# TECHNICAL REPORT

# ISO/TR 11150

First edition 2007-12-15

# Natural gas — Hydrocarbon dew point and hydrocarbon content

Gaz naturel — Point de rosée d'hydrocarbure et teneur en hydrocarbure



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ISO/TR 11150 was prepared by Technical Committee ISO/TC 193, *Natural gas*, Subcommittee SC 1, *Analysis of natural gas*.

### Introduction

With Resolution 6 at its Prague meeting in 2004, ISO/TC 193/SC 1, *Analysis of natural gas*, decided to publish a Technical Report on guidance for various International Standards on hydrocarbon dew point and hydrocarbon content.

The main purpose of this Technical Report is to explain to the wider gas community the complex issues behind the natural gas property called hydrocarbon dew point on the application of various International Standards on these subjects.

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# Natural gas — Hydrocarbon dew point and hydrocarbon content

### 1 Scope

This Technical Report describes the various means of estimating hydrocarbon dew point and hydrocarbon content of natural gas.

### 2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 6327, Gas analysis — Determination of the water dew point of natural gas — Cooled surface condensation hygrometers

ISO 6570:2001, Natural gas — Determination of potential hydrocarbon liquid content — Gravimetric methods

ISO 6974 (all parts), Natural gas — Determination of composition with defined uncertainty by gas chromatography

ISO 7504:2001, Gas analysis — Vocabulary

ISO 10715:1997, Natural gas — Sampling guidelines

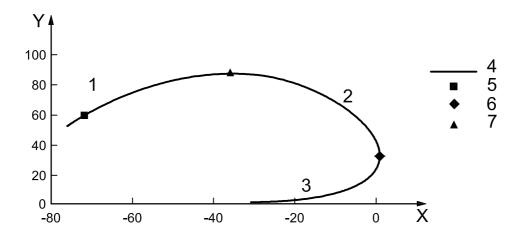
ISO 14532:2001, *Natural gas* — *Vocabulary* Technical Corrigendum:2002

ISO 23874, Natural gas — Gas chromatographic requirements for hydrocarbon dewpoint calculation

### 3 Background

Hydrocarbon dew point is often a requirement of gas quality specifications in sales contracts where gas is traded or crosses international borders. It can also be quoted in health and safety legislation. It is usually specified as a temperature at a defined pressure or over a range of pressures above which no hydrocarbon condensation will occur. It may alternatively be expressed as a maximum amount of hydrocarbon liquid which may condense under specific pressure and temperature conditions.

Under certain conditions, higher hydrocarbons present in natural gas or similar gases may condense and the condensate formed can cause difficulties in the operation of gas transport and distribution systems. Phase behaviour in hydrocarbon mixtures such as natural gas is highly non-ideal. More ideal behaviour, such as that of water in air, or, indeed, in natural gas, gives a dew point temperature which continually increases with pressure. Retrograde behaviour, which affects hydrocarbon mixtures, produces dew point temperatures which have a maximum value at an intermediate pressure. Figure 1 shows a typical phase diagram.



### Key

- temperature in degrees centigrade
- pressure in bar
- dense phase
- 2 gas only
- gas + liquid 3
- dewline
- 5 critical point
- cricondentherm 6
- cricondenbar

Figure 1 — Natural gas phase diagram

In Figure 1 the dew line is the phase boundary. To the right of and above this line only single-phase gas exists. Within the curve of the dew line, both gas and liquid phases are present, in proportions which are governed by the pressure and temperature. The closer to the line, the smaller is the proportion of liquid. The cricondentherm is the point of maximum dew point temperature. Above this temperature only single-phase gas exists, whatever the pressure. Similarly, at pressures above the cricondenbar, only single phase or dense phase gas exists, whatever the temperature.

A gas with a dew line similar to that in Figure 1 would be stable single-phase at -5 °C and 70 bar. If its pressure is reduced isothermally, it would remain single phase to about 55 bar, at which point it would encounter the phase boundary and condensate would start to separate. As pressure is further reduced, varying ratios of gas and condensate will be found until about 15 bar, when it returns to single phase for the remainder of its depressurization. In fact, once condensate has separated, it is unlikely that it will instantly return to the gas phase, and so liquids may continue to be present at lower pressures. Another consideration is that pressure reduction without the addition of heat is isenthalpic rather than isothermal, and Joule-Thomson cooling will cause the two-phase region to be encountered earlier, unless the gas has been pre-heated so that the cooling curve stays in the single phase region.

### Why is hydrocarbon dew point important?

Avoidance of condensate formation is important for pipeline operations. The presence of condensate can cause problems with filters and with measurement and control instrumentation. There is also an issue with gas turbines in power plants – significant damage can be caused by the presence of condensate in the burners.

A measured dew point temperature which is lower than the specification limit should give assurance that condensation will not occur. For certain needs, such as plant design, or if it is known that a certain amount of condensable material can remain after treatment, knowledge of the quantity of condensable hydrocarbons produced at specified conditions is useful. This can be physically measured using ISO 6570.

Operators require confidence in the measured result. At present, there is little or no information on the maximum permissible error of measurement, from any type of measurement which is strongly dependent on the type and nature of the natural gas. The single determined value as measured is accepted as the basis for decision making. However, for some natural gases, even a small decrease in temperature can result in a large liquid drop out.

### 5 What is the definition of hydrocarbon dew point?

The following definitions can be found in various ISO documents, such as in ISO 14532.

- 2.6.5 Dew points
- 2.6.5.2 Hydrocarbon dew point

### 2.6.5.2.1 Hydrocarbon dew point

temperature above which no condensation of hydrocarbons occurs at a specified pressure

NOTE 1 At a given dew point temperature there is a pressure range within which retrograde condensation can occur.

The **cricondentherm** defines the maximum temperature at which this condensation can occur.

NOTE 2 The dew point line is the locus of points for pressure and temperature which separates the single phase gas from the biphasic gas-liquid region.

### 2.6.5.2.2 Retrograde condensation

phenomenon associated with the non-ideal behaviour of a hydrocarbon mixture in the critical region wherein, at constant temperature, the vapour phase in contact with the liquid may be condensed by a decrease in pressure; or at constant pressure, the vapour is condensed by an increase in temperature

NOTE Retrograde condensation of natural gas is the formation of liquid when gas is heated or pressure is reduced.

### 2.6.5.2.3 Potential hydrocarbon liquid content (PHLC)

amount of liquid potentially condensable per unit volume of gas at a given temperature and pressure

Or alternatively in ISO 7504.

### 3.5.2 Dew point

at a specified pressure, the temperature at, or below which, condensation from the gas phase will occur

### 3.1 Equation of State

mathematical relationship between the state variables (pressure and temperature) of a gas or gas mixture, and the volume occupied by a given amount of substance

### 3.5.1 Critical point

single point in pressure-temperature phase diagram at which the composition and properties of the gas and liquid phases in equilibrium are identical

NOTE 1 The pressure at this point is known as the "critical pressure" and the temperature as the "critical temperature".

### 6 Specifications

Two examples from legislation and gas trading can be given.

### 6.1 EASEE-gas European association for the streamlining of energy exchange — Gas

Common business practice 2005-001/01 Harmonisation of natural gas quality 3/2/05. Hydrocarbon dew point shall be maximum of -2 °C at 1 bar to 70 bar.

NOTE EASEE-gas has not observed any technical constraints in conflict with the proposed harmonized values, and such values were adopted by 1/10/06. This same published document also made the comment "The need for introducing a harmonized measuring method has been identified".

### 6.2 United Kingdom Health and Safety Executive

A guide to the Gas Safety (Management) Regulations 1996.

Schedule 3 Content and other characteristics of gas.

Regulation 8 Part 1 Requirements under normal conditions.

**Hydrocarbon dew point** and water dew point shall be at such levels that they do not interfere with the integrity or operation of pipes or any appliance [within the meaning of regulation 2(1) of the 1994 Regulations] that a consumer could reasonably be expected to operate.

### 7 Hydrocarbon dew point measurement

### 7.1 General

The definition of the theoretical hydrocarbon dew point alone is not well understood by measurement technicians/scientists/engineers or those who draft sales gas contracts. At the most pedantic level, the dew point temperature is the minimum value at which no condensate is present, but only homogeneous gas phase. However this cannot and will never be physically measured as the first molecule will not be detected because the available methods are not sensitive enough (theoretical hydrocarbon dew point temperature).

So the method of determination of hydrocarbon dew point is critical, as each approach is based on different measurement principles, the hydrocarbon dew point can only be estimated with an associated uncertainty, and the true value cannot be achieved.

### 7.2 General sampling

Before any instrument or method can be deployed, a sample of the gas to be measured, has to be taken from the flowing gas in the pipeline and transferred unaltered to the measuring device.

ISO 10715 states:

### 3 Principles of sampling

### 3.1 Sampling methods

The main function of sampling is to take an adequate sample that is representative of the gas by direct sampling such that the sample is drawn from a stream and directly transferred to the analytical method. Care should be exercised to transfer a representative sample flowing in the pipeline unaltered and in a homogeneous single gas phase state to the analytical method. In general, turbulent flow is advantageous in a sampling system and in a gas line to be sampled because turbulence creates a well-mixed gas. Great care and consideration should be given for a gas near the dew point, as a reduction in line temperature will cause some condensation to occur, as will rapid reduction of pressure isothermally (adiabatic expansion causing cooling) resulting in two-phase sample gas flow.

### 7.3 Hydrocarbon dew point determination/estimation/monitoring

There are two principal methods: direct determination by physical observation of liquid condensation and calculation from detailed analysis. A third method measuring a similar/related property of potential hydrocarbon liquid formation (gravimetric method) is also discussed.

The first technique and apparatus for determining the dew point of gases under pressure was published by Deaton and Frost<sup>[1]</sup>. This manual method was widely adopted as it was the only method available and by default has become the *de facto* standard. However, there is currently no published ISO method with any performance characteristics. There is a method describing how manual cold mirrors operate in the ISO standard for water dew point. See ISO 6327. That International Standard also describes the procedures necessary for precautions against hydrocarbon or other liquid formation on the mirror prior to the water dew point determination (see Annex A for further information).

Similarly, the method for calculation from detailed analysis by gas chromatography is described in ISO 23874. That International Standard only deals with the chromatographic requirements and not with equation of state numerical methods. For the benefit of the user this draft is given in Annex B.

There is a published standard for potential hydrocarbon liquid content: ISO 6570. Explanation on the essentials is given in Annex C.

The real requirement is for an on-line automated method for the determination of the physical gas property of hydrocarbon dew point. The potential hydrocarbon liquid content method does not readily lend itself to automation.

### 7.4 Physical methods

### 7.4.1 General

Natural gas is passed through a cell at a defined pressure – typically in the range 25 bar to 35 bar. The cell contains a reflecting surface on to which light is directed and which can be observed. The surface is cooled and its temperature at the first appearance of liquid is recorded. This is regarded as the dew point temperature at the pressure of measurement. The operation can be controlled manually, in which case the appearance of liquid on the surface is usually detected by eye, or automatically, in which case the detection is by means of a photocell.

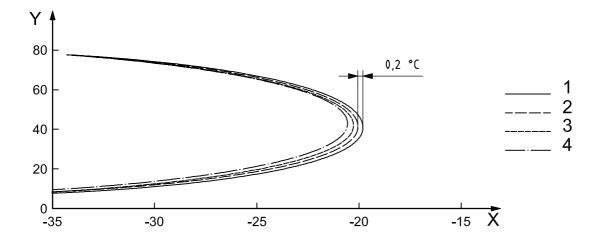
### 7.4.2 Physical methods — Advantages

- Condensation of liquid is clearly demonstrated.
- It is the *de facto* standard method, and experienced operators can achieve good agreement when using it.
- The manual equipment is portable, so sampling should not be a problem. The cooling can be done by expansion of carbon dioxide or air, avoiding the need for electrical power. Of the physical methods, it may be assumed that dew point temperature is a more rigorous specification than quantity of condensate (PHCL). It assumes, after all, "zero" condensate at the specified temperature rather than "not more than a defined amount".
- The automatic equipment conforms to safety requirements for installation on process plant.

### 7.4.3 Physical methods — Disadvantages

- A small power source is needed to illuminate the cooled surface with the manual equipment, but it is regularly used under a permit to work scheme.
- A defined amount of liquid needs to condense before it becomes visible. This will occur at a temperature below the theoretical dew point temperature (the first molecule) and the extent of the difference varies between gases from different sources. The effect may be significant. The rate at which liquid condensate forms as a function of the temperature below the theoretical dew point depends upon the composition of the gas. Figures 2 to 4 show the dew lines and iso-vapour fraction lines for three gases. The iso-vapour fraction lines correspond to condensate quantities of 50 mg/m³, 100 mg/m³ and 200 mg/m³ in each case.

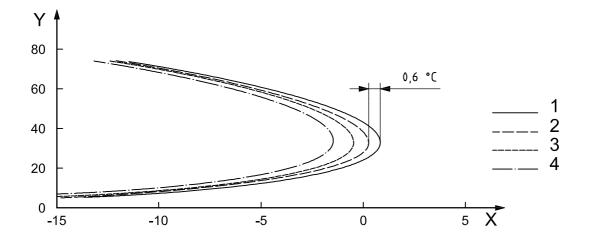
### ISO/TR 11150:2007(E)



### Key

- Χ temperature in degrees centigrade
- pressure in bar
- dewline
- 2 50 mg/m<sup>3</sup>
- 100 mg/m<sup>3</sup> 3
- 200 mg/m<sup>3</sup>

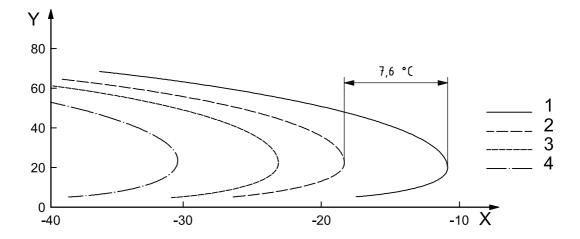
Figure 2 — Gas 1 condensation behaviour



### Key

- temperature in degrees centigrade
- pressure in bar
- dewline
- 50 mg/m<sup>3</sup> 2
- 3 100 mg/m<sup>3</sup>
- 200 mg/m<sup>3</sup>

Figure 3 — Gas 2 condensation behaviour



### Key

- X temperature in degrees centigrade
- Y pressure in bar
- 1 dewline
- $2 50 \text{ mg/m}^3$
- $3 \quad 100 \text{ mg/m}^3$
- 4 200 mg/m<sup>3</sup>

Figure 4 — Gas 3 condensation behaviour

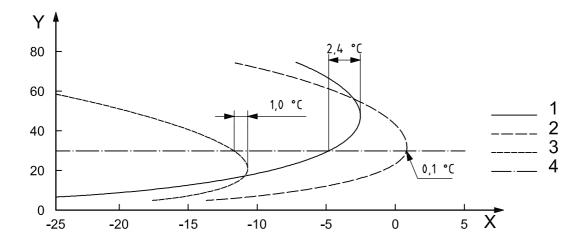
Gas 1 generates condensate at a rapid rate below the dew point temperature:  $50 \text{ mg/m}^3$  is found at a temperature of  $0.2 \,^{\circ}\text{C}$  below the dew point. Gas 2, which has a higher dew point value, is also reasonably prompt, at  $0.6 \,^{\circ}\text{C}$ ;  $50 \,^{\circ}\text{mg/m}^3$  is a reasonable estimate of the amount of condensate necessary to form a visible deposit on a cold mirror. The quantity will vary with cell design. Gas 3 is exceptional, generating  $50 \,^{\circ}\text{mg/m}^3$  at  $7.6 \,^{\circ}\text{C}$  below the dew point temperature.

The behaviour of gas 3 is unusual, but it is a genuine natural gas, accepted into the transmission system. It may be that the increasing use of a larger number of smaller supplies will lead to more such gases being delivered.

The point of maximum dew point temperature (the cricondentherm) is found at different pressures with different gases. Physical dew point measurement occurs at a selected pressure (default in Europe is 27,6 bar gauge or 400 psi). This default pressure may not reflect the actual cricondentherm as gas composition varies. It is not practicable to make a series of measurements at different pressures, and so significant bias may be present. Figure 5 shows dew lines for gases 2 and 3, as above, and also for gas 4, compared to a typical measurement pressure of 28 bar. The cricondentherm for gas 2 is at around 30 bar, and so the difference between the maximum dew point temperature and that at 28 bar is only 0,1 °C.

Gas 3 has a cricondentherm at around 20 bar, some way away from the measurement pressure, which means that the measured dew point would be underestimated by 1 °C from the maximum. The cricondentherm for gas 4 occurs at about 47 bar, which means that the measured value would be 2,4 °C below the maximum. These calculations assume that the theoretical dew point is instantly recognized; in fact, as we have seen from Figure 4, gas 3 will be subject to a larger error due to its slow rate of condensate generation. Figure 5 also shows that choice of a measurement pressure more suited to gas 3 or gas 4 would produce larger errors for the others.

It is possible (but relatively unlikely) that the condensed phase may be water or other liquid (glycols, methanol, etc.) rather than hydrocarbons. While experienced manual cold mirror operators claim they can identify the type of condensate, inexperienced operators may incorrectly identify other liquids as hydrocarbons.



### Key

- Х temperature in degrees centigrade
- pressure in bar
- 1 gas 4
- 2 gas 2
- gas 3
- 28 bar

Figure 5 — Effect of measurement pressure

### **Analysis and calculation**

#### 7.5.1 General

Equation of state software can calculate phase properties, including hydrocarbon dew point, from a detailed analysis. The analysis usually requires equipment and conditions that are laboratory-based, although there is increasing interest and an increasing use of on-line process analysers to perform the task. The analysis must be detailed, measuring major components and also, importantly, trace quantities of higher hydrocarbons. Simplifications such as measuring all C<sub>6</sub> and higher hydrocarbons as a single "pseudo-component", which is satisfactory for calorific value determination, are not acceptable. It is not possible to use a single analytical system, as is the case for calorific value applications; the detail required for higher hydrocarbons needs a different analytical system from that used for major components. It is possible to use a single instrument, but it needs to contain different analytical sub-systems.

The approaches taken for laboratory and process use are sufficiently different such that they are considered separately.

#### Laboratory analysis 7.5.2

#### 7.5.2.1 General

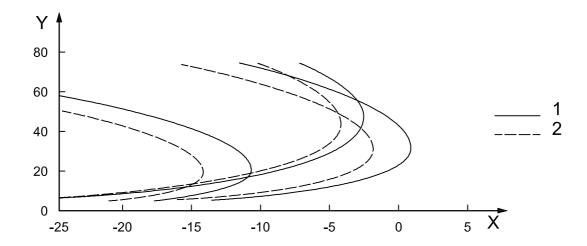
The sample must come to the analyser. The gas may be analysed directly, in which case the combination of sample size and column dimensions must be well adapted to allow the increasingly small quantities of increasingly higher-boiling hydrocarbons to be measured with sufficient precision. Alternatively, the higher hydrocarbons can be pre-concentrated in an adsorption tube and/or cold trap to allow larger quantities to be analysed. Lower boiling components are not amenable to pre-concentration and so the method must be well defined to ensure that the intended components are quantitatively pre-concentrated.

### 7.5.2.2 Laboratory analysis — Advantages

- Gas chromatography using capillary columns, temperature programming and a flame ionization detector (FID) is well established for the range of components, and has sufficient sensitivity to be applied to subparts per million levels.
- Pre-concentration techniques allow measurement of parts per billion levels.
- From a comprehensive analysis, equation of state software allows multiple calculations. The dew point at a selected pressure, or a range of dew points, or just the cricondentherm can be calculated as required. Alternatively, it is possible to calculate the amount of condensate at particular conditions in the two-phase region, and the properties and composition of the condensate and of the gas with which it is in equilibrium can be found.

### 7.5.2.3 Laboratory analysis — Disadvantages

- The quality of the result is totally reliant on the quality of the sample. Great care must be taken to ensure that the sample is representative, with no components lost in whole or in part, and no cross-contamination from previous use.
- Quantitative data is usually calculated using the assumption that the FID is a carbon counter. Components are then quantified relative to a component, such as butane or pentane, which has been measured as part of a major component analysis. This assumption may not be true, depending on the operating parameters of the analyser, and should be checked. Certified gas mixtures containing typical components of interest are not widely available (although that is improving) and expensive.
- There are clear differences in the result when using the same analytical data with different equations of state. Figure 6 shows the differences for gases 2, 3 and 4 when using the same analytical data with the Redlich-Kwong-Soave (RKS) and the Peng-Robinson (PR) equations of state. For results to be compared, the same equation must be used. There is little information as to which equation should be preferred. Current work in ISO/TC 193 should improve knowledge in this area as will the GERG studies.
- As with any laboratory measurement, there is an inevitable delay between sampling and reporting.



### Key

- X temperature in degrees centigrade
- Y pressure in bar
- 1 RKS
- 2 PR

Figure 6 — Different equations of state

### 7.5.3 Process analysis

#### 7.5.3.1 Process analysis — Advantages

- With a properly designed sampling system, the analyser will be presented with a representative sample, in the same way that physical dew point methods are.
- There is little delay between sampling and reporting.
- An analyser set up for dew point determination will also be capable of providing data for other physical properties, such as calorific value, density, Wobbe index and compression factor.

#### 7.5.3.2 Process analysis — Disadvantages

- Temperature programming is not available on process analysers. Some manufacturers offer FID models, and capillary columns can be used perfectly well. However, with isothermal analysis it is impossible to achieve the same performance as that of a laboratory analyser. This might be solved by breaking down the separation of, say, C<sub>5</sub> to C<sub>12</sub> hydrocarbons into simpler groups rather than trying to tackle it in a single operation.
- In the absence of an FID, the problem becomes greater. The ubiquitous thermal conductivity detector (TCD) can be used with capillary columns, but it cannot match the range and sensitivity of the FID.
- The comments on quantitative data given in laboratory analyser disadvantages are equally true for a process analyser using an FID. There is less available information about hydrocarbon responses from a TCD and so the need for certified mixtures to check performance is all the greater.
- The choice of equation of state for calculation is equally important as when using laboratory-based analyses.

#### Comparative studies 7.6

A number of comparative studies have been conducted between manual cold mirror and automated dew scope, and between both laboratory and site automated chromatographic approaches with dew scope methods. All of these studies show that the trend monitoring closely follow each other but do not always give exactly the same mean value. Some studies were not so well conceived, or conducted in a controlled manner, and are therefore not so helpful. However, two papers (Bibliography [2], [3]) show that with very careful and controlled operation of equipment a converging dew point value can be obtained if the gas quality is well defined and of constant composition.

There is extensive work currently being carried out by several working groups, i.e. GERG, NPL. These further studies will lead to an improvement or better understanding of hydrocarbon dew point determination in the next few years.

### Conclusions

The method of determination of hydrocarbon dew point should be carefully chosen to match the nature of the natural gas, the mode of operation and the end use for which the information is to be applied.

Different methods of determination of hydrocarbon dew point diverge in results for many reasons but the principle reasons are:

- the rate of deposition and the amount of liquid deposited on a mirror surface;
- how comprehensive the determination of the components in natural gas is made and the choice of EoS used for the calculation.

Although consensus results are required by all parties at the point of measurement, it is difficult to harmonize results obtained from direct determination by physical observation of liquid condensation and calculation from detailed analysis. These two methods are using fundamentally different measurement principles.

### 9 Recommendations

If the term hydrocarbon dew point is used in gas quality specifications it should be appended by the determined value, e.g. max.  $-2\,^{\circ}\text{C}$  at pressures from 1 bar gauge to 70 bar gauge with a maximum permissible error of  $\pm$  1,5  $^{\circ}\text{C}$  (from the accepted or true value) and the method of determination in case of a disputed value should be stated.

The term hydrocarbon dew point should be substituted by a new definition called technical or measurable hydrocarbon dew point to aid convergence of the determined value from the different approaches of measurement.

# Annex A

(informative)

### **Dew scope measurements (cold mirror)**

### A.1 Introduction

### A.1.1 General

Dew scope measurements can be made manually or automatically.

### A.1.2 Manual dew scope

This manual technique requires the observation, by eye, of the formation of a film of dew (mist) on the surface of an illuminated cooled mirror. It requires a skilled and practiced operator to achieve accurate results. It is established that with due skill, it is to be expected that there should be a maximum difference of 1,5 °C between the measurements for 95 % of the time. Because the method is manual, it is unsuitable for continuous monitoring of the gas dew point.

This method has been adopted in a lot of contracts between delivery terminals and shippers.

### A.1.3 Automatic dew scope

An automated instrument determines the temperature at which dew forms by cyclically cooling and heating a reflective surface while optically searching for the presence of dew on the surface. When the surface is free of dew, little if any light is transmitted to the detector, resulting in a correspondingly low signal from the detector. When dew forms, it increases the amount of light reaching the detector, thereby indicating that the surface's temperature is the dew point. It is necessary to decide the level of electrical output that is taken as indicating the presence of dew. This is generally a factory default figure, but most instruments allow adjustment by reference to a dew scope or other method of measurement. Manufacturers' accuracy claims are typically as good or better than those achievable with manual dew scopes.

### A.2 Individual instrument description

### A.2.1 Manual dew scope

### A.2.1.1 General

Manual measurements of hydrocarbon dew point are made using different dew scopes.

Some examples are U.G.C., Marquis and Chandler Engineering (AMETEK Process Instruments)<sup>1)</sup>.

Manual dew scopes have long been in use and the technique is included in different manual procedures. The technique is described in ISO 6327.

<sup>1)</sup> These trade names are examples of suitable products available commercially. This information is given for the convenience of users of this Technical Report and does not constitute an endorsement by ISO of these products.

### A.2.1.2 Principle of measurement

The dew point of the gas is determined by cooling a mirror, over which a slow stream of the gas is passed. The dew point is recorded as the temperature at which a film of condensate just appears on the mirror.

The general layout of equipment is common to the different manual dew scope instruments employed. The instrument consists of a cylinder divided by a stainless steel mirror. A slow stream of gas is passed through the part of the cylinder on the reflecting side of the mirror, which is illuminated and viewed through an eyepiece. Refrigerant (carbon dioxide) is passed into the other part of the cylinder, thus cooling the back of the mirror. The temperature of the mirror is determined with a thermistor in contact with its back. A fine needle control valve controls the flow of refrigerant. The apparatus is also fitted with inlet and outlet gas valves and a gas pressure gauge. The instrument is connected to the sample point via a high-pressure hose or tube made of clean, inert and non-porous material. Hydrocarbon dew point is by convention generally measured at 27,6 bar gauge (400 psig), which approximates the cricondentherm of natural gases. The hydrocarbon dew point is therefore estimated to be at a maximum at around this pressure. With the dew scope instrument, the formation of a hydrocarbon liquid film is observed as coloured interference fringes on the mirror. With some instruments, droplets are observed, rather than interference fringes, owing to the use of a ridged mirror.

### A.2.1.3 Advantages and disadvantages

The manual dew scope has been in operation throughout the world for many years in the gas industry. A measurement can be made relatively quickly – 10 minutes – and reproducibly – different trained operators can be expected to give results with the same gas and similar instruments differing by around 1 °C. Like most measurement techniques it is dynamic, i.e. a sample of natural gas has to be cooled, and the result can be dependent upon cooling rate. Detection of first formation of liquid is subjective and trained operators must be employed. Additionally, trained operators may also be able to characterize the type of dew detected as hydrocarbon, water, glycol or methanol, as each of these compounds exhibits differing characteristics of dew formation.

### A.2.2 Automatic dew scope

### A.2.2.1 General

There are several types of automated hydrocarbon dew point analysers produced by various manufacturers. While all devices employ automated heating and cooling of the measuring surface and automated optical dew detection, they vary in the method of heating/cooling, the length of the measuring cycle, sample conditioning, source/surface/detector configuration, and physical configuration.

### A.2.2.2 Principle of measurement

While there are variations in the specific measurement principles employed, virtually all automatic dew scope devices employ the following generic technique.

A natural gas sample stream is connected from the pipeline to the analyser at pipeline pressure (when appropriate, the analysis may take place at a regulated, defined pressure such as 27,6 bar gauge) using seamless stainless steel tubing. The tubing is sized to prevent pressure loss within the tubing when the device is drawing its maximum sample flow rate.

The sample gas is usually filtered to remove entrained liquids and solids which would otherwise contaminate the sample cell and measuring surface. This serves to minimize the necessity for cleaning the optical measuring surfaces within the instrument's sample cell.

The measuring surface is cyclically cooled and heated to allow dew to form for dew point detection and to evaporate to clean the surface for the next measuring cycle. An optical system consisting of a light source, the measuring surface, and detector is employed to detect when dew forms on the cooled surface.

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A beam of light is projected by the light source on to the measuring surface. When the surface is free of dew, little, if any, light is transmitted to the detector, resulting in a correspondingly low signal from the detector. When dew forms on the surface, the signal from the detector increases dramatically, indicating the presence of dew. A highly accurate thermocouple is used to constantly relay the temperature of the surface. The temperature at which the detector "sees" light is then reported as the hydrocarbon dew point temperature.

The accuracy of an automatic hydrocarbon dew point device depends upon several factors: the accuracy of the temperature measuring device, the amount of dew formation required to "trigger" the detector that dew is present, and the temperature gradient between the temperature measuring device and the measuring surface where the dew forms.

As highly accurate temperature measurement is easily achieved, the first factor is typically not a concern. (Be aware that the accuracy of the temperature measurement device is not promoted as the overall accuracy of the dew scope.) The second factor is a common disadvantage which was elaborated upon in 7.4.3. The third factor is where the true inherent inaccuracies often occur.

Verification of the accuracy of an automatic dew point device can be achieved by challenging the device with a hydrocarbon of known dew point such as pure propane at a controlled pressure but does not reflect the complex behaviour of real natural gas retrograde nature.

### A.2.2.3 Advantages and disadvantages

These devices have the advantage of directly measuring the physical property of dew formation. They continually provide an accurate and verifiable measurement of the dew point of the sample gas. The measurements are typically consistent and repeatable between automatic devices and even with manual devices operated by trained technicians.

There are several possible disadvantages. Some devices will trigger on water, glycol or methanol dew formation which may or may not be desirable. In addition, some devices require refrigeration gases which may be unavailable or undesirable to use in some installation locations. Lastly, some devices might have inadequate sample filtering systems which will lead to more frequent filter maintenance and cleaning of the measuring surface.

### A.3 Best use of instrument

### A.3.1 Manual dew scope

### A.3.1.1 Test methodology

Critical factors considered in the operating procedure are the flows of gas and refrigerant in order to achieve a slow (1 °C/min) cooling rate just prior (ca. 3,5 °C) to the appearance of liquid.

The methodology acknowledges that a hydrocarbon dew point is more difficult to observe than a water dew point. It also recognizes the problem of cooling the mirror too rapidly and suggests that the final result should be the average of the point of first appearance of liquid on cooling and the point at which liquid disappears on re-heating. The test methodology requires the dew points on cooling and on heating to be different by no more than 1 °C. The reported dew point under this condition is the dew point on cooling. Readings are repeated until constant results are obtained.

### A.3.1.2 Operator comparisons

In order to gain confidence in any comparisons between manual dew scope measurements, an intercomparison of operators and the measurement process was conducted. For both tests, operators measured hydrocarbon dew points and the results were compared.

Excellent agreement was obtained between the operators, with the measurement process showing zero difference observed for 21 of a total of 22 comparisons.

### A.3.2 Automatic dew scope

### A.3.2.1 General

Gas for determination is taken from the common sample point that also serves the manual dew scope. All sample lines are electrically heated and insulated.

The pressure of 28 bar gauge was set, as this is the pressure at which the dew point temperature is at its highest value. The instrument was configured with a 15 min cycle time and the factory default setting (275 mV) for calibration.

### A.3.2.2 Results

The results of one commercially available automatic dew scope were compared to the measurements by manual dew scope, gas chromatograph and Gastec, after making the appropriate time of flight adjustments for the gas flow through the pipeline.

The general level of dew point was around -8 °C. However, two major excursions occurred over the period. The automatic scope reliably followed the trends indicated by the gas chromatographs and dew scope. The manual dew scope readings were also generally in accordance with the automatic scope's indicated trend. However, the dew point values determined by the automatic scope were higher than those obtained from the gas chromatographs and manual dew scope.

Consistently, the automatic scope reads higher. This is in accordance with comments from the devices manufacturer.

# Annex B

(informative)

## Chromatographic methods

### **B.1 Introduction**

This annex gives the background information on the gas chromatographic requirements for hydrocarbon dew point calculation, as given in ISO 23874.

### **B.2 Scope**

This Technical Report describes the performance requirements for analysis of treated natural gas of transmission or pipeline quality in sufficient detail so that the hydrocarbon dew point temperature can be calculated using an appropriate equation of state. It may be applied to gases, which have maximum dew point temperatures (cricondentherms) between 0 °C and -50 °C. The pressures at which these maximum dew point temperatures are calculated are in the range 20 bar to 50 bar. Major components are measured using ISO 6974-1, and the ranges of components, which may be measured, are as defined in that standard. The procedure given here covers the measurement of hydrocarbons in the range  $C_5$  to  $C_{12}$ . n-Pentane, which is quantitatively measured using ISO 6974, is used as a bridge component, and all C<sub>6</sub> and higher hydrocarbons are measured relative to *n*-pentane.

### **B.3 Principle**

For hydrocarbon gas mixtures such as natural gas, the phase boundary or dew point line distinguishing singlephase gas from gas/liquid mixtures is a complex function of pressure, temperature and composition. For a given composition, the pressure at which the dew point temperature is at a maximum is intermediate between those found in transmission and distribution operations. The analysis shall be comprehensive for inert components and for hydrocarbons up to C<sub>12</sub>. Helium, hydrogen, water and sulfur compounds do not need to be measured unless any of these is present at greater than 0,01 mole fraction.

The analysis shall be performed in two parts. Major components (nitrogen, carbon dioxide and hydrocarbons from C<sub>1</sub> to C<sub>5</sub>) shall be analysed in accordance with ISO 6974. Higher hydrocarbons (C<sub>5</sub> to C<sub>12</sub>) shall be analysed to satisfy the requirements given in this standard. This allows the traceability of measurements according to ISO 6974 to be extended to the higher hydrocarbons.

It is not possible to identify all the measured higher hydrocarbons, nor is it possible to obtain a reference gas mixture that contains more than a few representatives of the higher hydrocarbons. The analytical data are therefore handled with a number of simplifying assumptions:

- unidentified components are allocated a carbon number or molar mass according to their positions in the chromatogram with respect to identified *n*-alkanes;
- alkanes of carbon number 7 and above are summed by carbon number and treated as fractions for input to the dew point calculation;
- average boiling points and densities of fractions are calculated from the individual boiling points and quantities of the components that comprise them; individual component boiling points are calculated by interpolation between the bracketing *n*-alkanes (Bibliography [4]);
- sample components are quantified by comparison with n-pentane, which has been measured in accordance with ISO 6974, using relative response factors based on their allocated carbon numbers.

NOTE When using ISO 6974, *n*-pentane may be measured as a direct component, which is also present in the calibration gas mixture, or as an indirect component using a response factor relative to a different component (for example, *n*-butane) in the calibration gas mixture. In either case, the uncertainty on the quantity of *n*-pentane can be calculated according to ISO 6974-2.

### **B.4 CRMs**

- **B.4.1** Certified-reference gas mixture for major components (CRM1), such as is required for ISO 6974. Depending upon the working range and the accuracy required, more than one CRM may be needed.
- **B.4.2 Certified-reference gas mixture for higher hydrocarbons** (CRM2), containing as a minimum, *n*-pentane, *n*-hexane, benzene, cyclohexane, *n*-heptane, toluene, methyl cyclohexane and *n*-octane. Ideally, CRM2 should also contain *n*-nonane, *n*-decane, *n*-undecane and *n*-dodecane in methane.

The mole fractions of components in CRM2 shall be chosen to be appropriate for the application, provided that the mixture is stable and free from the possibility of condensation both in storage and in use.

- **B.4.3** Major components, the system for measurement of major components shall have performance as described in ISO 6974.
- **B.4.4 Higher hydrocarbons**, the system for measurement of higher hydrocarbons shall satisfy the following requirements:
- capable of measuring alkanes up to and including *n*-dodecane;
- capable of measuring individual alkanes at a concentration of not less than 0,1 parts per million (0,000 000 1 mole fraction);
- capable of distinguishing and measuring benzene, toluene, cyclohexane and methyl cyclohexane as individual components;
- use a detection system that can at least in principle measure all hydrocarbons in the range C<sub>5</sub> to C<sub>12</sub>;
- use a detection system that has a predictable response to hydrocarbons, based on mass or carbon content, such that unidentified components of known molar mass or carbon number can be measured relative to other known components in the sample or in the calibration gas.

### **B.5 Advantages**

A lot of the compositional data is required for other reasons and does not duplicate equipment at the point of measurement.

Benefits are predictive of change or trends; this explains why there is a change, and can provide information about gas under different pressures and temperatures further down the pipeline from point of measurement.

It can calculate the amount of liquid formed under different P&T.

It determines the dew line (locus of HC DP at different P&T), defining the conditions between homogenous gas and two-phase conditions. Gas chromatographic analysis of natural gas for the purpose of hydrocarbon dew point calculation needs to be comprehensive and competent.

For the purpose of calculating heating value, density and Wobbe Index, the analysis can be simplified by, for example, recombining all  $C_6$  and heavier components and measuring them as a single entity  $(C_6^+)$ .

Composition from chromatographic analysis needs to be well defined but shall specify the calculation routine and the equation of state EOS. For the same raw data input, different hydrocarbon dew point values could be obtained, depending on the EOS used. The choice of equation of state for calculation is equally important as choice of laboratory-based or online analyses.

# Annex C (informative)

## Potential hydrocarbon liquid content

### C.1 Scope

This annex gives background based on the determination of potential hydrocarbon liquid content, as given in ISO 6570.

### C.2 Introduction

Under certain conditions, higher hydrocarbons present in natural gas or similar gases may condense and the condensate formed can cause difficulties in the operation of gas transport and distribution systems. Dew-point measurements, by condensation on a mirror, may give an indication of the conditions under which condensation starts. However, these measurements give no further information about the amount of liquid to be expected under operating conditions. For proper operation of transport and distribution systems, a knowledge of the quantities of condensate formed as a function of temperature and pressure is required. This knowledge is also required for the design of production and treatment systems as well as for subsequent handling and disposal of the liquid. The methods described in ISO 6570 are intended for the determination of the quantity of hydrocarbon condensate formed from a natural gas or similar gas as a function of the temperature and pressure of the gas. Instruments based on different measurement principles can give a figure related to potential condensate content or dew point. The dew point can only be determined by performing measurements at different temperatures followed by extrapolation of the measurements to a potential hydrocarbon liquid content value of zero. The methods described in this Technical Report can be used to calibrate such instruments.

### C.3 Principle

Determination of the quantity of hydrocarbon condensate which can be formed at a pressure, p, and a temperature, T, by passing a representative sample of the gas through an apparatus where it is first brought to pressure, p, and then cooled to the temperature, T. The temperature and pressure are selected according to the specific application (see Annex A). Prior to reducing the pressure of the sample of gas to that required for the determination, the gas is heated, so that, after pressure reduction, the temperature is well above the dew point temperature of the gas. Downstream of the reducer, the sample is cooled isobarically in a cooling bath to the required measurement temperature. The quantity of liquid accumulated during the measurement period is determined by either direct manual weighing of the collected liquid or weighing of the condensate cyclone separator at the start and at the end of a measurement period (Method A). Alternatively, the quantity of liquid accumulated in a vertical measuring tube may be determined automatically (indirect automatic weighing) by indication of the pressure difference caused by the liquid accumulated in a vertical measuring tube.

## **Bibliography**

- [1] DEATON, W.M. and FROST, E.M. JR., *Apparatus for determining the dew point of gases under pressure*, Bureau of Mines, USBM RI 3399, May 1938
- [2] PANNEMAN, H.J., *A traceable calibration procedure for hydrocarbon dew point meters*, presentation given at the AGA Operations Conference in Chicago, April 2005
- [3] RIDGE, A., *Hydrocarbon dew point measurement measuring systems*, presentation given at the Advantica 2002 Conference
- [4] COWPER, C.J., Natural gas hydrocarbon dew point; comparison of measurement and calculation methods, presentation given at 2nd Gas Analysis Symposium and Exhibition, Maastricht, 2002
- [5] WARNER, H.R. et al., *Hydrocarbon dew point determination of lean natural gases*, Gas Processors Association Annual Convention, 2001

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