



Research Article

Standard methods and related techniques for on-line detection of the total sulfur content in natural gas^{☆,☆☆}

Li Xiaohong^{a,*}, Shen Lin^a, Luo Qin^a, Zhou Li^a, Yang Fang^a, He Zhanxing^b & Yang Weizhao^c

^a Natural Gas Research Institute, PetroChina Southwest Oil & Gas Field Company, Chengdu, Sichuan 601213, China

^b Puguang Branch of Sinopec Zhongyuan Oilfield Company, Dazhou, Sichuan 635002, China

^c Gas Transmission Division, PetroChina Southwest Oil & Gas Field Company, Chengdu, Sichuan 601213, China

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Abstract

At present, many domestic total sulfur detection methods are accurate and reliable, but they are disadvantageous with a low detection frequency, a long detection period and delayed work. In this paper, the standards of the total sulfur content detection of natural gas were reviewed. Then, the standard methods and related techniques for on-line detection of the total sulfur contents in natural gas were discussed, and their principles were figured out. And finally, it was recommended to develop a domestic on-line detection standard method for sulfur compounds and the total sulfur contents in natural gas. It is concluded that on-line total sulfur content detection is the inevitable development trend in the future; and that there is neither methods nor standards at home available for on-line detection of the total sulfur contents in natural gas, so it is recommended to timely formulate a national standard correspondingly by referring to foreign standards, e.g. ASTM D7165-10(2015), ASTM D7166-10(2015) and ASTM D7493-2014.

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Keywords: Natural gas; Total sulfur content; On-line; Detection; National standard; International standard

The total content of sulfur is an important indicator for characterizing the quality of natural gas, and it is closely related to the safety, the environmental protection work as well as the corrosion and protection of pipelines and equipment. Therefore, it is an indispensable item in natural gas detection. China's current mandatory national standards GB 17820-2012 *Natural gas* [1] and GB 18047-2000 *Compressed natural gas as vehicle fuel* [2] stipulate the limit of the total sulfur content in natural gas. Therefore, the accurate, reliable, timely and

effective detection of the total sulfur content in natural gas is of great significance.

At present, data of the total sulfur content in natural gas is obtained basically by means of manual field sampling and laboratory offline detection in China. Common standard determination methods include the oxidative microcoulometry method provided in GB/T 11060.4-2010 [3], the hydrolysis and colorimetry method in GB/T 11060.5-2010 [4] and the ultraviolet fluorescence method in GB/T 11060.8-2012 [5], which are accurate and reliable yet the detection frequency is low and the period is long, so the detection result cannot be given in time, and sulfur compounds may be easily absorbed by the sampling container, thus the authenticity of the detection result may be influenced. The online detection method features such advantages as directness, real-time capacity and rapidity, and by using this method, sulfur adsorption and sample contamination problems caused by sampling can be avoided. Therefore, techniques and standard methods

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* Corresponding author.

E-mail address: hxiaohong_li@petrochina.com.cn (Li XH).

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for online detection of the total sulfur content in natural gas have attracted people's attention of the industry.

In this paper, the standard methods and related techniques for online detection of the total sulfur content in natural gas are discussed and their principles are figured out after the related standards are analyzed. And finally, a domestic online detection standard method is recommended to be developed for the total sulfur content in natural gas.

1. Related standards for the detection of the total sulfur content in natural gas

At present, there are many related domestic and foreign standard methods for the determination of the total sulfur content in natural gas (Table 1.), which include two main types. As for the first type, the detection is performed after various sulfur compounds are oxidized to SO₂, such as the oxidative microcoulometry method provided in ISO 16960:2014 [6] and GB/T 11060.4-2010 [3], the ultraviolet fluorescence method in ISO/DIS 20729:2017 (not released officially) [7], GB/T 11060.8-2012, ASTM D6667-14 [8] and ASTM D7551-10 [9], and the barium chloride titration method in ASTM D1072-06 [10]. The Lingener combustion method

provided in ISO 6326-5:1989 [11] and GB/T 11060.7-2011 [12] does not specify that the combustion product is SO₂, but in principle, the detection is performed after various sulfur compounds are oxidized to sulfur oxides. Among the above methods, the coulometry and ultraviolet fluorescence methods are commonly used in China, but the barium chloride titration and Lingener combustion methods are rarely used because their steps are tedious; in regard to the second type, the detection is performed after various sulfur compounds are reduced to H₂S, such as the hydrogenolysis and colorimetry method provided in ASTM D4468-85(2011) [13] and GB/T 11060.5-2010 [4]. Such method is also one of the common methods for the detection of the total sulfur content, and by using this method, the sulfur compounds are reduced to H₂S and then reacted with lead acetate, and the result is detected by and read out from the colorimetric reaction rate meter.

In addition, the gas chromatography method provided in ISO 19739:2004 [14] and GB/T11060.10 [15] is used to detect the sulfur compound content in natural gas. Although these standards do not specify that the results of each sulfur compound content can be summed up as the total sulfur content, in principle, as long as the peaks of all sulfur compounds in natural gas can be detected, this summation mode is feasible.

Table 1
Statistics of domestic and foreign standards for the detection of the total sulfur content in natural gas.

No.	Standard no.	Standard title	Description	Method of use
1	ISO 16960:2014 [6]	Natural gas – determination of sulfur compounds – determination of total sulfur by the oxidative microcoulometry method	–	Oxidative–microcoulometry method
2	GB/T 11060.4-2010 [3]	Natural gas – determination of sulfur compounds – part 4: determination of total sulfur content by the oxidative microcoulometry method	Consistent with the technical content of ISO 16960-2014 [6]	
3	ASTM D6667-14 [8]	Standard test method for determination of total volatile sulfur in gaseous hydrocarbons and liquefied petroleum gases by ultraviolet fluorescence	–	Oxidative–ultraviolet fluorescence method
4	ASTM D7551-10 [9]	Standard test method for determination of total volatile sulfur in gaseous hydrocarbons and liquefied petroleum gases and natural gas by ultraviolet fluorescence	–	
5	ISO/DIS 20729:2017 [7]	Natural gas – determination of sulfur compounds – determination of total sulfur content by ultraviolet fluorescence method	Registered draft international standard, not released officially.	Oxidative–ultraviolet fluorescence method
6	GB/T 11060.8-2012 [5]	Natural gas – determination of sulfur compounds – part 8: determination of total sulfur content by ultraviolet fluorescence method	Refer to ASTM D6667-14 [8]	
7	ASTM D1072-06(2012) [10]	Standard test method for total sulfur in fuel gases by combustion and barium chloride titration	–	Oxidative–titration method
8	ISO 6326-5:1989 [11]	Natural gas – determination of sulfur compound – part 5: Lingener combustion method	–	
9	GB/T 11060.7-2011 [12]	Natural gas – determination of sulfur compounds – part 7: determination of total sulfur content by Lingener combustion method	Apply the ISO 6326-5:1989 [11] mutatis mutandis	
10	ASTM D4468-85(2011) [13]	Standard test method for total sulfur in gaseous fuels by hydrogenolysis and rateometriccolorimetry	–	Hydrogenolysis–lead acetate colorimetry method
11	GB/T 11060.5-2010 [4]	Natural gas – determination of sulfur compounds – part 5: determination of total sulfur content by hydrogenolysis and rateometriccolorimetry method	Apply the ASTM D4468-85(2011) [13] mutatis mutandis	
12	ISO 19739:2004 [14]	Natural gas – determination of sulfur compounds by gas chromatography method	–	Gas chromatography method
13	GB/T 11060.10-2014 [15]	Natural gas – determination of sulfur compounds – part 10: determination of sulfur compounds by gas chromatography method	Apply the ISO 19739:2004 [14] mutatis mutandis	

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