Determination of Water Content of Nitrogen Containing Hydrogen Sulfide by Karl Fischer Coulometric Titration

Xuting ZHI,* Haifeng WANG,**† Baijun LIU,* Xiaoping SONG,** Zhanyuan LI,** and Jia LI**

* China University of Petroleum-Beijing, Beijing, 102249, China
** National Institute of Metrology of China, Beijing, 100029, China
† To whom correspondence should be addressed.

E-mail: wanghf@nim.ac.cn
Abstract

Measurement of water content in natural gas is important for the safety; however, the complex matrixes make the results inaccurate. Natural gas contains hydrogen sulfide (H₂S) which reacts with iodine (I₂), causing Karl Fischer coulometric titration (KFCT) to give higher results. The KFCT method for the determination of water content of nitrogen containing H₂S was investigated. A chilled mirror hygrometer offered the reference water content to calibrate the KFCT. The interfering of H₂S was reduced by the subtraction of I₂ consumed by H₂S according to the reaction mechanism of ISO 10101; however, the modified results remained higher. A possible reaction mechanism with a stoichiometry of H₂S to I₂ of 1: 2.5 was proposed. The improved KFCT method had an error of water content no more than (3+2%·x) mg/kg (x, water content in mg/kg) and had a potential of online monitoring of natural gas.

Keywords: natural gas, water content, Karl Fischer coulometric titration, hydrogen sulfide
Introduction

Water can combine with contaminants in natural gas, such as hydrogen sulfide (H₂S) and carbon dioxide (CO₂), to create acid, which accelerates corrosion of pipelines and associated equipment. Ice and methane hydrate formed at high pressure and low temperature can reduce or even block pipeline flow; therefore, all countries specify the limit of water content or dew point of natural gas. In China, the dew point of natural gas transported through pipeline should be 5 °C lower than the temperature of the surrounding environment. In the United States, the water content of natural gas should be no more than 112 mg/m³ (about 157 mg/kg). However, the dehydration of natural gas requires both energy and chemical reagents. To ensure both operational safety and economic efficiency, the water content of natural gas should be determined accurately. There are two types of analyzers for the determination of the water content or dew point of natural gas. The first is the chilled mirror hygrometer (CMH) which is used to determine the dew point or frost point (FP) of natural gas, and the second is the water content analyzers or moisture analyzers which include those based on Karl Fischer titration (KFT), capacitance-based sensors, quartz crystal microbalances (QCM), electrolytic-based sensors, and tunable diode laser absorption spectroscopy (TDLAS). The frost point and water content can be converted to each other.

For the CMH, the liquid of hydrocarbons formed at low temperature might interfere with the determination of the water dew point. Furthermore, ethylene glycol, a common dehydrating agent of natural gas, with a concentration of less than 1 μmol/mol, results in an obvious error of dew point. Ethylene glycol also results in an irreversible shift of analyzers based on capacitance-based sensors and QCM. Besides ethylene glycol, the electrolytic-based sensor is also affected by oxygen and hydrogen.

KFT methods, including coulometry and volumetry, are widely used for determination of
the water content of liquid and solid samples, as well as gas samples.\textsuperscript{4, 5, 12-17} In Karl Fischer reaction, water reacts with iodine (I\textsubscript{2}) according to the stoichiometry of 1: 1, and thus the amount of water in the analyte is equal to that of I\textsubscript{2} which is calculated through electric quantity according to \textit{Faraday}'s law.\textsuperscript{13} Karl Fischer coulometric titration (KFCT) is a direct method, therefore it is regarded as not only the reference method,\textsuperscript{11} but also an international standard method (ISO 10101) for determination of water content in natural gas.\textsuperscript{4, 5} Hydrogen sulfide (H\textsubscript{2}S) and mercaptan (RSH) in natural gas can be oxidized by iodine during Karl Fischer titration, causing higher water content.\textsuperscript{5} As specified by ISO 10101, iodine consumed by H\textsubscript{2}S and RSH can be subtracted from total iodine consumed, by which the modified water content can be achieved.\textsuperscript{5} However, when the content of sulfur is more than 20\% of the water content, the residual systematic error is too big to be neglected, and thus this method is not recommended.\textsuperscript{5} The systematic error of water content of natural gas determined by the KFCT method remains to be explored. Although KFCT is a direct method, the recovery of water is affected by the current density of electrolysis and the side reaction such as Bunsen reaction.\textsuperscript{18, 19} In the determination of water content of liquid and solid samples, the home-made water standard prepared by the gravimetry was used to calibrate KFCT to make the result traceable and accurate.\textsuperscript{19, 20} Up to now, there is no report on the calibration of KFCT for the determination of water content of gas sample.

The lack of the accurate determination of the water content of natural gas leads to the inconsistency of results determined by analyzers based on different principles.\textsuperscript{9, 10} There remains an urgent need of an accurate determination of the water content of natural gas for the online monitoring and calibration.

In the present study, the KFCT method for the determination the water content of nitrogen containing H\textsubscript{2}S was investigated. The CMH offered the reference water content to calibrate the KFCT. The measured water contents by the KFCT were modified by the subtraction of I\textsubscript{2}
consumed by H$_2$S according to the reaction mechanism of ISO 10101; however, the modified results remained higher than the reference values. A possible mechanism of H$_2$S and iodine was proposed based on the experiment results. The KFCT method modified according to the proposed mechanism had an improved accuracy.

**Experimental**

*Reagents and chemicals*

Hydranal Coulomat AG Oven and Hydranal Coulomat CG (Honeywell, USA) was used as the anolyte and catholyte, respectively. A certified reference material (CRM) for H$_2$S in nitrogen was developed by National Institute of Metrology of China.

*Apparatus*

Fig. 1

A test rig of a mixed flow humidity generator of nitrogen containing H$_2$S was constructed as shown in Fig. 1. The nitrogen (>99.999% purity) flow from the gas cylinder (G-1) was split into three lines, one for the generation of water saturated gas (V-3) and the other two for the generation of dry gas (V-4 and V-5). At room temperature, the nitrogen was bubbled through water in the glass cylinder with a volume of 25 mL (E-1) for saturation. The saturated gas was mixed with the dry gas from the molecular sieve drier (E-2) for the generation of primary humid gas. The proportion of the saturated gas and the dry gas was regulated through their flowrates. Part of primary humid gas was mixed with the dry gas from the molecular sieve drier (E-3) for the generation of second humid gas. The proportion of the primary humid gas and the dry gas
was regulated through their flowrates and thus the second humid gas with a frost point ranging from -60 °C to -20 °C was generated. The room temperature was kept about 25 °C. The second humid gas was subsequently mixed with the CRM of H\textsubscript{2}S in nitrogen with a certified concentration of 307 μmol/mol (G-2). The proportion of the second humid gas and the CRM of H\textsubscript{2}S in nitrogen was regulated through their flowrates and thus the concentration of H\textsubscript{2}S of the mixed gas ranged from 0 to 50 μmol/mol. The final humid nitrogen containing H\textsubscript{2}S was split into three lines, one for the CMH (H-1), one for the KFCT (H-2) and one for ventilation.

**Instrument**

A CMH (H-1, 373 LX, MBW Co., Switzerland) was used to measure the frost point of gas. A Karl Fischer coulometric titrator (H-2, 875, Metrohm AG, Switzerland) was used to measure the water content of gas. An electrolysis electrode with a diaphragm was used to generate iodine through the electrolysis. A flowmeter (GSC-B9KS-BB26, Voeglin, Switzerland) was used to measure the flowrate of the sample and carrier gas.

**Analytical methods**

The KFCT method was performed as described below. First, the carrier gas of dried nitrogen was fed into the titrator to drive off the residual water in the pipeline, valves and titration cell, and simultaneously the electrolysis electrode started to generate iodine. As the iodine reacted with the residual water, the drift decreased gradually. Second, when the drift was no more than the start drift, namely 2 μg water per min (μg/min), the sample gas was fed into the titrator at a flowrate of 400 mL/min. The drift increased abruptly, indicating the rate of generation of iodine increased greatly. Third, after 1.00 g of sample gas was fed into the titrator, the carrier gas of dried nitrogen was again fed to drive off the residual water in the pipeline and
titration cell. When the drift was no more than 5 μg/min, the titration was terminated.

The measured water content ($x_1$) was calculated using the mass of sample gas, the start drift, time of titration and the amount of iodine. The saturation vapor pressure over ice ($e_i(FP)$) was calculated using $x_1$ (Eq. 1).

$$e_i(FP) = \frac{101325 \times 28.013x}{18.015}$$  \hspace{1cm} (1)

where, $e_i(FP)$ is the saturation vapor pressure over ice, Pa; $FP$ is the frost point, K; 101325 Pa is the standard atmospheric pressure; 28.013 g/mol is the molecular weight of nitrogen; $x$ is the water content of nitrogen, mg/kg; 18.015 g/mol is the molecular weight of water.

$s_i(FP)$ and $FP$ can be converted to each other using the formula developed by Sonntag (Eq. 2).\(^{21}\)

$$\ln e_i(FP) = -6024.5282FP^{-1} + 29.32707 + 1.0613868 \times 10^{-2}FP - 1.3198825 \times 10^{-5}FP^2 - 0.49382577 \ln FP$$  \hspace{1cm} (2)

ISO 10101 reported that H$_2$S reacts with iodine, and thus hydrogen iodide (HI) and sulfur (S) are produced, as shown in Eq. 3.\(^5\)

$$H_2S + I_2 \rightarrow 2HI + S$$  \hspace{1cm} (3)

According to the stoichiometry of H$_2$S to I$_2$ (1:1) (Eq. 3), the contribution of iodine consumed by H$_2$S was subtracted from the measured water content ($x_1$) to give the modified value ($x_2$) (Eq. 2).\(^5\)

$$x_2 = x_1 - 0.643C_{H_2S}$$  \hspace{1cm} (4)

where, $x_2$ is the water content after modification of H$_2$S, mg/kg; $x_1$ is the measured water content, mg/kg; 0.643 is the ratio of the molecular weight of water (18.015 g/mol) to that of nitrogen (28.013 g/mol); and $C_{H_2S}$ is the concentration of H$_2$S of nitrogen, μmol/mol.

The water content converted from the frost point by the CMH according to Eq. 1 and Eq. 2
was used as the reference value \(x_{\text{ref}}\) to calibrate the KFCT.\(^{21}\)

**Results and Discussion**

*Calibration of Karl Fischer coulometric titration*

The water content results were affected by the sample mass, sample gas flowrate and start drift. The optimized KFCT was performed using a sample mass of 1.00 g, a sample gas flowrate of 400 mL/min and a start drift of 2 μg/min. Furthermore, during a series of measurements, methanol was added to keep the volume of the anolyte constant.

Compared with the reference water content by CMH, the recovery of the water content and the error of the frost point at varied frost points were achieved (Fig. 2).

As shown in Fig. 2, when the measured frost point of humid nitrogen was -54.1 °C, -40.9 °C, -34.2 °C, -26.9 °C and -16.4 °C, the recovery of water content (its standard deviation) was 89.2% (4.1%), 111.6% (1.0%), 115.1% (1.8%), 117.5% (1.2%) and 120.7% (0.6%), respectively, and the error of the frost point was -0.92 °C, 0.97 °C, 1.29 °C, 1.61 °C and 2.01 °C, respectively. Løkken reported that the frost point determined using KFCT was higher than that using the CMH.\(^{6}\) The results above indicate that the recovery of water content and the error of the frost point increased with increasing water content. After the termination of titration, trace water might remain in the titration cell. As the water content of the analyte increases, the proportion of residual water to the total water decreased, which results the recovery of water content increased.

As the water content increased, its relative standard deviation decreased (Fig. 2). The
relative standard deviation (1.0%–4.1%) at a range of frost point from -54.1 °C to -40.9 °C was close to that reported by Løkken (2.15% at a FP of -47.7°C).\textsuperscript{7}

The KFCT for gas has obvious errors that could not be explained well and reduced at present. Although it is a direct method, it should be calibrated using the CMH to make the water content result traced to the International System of Unit (SI unit) of humidity. The data of water content recovery versus measured frost point was fitted to a polynomial function with a polynomial order of 3 (Eq. 5).

\[ Rec = 1.459 + 2.77 \times 10^{-2} \, FP + 9.46 \times 10^{-4} \, FP^2 + 1.160 \times 10^{-5} \, FP^3 \quad (5) \]

where, \( Rec \) is the recovery of water content; \( FP \) is the measured frost point converted from the measured water content, °C.

**Water content of nitrogen containing H\(_2\)S**

The humid nitrogen containing H\(_2\)S was determined by the KFCT and the CMH simultaneously. Fig. 3 shows the relative error of measured water content of the humid nitrogen containing H\(_2\)S with a concentration of 5.37 μmol/mol at varied frost points (\( \Delta x(x_1) \)), namely the ratio of error to \( x_{\text{ref}} \). As the frost point ranged from -51.27 °C to -15.30 °C, namely the water content from 21.33 to 1022.13 mg/kg, \( \Delta x(x_1) \) decreased from 41.1% to 22.2% (Fig. 3). These positive errors were contributed to the side reaction of H\(_2\)S and iodine.\textsuperscript{5} When the frost point of nitrogen increased, \( \Delta x(x_1) \) decreased because of a decrease of the proportion of iodine consumed by H\(_2\)S.
Figure 4 shows $\Delta r(x_1)$ of the humid nitrogen with a frost point of about -40 °C at varied concentrations of H$_2$S. As the concentration of H$_2$S ranged from 5.37 to 50.49 μmol/mol, $\Delta r(x_1)$ increased from 27.7% to 128.9% (Fig. 4). These positive errors were also because of side reaction of H$_2$S and iodine.\textsuperscript{5} When the concentration of H$_2$S increased, $\Delta r(x_1)$ increased because of an increase of the proportion of iodine consumed by H$_2$S.

The systematic error due to the side reaction of H$_2$S and iodine can be partly reduced by the modification using Eq. 4 and thus the modified water content ($x_2$) was calculated. The frost point ($FP_2$) converted from $x_2$ was substituted into Eq. 5, by which the recovery of the water content ($Rec$) was achieved. Finally, $x_2$ was modified by this recovery ($Rec$) and thus the water content after modification of H$_2$S and recovery ($x_3$) was achieved. For nitrogen containing H$_2$S with a concentration of 5.37 μmol/mol, as the frost point ranged from -51.27 °C to -15.30 °C, the relative error of $x_3$ ($\Delta r(x_3)$) decreased from 25.2% to -1.13% (Fig. 3). Compared with the measured water content ($x_1$), $x_3$ had an improved accuracy. However, for the nitrogen with a low frost point (-51.27 °C), $\Delta r(x_3)$ (25.2%) remained high (Fig. 3), limiting the applicability of KFCT for natural gas with a low water content. For humid nitrogen with a frost point of about -40 °C, as the concentration of H$_2$S increased from 5.37 to 50.49 μmol/mol, $\Delta r(x_1)$ increased from 8.97% to 60.36% (Fig. 4), which limits the applicability of KFCT to natural gas containing a high concentration of H$_2$S.

**Reaction Mechanism of H$_2$S and iodine**

It is well known that, in aqueous solution, H$_2$S is oxidized to sulfur by iodine as shown in Eq. 3. ISO 10101 regards Eq. 3 to still be applicable in the anhydrous Karl Fischer anolyte;\textsuperscript{4,5} thus, the stoichiometry of H$_2$S to I$_2$ remains 1: 1. Bruttel \textit{et al.} reported that H$_2$S is oxidized to sulfur by iodine, but the reaction of H$_2$S and iodine does not occur stoichiometrically.\textsuperscript{22} However, there is no experimental results supporting the mechanism of H$_2$S and iodine in...
anhydrous Karl Fischer anolyte as shown in Eq. 3.

The elementary sulfur, the predicted product of the reaction shown in Eq. 3, will make the anolyte cloudy and cause the polarity potential to be less than the equilibrated one (70 mV) because of its polarization. In fact, after more than forty times of measurements, a 150-mL fresh anolyte turns cloudy and the polarity potential is stably less than 70 mV, which indicate the formation of elementary sulfur. Therefore, during the forty times of measurements, there seemed no elementary sulfur formed in the anolyte, namely H$_2$S and iodine might not undergo the reaction as shown in Eq. 3.

The results above showed that the modified water content ($x_3$) was higher than the reference value, especially for nitrogen with a low water content (Fig. 3) or a high concentration of H$_2$S (Fig. 4), which indicates that the actual stoichiometry of H$_2$S to I$_2$ should differ from 1:1.

For the sample with a high concentration of H$_2$S and a low water content, most iodine is consumed by H$_2$S, therefore the ratio of the amount of H$_2$S to I$_2$ consumed by H$_2$S is close to the true stoichiometry of H$_2$S to I$_2$. As shown in Table S1 (Supporting Information), for nitrogen containing a 50.49 μmol/mol of H$_2$S and a frost point of -54.06 °C (a water content of 15.00 mg/kg), the measured water content ($x_1$) was 95.30 mg/kg. In other words, 1 g of the sample consumed 5.29 μmol of I$_2$ (Eq. 6), in which the contribution of water and H$_2$S was 0.83 and 4.46 μmol, respectively (Eq. 7 and 8). 1g nitrogen contained 1.80 μmol of H$_2$S (Eq. 9). Therefore, the ratio of amount of H$_2$S to I$_2$ consumed by H$_2$S was 1: 2.48 approximate to 1: 2.5 which is very different from that of 1: 1. Similarly, for nitrogen with a frost point about -52 °C and a concentration of H$_2$S of 5.37, 14.19, 20.41 and 30.12 μmol/mol respectively, the ratio of amount of H$_2$S to I$_2$ consumed by H$_2$S was 1: 2.54, 1: 2.54, 1: 2.43 and 1: 2.42, respectively (Table S1). These findings indicate that in the anhydrous Karl Fischer anolyte, H$_2$S and I$_2$ might undergo a reaction with a stoichiometry of 1: 2.5.
In aqueous solution without sulfur dioxide (SO$_2$), H$_2$S reacts with I$_2$, leading to the formation of elementary sulfur (Eq. 3). However, in anhydrous Karl Fischer anolyte with a high concentration of base, monomethyl sulfite ([RNH]SO$_3$CH$_3$) formed from SO$_2$, H$_2$S might react with [RNH]SO$_3$CH$_3$, and then elementary sulfur and water formed as shown in Eq. 10. The product of water would react with [RNH]SO$_3$CH$_3$ and I$_2$ according to Karl Fischer reaction as shown in Eq. 11. The product of elementary sulfur probably reacts with [RNH]SO$_3$CH$_3$ and I$_2$ according to Eq. 12, leading to a formation of base, monomethyl trithionic ([RNH]S$_3$O$_6$CH$_3$). As a result, the overall reaction equation is shown as Eq. 13, which indicates that the stoichiometry of H$_2$S to I$_2$ is 1: 2.5.

$$\frac{95.30\text{mg/kg} \times 1\text{g}}{18.015\text{g/mol}} = 5.29\mu\text{mol} \quad \text{(Eq. 6)}$$

$$\frac{15.00\text{mg/kg} \times 1\text{g}}{18.015\text{g/mol}} = 0.83\mu\text{mol} \quad \text{(Eq. 7)}$$

$$5.29 - 0.83 = 4.46\mu\text{mol} \quad \text{(Eq. 8)}$$

$$\frac{50.49\mu\text{mol/mol} \times 1\text{g}}{28.013\text{g/mol}} = 1.80\mu\text{mol} \quad \text{(Eq. 9)}$$

$$2\text{H}_2\text{S} + [\text{RNH}]\text{SO}_3\text{CH}_3 \rightarrow 3\text{S} + 2\text{H}_2\text{O} + \text{CH}_3\text{OH} + \text{RN} \quad \text{(Eq. 10)}$$

$$\text{H}_2\text{O} + [\text{RNH}]\text{SO}_3\text{CH}_3 + \text{I}_2 + 2\text{RN} \rightarrow [\text{RNH}]\text{SO}_4\text{CH}_3 + 2[\text{RNH}]\text{I} \quad \text{(Eq. 11)}$$

$$\text{S} + 2[\text{RNH}]\text{SO}_3\text{CH}_3 + \text{I}_2 + 2\text{RN} \rightarrow [\text{RNH}]\text{S}_3\text{O}_6\text{CH}_3 + 2[\text{RNH}]\text{I} \quad \text{(Eq. 12)}$$

$$2\text{H}_2\text{S} + 9[\text{RNH}]\text{SO}_3\text{CH}_3 + 5\text{I}_2 + 9\text{RN} \rightarrow 2[\text{RNH}]\text{SO}_4\text{CH}_3 + 3[\text{RNH}]\text{S}_3\text{O}_6\text{CH}_3 + \text{CH}_3\text{OH} + 10[\text{RNH}]\text{I} \quad \text{(Eq. 13)}$$

It should be noted that the reaction shown in Eq. 12 is hypothesized. So Eq. 12 and overall reaction (Eq. 13) remain to be validated by the composition analysis.
By the stoichiometry of H$_2$S to I$_2$ (1: 2.5) according to the proposed mechanism (Eq. 13), the contribution of iodine consumed by H$_2$S was subtracted from the measured water content ($x_1$), and then the water content after modification of H$_2$S ($x_4$) was achieved (Eq. 14).

$$x_4 = x_1 - 2.5 \times 0.643C_{H_2S}$$  \hspace{1cm} (14)

where, $x_4$ is the water content after modification of H$_2$S, mg/kg; $x_1$ is the measured water content, mg/kg; 2.5 is the stoichiometry of I$_2$ to H$_2$S; 0.643 is the ratio of the molecular weight of water to that of nitrogen; $C_{H_2S}$ is the concentration of H$_2$S of the sample, μmol/mol.

The modified frost point ($FP_4$) converted from $x_4$ was substituted into Eq. 5, after which recovery of the water content ($Rec$) was achieved. Finally, the $x_4$ was modified by the recovery ($Rec$) and thus the water content after modification of H$_2$S and recovery ($x_5$) was achieved. For the nitrogen containing H$_2$S with a concentration of 5.37 μmol/mol, as the frost point ranged from -51.27 °C to -15.30 °C, the relative error of $x_5$ ($\Delta(x_5)$) ranged from -1.48% to 4.6% (Fig. 3). For the humid nitrogen with a frost point of about -40 °C, as the concentration of H$_2$S ranged from 5.37 to 50.49 μmol/mol, $\Delta(x_5)$ ranged from 2.15% to 4.54% (Fig. 4). Compared with $x_3$, the accuracy of $x_5$ were obviously improved.

Fig. 5

Figure 5 shows the relative errors of water contents of the humid nitrogen with a frost point ranging from -54.1 °C to -15.3 °C and a concentration of H$_2$S ranging from 5.37 to 50.49 μmol/mol modified according to different reaction mechanisms ($\Delta(x_3)$ and $\Delta(x_5)$). Table S1 in Supporting Information shows all water contents and their relative errors, and frost points and their errors. The water contents modified according to the stoichiometry of H$_2$S to I$_2$ of 1: 1 have relative errors ranging from -1.13% to 280.9% (Fig. 5 and Table S1). Comparatively, those modified according to the stoichiometry of 1: 2.5 have relative errors ranging from -1.48% to
7.20% (Fig. 5 and Table S1). The frost points modified according to the stoichiometry of 1: 1 have errors ranging from -0.15 °C to 10.95 °C (Table S1). Comparatively, those modified according to the stoichiometry of 1: 2.5 have relative errors ranging from -0.29 °C to 0.50 °C (Table S1). Modification of the water content according to the proposed reaction mechanism (Eq. 13) gave the KFCT a better accuracy.

As shown in Table S1, for the nitrogen with a frost point ranging from -54.1 °C to -15.3 °C and a concentration of H$_2$S ranging from 5.37 to 50.49 μmol/mol, the error of the water content ($\Delta(x_5)$) was no more than $(3 + 2\% \cdot x) \text{ mg/kg}$ ($x$, the water content in mg/kg).

**Discussion**

Determination of the water content of gas by Karl Fischer volumetric titration was first reported in 1975. The application of KFCT was partly restricted by the inaccurate determination of gas volume and rather high drift before titration. Measurement using the commercial Karl Fischer coulometric titrator (875, Metrohm) equipped with a mass flowmeter employed a procedure that involved two rounds of purging with dried nitrogen, one before and one after titration, to drive off the residual moisture in the pipeline. Therefore, repeatable results can be acquired conveniently.

In present study, the calibration of KFCT using a CMH reduced its systematic error over a wide range of frost points. Additionally, modification of the water content based on a proposed mechanism reduced the systematic error from the side reaction of H$_2$S and iodine. The reduction of these two systematic errors makes the KFCT traceable and accurate.

The source of uncertainty of the modified KFCT might mainly come from the repeatability, the accuracy of the concentration of H$_2$S, the stability of the humidity generator and the accuracy of the CMH. The repeatability remains the major source of uncertainty, especially for gas with a low frost point or a high concentration of H$_2$S.
Natural gas usually contains not only H₂S, but also mercaptan. The reaction mechanism of mercaptan and iodine should be investigated. Additionally, the accuracy, stability and anti-interference of the KFCT method should be validated by the comparison with other water content analyzers online in actual natural gas pipelines. Such studies are currently being conducted.

Conclusions

In the present study, the KFCT was calibrated using a CMH, which ensured the water content results traceable. Humid nitrogen containing various concentrations of H₂S was then measured using the KFCT and the CMH. The measured results of the KFCT were obviously higher than the reference value from CMH because of the side reaction of H₂S and iodine. The results modified by the stoichiometry of H₂S to I₂ (1:1) according to the mechanism specified by ISO 10101 remained higher than the reference value. A possible reaction mechanism of H₂S and I₂ in the Karl Fischer anolyte was proposed. The water content modified by the stoichiometry of H₂S to I₂ of 1:2.5 according to the proposed mechanism had a better accuracy. The error of the water content of nitrogen with a frost point ranging from -54.1°C to -15.3°C and a concentration of H₂S ranging from 5.37 to 50.49 μmol/mol was no more than (3 +2%·x) mg/kg (x, the water content in mg/kg). The improved KFCT has the potential for monitoring the water content of natural gas online because of its good accuracy and anti-interference against H₂S.

Acknowledgements

This study was supported by the National Quality Infrastructure Program of China (Grant No.2017YFF0205300 and No. 2017YFF0205803) and the Ability Promotion Program of National Institute of Metrology of China (No. 31-ANL1814). We thank Jeremy Kamen, MSc,
Supporting Information

Table S1 (Supporting Information) shows the measured water content ($x_1$) and modified water content ($x_3$ and $x_5$), their relative errors ($\Delta_r(x_1)$, $\Delta_r(x_3)$ and $\Delta_r(x_5)$), the measured frost point ($FP_1$) and modified frost point ($FP_3$ and $FP_5$), and their errors ($\Delta(FP_1)$, $\Delta(FP_3)$ and $\Delta(FP_5)$). This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/.

References

1. J. Carroll, “Natural Gas Hydrates: a Guide for Engineers”, Second Ed., 2009, Elsevier, Burlington, USA.
2. GB 17820, Natural gas, GB, Beijing, China, 2012.
3. ISO 6327, Gas analysis – Determination of the water dew point of natural gas – Cooled surface condensation hygrometers, ISO, Geneva, Switzerland, 1981.
4. ISO 10101-1, Natural gas - Determination of water by the Karl Fischer method - Part 1: Introduction, ISO, Geneva, Switzerland, 1993.
5. ISO 10101-3, Natural gas - Determination of water by the Karl Fischer method - Part 3: Coulometric procedure, ISO, Geneva, Switzerland, 1993.
6. T. V. Løkken, J. Nat. Gas. Sci. Eng., 2012, 6, 24.
7. T. V. Løkken, J. Nat. Gas. Sci. Eng., 2012, 7, 7.
8. T. V. Løkken, J. Nat. Gas. Sci. Eng., 2013, 12, 13.
9. J. G. Gallegos, R. Benyon, S. Avila, A. Benito, R. M. Gavioso, H. Mitter, S. Bell, M. Stevens, N. Böse, V. Ebert, M. Heinonen, H. Sairanen, A. Peruzzi, R. Bosma, and M. Val’ková, J. Nat. Gas. Sci. Eng., 2015, 23, 407.
10. J. G. Gallegos, S. Avila, R. Benyon, G. McKeogh, and A. Stokes, *J. Nat. Gas. Sci. Eng.*, 2016, 31, 293.

11. ISO 18453, Natural gas – Correlation between water content and water dew point, ISO, Geneva, Switzerland, 2004.

12. K. Fischer, *Angew. Chem.*, 1935, 48, 394.

13. E. Scholz, “*Karl Fischer Titration*”, 1984, Springer Verlag, Heidelberg, Germany.

14. S. Inagaki, T. Asakai, M. Numata, N. Hanari, K. Ishikawa, K. Kitanaka, M. Hagiwara, and S. Kotaki, *Anal. Methods*, 2014, 6, 2785.

15. W. Liu, H. F. Wang, X. F. Gu, C. Quan, and X. H. Dai, *Anal. Methods*, 2016, 8, 2845.

16. R. J. Davies, *Analyst*, 1975, 100, 163.

17. H. R. Dong, *Anal. Sci.*, 2005, 21, 421.

18. H. Katoh, Y. Fujimoto, and M. Kakuda, *Anal. Sci.*, 1992, 8, 575.

19. H. F. Wang, K. Ma, W. Zhang, J. Li, G. H. Sun, and H. M. Li, *Food Chem.*, 2012, 134, 2362.

20. W. Liu, H. F. Wang, X. F. Gu, C. Quan, and X. H. Dai, *Anal. Meth.*, 2016, 8, 2845.

21. D. Sonntag, *Z. Meteorol.*, 1990, 40, 340.

22. P. Bruttel and R. Schlink, “*Water determination by Karl Fischer titration*”, Monography 8.026.5003, 2003, Metrohm Ltd, Herisau, Switzerland.
Figure Captions

Fig. 1 Schematic of the humid nitrogen containing H$_2$S generator. (G-1, nitrogen cylinder; G-2, reference material for H$_2$S in nitrogen; V-1 and V-2, pressure regulator; V-3, V-4, V-5, V-13 and V-14, valve; E-1, saturator; E-2 and E-3, molecular sieve drier; V-6 to V-12, mass flowmeter; H-1, chilled mirror hygrometer; H-2, Karl Fischer coulometric titrator)

Fig. 2 Water content recovery and error of frost point vs measured frost point by KFCT. Line in black and red is the fitted line of recovery and error of frost point versus measured frost point, respectively.

Fig. 3 Relative error of water content vs reference frost point of nitrogen containing H$_2$S with a concentration of 5.37 μmol/mol. Δr($x_1$), Δr($x_3$) and Δr($x_5$) is the relative error of measured water content ($x_1$) and modified water content ($x_3$ and $x_5$), respectively.

Fig. 4 Relative error of water content vs concentration of H$_2$S nitrogen with a frost point of about -40 °C. Δr($x_1$), Δr($x_3$) and Δr($x_5$) is the relative error of measured water content ($x_1$) and modified water content ($x_3$ and $x_5$), respectively.

Fig. 5 Relative error of water contents modified according to different mechanism vs concentration of H$_2$S and reference frost point. Δr($x_3$) and Δr($x_5$) is the relative error of modified water content, $x_3$ and $x_5$, respectively.
Fig. 1 Schematic of the humid nitrogen containing H\textsubscript{2}S generator.
Fig. 2 Water content recovery and error of frost point vs measured frost point by KFCT.
Fig. 3 Relative error of water content vs reference frost point of nitrogen containing H$_2$S with a concentration of 5.37 μmol/mol
Fig. 4 Relative error of water content vs concentration of H$_2$S of nitrogen with a frost point of about -40 °C.
Fig. 5 Relative error of modified water contents by two methods vs concentration of H$_2$S and frost point.