PAC | Application Note

Total and Speciated Trace Sulfur Analysis in Beverage Grade CO_2

- Speciated and Total Sulfur in 1 run
- Results in less than 10 minutes
- High Sensitivity, excellent Linearity
- No CO_2 Matrix Interference

Keywords: Trace Sulfur, Beverage Grade CO_2, SCD, Chemiluminescence

INTRODUCTION

Guidelines for food and beverage industry concerning sulfur impurities in carbon dioxide are most stringent; ISBT lists 100 ppb for individual species such as COS and Hydrogensulfide in beverage grade CO_2. At the same time, total sulfur cannot exceed 100 ppb.
These limits demand labs can measure 20 ppb or lower for both total and individual sulfur-species.This combined requirement usually involves having two analytical solutions in the lab.AC has developed a unique solution that combines total *and* speciated sulfur in one fast and convenient 10 minute run at the detection levels required, that saves space, and delivers accurate results fast.

System Description

The sample is introduced into the system via inert Hastelloy C Gas Sampling Valve injection. In order to minimize surface adsorption of sulfur species – in particular H_2S – the system is configured with special sulfur deactivated materials.
Dual valves alternate injections into different columns, both connected to 1 detector. Components of interest are detected Sulfur Chemiluminescense Detection. The SCD is very sensitive and selective for sulfur and is not affected by the presence of bulk CO_2 matrix. Also, chemiluminesence detection has excellent linearity and equimolarity compared to other sulfur specific detectors.
Speciated sulfur and total sulfur can be analysed in under 10 minutes in a single run. Figure 1 shows the chromatogram at ppm level. Following components are detected: H_2S, COS, MeSH, EtSH, DMS and CS_2. SO_2, and other components may be added, but are not displayed here.
The system can be used in a 2 minute total sulfur mode displaying only the single peak for total sulfur, a combined mode (see Figure 1&2), or just speciated sulfur (Figure 3). The latter two take less than 10 minutes.

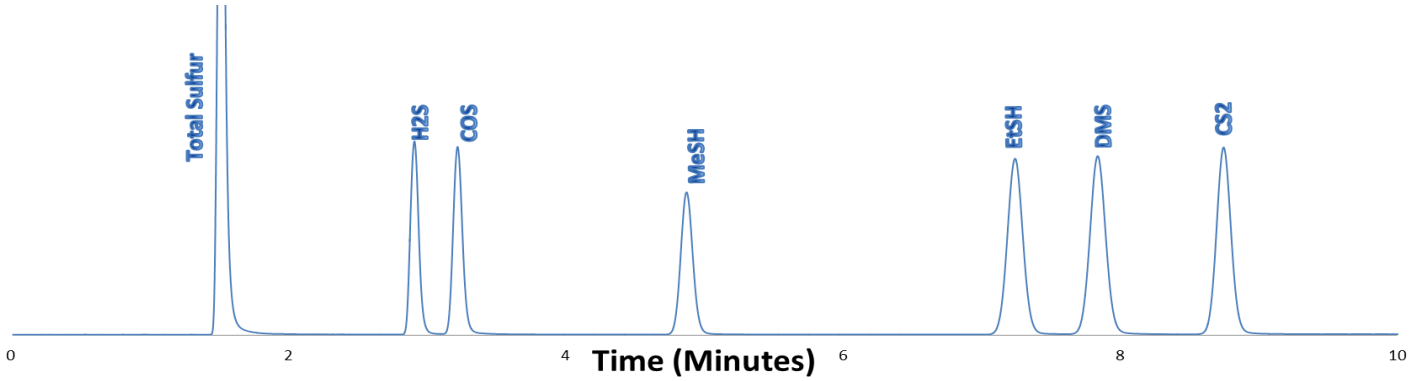

Figure 1. Total and Speciated Sulfur in 1 analysis. Mixture of 5-10 ppm mole Sulfur per species.

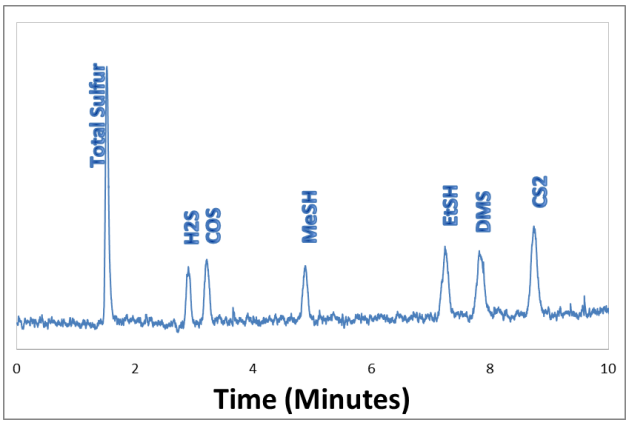

Figure 2. Typical Chromatogram of Combined Total Sulfur and Speciated Sulfur Analysis in CO_2 at working range (20-50 ppb per species, 270 ppb in total)

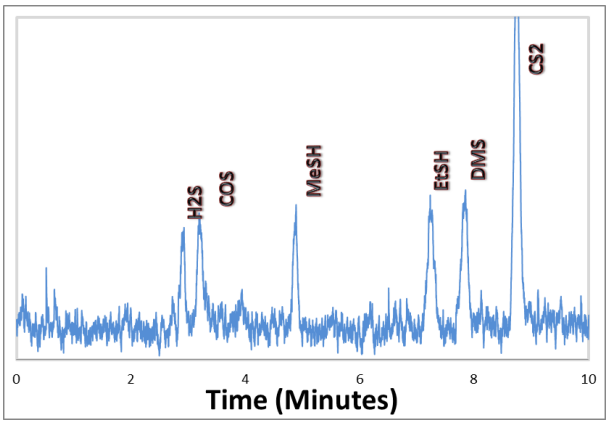

Figure 3. Shows a Typical Chromatogram of Speciated Sulfur Analysis in CO_2 (5-10 ppb mole level, except CS2)

Results

Figures 2 and 3 show calibration working range (Fig 2) and appr. detection limit level (Fig 3). Note that Figure 3 has total sulfur switched off, and just reports individual species.

Linearity

Both Speciated and Total Sulfur have a linear dynamic range of >3 orders of magnitude.

Calibration

For optimal calibration accuracy the system can optionally be fitted with a system integrated permeation device. Such an integrated device takes no lab space and is more flexible in generating different calibration levels for different components. Moreover, it generally yields calibration mixtures with better accuracy at values of interest.
It also omits having to search and order cylinders with very low concentration sulfur components in CO_2 which are often quite unreliable.

Equimolarity

Table 1 shows equimolarity data of the system. As can be seen, the SCD demonstrates excellent equimolarity that is not disturbed by the elution of bulk CO_2 or programming of the oven.

	Conc. (ppm Mole)	Equimolarity Relative Bias
H2S	7.1	9.0
COS	7.0	-1.5
MeSH	7.0	0.6
EtSH	10.9	-0.9
DMS	10.9	-4.7
COS	5.3	-2.5

Table 1. Demonstration of Equimolarity of the System

Precision

Precision data is displayed in table 2 and figure 4. Even at low ppb levels the RSD values are well within 10%, which is extremely good considering the nature of the components.

As can be expected, total sulfur measured as a single peak has significantly better precision (<1%) than total sulfur calculated by summarizing individual species (4%). The absence of multiple Integration variances on the low ppb level lead to higher precision for total sulfur measured as a single peak. Calculated value for both ways of determination was found identical.

	Conc. (ppb Mole)	RSD (%) (n=11)
Total Sulfur	241	0.9
H2S	36	6.2
COS	35	8.4
MeSH	35	8.4
EtSH	55	5.3
DMS	55	6.6
CS2	27	4.9
∑ Sulfur	241	4.1

Table 2: Precision at working levels (30-50 ppb per species)

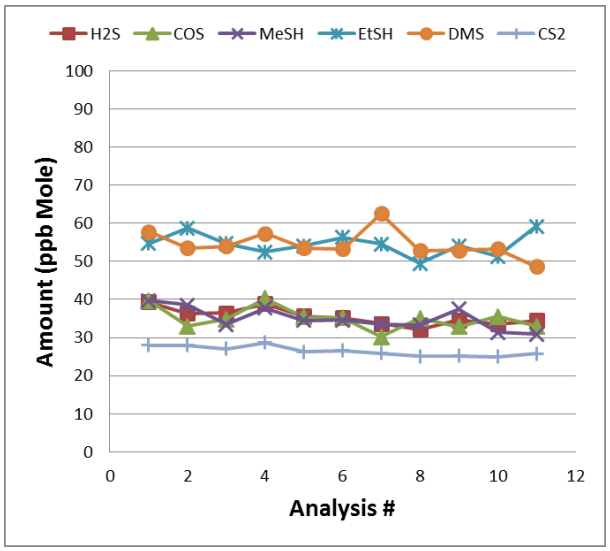

Figure 4: Precision at working levels (30-50 ppb per species)

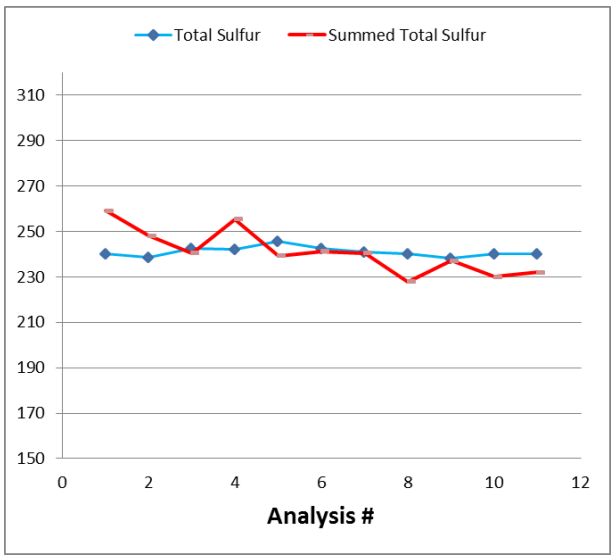

Figure 5: Precision for Total Sulfur measured (blue) versus ∑Total Sulfur (red)

CONCLUSION

A unique solution has been demonstrated for the combined analysis of sulfur species in beverage grade CO_2. Unlike any other system, this AC solution can be set up to provide total *and* speciated sulfur data in a single 10 minute run, or do total sulfur in only 2 minutes.
Results show that sensitivity, equimolarity, precision and accuracy make this solution a fast and easy spacesaver for beverage grade CO_2 quality control worldwide.

Typical LDL (3*N)	Below 20 ppb Mole speciated S Below 20 ppb Mole Total S
Linear Range	10^3
Matrix	Beverage Grade CO_2
Precision	Below 10% RSD
Analysis Time	10 min - Total + Speciated Sulfur 2 min - Total Sulfur

Table3. Analysis Specifications Speciated & Total Sulfur Analysis

AC Analytical Controls® has been the recognized leader in chromatography analyzers for gas, naphtha and gasoline streams in crude oil refining since 1981. AC also provides technology for residuals analysis for the hydrocarbon processing industry. Applications cover the entire spectrum of petroleum, petrochemical and refinery, gas and natural gas analysis; ACs Turn-Key Application solutions include the AC Reformulyzer ® , SimDis, DHA, Hi-Speed RGA and Customized instruments.