Comparison of hygrometers for monitoring of water vapour in natural gas

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A R T I C L E   I N F O

A B S T R A C T

Hygrometers for monitoring of water vapour (moisture) in natural gases were compared with respect to accuracy, long term stability and response time. The hygrometers were based on capacitor sensor, quartz crystal microbalance (QCM), electrolytic cell, fibre-optic sensor and conversion of water to ethyne with calcium carbide (CaC_2-GC), respectively. In the latter technique, ethyne was quantified by a gas chromatograph (GC). Monitoring of water vapour concentrations between 20 μmol/mol and 120 μmol/mol was carried out in the laboratory, using nitrogen as the matrix gas. The capacitor hygrometers and the electrolytic cell hygrometer tested in this work showed a tendency to drift, which reduced their accuracy. The QCM, fibre-optic and CaC_2-GC hygrometer showed good accuracy and long term stability. The QCM hygrometer had the overall shortest response times. The results demonstrated the need for careful quality control of the hygrometers, and monitoring systems which are thoroughly fitted to the requirements of individual natural gas applications.

1. Introduction

1.1. Background

Accurate determination of water vapour in natural gases, often referred to as moisture, is crucial for maintaining a stable and safe processing and transport of natural gas. These are important reasons why natural gas producers have a defined moisture specification in their sales contracts. The moisture specification is often expressed as a water dew point. Underestimating the moisture concentration in the natural gas can lead to condensation of liquid water in process equipment or pipelines. Condensed water will increase the corrosion potential when combined with compounds such as hydrogen sulphide and carbon dioxide (Mychajliw, 2002). Another possible consequence of underestimation of moisture is the formation of gas hydrates (Jamieson and Sikkenga, 1986). Gas hydrates can plug pipelines or process units, resulting in loss of production or obstructed transportation of natural gas.

Even though analysis of moisture in various gases has been performed for more than 50 years, this is still regarded as one of the most challenging trace gas analyses. One important reason for this is the high polarity of water making it extremely adsorptive. Consequently surfaces regarded as dry are usually coated with a thin film of moisture (Carr-Brion, 1986; Knight and Weiss, 1962).

The abundance of water in the atmosphere also makes trace analysis challenging, with high potential for background moisture interference.

In this work several devices for monitoring of moisture in gases, referred to as hygrometers, more or less frequently used in natural gas business were compared. The focus was to investigate and compare the performance of the hygrometers, mainly with respect to accuracy, long term stability and response time. The range of moisture concentration examined was (20–120) μmol/mol, which is a relevant range for many natural gas applications. For practical and safety reasons, the measurements were performed in the laboratory at ambient conditions using nitrogen as the matrix gas.

1.2. Measuring techniques

Throughout the years numerous methods for moisture measurements in gases have been developed and established. Most of them are thoroughly described in published literature (Blakemore et al., 1986; Bruttel and Regina, 2006; Carr-Brion, 1986; Funke et al., 2003; ISO, 1993a,b; Keidel, 1959; Knight and Weiss, 1962; McAndrew and Boucheron, 1992; McAndrew, 1997; Monroe, 1998; Wiederhold, 1997, 2000; Willsch et al., 2005). Hygrometers based on capacitor sensor, quartz crystal microbalance (QCM), electrolytic cell, fibre-optic sensor, CaC_2-GC, chilled mirror and Karl Fischer titration have been investigated in this work. The basic principles for these methods are briefly summarised in Table 1. Karl Fischer titration and chilled mirror hygrometry

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Table 1
Summary of methods for moisture measurements in gases.

Method	Typical uncertainty	Working principle
Capacitor sensor	(1–3) °C	Capacitance or impedance measured as a function of water molecules adsorbed to the porous dielectric (usually metal oxides like Al_2O_3 or SiO_2) of a capacitor (Carr-Brion, 1986; Funke et al., 2003; McAndrew and Boucheron, 1992; McAndrew, 1997; Wiederhold, 1997).
Quartz crystal microbalance (QCM)	±10%	Measures the resonance frequency of an oscillating quarts crystal (piezoelectric) coated with a hygroscopic polymer. The frequency changes with mass as water molecules adsorb on the quartz crystal (Blakemore et al., 1986; Carr-Brion, 1986; Funke et al., 2003; McAndrew and Boucheron, 1992; McAndrew, 1997; Wiederhold, 1997).
Electrolytic cell	±10%	Measures current generated from electrolytic decomposition of water adsorbed in strongly hygroscopic P_2O_5 (Keidel, 1959).
CaC₂-GC	±10%	Conversion of water molecules to ethyne with CaC_2, followed by gas chromatographic (GC) separation and detection with e.g. a thermal conductivity or a flame ionisation detector (Knight and Weiss, 1962; Monroe, 1998).
Fibre-optic sensor	±2 °C	Measures a shift in reflection spectrum dependent on the amount of adsorbed water in a hygroscopic Fabry-Perot filter. "Fibre-optic" in the sense that light is emitted and reflected via fibre-optic cables (Willsch et al., 2005).
Karl Fischer titration	±10%	The Karl Fischer reaction: $ROH + SO_2 + R'N \rightarrow (R'NH)SO_3R$ $(R'NH)SO_3R + 2R'N + I_2 + \textbf{H}_2\textbf{O} \rightarrow (R'NH)SO_4R + 2(R'NH)I$ ROH = alcohol, R′N = basic nitrogen compound For coulometric titration the amount of water is calculated by measuring the current needed for the electrochemical generation of iodine (I_2) from iodide (I^-) (Bruttel and Regina, 2006; ISO, 1993a,b).
Chilled mirror	±0.1 °C	Measures the temperature at which water molecules condense from the gas to form dew or frost on a mirror surface (Wiederhold, 1997, 2000).

are usually regarded as direct or absolute methods as they utilise a direct relationship between the measured quantity and the amount of moisture. Hence they often are preferred as reference methods.

1.3. Interpretation of moisture measurements

The amount of moisture in a natural gas can either be expressed as concentration (e.g. µmol/mol or mg/Sm³ at some defined standard temperature and pressure) or as dew or frost point in degrees Celsius. The dew point is the highest temperature, at a specified pressure, where water can condense from the gas. The frost point is the highest temperature, at a specified pressure, where ice can precipitate from the gas (Løkken et al., 2008). In the temperature region between 0 °C and −20 °C it is difficult to predict whether the moisture will condense as dew or precipitate as ice. It is necessary to distinguish between the dew point and the frost point, as these could deviate with several degrees for the same moisture concentration. Accurate formulas for conversion between dew or frost point at atmospheric pressure and concentration (via saturation vapour pressure) are published by Sonntag (Sonntag, 1990, 1994). The following formula converts frost point to saturation vapour pressure:

For the given temperature range

$$173.15 \text{ K} \leq T_K \leq 273.16 \text{ K} \quad (-100\,°C \leq T_C \leq 0.01\,°C)$$

$$\ln e_i(T_K) = -6024.5282 T_K^{-1} + 24.7219 + 1.0613868 \times 10^{-2} T_K$$
$$- 1.3198825 \times 10^{-5} T_K^2 - 0.49382577 \ln T_K, \quad (1)$$

$e_i(T_K)$ is the saturation vapour pressure with respect to ice in hPa (hectopascal), T_K is frost point temperature in K.

Saturation vapour pressure can be converted to frost point by formula (2), which is derived from equation (1):

$$T_K = 12.1197y + 5.25112 \times 10^{-1} y^2 + 1.92206 \times 10^{-2} y^3$$
$$+ 3.84403 \times 10^{-4} y^4 + 273.15 \quad (2)$$

In the conversion formula (2)

$$y = \ln(e_i(T_K)/6.11153) \quad (3)$$

For conversions between saturation vapour pressure and concentration the following formula can be used:

$$c_w = \frac{e_i(T_K) \times 10^6}{1013.26}, \quad (4)$$

c_w is concentration in µmol/mol. At elevated pressures the formulas of Sonntag are not applicable because of increasing non ideal behaviour of the gas.

Conversion between moisture concentration and dew point at elevated pressure has traditionally been performed by use of the correlation charts from McKetta and Wehe (1958) or by the formulas of Bukacek (1955). The methods are based on empirical data produced between the years of 1927 and 1955. The conversions always relate the moisture concentration to condensed water (dew), despite the thermodynamic most stable phase in the lower temperature regions being gas hydrates or ice (dependent of the pressure and temperature). These methods have gained widespread use when it comes to calculations of the moisture concentration or the dew point of unprocessed natural gas, and they have been important for design of dehydration processes.

The hygrometers returning dew or frost points as their primary unit of measurement are usually calibrated at ambient pressure using a high precision chilled mirror as the reference. The calibration process will start at the lowest moisture concentration, typically cooling the mirror to well below −40 °C, to make sure the temperature reading relates to ice. When ice is formed on the mirror surface, the condensed water phase will remain as ice until the mirror temperature increases to 0 °C again. As a consequence these hygrometers will return frost points for negative temperatures and dew points for positive temperatures. Converting frost points or dew points to concentration at atmospheric pressure is easy using Sonntag's formulas ((1)–(3)). Conversion utilising the chart of McKetta and Wehe or the formulas of Bukacek, should only be performed on dew points (≥0 °C). The errors involved using these methods directly on frost points (<0 °C) will increase as the temperature decrease.

Thermodynamic modelling is often a preferred alternative for calculating equilibrium water content of natural gas. In contrast to charts and simple formulas thermodynamic models usually have the possibilities of covering a broad range of compositions, pressure and temperature ranges. The equations of state (EoS) traditionally