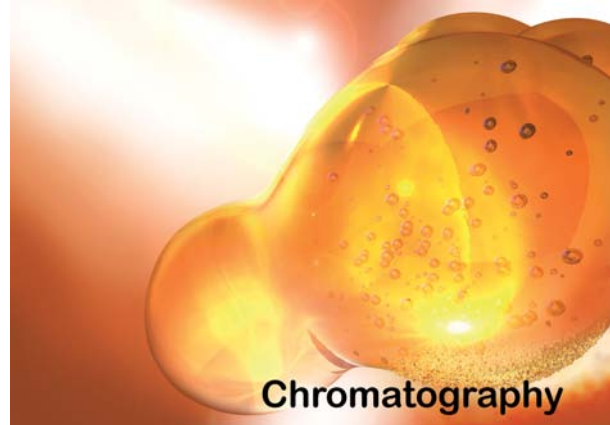# Application Note

Determination of Sulphur Compounds in Carbondioxide

Chromatography

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Introduction:

A large part of all the GC applications concerns the analysis of gases, permanent gases as well as traces of impurities in these gases. For large concentrations of gases, several detectors are available. The vast majority is analysed with the Thermal Conductivity Detector (TCD) and in many cases also a FID will satisfy. If impurities in the gases are of interest the conventional detectors are not sensitive enough. More special devices could be used like the Pulsed Discharge Detector or in case of Sulphur containing compounds a FPD or a Sulphur Chemiluminescence Detector could be used. Robustness, linearity and ease of use hamper all three detector devices. For sensitive and selective trace analysis a mass spectrometer could be a good solution. Sulphur trace analysis is extremely difficult because the low volatile compounds will stick to all metal surfaces throughout the complete instrumentation. As a result bad detection limits and severe memory problems can be expected.

In this Application Note the instrumental set-up and method is described for the analysis of H_2S, COS and DMS in Carbon-dioxide. The regenerated CO_2 is used for brewery applications. The system described here is a **F**ully **A**utomated **S**ulphur **T**race **G**as **A**nalysis **S**ystem (**FASTGAS**) and for this purpose a sampler was developed which can contain 10 sample bags of a volume of 3 Litre each. Specially developed software controls the gas sampler and this software is adapted to Shimadzu's GCMSsolution software.

Instrument Set-up:

The gas sampler contains several switching valves and the sample is introduced to the GCMS via a loop/ backflush valve. All parts in the **FASTGAS** set-up are Cheminert treated or made of teflon. The Shimadzu QP-5050A GCMS is used.

Calibration samples:

500 ppb standard: COS and H_2S each 727 ppb DMS

300 ppb standard: COS and H_2S each 381 ppb DMS

200 ppb standard: COS and H_2S each 99 ppb DMS

100 ppb standard: COS and H_2S each 18 ppb DMS

50 ppb standard: COS and H_2S each 9 ppb DMS

30 ppb standard: COS and H_2S each

The standards were prepared and diluted with ultra clean carbondioxyde and stored in Tedlar sample bags.

Method description:

Equipment:

Autosampler: **FASTGAS** autosampler, containing 10 Tedlar sample bags of a volume 3 litre each.

GCMS: Shimadzu QP-5050A GCMS (with EI)

Column: GasPro fused silica 30m x 0.32mm ID.

The gas chromatograph accommodates one 10-port 2-position valve, a 6-port valve and a 4-port valve for back flush and column switching purposes.

The **FASTGAS** autosampler contains a 10-port multiposition valve and a 10-port 2-position valve.

Also a AreoTrap 6000, Tekmar, is incorporated in the system, and is using a second flow line. The column used is an 75m, 0.45mm ID DB624.

The software to control the gas sampler is totally adapted to the Shimadzu GCMSsolution software.

Chromatographic conditions:

Gasloop temperature: 50 °C

Loop volume: 250 µL

Column oven: isothermal 50 °C

Carrier gas (helium) flow: 2 ml/min, constant flow

MS-parameters:

Detector Volts: 1.5 kV

Acquisition mode: SIM (single ion monitoring)

Ion set 1 : M/Z = 60, acquisition time = 0.0 – 2.10 min

Ion set 2 : M/Z = 34, acquisition time = 2.10 – 3.75 min

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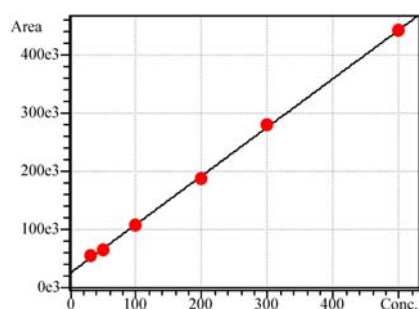*Solutions for Science*
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Results, calibration curve

Figure 1: Calibration curves for COS in Carbondioxide standards (concentration range 30 ppb to 500 ppb)
For H_2S, the same concentration range was used. The R-coefficient was 0.9981. For DMS (range 9 to 700 ppb) R-coef. was 0.99998.
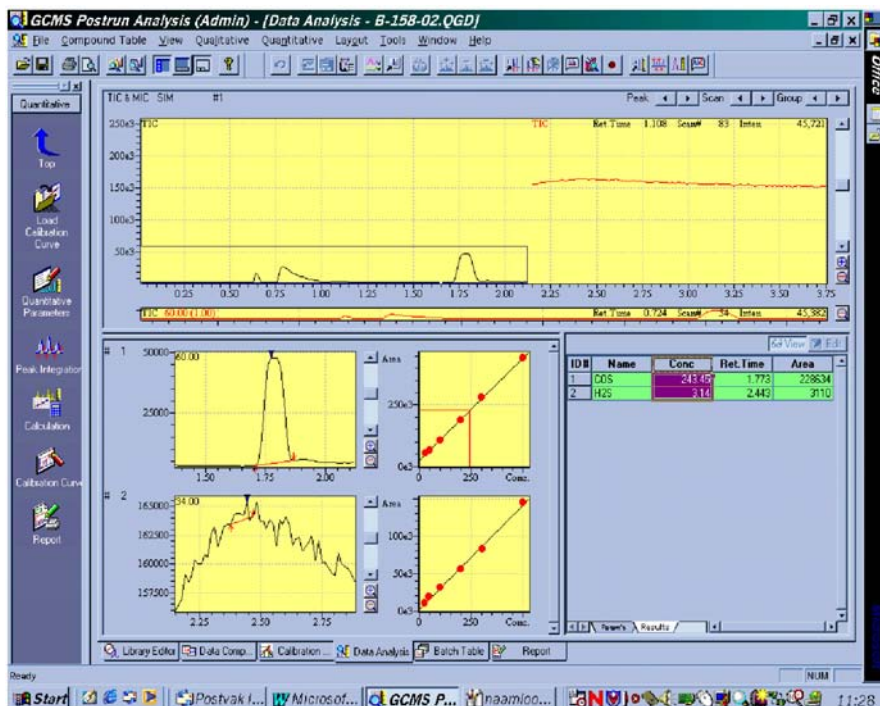

Figure 2: Quantitation window of a real sample obtained from a brewery. COS concentration is 243 ppb and H_2S level is less than 20 ppb. In the upper windows both the mass signals of COS and H_2S are visible. In the lower part the quantitation is depicted.

Conclusions

The obtained detection limit for H_2S, COS and DMS is 20, 0.5 and 1 ppb resp.. This is achieved with a 250 µL sample loop. Especially in case of H_2S, this is very acceptable. In general sulphur compounds are very difficult to analyse.

The use of Teflon tubing and parts and the Cheminert treatment of several switching valves is necessary. The flexibility of the system for general gas analysis is proved by the fact that also a Tekmar AreoTrap 6000 is incorporated in the system.

The possibility to control the complete system with GCMSsolution makes this **FASTGAS** analyzer a sensitive and selective tool for all kind of gases, with an optimal ease of use.

Figure 3: Detail of the autosampler.