International Gas Union Research Conference 2014

THE NEW QUANTITATIVE ANALYTICAL METHOD FOR ULTRATRACE SULFUR COMPOUNDS IN NATURAL GAS

Main author
Hironori IMANISHI
Tokyo Gas Co., Ltd.
JAPAN
himanishi@tokyo-gas.co.jp

Co-authors
Tohru TAKAHASHI

1. Abstract

Recent improvements to gas consumption equipment have necessitated the need for natural gas with different levels of quality for specific applications. In some cases, quantification technology for ultratrace impurities at ppb (parts per billion) levels is required. Consequently, there is increased importance for the development of gas quality management technology and trace component analysis methods as fundamental technologies. In particular, quantitative analysis of sulfur compounds is required in the management of odor concentration, detection of gas leakage, and lifetime prediction of the desulfurizing agent of hydrogen generators similar to the fuel processing system of a fuel cell.

However, the maximum limit of quantification (LOQ) of conventional analytical methods is a few tens of ppb. Thus, these methods are ineffective for sulfur detection if the concentration of sulfur compounds is lower than several ppb. Therefore, Tokyo Gas Co. developed a technique for the quantitative determination of sulfur compounds in natural gas. In this study, the target value of the LOQ is 1.0 ppb, which is the concentration level required in the reforming catalyst evaluation of hydrogen generators. The target sulfur compounds are *tert*-butyl mercaptan (TBM), dimethyl sulfide (DMS), hydrogen sulfide (H_2S), and carbonyl sulfide (COS).

A preconcentration method using a gas chromatograph/sulfur chemiluminescence detector (GC/SCD) was employed to quantify sulfur compounds with very high sensitivity. However, the conditions for the complete separation of hydrocarbon components from the sulfur compounds should be determined when applying this method. In this method, the sulfur compounds in the sample gas were concentrated by condensing at a suitably cooled trap column, and the hydrocarbons could be eliminated without condensing because of the difference in the boiling points of the sulfur compounds and hydrocarbons. Here, the separation of COS from propane was particularly difficult because their boiling points are quite close. Therefore, the goal of the development was to determine unique separation conditions for analytes with a small difference in their boiling points.

After optimizing the trap temperature and flow rate of sample transfer, the conditions for the efficient separation of COS from propane were determined. Under these conditions, COS could be detected with a good peak shape, the limit of detection (LOD) was 0.1 ppb, and the LOQ was 1.0 ppb. Moreover, TBM, DMS, and H_2S could be analyzed with the same LOD and LOQ. In conclusion, the developed analytical method was suitable for quantifying ppb levels of sulfur compounds. Ultratrace compounds, which cannot be determined using the conventional method, were identified using the proposed method.

The developed method was applied for the evaluation of odorization and deodorization performance, detection of gas leakage, and optimization of the desulfurizing agent of a hydrogen generator. Thus, safe and sophisticated use of energy is expected to be achieved.

TABLE OF CONTENTS

2. Introduction

In recent years, the quality of natural gas has become more sophisticated and diversified in accordance with the improvement in the gas consumption equipments. Therefore, there is increased demand for methods to quantify ultratrace impurities at ppb levels. In particular, the quantitative analysis of sulfur compounds has become important in the management of odor concentration, detection of gas leakage, and lifetime prediction of the desulfurizing agents and catalysts of hydrogen generator systems.

A gas chromatograph (GC) is typically used for gas analysis. A sulfur chemiluminescence detector (SCD) is widely used as a selective detector for sulfur compounds. However, the limit of quantification (LOQ) of this conventional GC/SCD method is more than tens of ppb. For example, the analytical method used for sulfur compounds in natural gas has an LOQ of a few tens of ppb when the GC/SCD system is used [1].

To analyze trace amounts of sulfur compounds at the sub-ppb level, a preconcentrator is used before injecting the sample into the GC/SCD system. In this method, the sample gas is passed through a trap column that is cooled with liquid nitrogen. The sulfur compounds in the sample gas are trapped and concentrated on the basis of the difference in the boiling points of the constituents in the bulk gas. After the concentration of the analytes, the trap column was heated to desorb the sorbed analytes, which were then injected into a GC/SCD system. In the analysis of trace amounts of sulfur compounds in pure hydrogen, the GC/SCD equipped with a preconcentrator resulted in an LOQ of 0.02 ppb [2]. Furudate et al. used a trap column packed with an adsorbent to condense methyl mercaptan by cooling and detected sub-ppb levels of this compound [3].

Thus, a GC/SCD equipped with a preconcentrator has sufficient sensitivity to detect sulfur compounds in pure hydrogen. However, an appropriate method is required to concentrate the sulfur compounds and remove the hydrocarbon components from the bulk gas in order to achieve sub-ppb levels of LOQ. The melting and boiling points of various hydrocarbon and sulfur compounds are shown in Table 1. Methane and ethane can be removed easily by cooling to a suitable temperature, because their boiling points are much lower than those of the sulfur compounds. In contrast, the boiling point of propane is close to that of carbonyl sulfide (COS). Therefore, both COS and propane would be concentrated simultaneously by cooling. Moreover, the chromatographic separation of highly concentrated propane and COS is difficult, and their coelution causes the quenching of the sulfur signals at the SCD.

Therefore, a new measurement technique had to be developed for effectively removing propane from the sample gas at the preconcentrator, in order to achieve ppb levels of LOQ for the sulfur compounds in natural gas. In this study, the effects of different trapping conditions were evaluated to develop an appropriate method for selectively concentrating COS in the presence of propane. Moreover, the limit of detection (LOD) and LOQ of other representative sulfur compounds, hydrogen sulfide (H_2S), dimethyl sulfide (DMS), and *tert*-butyl mercaptan (TBM), were evaluated using the same concentration method.

Table 1 Melting and boiling points of compounds. ([4][5])

Compound		Melting point (°C)	Boiling point (°C)
Nitrogen		−210	−196
Oxygen		−218	−183
Hydro-carbons	Methane	−187	−162
	Ethane	−184	−89
	Propane	−188	−42
	n-Butane	−137	−0.1
	i-Butane	−133	−11
	n-Pentane	−130	36
	i-Pentane	−160	28
	n-Hexane	−95	69
Sulfur compounds	Carbonyl sulfide	−139	−50
	Hydrogen sulfide	−82	−60
	Dimethyl sulfide	−98	38
	tert-Butyl mercaptan	0.8	64

3. Experimental

3.1. Instrumentation

The analyses were carried out using the system shown in Figure 1; the system consists of a preconcentrator (Entech Instruments Inc., USA, Model 7100A), a GC (Agilent Technologies, USA, Model GC7890A), an SCD (Agilent Technologies, USA, Model SCD355), and a mass spectrometer (MS, Agilent Technologies, USA, Model 5973inert). For the identification of hydrocarbons, the SCD and MS instruments were used in parallel.

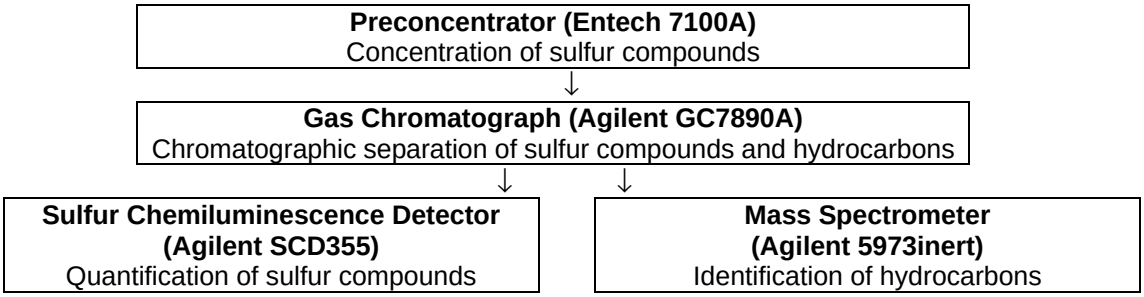

Figure 1 Schematic of the analytical system.

Figure 2 shows the schematic diagram of the preconcentrator. First, the sample gas was passed to the trap 1 column packed with an adsorbent. The trap column was cooled with liquid nitrogen to concentrate the sulfur compounds, and the bulk gas was passed through the column (1). After a predetermined volume of the sample gas was allowed to pass, the trap column was heated using a mounted electric heater, and the desorbed sulfur compounds were directed to the trap 2 column by a carrier gas flow (2). Then, the trap 2 column, which was packed with an adsorbent different from adsorbent packed in the trap 1 and cooled with liquid nitrogen, was heated using a mounted electric heater, and the desorbed sulfur compounds were directed to a cryofocus module cooled with liquid nitrogen (3). Finally, the cryofocus module was heated rapidly, and the desorbed sulfur compounds were injected into the GC/SCD system (4).

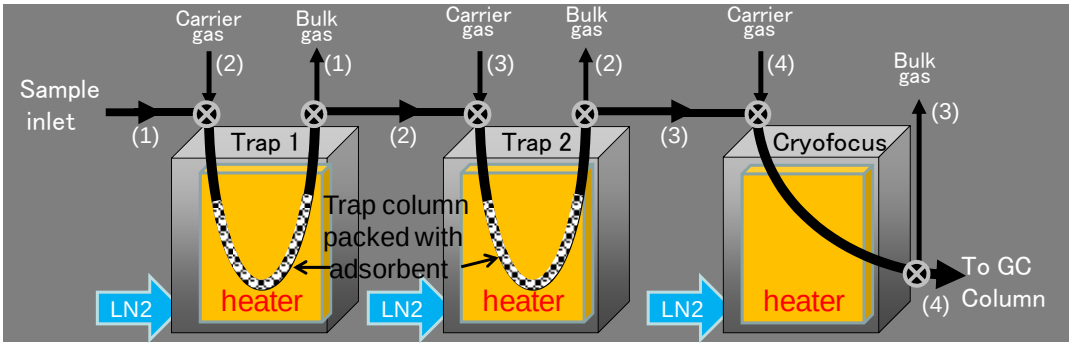

Figure 2 Schematic of the preconcentrator assembly.

3.2. Materials

The sample gas was prepared with pure nitrogen, pure hydrocarbons, and a standard gas containing each of the investigated sulfur compounds. The gas sampling canisters (1.0 L each) were manufactured by Entech Instruments Inc. (Minican^{TM}). Their inner wall surface was coated with fused silica to prevent losses due to the adsorption of sulfur compounds. The canisters were first washed with 350 kPa pressurized and humidified nitrogen and then evacuated to ~1 Pa. After the washing and evacuation steps were repeated five times, the canister was ready for sample preparation. The sample gas was prepared by introducing pure hydrocarbons and the sulfur standard gas using a gas-tight syringe into the canisters and diluting with pure nitrogen gas to obtain the volume ratio shown in Table 2. The concentrations of ethane, propane, n-butane, and i-butane were prepared to be typical components of natural gas. And methane was replaced to nitrogen, because their separation characters were expected to resemble.

The concentrations of COS, DMS, TBM, and H_2S in the standard gas were 11 ppm, 10 ppm, 10 ppm, and 10 ppm/5 ppm (two cases), respectively. The purity of ethane, propane, *n*-butane, and *i*-butane were >99.95%. The purity of nitrogen gas was 99.99995%.

Table 2 Compositions of sample gases.

Compound	Blank	Concentration
COS	-	11 ppb
H_2S	-	10 ppb
DMS	-	10 ppb
TBM	-	10 ppb
Ethane	6.3%	6.3%
Propane	2.3%	2.3%
n-Butane	0.6%	0.6%
i-Butane	0.4%	0.4%
Nitrogen	90.4%	90.4%

3.3. Analytical method development

An appropriate method to achieve an LOQ of 1.0 ppb for the sulfur compounds in natural gas was developed by optimizing the concentration parameters to remove propane from the sample gas. In this study, the “Trapping temperature at trap 1” and “Transfer rate from trap 1 to trap 2” were selected for optimization. The adsorbents of the traps provided by the manufacturer were glass bead, Tenax TA, and their mixture. The results of the preliminary performance tests show that the glass bead had a poor adsorption performance for COS and propane. Tenax TA showed strong adsorption performance for both the compounds. If the glass bead was used alone for trap 1, COS would not be well concentrated. On the other hand, if Tenax TA was used alone, propane would not be removed well. Therefore, a mixture of glass bead and Tenax TA was used as the adsorbent of trap 1. Tenax TA was selected as the adsorbent of trap 2 because the propane concentration in the sample gas would be reduced at trap 1. Then, the trap temperature and transfer rate were optimized by analyzing the prepared sample gases.

The trapping temperature at trap 1 should be lower to achieve efficient concentration because of the advantages of the adsorption performance and condensation of sulfur compounds. However, a lower trapping temperature would also cause the concentration of propane. Thus, three temperatures—−70 °C, which is lower than the boiling points of COS and H_2S; −88 °C, which is lower than the melting point of H_2S; and −150 °C, which is lower than the melting point of COS and H_2S—were investigated.

The transfer rate was selected as one of the parameters for optimization because compounds with weak adsorption performance would be desorbed easily at a higher transfer rate. Assuming that there is a difference in the adsorption performances of COS and propane, propane can be removed more efficiently by optimizing the transfer rate. These conditions are listed in Table 3, and analytical parameters for GC, SCD, and MS are listed in Table 4.

Table 3 Analytical parameters for Trap 1 and transfer conditions between the traps.

		#01	#02	#03	#04	#05	#06	#07	#08	#09	#10	#11	#12	#13
Trap 1	Adsorbent	Tenax TA/Glass bead mixture												
	Trap temp. (°C)	−150	−88	−70	−70									
	Desorption temp. (°C)	−45			−45									
Transfer rate between traps (mL/min)		40			40	200	100	200	10	100	130	150	160	200
Transfer volume (mL)		200			40	40	100	100	200	200	200	200	200	200
Trap 2	Adsorbent	Tenax TA												
	Trap temp. (°C)	−150	−88	−70	−70									
	Desorption temp. (°C)	180												
Cryofocusing	Trap temp. (°C)	−160												
	Injection temp. (°C)	80												

Table 4 Analytical parameters for GC, SCD, and MS.

GC	Separation column		Silica PLOT (Agilent J&W GS-GasPro) 30 m × 0.32 mm ID.
	Oven Temp.	Initial	32 °C (10 min hold)
		ramp rates	20 °C/min
		Final	260 °C (9 min hold)
	Flow rate of carrier gas		5.0 mL/min
SCD	Detector temp.		800 °C
	H_2 flow rate		45 mL/min
	Air flow rate		66 mL/min
MS	Ionization method		Electron Ionization (EI) method
	Ion source temp.		230 °C
	Scan range		m/z = 30–230
	Quadrupole temp.		150 °C

4. Results and discussion

4.1. Effect of trap temperature on peak area/characteristics

The analysis results show that the optimized trap temperature is −88 °C (condition #02), as indicated in Figure 3. A large propane peak and a broad COS peak were observed, and these peaks overlapped. This indicates that propane was concentrated in excess and coeluted with COS into the SCD, thus quenching the SCD and obscuring the COS peak. A more significant quenching effect was observed in the case of the −150 °C trap (condition #01). In contrast, the result for the trap at −70 °C (condition #03) shows a smaller peak of propane and a relatively sharp peak of COS, as seen in Figure 4.

Thus, the trap temperature should be moderate because of the limited removal of propane at extremely low temperatures. Nevertheless, it was impossible to determine the COS amount by the peak shape at −70 °C trap. By increasing the trap temperature further, the concentration efficiency of COS may be lowered. Therefore, the transfer rate as another parameter should be optimized.

4.2. Effect of transfer rate on peak area/characteristics

Figure 5 shows the COS peak area of the SCD and the propane peak area of the MS against the transfer rate from trap 1 to trap 2 for the same transfer volume. For transfer volumes of 40 mL (conditions #04 and #05) and 100 mL (conditions #06 and #07), the peak area of COS and propane increased as the transfer rate decreased. In this case, the transfer time, which is expressed as the quotient of transfer volume and transfer rate, increased with a decrease in the transfer rate. Thus, the peak areas of COS and propane may have increased with an increase in transfer time. Figure 6 shows the peak areas of COS and propane against the transfer volume for the same transfer rate (conditions #05, #07, and #13). The result shows that the peak areas of COS and propane increased as the transfer volume increased. In another view point, in this case, the increase in the transfer time increased the sensitivity. Therefore, a higher transfer time may result in higher COS sensitivity.

Therefore, to optimize the transfer rate and volume for the same transfer time, three cases of transfer rate and volume (#04, #06, and #13) were compared. Figure 7 shows that the peak area of COS increased as the transfer rate and volume increased. However, no significant change in the peak area of propane was observed. This difference in the trend can be attributed to the differences in the vaporization and desorption characteristics between propane and COS. It is considered that the desorption and vaporization rates of propane are low; therefore, the amount of desorbed and vaporized propane did not change significantly during the same transfer time. In contrast, COS is considered to be desorbed and vaporized easily. Thus, the more the increase in the transfer rate and volume, the greater is the desorption and vaporization of COS for the same transfer time.

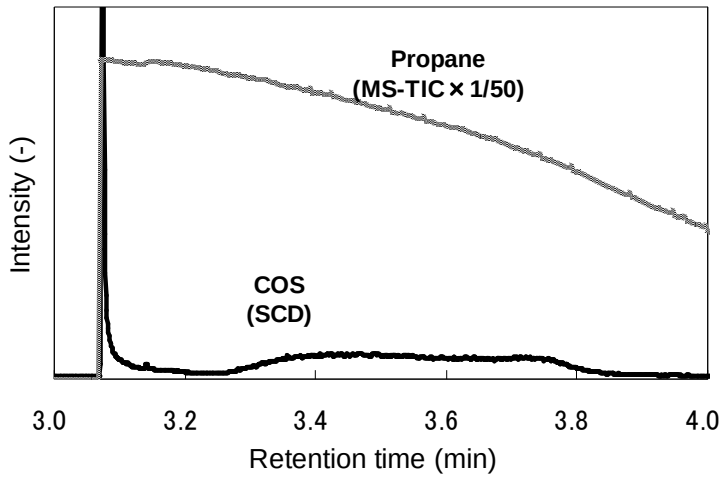

Figure 3 Chromatogram of the analysis result for condition #02.
(Trap temp.: –88 °C, Transfer rate: 40 mL/min, Transfer volume: 200 mL)

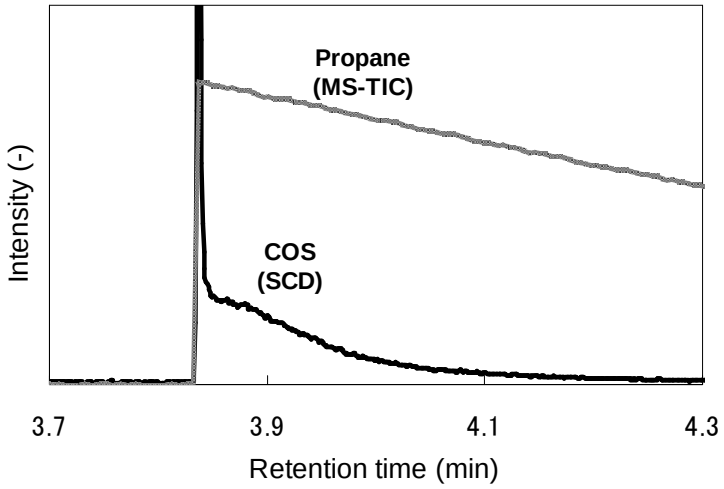

Figure 4 Chromatogram of the analysis result for condition #03.
(Trap temp.: –70 °C, Transfer rate: 40 mL/min, Transfer volume: 200 mL)

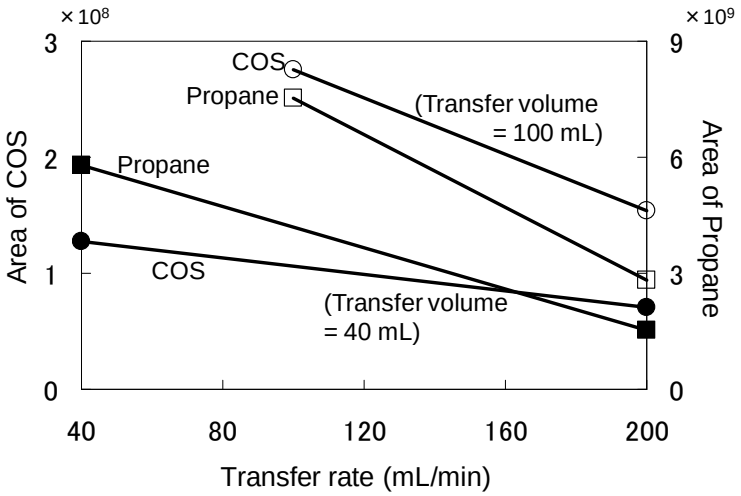

Figure 5 Effect of transfer rate on peak area for the same transfer volume.
(Trap temp.: –70 °C)

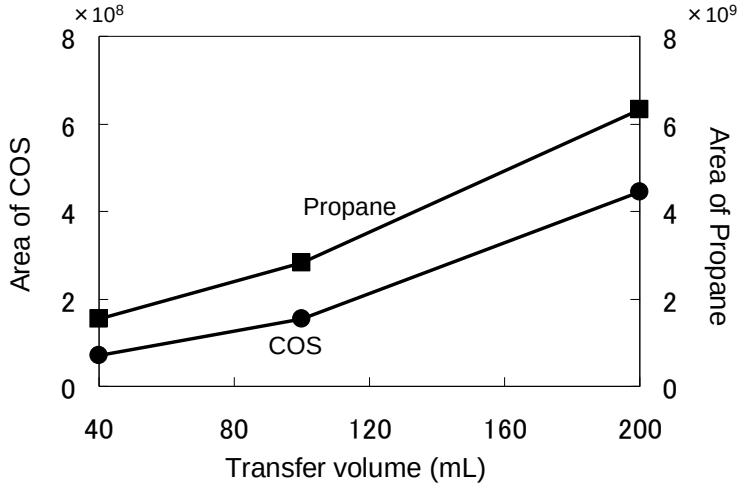

Figure 6 Effect of transfer volume on peak area for the same transfer rate. (Trap temp.: -70 °C, Transfer rate: 200 mL/min)

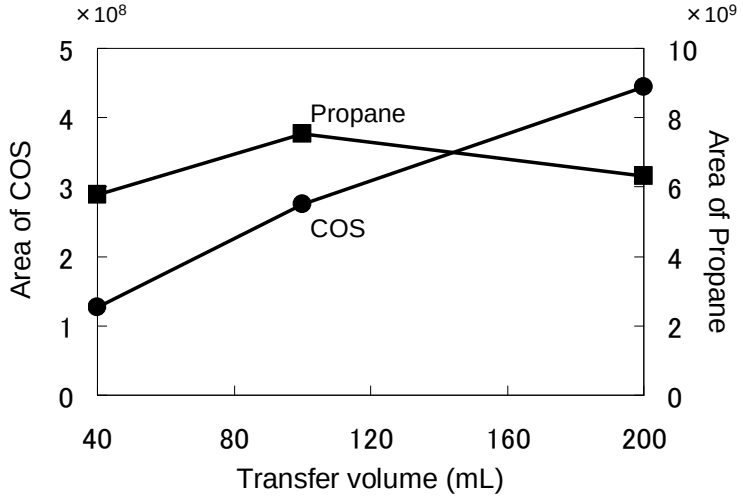

Figure 7 Effect of transfer volume on peak area for the same transfer time (1 min). A horizontal axis shows also transfer rate (mL/min), because transfer time of each transfer volumes are 1 min. (Trap temp.: –70 °C)

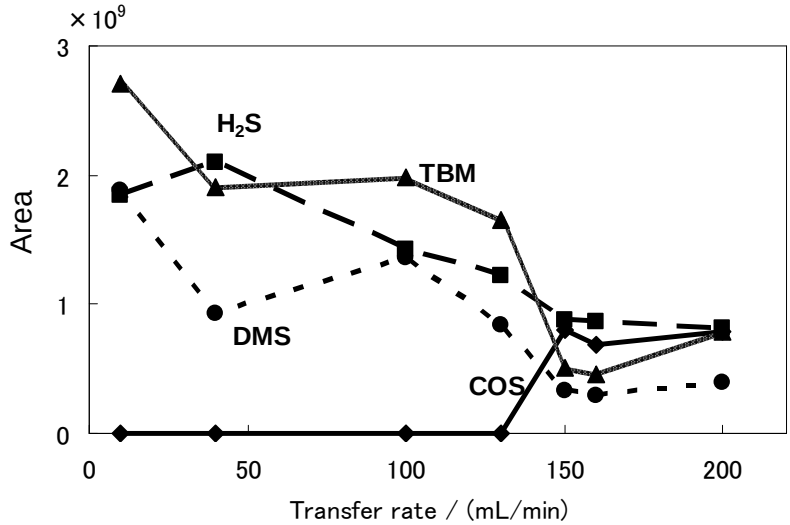

Figure 8 Effect of transfer rate on peak area for the same transfer volume. (Trap temp.: -70 °C, Transfer volume: 200 mL)

According to the above results, the transfer volume was optimized as the maximum value of the facility specifications. To optimize the transfer rate, seven cases of transfer rate (#03 and #08–13) were compared, as shown in Figure 8. The results show that the peak areas of the sulfur compounds other than COS increased with decreasing transfer rate. However, a lower transfer rate caused quenching of the SCD because of the coelution of highly concentrated propane with COS. A clear peak shape for COS was obtained when the transfer rate was >150 mL/min. No significant change in the peak areas of COS was observed when the transfer rate was 150–200 mL/min. By considering the stability of the determination and shortening of the runtime, the transfer rate should be fixed at 200 mL/min.

After the development, the method for COS concentration was optimized. The chromatograms of COS and propane under the optimized conditions are shown in Figure 9. A clear peak shape of COS was obtained using this method.

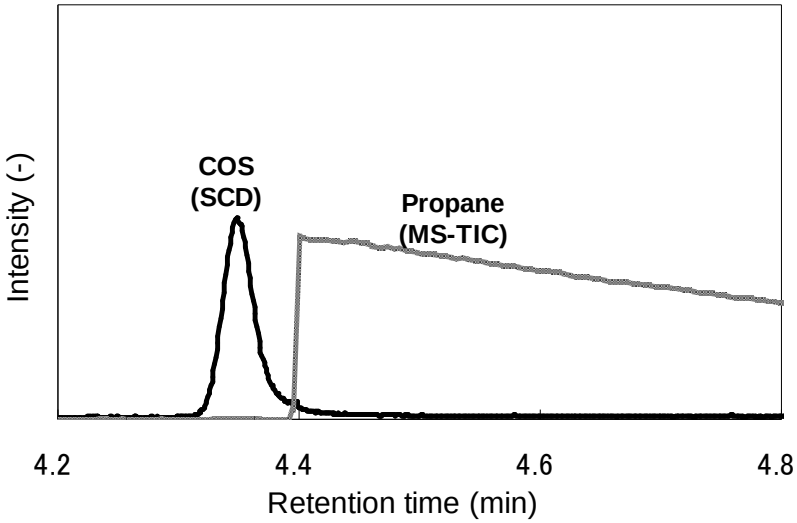

Figure 9 Chromatogram for the optimized method (#13).
(Trap temp.: −70 °C, Transfer rate: 200 mL/min, Transfer volume: 200 mL)

4.3. Limits of detection and quantification of the developed method

To evaluate the accuracy of the developed method, the LOQ and LOD of the sulfur compounds were determined. The COS peak in the sample gas analysis (Figure 9) shows the signal-to-noise (S/N) ratio to be 220. Thus, the LOQ and LOD were calculated to be 1.0 ppb and 0.1 ppb, respectively. Furthermore, the LOQ and LOD of TBM and DMS were 1.0 ppb and 0.1 ppb, respectively. These compounds could be detected and determined at equivalent levels using the same method as that for the COS analysis. The LOD of H_2S was calculated to be 1.0 ppb because of a broad peak shape; however, the peak area was equivalent to that of the other sulfur compounds. This indicates that H_2S was also sufficiently concentrated as the other compounds.

Thus, using this analysis method, it was possible to analyze sulfur compounds at ppb levels of sensitivity. However, the relative standard deviation (RSD) was calculated to be 20%. To improve the analytical precision, the dispersion should be decreased.

5. Conclusions

A new method was developed for the quantitiative analysis of sulfur compounds in natural gas. In particular, COS could be determined in the presence of propane using this method; this was achieved by removing propane using a preconcentrator. After the optimization of concentration parameters such as trap temperature and transfer rate, an LOD of 0.1 ppb and an LOQ of 1.0 ppb were achieved. Moreover, TBM and DMS could be determined at the same LOD and LOQ. The LOD of H_2S was also obtained at the ppb level; however, it was slightly higher than those of the other sulfur compounds.

In the future, the LOQ of sulfur compounds other than COS, TBM, DMS, and H_2S will be evaluated, and the analytical accuracy of the method will be improved. Therefore, it is necessary to evaluate the uncertainty in the analysis, including that in the preparation of the calibration gas.

6. References

1. ASTM D5504-08 Standard Test Method for Determination of Sulfur Compounds in Natural Gas and Gaseous Fuels by Gas Chromatography and Chemiluminescence
2. ASTM D7652-11 Standard Test Method for Determination of Trace Hydrogen Sulfide, Carbonyl Sulfide, Methyl Mercaptan, Carbon Disulfide and Total Sulfur in Hydrogen Fuel by Gas Chromatography and Sulfur Chemiluminescence Detection
3. Furudate et al. Analysis of Flavor Ingredients in Foods/Beverages/Liquors Using Large Volume Headspace and Pre-concentration by GC-MS, PITTCON 2006
4. National Institute of Standards and Technology (NIST) Standard Reference Database Number 69, NIST Chemistry WebBook
http://webbook.nist.gov/chemistry/ (Last accessed 26 Aug 2014.)
5. U.S. Environmental Protection Agency (EPA) Chemical Fact Sheets 749-F-94-009, Aug, 1994

7. List of Tables

8. List of Figures