FOCUS ON SULPHUR ANALYSIS

The analysis of impurities like Sulphur components, Arsine and Phosphine at low ppb level is highly important when critical catalytic processes are involved like several refining stages or feedstock characterisation for fuel cell development. Gas chromatography coupled with sensitive and selective detectors like FPD, PFPD, SCD and Mass Spectrometer is the proven technique for analysing individual species at ppb level in several matrices.

Applications

Gaseous samples like Natural Gas and Ethylene are injected using GSV (Gas Sampling Valve), according to ASTM D6228, D5303, D5504, UOP791 and ISO 19739. Liquid samples like finished fuels are injected using SSL (Split injector) or PTV (Programmable Temperature Vaporiser), according to ASTM D5623.

LPG samples are analysed by GSV after vaporising or by LSV (Liquid Sampling Valve). The Sample Securitiser is used for guaranteed quantitative liquid injection of LPG (see figure 1), handling all involved laboratory safety issues.

Figure 1: Sample Securitiser for guaranteed quantitative and safe injection of LPG samples

FPD or PFPD?

FPD (Flame Photometric Detector) and PFPD (Pulsed-FPD) both provide robust and reliable analysis. With PFPD the highest sensitivity is achieved: 15-35 ppb (depending on component), while LODs for FPD are in the 100-200 ppb range (based on signal to noise factor 3). Good selectivity is offered as well; hydrocarbon components show no positive response. However co-elution with very high amounts of hydrocarbons (bulk) decreases sensitivity and therefore chromatographic separation is optimised for each standardised method. Since selectivity and dynamic range of FPD and PFPD are comparable for both detectors, the choice is often determined by the needed sensitivity. PFPD offers 5 times better LODs, but its price is more than double. Figure 2 shows low level Sulphur analysis using GSV.

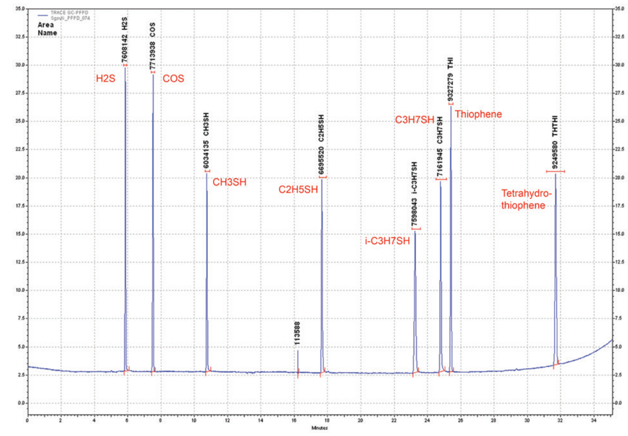

Figure 2: GSV injection of Sulphur components. 500 ppb level; PFPD.

GCMS

The Mass Spectrometer is usually not considered for low level Sulphur species analysis; (P)FPD and SCD have traditionally dominated this application. However GC-quadrupole MS is a very interesting alternative, providing in fact better sensitivity and selectivity and positive component identification as added value. Figure 3 shows the mass chromatograms of H2S and COS at low ppb level while figure 4 demonstrates good linearity.

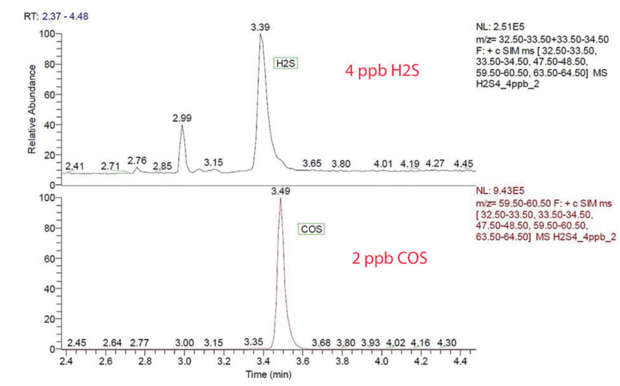

Figure 3: low level ppb Sulphur analysis using GCMS, SIM mode.

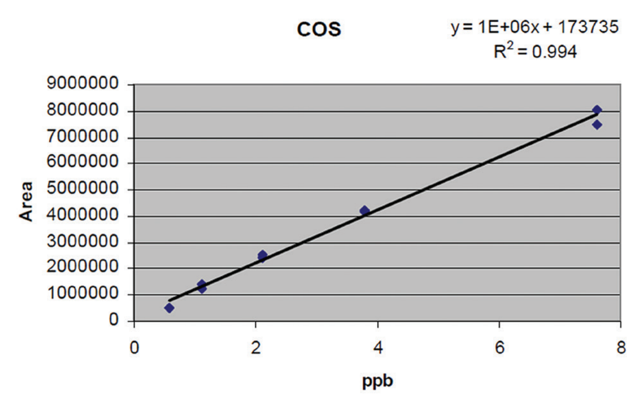

Figure 4: GCMS analysis of COS, linearity: R2 = 0.994 from 2 to 10 ppb.

Arsine and Phosphine

Catalysts are not only extremely prone to poisoning by feedstock impurities such as Sulphur components, but also by contaminants like Arsine (AsH3) ad Phosphine (PH3). GCMS provides low level single digit ppb analysis of these components, see figure 5. Beside better sensitivity, GCMS offers positive component identification for a variety of components groups, for instance oxygenates.

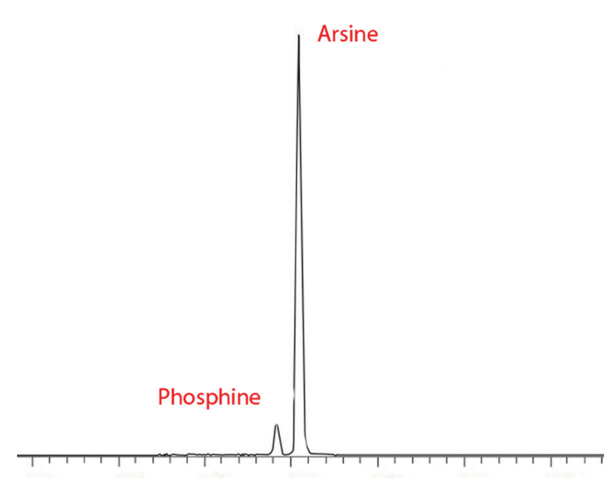

Figure 5: GCMS analysis of Arsine and Phosphine. Limit of detection is below 10 ppb.

Inert sample path

Sulphur components very easy adsorb on active surfaces, therefore Sulfinert deactivation is applied to the full sample path, which is vital for accurate quantification.

Calibration

Calibration is often based on a single calibration gas which is adequate when concentration levels of sample and calibration gas are comparable. A multipoint calibration is advised when larger concentration ranges have to be covered. The ACU module (figure 6 and 7) is utilised to create multiple calibration levels using a single calibration gas or using permeation tubes. The various levels can be pre-programmed and synchronised with the GC sequence, resulting in a completely automated multipoint calibration, running for instance overnight. Fig 8 shows excellent linearity for Sulphur components using dynamic blending.

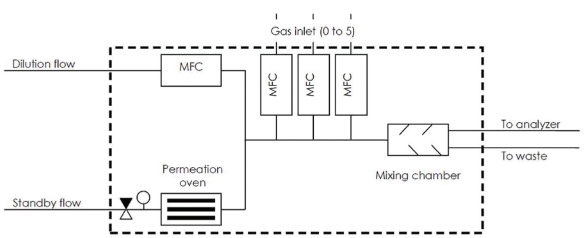

Figure 6: ACU Calibrator diagram with dynamic dilution and permeation oven.

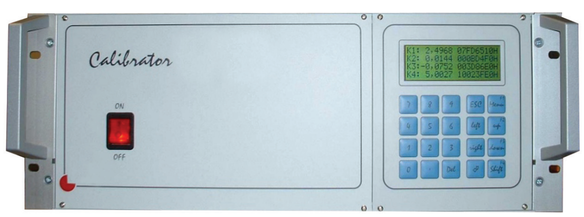

Figure 7: ACU calibrator for automated multipoint calibration for Sulphur analysis.

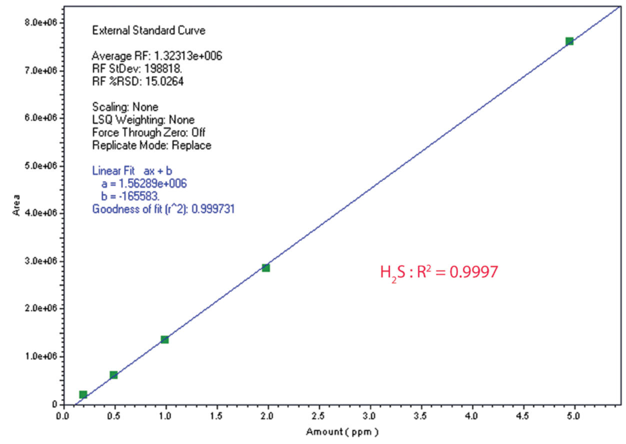

Figure 8: Excellent linearity for 100 ppb-5 ppm H2S using dynamic dilution from a single calibration standard (GSV-PFPD).

CGC-TD

Sample pre-concentration using a thermal desorption trap is successfully applied for the analysis of sub ppb level Sulphur components. Figure 9 shows the basic principle: the components of interest are trapped on a Peltier cooled adsorbent, and then injected on the column by very fast heating of the trap. This thermal desorption option is placed in CompactGC$^{4.0}$ (figure 10). With PFPD a limit of detection of 0.5 ppb is achieved in this way for Hydrogen sulfide, Methylmercaptane, Dimethyl sulfide and Dimethyl disulfide (see figure 11).

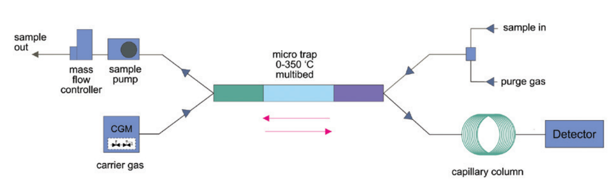

Figure 9: Principle Thermal Desorption for low level Sulphur analysis.

Figure 10: CompactGC$^{4.0}$: 19" analyser with thermal desorption module and PFPD.

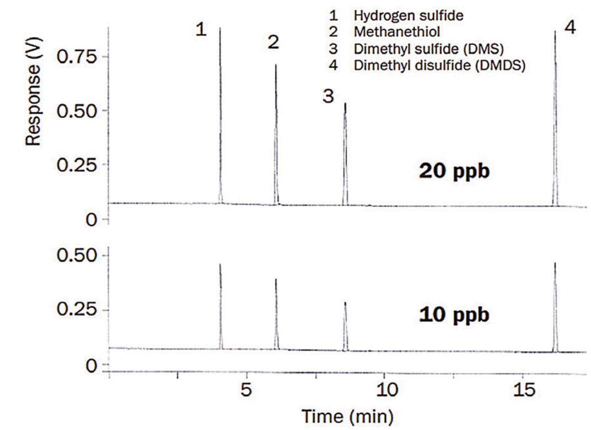

Figure 11: Sulphur components in air using TD-PFPD. Limit of detection: 0.5 ppb.

Summary

Sulphur components are traditionally analysed by selective Sulphur detectors like FPD and PFPD. Both provide robust and sensitive analysis; the maximum achievable sensitivity for PFPD is 15-40 ppb (depending on component), while FPD shows LODs between 100 and 200 ppb. GCMS is a highly interesting alternative: good linearity and improved sensitivity and selectivity were found in the low ppb range (below 10 ppb). GCMS offers positive component identification as well, and besides Sulphur components other impurities like Arsine, Phosphine and Oxygenates are also analysed. A Compact solution was shown based on thermal desorption-PFPD, with 0.5 ppb detection limit for Sulphur components in air.

Author Contact Details

Wilco Agterhuis, Ronald Verbeek, G.A.S – Global Analyser Solutions • Tinstraat 16, 4823 AA Breda, The Netherlands

• Tel +31 (0)76 5411800 • Email: : info@gas-site.com • **Web: www.gas-site.com**