Rapid determination of ethylene glycol content in the produced water of coalbed methane wells by gas chromatography-mass spectrometry

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Abstract. In the process of gas field exploitation in cold regions, the formation of gas hydrate in the gas collection pipeline has always been a great technical difficulty. In order to effectively prevent the formation of gas hydrates in the gas collection pipeline, ethylene glycol is mainly injected into the pipeline as an inhibitor. In order to ensure the normal production of oil and gas wells and the optimal use of ethylene glycol, it is necessary to monitor the changes of ethylene glycol in the production process in real time. Due to the advantages of gas chromatography-mass spectrometry (GC-MS) such as separation efficiency and detection sensitivity, the content of ethylene glycol in the produced water of coalbed methane wells was tested by this method. The results showed that the precision of ethylene glycol samples with different concentrations prepared from produced water was 0.7%~2.1%, and the recovery rate was in the range of 98.5%~101.2%, which proved that the precision, repeatability and spike recovery rate of GC-MS were good, meeting the requirements of analysis and determination. The method and test conditions are used to detect the content of ethylene glycol in the produced water of YI3 well in Hancheng coalbed methane field. The results show that the method is simple, rapid and accurate, and can be used for real-time monitoring of the content of ethylene glycol in the produced water of a gas well.

Keywords: Gas chromatography-mass spectrometry (GC-MS) ; Ethylene glycol; Antifreeze; Produced water; Coalbed methane wells.

1. Introduction

The chemical formula of ethylene glycol is $(CH_2OH)_2$, also known as glycol, 1,2-ethylene glycol, referred to as EG, is the simplest diol[1]. It is a colorless, odorless, high boiling point and sweet liquid, which can dissolve with ethanol, water, acetone and so on, but its solubility in ethers is small[2]. Ethylene glycol can be used as a solvent, antifreeze, and raw material for the synthesis of polyester[3,4].It is toxic to the human body and can cause damage to the central nervous system and kidneys when excessive amounts enter the human body[5-8].

In the development and gathering process of conventional oil and gas reservoirs, unconventional coalbed methane reservoirs or shale gas reservoirs, under the condition of high pressure and low temperature, especially in the cold winter of the seabed and the north, the temperature is in the range of 0 °Cto about 20 °C below zero. It is easy to form natural gas hydrate when water and natural gas are mixed in the oil and gas gathering and transportation trunk line[9].Even under high pressure conditions, hydrates can be formed above 0 °C [10]. Natural gas hydrate composed of water molecules and gas molecules mainly composed of light hydrocarbons is a white solid material with ice-like crystals, which can easily cause the blockage of gas gathering pipeline equipment and affect the normal production of oil and gas fields. Hammerschmidt first discovered the phenomenon of hydrate blockage in the pipeline, and believed that the formation of hydrate blockage was related to pressure, temperature and gas-water composition[11]. Hydrate blockage usually occurs in low temperature and high pressure environment. Natural gas transportation pipeline is the main area where hydrate blockage occurs. In the process of gas transmission, due to the decrease of seawater temperature and long-distance transportation, the gas temperature in the pipeline will decrease and the pressure will increase, which is conducive to the formation of hydrate. Zhang et al. [12], Martín et al. [13], Lekvam et al. [14] predicted the formation conditions of natural gas hydrates. At present, by removing water[15], depressurizing control, pipeline heating[16], and injecting hydrate inhibitors[17], the problem of hydrate blockage in oil and gas pipelines can be effectively solved.

At present, the main measures to solve hydrate blockage in industry are to add hydrate thermodynamic inhibitors such as ethylene glycol and methanol in the mining process. Although methanol is cheaper than ethylene glycol, ethylene glycol is based on hydrate inhibition effect and is easier to recycle and reuse[18].In addition, considering the investment cost, the injection of ethylene glycol is considered to be more advantageous than methanol[19]. Therefore, the injection of ethylene glycol is widely used in industry. Reasonable ethylene glycol content can reduce equipment blockage, avoid ethylene glycol waste, and achieve the purpose of improving economic benefits. Therefore, it is necessary to monitor the changes of ethylene glycol in the process of gas reservoir development in real time.

2. The Mechanism of Ethylene Glycol Inhibiting Hydrate Formation

2.1 Intermolecular interactions

2.1.1 Altering thermodynamic conditions

There are interactions between ethylene glycol (EG) molecules and water molecules. During the formation of hydrates, certain thermodynamic conditions need to be met, including temperature, pressure, and chemical potential, etc. The addition of ethylene glycol molecules alters the chemical potential of water.

Ethylene glycol molecules reduce the tendency of water molecules to form the cage-like structures of hydrates through interactions such as forming hydrogen bonds with water molecules. The formation of hydrates is an exothermic process, according to Le Chatelier's principle, when ethylene glycol interacts with water molecules, it will change the energy distribution of the system, which is unfavorable for the formation of hydrates.

2.1.2 Altering kinetic conditions

From a kinetic perspective, the formation of hydrates requires water molecules to aggregate and arrange in a certain crystal structure. The presence of ethylene glycol molecules hinders the process of aggregation and arrangement of water molecules.

Ethylene glycol molecules are constantly in motion in the solution. They collide with and interact with water molecules, interfering with the process in which water molecules form an orderly crystal structure of hydrates, thus inhibiting the formation rate of hydrates.

2.2 Destruction of the Hydrogen Bond Network

2.2.1 Importance of the Hydrogen Bond Network

During the formation of hydrates, water molecules form regular cage-like structures through hydrogen bonds to encapsulate guest molecules. The stability of the hydrogen bond network is crucial for the formation of hydrates.

2.2.2 Destructive Effect of Ethylene Glycol

Ethylene glycol molecules contain multiple hydroxyl groups (-OH), which are able to form hydrogen bonds with water molecules. When ethylene glycol is added to water, it will form new hydrogen bonds with water molecules, thus disrupting the original hydrogen bond network among water molecules. This destructive effect makes it difficult for water molecules to form stable cage-like structures to accommodate guest molecules, and further inhibits the formation of hydrate crystal structures.

In conclusion, ethylene glycol effectively inhibits the formation of hydrates by altering the thermodynamic and kinetic conditions for hydrate formation and by disrupting the hydrogen bond network among water molecules.

3. Test part

3.1 Principle of the method

In this method, water samples were directly taken and imported into a gas chromatography column with an automatic sampler, and analyzed by gas chromatography-mass spectrometry[20-22].

3.2 Instruments and reagents

3.2.1 Instruments

7890B-5977B gas chromatography-mass spectrometer (Agilent, USA); electronic balance; 10 μL, 25 μL micro-syringe; 2 mL brown injection bottle, 10 mL volumetric bottle.

Chromatographic conditions: DB-624 chromatographic column, 30m long, inner diameter of 0.25 mm, film thickness of 0.25 mm; the carrier gas is high purity helium (99.999 %); the temperature of gasification chamber is 230 ℃; the detector temperature was 280 ℃. The column temperature was maintained at 50 ℃ for 1.0 min, and then increased to 220 ℃ at 15.0 ℃/min for 1.0 min. The injection volume was 1.5 μL.

3.2.2 Reagents

Ethylene glycol, analytically pure (99.9 %); dichloromethane; anhydrous sodium sulfate; t he sample to be tested: the produced water of YI3 in coalbed methane well before injectio n of antifreeze (Na^+: 1115.00 mg/L, K^+: 129.70 mg/L, Ca^{2+}: 159.30 mg/L, Mg^{2+}: 33.79 mg/ L, Cl^-: 1012.45 mg/L, SO_4^{2-}: 37.80 mg/L, HCO_3^-: 794.54 mg/L, OH^-: 0.0309 mg/L, total sal inity: 3282.61 mg/L).

4. Results and discussion

4.1 Establishment of standard curve

4.1.1 Preparation of standard solution

Sample pretreatment : 50.0 mL of the produced water sample was taken in the separation funnel, and 5.0 mL of dichloromethane was added. After shaking and standing, the lower organic phase was taken, and finally dehydrated with anhydrous sodium sulfate and analyzed on the machine.

Preparation of standard solution: 10.0 mg of ethylene glycol standard was accurately weighed in a 10.0 mL volumetric flask and diluted to the scale with dichloromethane to prepare a standard stock solution of 1000.0 μg/mL.

4.1.2 Establishment of standard curve

The working curves of 10.0, 20.0, 50.0, 100.0 and 200.0 μg/mL of ethylene glycol standard solution were prepared by drawing 10.0, 20.0, 50.0, 100.0 and 200.0 μg of ethylene glycol standard solution in 1.0 mL volumetric flask and constant volume to scale with dichloromethane. Each 1 mL of standard solution of different concentrations was added to the injection bottle. After the injection bottle was shaken well, 1.5 μL was taken and injected from low concentration to high concentration according to the steps specified in the standard, and the regression equation was calculated. The results are shown in Fig. 1.

The linear regression equation of ethylene glycol is f (x) = 2510x-14698, the correlation coefficient (R) = 0.9997744, the fitting degree (R^2) = 0.9995.

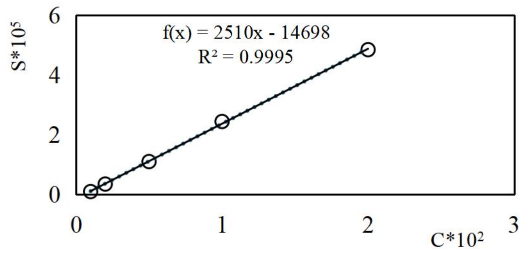

Fig. 1 Glycol standard curve

4.1.3 Standard test

Each 1.5 μL of five known concentration standard solutions was measured, and the samples were injected in turn according to the steps specified in the standard. The test results were substituted into the regression equation to calculate the concentration of ethylene glycol, and the calculation results were compared with the known concentration. The results are shown in Table 1. The standard deviation is less than 0.15, and the relative standard deviation is less than 1.4 %, which is within the allowable range of error, indicating that the standard curve established in this paper can be used for the next test.

Table 1. The results of the standard solution test

Sample number	Known ethylene glycol concentration/(μg/mL)	Tested ethylene glycol concentration/(μg/mL)	Average value/(μg/mL)	Standard deviation	RSD/%
1	5.19	5.34	5.27	0.08	1.4
2	10.20	10.48	10.34	0.15	1.4
3	18.68	18.75	18.72	0.04	0.2
4	25.42	25.38	25.35	0.07	0.3
5	32.65	32.41	32.53	0.12	0.4

4.2 Precision of the method

4.2.1 Precision test results

The produced water of coalbed methane wells with ethylene glycol concentrations of 10.25, 7.16, 12.20 and 5.61 μg/mL were prepared, and each 10.00 mL was placed in a 50 mL volumetric flask. Each sample was continuously injected for 6 times, each injection was 1.5 μL, and the determination was carried out according to the chromatographic conditions. The gas chromatography diagram of ethylene glycol concentration is shown in figure 2, and the concentration of ethylene glycol is calculated by the regression equation. The results are shown in table 2.

It can be seen from table 2 that the standard deviation is less than or equal to 0.15, the relative standard deviation is less than or equal to 2.1 %, which is within the allowable range of error (the standard deviation of gas chromatography analysis is less than 2 % ~ 3 %). This precision fully meets the analysis requirements and can be used for real-time monitoring of ethylene glycol content in produced water of coalbed methane wells.

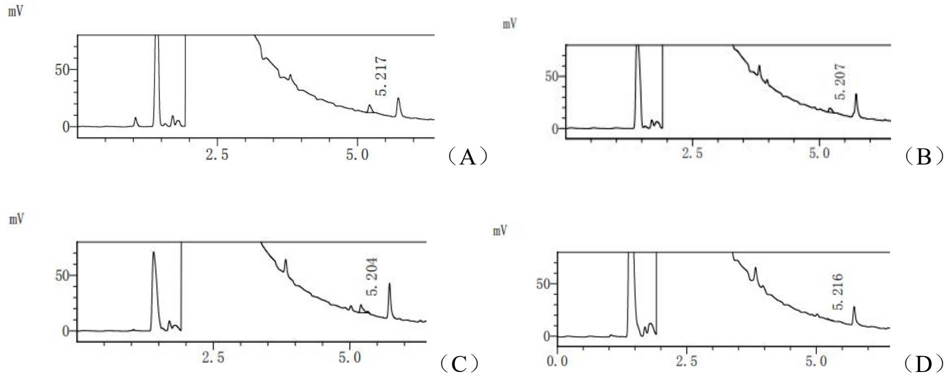

Fig. 2 Gas chromatogram of ethylene glycol at different concentrations

Table 2. Results of precision tests

Sample number	Ethylene glycol concentration /(μg/mL)						Average value /(μg/mL)	Standard deviation	RSD/%
A	10.28	9.95	9.89	9.92	10.22	10.15	10.07	0.15	1.5
B	7.19	7.01	7.21	7.15	7.09	7.24	7.15	0.08	1.1
C	12.23	12.15	12.08	12.28	12.11	12.06	12.15	0.08	0.7
D	5.64	5.38	5.51	5.68	5.49	5.72	5.57	0.12	2.1

4.2.2 Repeatability test results

The same batch of samples to be tested was taken and 6 copies were prepared respectively. According to the chromatographic conditions, the content of ethylene glycol was calculated by the regression equation. The repeatability results are shown in Figure 3.

As can be seen from table 3, the relative standard deviation is ≤ 2.4 %, which is within the allowable range of error. It shows that the method has good repeatability and can be used for real-time monitoring of ethylene glycol content in produced water of coalbed methane wells.

Table 3. Results of repeatability tests

Ethylene glycol concentration/(μg/mL)						Average value/(μg/mL)	RSD/%
6.75	6.79	6.51	6.96	6.58	6.52	6.69	2.4

4.2.3 Test results of recovery rate

A total of 6 samples with different ethylene glycol contents were prepared, 10 mL for each, and 1 mL standard solution (1000 μg ethylene glycol per 1 mL solution) was added accurately. The ethylene glycol content was measured according to the test method and the recovery rate was calculated. The results are shown in Table 4.

The results show that the relative standard deviation is less than 2.0 %, indicating that the test has good accuracy and can be used for real-time monitoring of ethylene glycol content in produced water of coalbed methane wells.

Table 4. Results of spiked recovery tests

Sample number	Ethylene glycol content in the sample/(μg)	Spiked/(μg)	Measured value after spiking/(μg)	Recovery /%	Average recovery/ %	RSD/%
1	117.91	1000.00	1116.22	98.6	99.6	1.2

2	117.91	1000.00	1117.15	99.4		
3	140.81	1000.00	1141.90	100.8		
4	140.81	1000.00	1142.51	101.2		
5	185.84	1000.00	1184.13	99.1		
6	185.84	1000.00	1183.09	98.5		

5. Sample measurement

Hancheng CBM field is located in the southeastern margin of Ordos Basin, Shaanxi Province, with an area of 1532 km^2. The overall structure of the gas field is monoclinic, the formation tends to the northwest, and the average temperature in winter is-3 °C. It is one of the main development zones of coalbed methane in China. The daily gas production of single well is mostly concentrated in 200 ~ 1000 m^3, and the casing pressure of gas well is generally less than 1 MPa. Due to the low temperature, in order to prevent the formation of natural gas hydrate and block the pipeline during the exploitation of coalbed methane wells in this area, it is necessary to add ethylene glycol as antifreeze. However, when the concentration of ethylene glycol is too low, if the antifreeze effect is not too high, it will cause waste. Therefore, it is necessary to monitor the content of ethylene glycol in the produced water of coalbed methane wells in real time. The average winter temperature in the Hancheng area is shown in Figure 4.

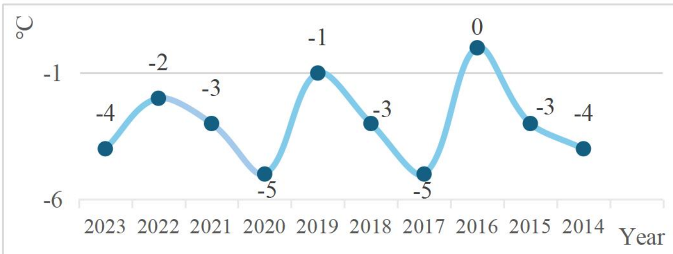

Fig. 4 The average winter temperature in the Hancheng area

On January 4,2023, antifreeze was injected into the coalbed methane well YI3. By detecting the ethylene glycol content in the produced water of the well, the changes of ethylene glycol concentration on the 3rd, 18th, 20th, 22nd and 36th days were recorded, and the changes of ethylene glycol content in the produced water with time were observed. The results are shown in Figure 5.

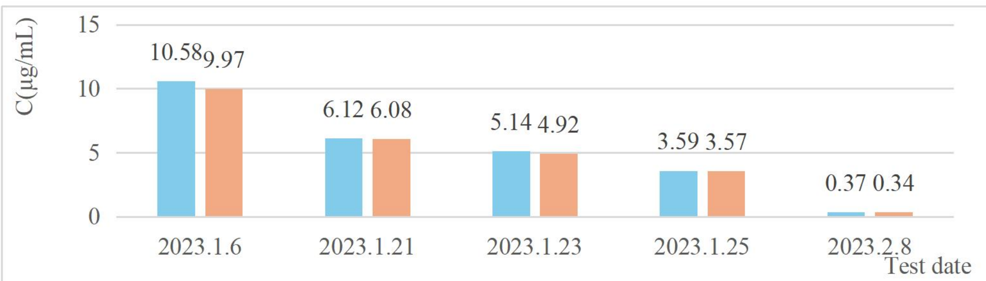

Fig. 5 Graph of Ethylene Glycol Concentration Variation over Time

From Table 5, it can be seen that the two parallel experimental results of each time period show that the sample has good parallelism, and the relative deviation is less than 4.23 %, which meets the test requirements. It was found that the concentration of ethylene glycol in the produced water of the coalbed methane well injected with ethylene glycol was reduced to 0.36 μg/mL on the 30th day. Combined with the actual situation, in order to ensure the smooth exploitation of coalbed methane wells, it is necessary to inject ethylene glycol antifreeze again in the near future.

Table 5. Real-time monitoring of ethylene glycol concentration changes

Detection time	Ethylene glycol concentration/(μg/mL)		Average value/(μg/mL)	Relative deviation/%
YI3(2023.1.6)	10.58	9.97	10.29	2.97
YI3(2023.1.21)	6.12	6.08	6.10	0.33
YI3(2023.1.23)	5.14	4.92	5.03	2.19
YI3(2023.1.25)	3.59	3.57	3.58	0.28
YI3(2023.2.8)	0.37	0.34	0.36	4.23

6. Conclusion

(1) Different concentrations of ethylene glycol samples were tested and analyzed. The test precision was calculated to be between 0.7 % and 2.1 %, and the recovery rate ranged from 98.5 % to 101.2 %. It is proved that based on the established test conditions, the precision, repeatability and spiked recovery of the gas chromatography-mass spectrometry are good, which meets the requirements of analysis and testing.

(2) Through the real-time monitoring of the ethylene glycol content in the YI3 well injected with antifreeze in the Hancheng coalbed methane field, the relative deviation of the sample is less than 4.23 %, indicating that the sample has good parallelism. It was found that the concentration of ethylene glycol in the produced water of the well was reduced to 0.36 μg/mL on the 30th day. In order to prevent the formation of natural gas hydrate in the acquisition pipeline, it is necessary to inject antifreeze again in the near future.

(3) Based on the test parameters, the method of determining the content of ethylene glycol in the produced water of coalbed methane wells by gas chromatography-mass spectrometry has the advantages of simple, rapid and accurate results. It can be used to monitor the content of ethylene glycol in the produced water with different salinity in real time.

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