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GC-2030 Gas Chromatograph

Application News

Determination of Trace Amounts of Sulfur Compounds in Gases by GC-SCD

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User Benefits

- Trace amounts of sulfur compounds can be detected to exceed ISO/DIS 14687 and DIN EN 17124:2019-07 requirements on hydrogen quality for proton exchange membrane fuel
- Equimolarity of sulfur compounds with GC-SCD allows analysis without individual compound calibration

■ Introduction

Recent development in proton exchange membrane (PEM) fuel cell research has opened a strong potential for hydrogen gas as fuel, especially used in PEM fuel cells. In this context, tolerances of impurities in hydrogen gas have been reconsidered to fulfill requirements to be used on catalysts surfaces.

In the ISO/DIS 14687 and DIN EN 17124:2019-07, respectively, a quantification limit of 4 ppb total sulfur compounds is defined [1, 2]. Sulfur compounds analysis includes at least the measurement of H_2S, COS, CS_2 and mercaptans. To reach this challenging requirement, a sensitive technique to determine sulfur content is necessary.

In this application, we present a valve system for gas sampling connected to a gas chromatograph (GC). Detection was performed with sulfur chemiluminescence detection (SCD). To allow analysis of big sampling volumes (20 mL) for highly volatile compounds, focusing prior to detection was done with a cryogenic cold trap (Frontier Laboratories) by liquid nitrogen cooling (Fig. 1).

To avoid any adsorption, absorption, and reaction of sulfur compounds, the tubing and valves were Sulfinert® treated.

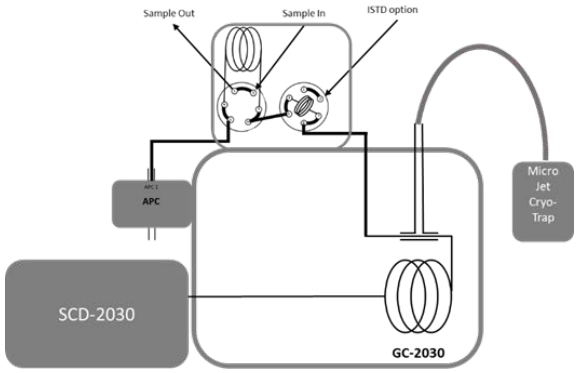

Fig. 1 Schematic representation of the system used

■ Sample Preparation and Calibration

Standard gases of tert-butyl-mercaptan (TBM), Hydrogen-sulfide (H_2S) and Carbon oxide sulfide (COS) were used as sulfur samples from stocks at low ppm range in 20 L gas cylinders. Dilution was performed using a Wösthoff Digamix gas mixing pump [3]. The outlet of the gas mixing pump was connected to the GC valve box. 20 mL sample volume were injected onto the GC column via sample loop. Prior to injection via valve switching, gas flow to the sample loop was stopped to allow pressure equilibration to atmospheric pressure.

Calibration standards were prepared from COS stock in the concentration range from 1.3 to 13 ppb. Due to the equimolarity of SCD-2030 a single sulfur compound standard is sufficient [4].

■ Results

By optimizing the trapping time to 5 min for the 20 mL sample volume, sufficient to quantitatively elute the sample onto the column (Fig. 2), it was possible to keep the chromatographic runtime as short as 7 min. Taking into consideration the cool down time, the method allows the analysis of approximately 6 samples per hour.

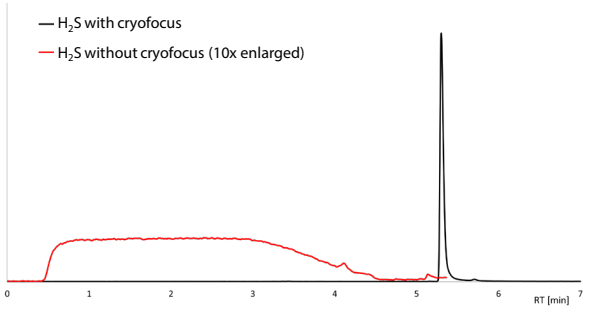

Fig. 2 Evaluation of trapping time

Carryover experiments injecting 6.3 ppm sulfur standard by loop injection revealed no detectable carryover in the subsequent sulfur-free hydrogen blank (Fig. 3).

This result underlines the possibility to reliably analyze sulfur content at the trace amount levels required.

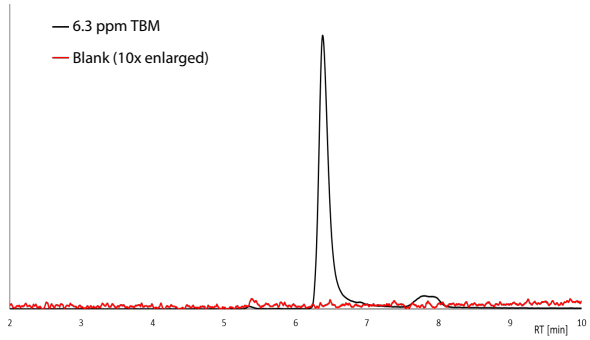

Fig. 3 No carryover observed in blank samples

Calibration was performed measuring duplicates of COS standards in concentrations of 1.3, 3.9, 6.5, and 12.9 ppb, respectively. The calibration curve showed a very good linearity within the calibration range (Fig. 4).

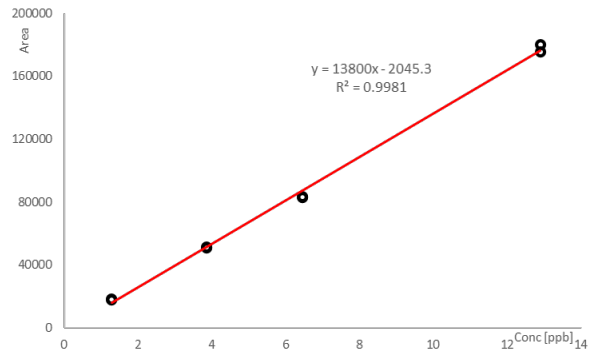

Fig. 4 Calibration curve for COS

To determine reproducibility of the analytical method, a 3.9 ppb of COS standard was injected 10 times. Calculation of the relative standard deviation (%RSD) for peak areas and concentrations revealed the reliability of the setup (Table 1). Area and concentration reproducibility was below 2%, ensuring reliable detection and quantitation of the sulfur compounds at low concentrations.

Table 1 Reproducibility of 10 consecutive measurements of a 3.87 ppb COS standard

#	Area	Conc [ppb]
1	51151	3.879
2	50914	3.861
3	52193	3.958
4	51838	3.931
5	51800	3.928
6	50768	3.850
7	50815	3.854
8	50716	3.846
9	50557	3.834
10	50300	3.814
Average	**51.105**	**3.876**
%RSD	**1.23**	**1.23**

To investigate consumable aging effects on the sulfur content detector response, two external calibration curves were performed, with a freshly installed pyrotube (main SCD consumable), and after 3 months use, respectively (Fig 5). With the used pyrotube, we observed 8-fold decreased detector response compared to using a new pyrotube.

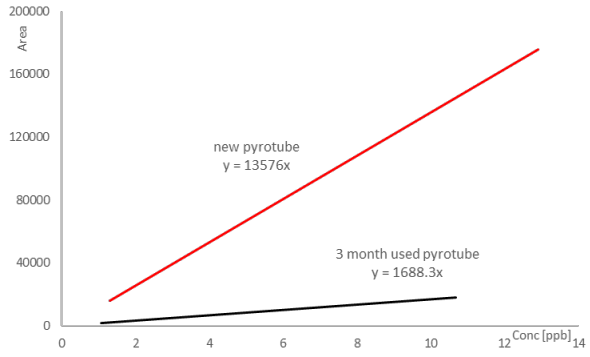

Fig. 5 Effect of consumable usage time on detector response

To compensate these consumable aging effects, an additional valve equipped with 1 mL sample loop for internal standard addition was implemented (Fig 1). Internal standard (TBM) was injected to the column after the sample (H_2S) was completely eluted (Fig. 6). The calibration curve using internal standard option was created (Fig. 7).

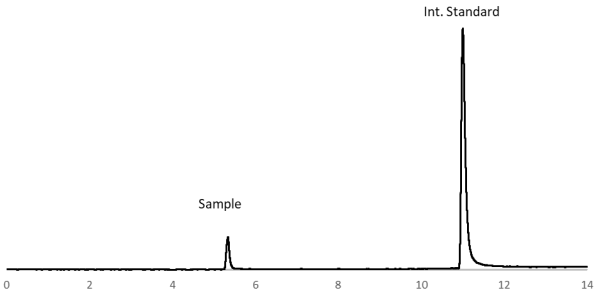

Fig. 6 Chromatogram of sulfur sample including internal standard

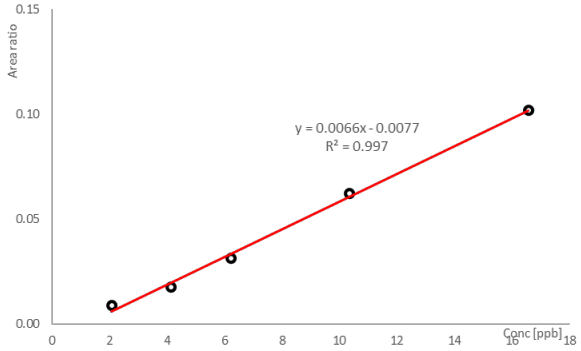

Fig. 7 Calibration curve for H_2S using internal standard

■ The Package

The recommended analytical hardware and software configuration is listed below.

❑ *Main Unit*

Nexis™ GC-2030 plus Nexis SCD-2030: Gas chromatograph plus sulfur chemiluminescence detector

❑ *Accessory*

Top mounted valve box (LVO-2030), MicroJet Cryo-Trap (Frontier Laboratories)

❑ *Main Consumables*

SH-Q-Bond column (1 m x 0.32 mm x 10 µm)

SH-I guard column (5 m x 0.32 mm)

❑ *Software*

LabSolutions™ LCGC

Fig. 8 Nexis™ GC-2030 equipped with SCD-2030 detector and LVO-2030 valve box

■ Conclusion

Sulfur chemiluminescence detection using Nexis SCD-2030 allows to selectively detect total sulfur content in gases without any effect of matrix. The total sulfur content can be determined with a quantification limit of less than 4 ppb, exceeding requirements of ISO/DIS 14687 and DIN EN 17124:2019-07. As no carryover was observed, elevated amounts of sulfur in single samples do not affect subsequent analysis, allowing high throughput without the need of additional blank injections. Furthermore, high reproducibility and the use of internal standard allows reliable long-term analysis. Finally, equimolarity of the sulfur detection by SCD-2030 allows analysis without individual compound calibration.

■ Acknowledgements

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<References>

1) ISO/DIS 14687(en) Hydrogen fuel quality — Product specification, online available:
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2) DIN EN 17124:2019-07, Hydrogen fuel - Product specification and quality assurance - Proton exchange membrane (PEM) fuel cell applications for road vehicles
3) Wösthoff Digamix gas mixing pump; information online available: wösthoff.com/gas-mixing-pumps
4) Shimadzu Application News G330 Comparison of Sensitivity for Sulfur Compound Species by Nexis™ SCD-2030: Equimolar Sensitivity Measurement

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