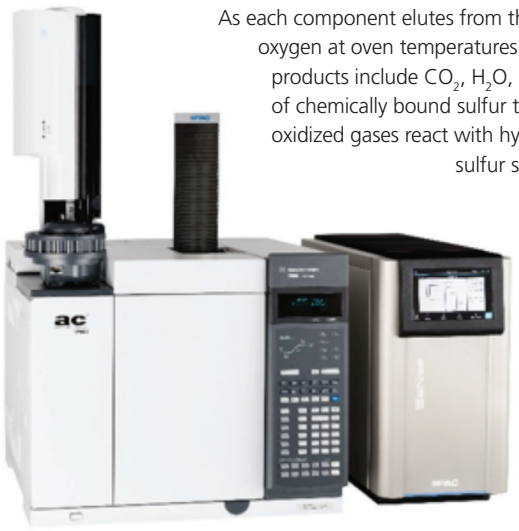
THE NEW STANDARD IN SPECIATING SULFUR AND NITROGEN BY GAS CHROMATOGRAPHY

SeNse is a new detector that has been developed by AC Analytical Controls (PAC) for Gas Chromatography applications aiming to determine Sulfur species in hydrocarbon type matrices. While still based on the Chemiluminescence principle that was employed first in the Antek 7090NS model, the detector has undergone a significant redesign to provide unsurpassed sensitivity resulting in lower detection limits, excellent equimolar response, dynamic range and selectivity. A fast cold start-up, unrivalled signal stability, the sturdy but compact design, and the touchscreen interface makes it the easiest to work with.

The SeNse Sulfur Chemiluminescence Detector (SCD) and/or Nitrogen Chemiluminescence Detector (NCD) is a detector used in GC applications. The effluent of the GC application is led to the base of the SeNse furnace. The components are mixed with air and hydrogen and oxidized in the furnace on top of the GC. The effluent of the furnace is directed into the reaction cell under influence of an oil free vacuum pump. In the reaction cell, a Chemiluminescence reaction of Sulfur or Nitrogen containing molecules takes place under influence of ozone. The emitted light passes an optical filter and enters the PhotoMultiplier Tube (PMT) where a small current is generated.

INTRODUCTION:

The principle of operation for sulfur detection begins with the complete, high temperature oxidation of the entire sample matrix.



As each component elutes from the GC column, the component reacts with oxygen at oven temperatures ranging from 700- to 900°C. Oxidation products include CO_2, H_2O, SO_2 (under ideal conditions). The conversion of chemically bound sulfur to SO_2 (sulfur dioxide) is quantitative. The oxidized gases react with hydrogen (reduction), generating reduced sulfur species. The reduced sulfur species are then passed through the reaction chamber where they react with ozone. The reduced sulfur species react with O_3 (ozone), produced by an on-board ozone generator to form SO_2* (sulfur dioxide in the excited state). As the excited species decays to the ground state, light is emitted and detected, at specific wavelengths, by a photomultiplier tube. This Chemiluminescent emission is selective for sulfur and is proportional to the amount of sulfur in the original sample.

DEVELOPMENT:

In the development process of the new SCD unit all aspects of the Chemiluminescence phenomenon were considered and optimized to create a detector with unsurpassed signal stability over longer periods of time. Extensive studies on ceramic tube material, together with the optimization of the oxidation and reduction reaction conditions, has resulted in a unit performing with best in market stability over longer periods of time. Figure 1 represents a stability run of 30 injections over a period of

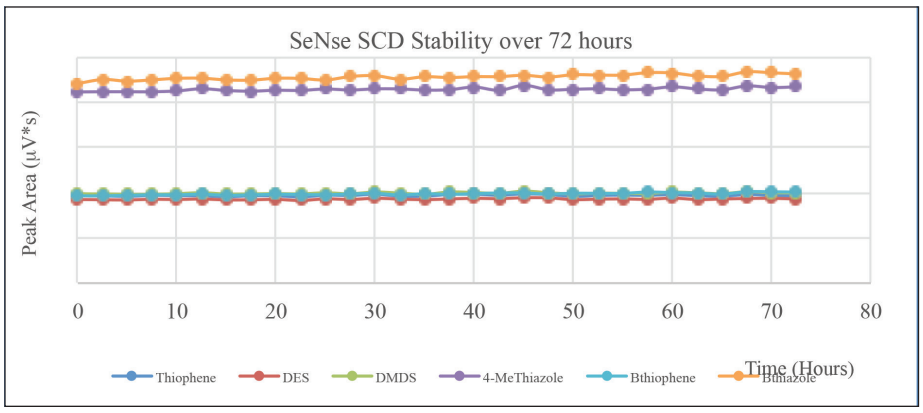


Figure 1: Sense Stability over a timeperiod of 72 hours.

72 hours. The obtained response for each individual compound were found to be within 1.5% RSD.

The optimized Chemiluminescence process together with improved electronics and digital flow control has resulted in a unit with surpassed sensitivity, excellent equimolar response, dynamic range and selectivity.

The performance specifications of the new SeNse SCD Chemiluminescence detector were cross-checked against ASTM D5504 (Sulfur compounds in Natural gas) based on the GC configuration shown in Figure 2.

SENSITIVITY:

The Detection limit is calculated based on a ~ 50 ppb dilution (using a Mass Flow Controller) from a calibration standard containing Hydrogen Sulfide (H_2S), Carbonyl Sulfide (COS), Methyl Mercaptane (MeSH), Ethyl Mercaptane (EtSH) and Dimethylsulfide (DMS), presented in Figure 3. The calculated limit of the detector for each individual compound is below <5 ppb (LDL 3*N).

EQUIMOLARITY:

The SCD is an equimolar detector; therefore, all sulfur compounds are assumed to produce an equivalent response as sulfur. The response factors for all calibration components in the calibration gas are calculated and listed in Table 1. The response factor of each single sulfur compound are within 5% of the response factor for hydrogen sulfide.

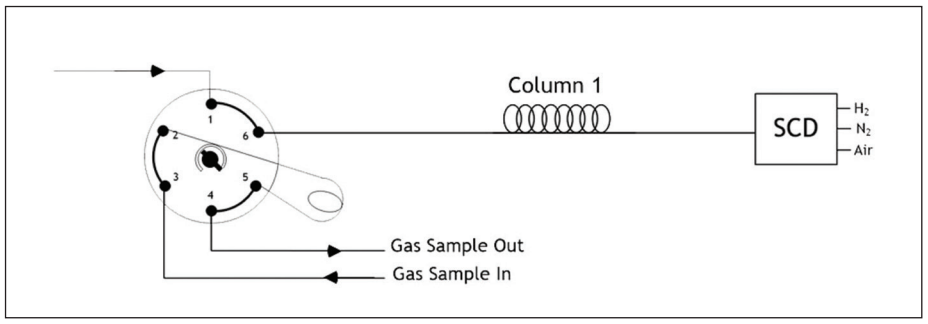


Figure 2: ASTM D5504 GC Configuration

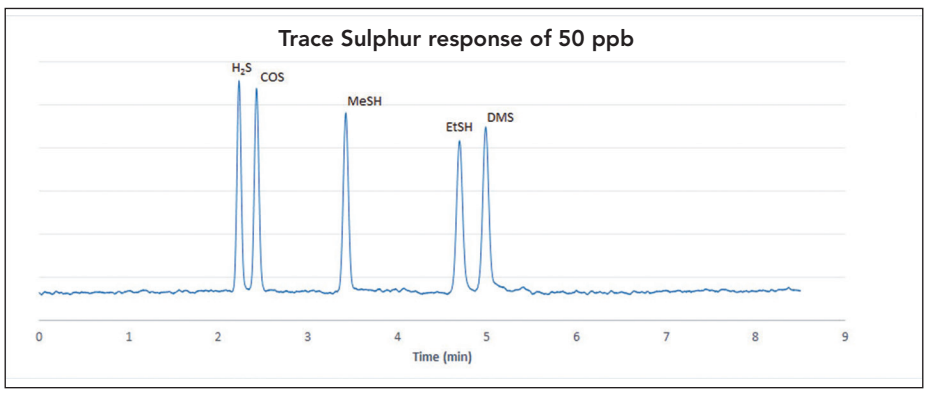


Figure 3: ~ 50 ppb dilution (MFC) from a calibration standard contain H_2S. COS, MeSH, EtSH and DMS.

Component	Concentration (ppm)	RF	Deviation RF to H_2S	Repeatability Measured	Repeatability St.dev ASTM D5504
H_2S	0.49	0.00143	0.0%	0.002	0.1
COS	0.48	0.00136	-4.9%	0.003	0.06
MeSH	0.48	0.00137	-4.1%	0.002	0.1
EtSH	0.50	0.00143	-0.3%	0.003	
DMS	0.50	0.00137	-4.3%	0.003	

Table1: Equimolarity and precision data (results in ppm).

LINEARITY

The linearity of response for the analyzer is verified by creating dynamic dilutions of a certified calibration gas. Concentrations from 10 ppm down to 5 ppb have been created for Hydrogen Sulfide (H_2S), as outlined in Figure 4. The calibration line has a linearity correlation > 0.9999.

Concentration repeatability according ASTM D5504-12 is measured for 8 consecutive runs for a calibration standard blend diluted to ~ 500 ppb single peak. Repeatability is compared with the precision statement of the method. Table 1 also represents precision data.
The obtained precision (r) is well within the limits of ASTM D5504.

NATURAL GAS SAMPLE:

A natural gas sample (taken from the local distribution network) is analysed with an ASTM D5504 configuration using SeNse. The main peak is THT (Tetra Hydro Thiophene) which is added to the natural gas network as an odor component by the supplier at ~18 mg/m3. The measured concentration is 4.55 ppm mol THT, which complies with 16.99 mg/m3.

Zoomed in on the baseline, various sulfur compounds (i.a. DMS) are determined at single digit ppb levels.

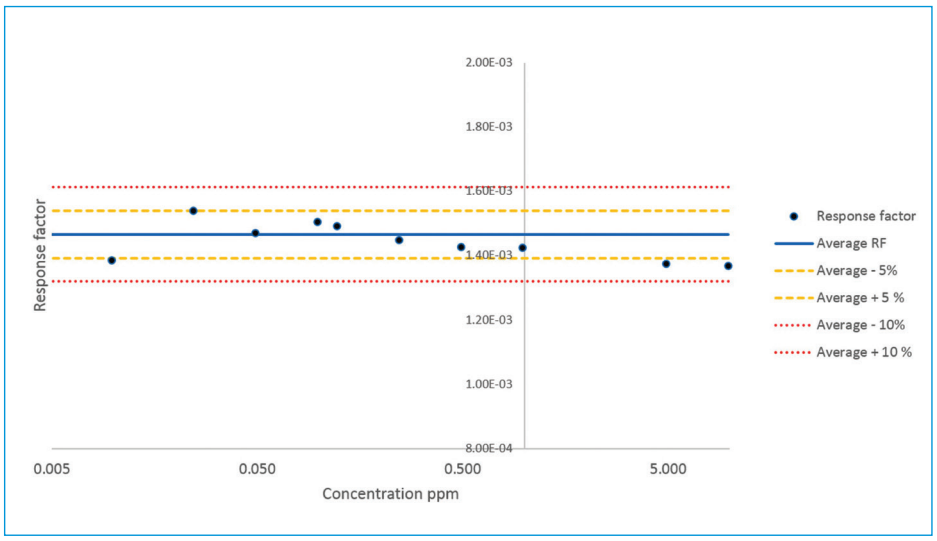


FIGURE 4: Linearity plot H_2S - Response factors from 5ppb - 10ppm

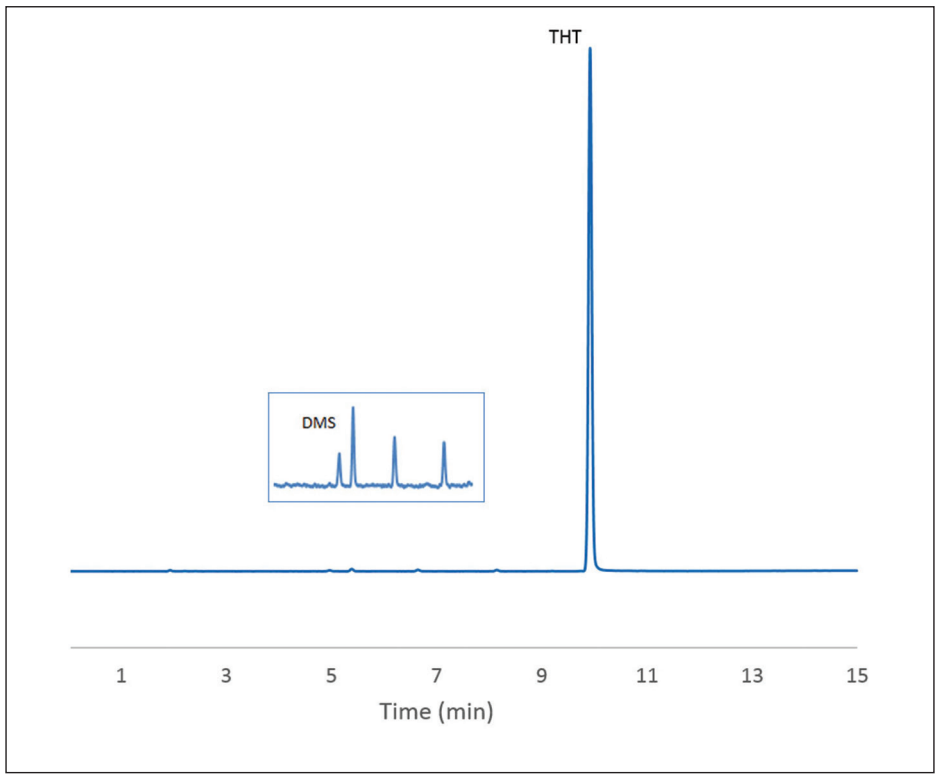


Figure 5: Oder component Tetra Hydro Thiophene in Natural gas.

CONCLUSION

Item	Target
Sensitivity	< 0.3 pgS/s
Stability	< 2% RSD per 2 hrs < 3% RSD per 24 hrs
Linearity	> 10^4
Equimolarity	< 10 %
Selectivity	> 10^7

The redesign of the new Sulfur Chemiluminescence Detector has resulted in a unit with unsurpassed stability, increased sensitivity, and provides an excellent equimolar response in addition to a large dynamic range and selectivity. Its performance not only meets but exceeds ASTM D5504 requirements, ensuring the best quality data that can be used to estimate effects of Sulfur compounds in Natural Gas and Gaseous Fuels.

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