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

Analyse des gaz — Détermination du point de rosée des gaz naturels — Hygromètres à condensation à surface refroidie

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Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council.

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No member body expressed disapproval of the document.

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

1 Scope

This International Standard describes hygrometers used for the determination of the water dew point of natural gases by detecting water vapour condensation occurring on a cooled surface or by checking the stability of the condensation on this surface.

2 Field of application

The water dew point of processed natural gases in transmission lines normally lies between $-25\text{ }^{\circ}\text{C}$ and $+5\text{ }^{\circ}\text{C}$, which corresponds to water concentrations of 50 to 200 ppm (V/V), according to the pressure of the gas.

The hygrometers considered in this International Standard may be used for determining water vapour pressure, without requiring calibration, in a system operating under total pressures greater than or equal to atmospheric pressure. The relationship between water vapour partial pressure and the observed dew point confers on the method the quality of absolute measurement.

If the test atmosphere contains gases which condense at a temperature in the region of, or above, that of the water dew point, it is very difficult to detect the condensed water vapour.

3 Principle

3.1 Principle of the apparatus

With this type of apparatus, which determines the water content of a gas by measuring the corresponding dew point, a surface (generally a metallic mirror), the temperature of which may be artificially lowered and accurately measured, is exposed to a sample of the gas being tested. The surface is then cooled to a temperature at which condensation occurs and is observed as dew.

Below this temperature, condensation increases with time, whilst above it, condensation decreases or does not occur. This surface temperature is then (for practical applications) taken as the dew point of the gas flowing through the apparatus.

3.2 Determination of water vapour pressure

The partial water vapour pressure in the gas samples is the saturated vapour pressure corresponding to the observed dew point, provided that the gas in the hygrometer is at the same pressure as the gas at the time of sampling.

Published documents are available giving the relationship between saturated vapour pressure and temperature.

It should be noted that if methanol is present, this method determines methanol in addition to water. However, if the methanol content is known, the annex gives, for information, correction factors allowing determination of the actual water dew point.

3.3 Precautions to be taken

It is essential that all sample lines be as short as possible and be sized to produce a negligible pressure drop during measurement. The sample lines and the hygrometer, apart from the mirror, shall be above the water dew point temperature.

4 Characteristics of the apparatus

4.1 General

Condensation apparatus may be designed in various ways. The differences lie mainly in the nature of the condensation surface, the methods used for cooling the surface and for controlling its temperature, the methods used for measuring the surface temperature and the method of detecting the condensation. The mirror and its associated components are normally placed in a small cell through which a sample of the gas flows; at high pressures, the mechanical strength and leak tightness of the cell have to be suitable.

It is recommended that the mirror should be easily removable for cleaning.

Adequate precautions shall be taken if measurements are to be made in the presence of condensable hydrocarbons.

Measurements can be carried out manually or automatically.

Caution : Manufacturers' instructions should be carried out before gas at high pressure is admitted to the cell.

4.2 Automatic and manual types

Devices for measuring dew point can be designed to make isolated measurements at different times or to make more or less continuous measurements. For isolated measurements, methods of mirror cooling may be chosen which require continuous attention by the operator responding to changes in the condensed deposit which is observed by the naked eye. If there is less moisture in the gas sample, i.e. if the gas has a lower dew point, the rate at which water vapour flows through the apparatus per unit time decreases so that condensation forms more slowly, and it becomes more difficult to judge whether condensation is increasing or diminishing. Observation of the deposit can be made easier by using a photoelectric cell or any other device which is sensitive to light, if a simple indicator is needed, while maintaining manual control of the cooling device.

With certain types of manually operated instruments, it is very difficult to observe the water dew point in the presence of condensed hydrocarbons. In such cases, a liquid paraffin bubbler may be used to assist such observations. It is very important, however, that the principles involved and the limitations in the use of such a bubbler are understood.

An equilibrium is established between the gas passing through the bubbler and the liquid paraffin oil contained in it, at the temperature and pressure of the bubbler. This involves the following reactions :

- a) The first gas passing through fresh liquid paraffin loses water to the paraffin until equilibrium is achieved, at which time the water content of the exit gas is the same as that of the inlet gas. Therefore, the temperature of the bubbler must be above that of the water dew point of the gas to be tested and sufficient gas must be passed into the bubbler for equilibrium to be established before observations can be made.
- b) Until equilibrium is established, heavy hydrocarbon components pass from the gas into the liquid paraffin. It is this exchange that reduces the volume of potentially condensable hydrocarbons in the gas, thereby reducing the masking effect of the condensed hydrocarbon liquid. As there is a continuing exchange of components, the liquid paraffin becomes saturated with condensible hydrocarbons the content of which increases in the gas. The liquid paraffin must then be replaced and the bubbler conditioned before further observations can be made.

The device can be fully automated by using the output signal of the photoelectric cell to stabilize the mirror at the required condensation temperature. Automatic operation is indispensable for continuous reading or recording.

4.3 Mirror illumination

Manual devices can involve observation of condensation with the naked eye; if a photoelectric cell is used, the mirror is illuminated by a light source built into the test cell. The lamp and photoelectric cell can be arranged in various ways, provided that diffusion in the direction of the light source from the mirror is reduced by the polishing of the mirror. In any case, the mirror must be clean before use.

In the absence of any condensation, the diffused light falling on the photocell must be reduced. The effects of light diffused from internal surfaces of the cell can be reduced by blackening these surfaces and this precaution can be supplemented by an arrangement of the optical system so that only the mirror is illuminated and the photocell views only the mirror.

4.4 Methods for cooling the mirror and controlling its temperature

The following methods are used for reducing and adjusting the mirror temperature. The methods described in 4.4.1 and 4.4.2 require constant attention from the operator and are not suitable for automatic devices. For automatic devices, two cooling methods are used : indirect contact with a coolant or cooling by the thermoelectric (Peltier) effect as described in 4.4.3 and 4.4.4. In any case, the rate of cooling of the mirror shall not exceed 1 °C per minute.

4.4.1 Solvent evaporation

A volatile liquid in contact with the rear face of the mirror can be evaporated and cooled by an air flow. Hand bellows are generally used for this purpose, but an adjustable source of low pressure compressed air or any other suitable pressurized gas is preferable. The liquid used can be ethylene oxide, a very efficient liquid giving cooling of the mirror of approximately 30 °C, without effort, when hand bellows are used. However, if toxicity is a risk, acetone can be used to obtain cooling of approximately 20 °C with hand bellows or even greater cooling with compressed air or other suitable pressurized gas.

4.4.2 Gas cooling by adiabatic expansion

The mirror can be cooled by discharging onto its rear face a gas which has just expanded through a nozzle. Compressed carbon dioxide, available from small cylinders, is often used for this purpose, but other gases such as compressed air, compressed nitrogen, propane or halogenated hydrocarbons can also be used. Mirror temperatures of at least 40 °C below the gas sample temperature can be obtained.

4.4.3 Indirect contact with a coolant

The mirror is connected to a cooler through a thermal resistor. Normally, a solid copper rod is plunged into the cooler and connected to the mirror by a small piece of insulating material forming the thermal resistor. The mirror is heated by an electric element. Current intensity should be controlled so that the mirror temperature can be adjusted easily and accurately. Using liquid nitrogen as coolant, temperatures of – 70 °C to – 80 °C may be obtained; for temperatures down to approximately – 50 °C (according to the apparatus design), a mixture of solid carbon dioxide plus acetone may be used, and for temperatures around – 30 °C liquefied propane can be used.

4.4.4 Cooling by thermoelectric (Peltier) effect

A single stage Peltier effect element normally allows maximum cooling of approximately 50 °C. With two stages, cooling of approximately 70 °C can be obtained.

The mirror temperature can be adjusted by varying the current in the Peltier effect elements, but thermal inertia tends to be high, and more rapid adjustment is achievable by maintaining a constant cooling current, connecting the mirror to a thermal resistance, and heating the mirror with an adjustable electric heating device.

4.5 Temperature measurement

It is essential that the temperature of the mirror on which the deposit is formed is measured as accurately as possible. To avoid temperature differences on the surface, a mirror of high thermal conductivity is preferred. Manual devices generally incorporate a mercury thermometer, and with automatic devices a thermoelectric probe is used (for example a resistance thermometer, a thermistor or a thermocouple).

5 Sources of error — General precautions for operation

5.1 Interfering substances

5.1.1 General

Substances other than the gas or water vapour can enter the device and affect its operational characteristics. Such substances may be solid particles, dust, etc., which can be deposited on the mirror. Vapour other than water vapour can condense on the mirror. Gases soluble in water, voluntarily or accidentally introduced into the test cell, can also induce an observed dew point different from the dew point which would correspond to the actual water vapour content.

5.1.2 Solid impurities

If solid impurities are absolutely insoluble in water, they do not modify the observed condensation temperature, but can hinder condensation observation. In an automatic device, without a compensation device for such impurities, these tend to obstruct the operation of the device if the amount of condensate is low. Defects resulting from an excess of solid impurities on the mirror generally result in an unexpected increase of the mirror temperature for a few minutes and call for dismantling of the device and cleaning of the mirror. (It is essential for this purpose that the hygrometric cell can be rapidly dismantled.) It may be desirable to remove solid impurities by using a non-hygroscopic filter¹⁾ to avoid such difficulties.

To prevent the influence of dust particles, some automatic devices are fitted with a "calibration" sequence. This consists of an optional superheating of the mirror, so as to remove all condensate, water and hydrocarbons, followed by a rebalancing of the measuring bridge.

5.1.3 Impurities in vapour form

Hydrocarbons can condense on the mirror. In principle these do not interfere because hydrocarbon surface tension is very different from that of water. They spread on the mirror and form a continuous layer which does not diffuse light. Manual detection of condensates is, nevertheless, not easy because although the dew point is very much lower than the condensation temperature of hydrocarbons, only a few water droplets can be detected in a large hydrocarbon droplet (see clause 6).

The presence of a hydrocarbon condensate does not modify the water dew point since the condensates are not miscible.

If the gas contains methanol, this will be deposited with the water, and a dew point for the mixture water and methanol will be obtained. If hydrocarbons are also present, then two condensates are formed, one aqueous, the other oily. In this case, the condensation temperature of the aqueous condensate is not due solely to the water content.

5.2 Cold wall error

It is essential that the parts of the pipes and device other than the mirror are at a temperature greater than the condensation temperature; if not, water vapour will condense at the coldest points and modify the moisture content of the gas sample.

5.3 Equilibrium temperature approach

If the quantity of water conveyed to the mirror per unit time is small, the mirror shall be cooled as slowly as possible because of the risk of greatly exceeding the actual condensation temperature without observing the first deposit.

The quantity of dew which can normally be observed with the naked eye is about 10^{-5} g/cm². Automatic devices, if very sensitive, can detect considerably lower quantities of water.

If a manual device is necessary, and especially for lower dew points, the following precautions shall always be taken :

- a) The mirror cooling rate shall be as small as possible in the condensation temperature range. (It is good practice to carry out a rapid test to determine the approximate condensation temperature before an accurate measurement is made.)
- b) The mean value of the temperature measured at the time of first dew appearance, while the mirror temperature slowly decreases, and of the temperature at which dew disappears, while the mirror temperature slowly increases, may be considered as the approximate dew point.

1) If a filter is used, even if it is stated to be non-hygroscopic, it should be in equilibrium with the water vapour content of the gas; this is obtained by allowing gas to flow through it for a period of time before the test at a rate considerably higher than that to be used during the test.

The difference between the temperature of appearance and disappearance should not be greater than 2 °C in the case of automatic apparatus and not greater than 4 °C in the case of manual apparatus.

6 Elimination of hydrocarbon condensates

If the hydrocarbon dew point is below the water vapour dew point, no special problem is presented. In the opposite case, as much hydrocarbon condensate as possible must be trapped before measurement is carried out; this assumes that it is condensed and removed from the mirror and from the measuring cell.

6.1 Condensation on the mirror

This can be achieved by fitting a device (or "cap"), of an appropriate shape, specified by the manufacturer, onto the mirror and directing the gas onto it when it enters the measuring cell through a small-bore tube.

Since it is connected to it, the "cap" is at a temperature close to that of the mirror, but slightly higher because it is heated by the incoming test gas.

6.2 Removal of condensates from the mirror

It is essential to aid the removal of the hydrocarbon condensates. This is even more important if the mirror is fitted with a cap.

This can be achieved by positioning the mirror vertically, or at least by giving it a marked inclination, and by fitting the mirror with a part which projects at its lower point. This projecting part may be the cap itself.

The hydrocarbon condensate thus flows permanently across the mirror and forms a drop on the projecting part; this assists its removal. This drop falls from time to time and flows to the bottom of the cell. It can also, if necessary, be re-evaporated in certain cases, for example at the time of calibration.

6.3 Removal of condensates from the cell

Condensates flowing from the mirror shall be removed from the cell.

This may be done by placing the measuring cell outlet at its lowest point. Condensates then vaporize into the discharge pipes.

7 Accuracy

Over a measuring range from - 25 °C to + 5 °C, the dew point is generally measured with an accuracy of ± 1 °C when using an automatic device. With a manual device, accuracy depends on the hydrocarbon content and, in most cases, an accuracy of ± 2 °C may be obtained.

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Annex

Correction of water dew point

(This annex forms part of the Standard.)

If the gas contains methanol, this will deposit with the water and a joint dew point will be obtained for water and methanol. The following table indicates the correction for methanol to be deducted from the measured dew point to obtain the true water dew point.

Table — Corrections to be deducted from water dew points in the presence of methanol

Methanol content mg/m ³	Pressure bar	Uncorrected dew points, °C			
		-10	-5	0	5
250	15	1	1	0,5	0,5
250	30	2	1,5	1	0,5
250	40	3	2	1,5	1
250	55	4	3	2	1,5
250	70	4,5	3,5	3	2
400	15	1,5	1	1	0,5
400	30	3,5	3	1,5	1
400	40	5	4	2	1,5
400	55	6,5	4,5	3,5	2
400	70	8	5,5	4	3

NOTE — The values given in this table have been determined by conversion into metric units of the figures given in table 2 of the "British Gas analytical methods" publication 2.5.1, October 1971.

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