Evaluation of the Performance of Various Universal and Selective Detectors for Sulfur Determination in Natural Gas

Hai Pham Tuan, Hans-Gerd M. Janssen*, and Carel A. Cramers
Eindhoven University of Technology, Laboratory for Instrumental Analysis, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Ellen M. Kuiper-van Loo and Harm Vlap
N.V. Nederlandse Gasunie, P.O. Box 19, 9700 MA Groningen, The Netherlands

Key Words:
Natural gas analysis
Sulfur components
Sulfur selective detection
Universal detectors

Summary

In the present contribution, the performance of a number of commercially available selective and universal detectors that can be used in the analysis of sulfur components in natural gas is evaluated in terms of sensitivity, selectivity, reproducibility, quenching effect, stability, and compound dependence of the sulfur response. Investigated detectors include the sulfur chemiluminescence, the flame photometric, the electron capture, the mass spectrometric, the thermal conductivity, and the flame ionization detector. The sulfur chemiluminescence detector was found to have the best overall performance, e.g., low picogram amounts of sulfur can be detected accurately and the linear dynamic range is more than five orders of magnitude. After careful optimization, the sulfur response of this detector was found to be almost compound independent. All other detectors, including the flame photometric and the electron capture detector, have more or less compound dependent responses.

1 Introduction

Apart from nitrogen and helium, the most important non-hydrocarbons that can occur in natural gas and associated condensates are sulfur compounds. The presence of sulfur compounds in natural gas constitutes a source of concern because of the corrosive nature of these compounds as well as their potential hazards for human health and for the natural environment. Furthermore, sulfur species are also well-known poisons to the catalysts involved in industrial chemical processes, where natural gas is used as a starting material.

The group of components that should be analyzed includes hydrogen sulfide, carbonyl sulfide, the C1 to C4 mercaptans, lower sulfides, and odorants such as for example tetrahydrothiophene. These odorants are added to the gas to impart a characteristic smell for safety purposes. The concentrations of sulfur components range typically from a few to several tens of parts per million on a volume basis. An exception is H2S which can be present at concentration levels up to one percent [1].

More stringent environmental regulations and higher demands presently being posed on the sulfur content of natural gas feedstocks necessitate the development of new analytical procedures for sulfur determination in natural gas. Only analytical procedures based on gas chromatography can meet the sensitivity and accuracy requirements dictated by environmental regulation in-stitutions and modern chemical industry. The complexity of the natural gas matrix as well as the extremely low concentration levels at which the sulfur species occur make the development of these analytical methods a true challenge. In the development of gas chromatographic systems for sulfur determination the choice of the detector plays a key role as this determines the requirements that have to be posed on sample pretreatment and chromatographic separation. Selective detection enables target compounds to be measured while other coeluting compounds are not sensed. Universal detectors such as the flame ionization detector (FID) and the thermal conductivity detector (TCD) respond to virtually all components amenable to gas chromatography; hence, if these detectors are used, high demands have to be posed on sample preparation and chromatographic separation.

Gas chromatography with flame photometric detection (FPD) is nowadays widely used for sulfur speciation in natural gas [2-7]. The detection limits of the standardized methods are approximately 0.1 mg S/m3 [3]. Although the FPD has proven to be reliable and sensitive it also suffers from a number of important disadvantages such as the well-known quenching effect and the inconvenient square dependence of the output signal on the concentrations of sulfur species [4-13].

In contrast to the flame photometric detector which has already been commercially available for over 25 years, the sulfur chemiluminescence detector (SCD) became available only some six years ago. Owing to the significantly higher sensitivity, the great advantage of linear response vs concentrations of sulfur species, the larger linear dynamic range, the higher selectivity, and the absence of quenching effects, the SCD has gained widespread acceptance for trace-level sulfur determination in complex matrices [14-18].

The combination of gas chromatography with mass spectrometric detection is an extremely powerful tool in the analysis of unknown samples. The mass spectrometric detector (MSD) offers a selectivity unsurpassed by any of the other selective detection devices. Whereas selective detectors such as those described above only reveal the presence of a certain hetero-atom, the mass spectrometer gives detailed information on various structural groups present in a molecule. In the particular case of petrochemi-
universal and selective detectors for sulfur determination in natural gas

Figure 1. Comparison between hot split and cold splitless injection techniques. Concentration of sulfur compounds in hexane (mg/L): 1 - EtSH 127.6; 2 - DMS 130.0; 3 - i-PrSH 115.9; 4 - n-BuSH 90.5; 5 - THT 99.1. A) Hot split injection: 1 µL, split ratio 1:30, inj. temperature 250 °C, oven 40 °C (2 min) to 150 °C at 20 °C/min; B) cold splitless injection: 0.1 µL, PTV 30 °C to 250 °C at 12 °C/min, oven see A, no cryofocusing; C) cold splitless injection: see B, oven 30 °C (5 min) to 150 °C at 20 °C/min, no cryofocusing; and D) cold splitless injection: see B, oven see C, focusing time 1.75 min.

cal analysis, e.g., analysis of gasoline and higher boiling fractions, GC/MS systems have been used almost exclusively [19–22] because of the higher complexity of the matrix involved.

A large disadvantage of universal detectors such as the FID or the TCD is the lack of selectivity needed for sensitive trace analysis in complex matrices. If, however, the analytical system incorporates an efficient sample pretreatment and adequate separation of the compounds of interest from interfering compounds in the matrix, these universal detectors become very attractive because of their ruggedness, reliability, low costs, and ease of use.

In this work the performance of a number of universal and selective detectors for the determination of sulfur species in natural gas is evaluated. Special attention will be paid to the sensitivity and the sulfur-to-carbon selectivity of the various detectors as well as to their quenching characteristics, the compound independence of the sulfur response, and the stability of the detectors.

2 Experimental

2.1 Chemicals

All pure liquid sulfur compounds except tetrahydrothiophene (THT), dimethyl sulfide (DMS), and carbon disulfide (CS₂) were purchased from Polyscience (Niles, Illinois, USA). THT was bought from Aldrich (Milwaukee, Wisconsin, USA), DMS from Janssen Chimica (Beerse, Belgium), and CS₂ from Merck (Darmstadt, Germany). The main characteristics of these compounds such as their purities, boiling points, etc. are listed in Table 1. Because of the limited range of sulfur components that possibly occur in natural gas, higher boiling sulfur compounds were not taken into consideration.

Table 1. Main characteristics of liquid sulfur compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Abbrev.</th>
<th>Mol. wt.</th>
<th>B.p. (°C)</th>
<th>Purity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylmercaptan</td>
<td>EtSH</td>
<td>62.13</td>
<td>35.0</td>
<td>97.11</td>
</tr>
<tr>
<td>Dimethyl sulfide</td>
<td>DMS</td>
<td>62.13</td>
<td>37.3</td>
<td>97.77</td>
</tr>
<tr>
<td>Carbon disulfide</td>
<td>CS₂</td>
<td>76.14</td>
<td>46.3</td>
<td>99.95</td>
</tr>
<tr>
<td>i-Propylmercaptan</td>
<td>i-PrSH</td>
<td>76.16</td>
<td>52.6</td>
<td>96.24</td>
</tr>
<tr>
<td>n-Butylmercaptan</td>
<td>n-BuSH</td>
<td>90.19</td>
<td>64.2</td>
<td>98.41</td>
</tr>
<tr>
<td>n-Propylmercaptan</td>
<td>n-PrSH</td>
<td>90.19</td>
<td>67.5</td>
<td>98.24</td>
</tr>
<tr>
<td>sec-Butylmercaptan</td>
<td>sec-BuSH</td>
<td>90.19</td>
<td>85.0</td>
<td>98.28</td>
</tr>
<tr>
<td>i-Butylmercaptan</td>
<td>i-BuSH</td>
<td>90.19</td>
<td>88.7</td>
<td>98.38</td>
</tr>
<tr>
<td>Diethyl sulfide</td>
<td>DES</td>
<td>90.19</td>
<td>92.1</td>
<td>97.91</td>
</tr>
<tr>
<td>n-Butylmercaptan</td>
<td>n-BuSH</td>
<td>90.19</td>
<td>98.5</td>
<td>98.30</td>
</tr>
<tr>
<td>Tetrahydrothiophene</td>
<td>THT</td>
<td>88.17</td>
<td>119.0</td>
<td>99.82</td>
</tr>
</tbody>
</table>
Stock solutions of sulfur compounds in hexane (Merck, p.a.), cyclohexane (Merck, p.a.), and n-nonane (Janssen, p.a.), respectively, were prepared gravimetrically in narrow-neck glass flasks to minimize vaporization of volatile sulfur components and were stored in a refrigerator. Working standard solutions in n-nonane were gravimetrically prepared freshly every day in small glass flasks.

2.2 Instrumental Set-Up

GC: HP 5890A Hewlett-Packard (Avondale, Pennsylvania, USA); oven temperature program: 30 °C (5 min) to 150 °C at a rate of 15 °C/min in the case of MS detection and of 20 °C/min in the case of other detection techniques.

PTV: KAS II (Gerstel, Mülheim a/d Ruhr, Germany); empty deactivated glass liner; injection technique: cold splitless, inj. volume: 1 μL of liquid solutions, splitless time: 1 min; temperature program: 30 °C to 250 °C at 12 °C/s;

Column: 35 m × 0.32 mm × 1.1 μm CP Sil-5 CB (Chrompack, Bergen op Zoom, The Netherlands).

Carrier gas: Helium, column head pressure 10 psi, column flow 1.6 mL/min, total flow rate 100 mL/min.

Cryotrap: DKK Cryofocuser (Atas, Veldhoven, The Netherlands) using gaseous CO₂ at 50 bar, restrictor 8 cm × 250 μm i.d. stainless steel inserted into a 60 cm × 3 mm i.d. Teflon tube; focusing time 1.75 min.

Detectors: Four detectors were included in the experimental work. A Sievers SCD 350B was purchased from Gerstel Benelux B.V. (Brielle, the Netherlands). The FPD was a Unicam 4600/04 FPD installed on a Unicam 4600 GC (Cambridge, UK). For mass spectrometric detection an HP 5970B MSD with an open split interface was used. The helium purge gas flow rate was set at 0.5 mL/min. The temperature of the interface was 200 °C. TCD experiments were performed on a Gow Mac TCD (Clare, Ireland) installed in a Varian 3400 GC. Helium was used as the make-up gas for both the analytical and reference channel with a flow rate of 30 mL/min. The detector temperature was set at 200 °C, the filament temperature at 300 °C. The operating range was 0.05 mV with attenuation 1. Because the FPD and the TCD were installed in separate gas chromatographs, a transfer line was used to lead the compounds eluted from the analytical column to the detector. In case of the FPD the transfer line was a 10 m × 0.32 mm × 0.2 μm OV-1 column coupled to the analytical column with a 0.32-0.32 glass press-fit connector purchased from Hewlett-Packard. For the TCD the last part (approximate 1 m long) of the analytical column was drawn out from the oven and led to the Varian GC where the TCD was installed. Details of the detector settings are presented in the Results and Discussion section.

3 Optimization of the Experimental Conditions

For the accurate determination of detector sensitivities, accurately known amounts of the test components must be introduced onto the chromatographic column. Moreover, the solvent should not interfere with the peaks of the components of interest.

3.1 Choice of the Injection Technique

Because of the high volatility and wide boiling point range of the investigated sulfur compounds, discrimination occurs when using hot split injection. Figure 1 clearly shows that the cold splitless injection technique in combination with a simple cryofocusing device is the best choice. Using this approach, accurately known amounts can be introduced free of discrimination or loss due to volatility as sharp symmetrical peaks.

3.2 Choice of the Solvent

Signals of sulfur compounds can be reduced, totally lost or become undetectable in the case of co-elution with the solvent peak. To avoid this problem, n-nonane was chosen for subsequent experiments because it elutes after all sulfur components of interest (Figure 2).

4 Results and Discussion

4.1 Sulfur Chemiluminescence Detector

Sulfur chemiluminescence detection is based on the reaction of SO formed during the combustion of sulfur containing species in a hydrogen rich FID flame with ozone to form electronically excited SO₂·. The SO₂· species relax afterwards by emission of light in the wavelength range of 280–420 nm. The SO is drawn into the SCD by means of a ceramic sampling probe attached to the FID flame housing and a vacuum system. In this flame-based system apart from the SCD signal also an FID signal is obtained. To facilitate the positioning of the ceramic sampling probe in the FID flame a Gerstel adjustable connector was used, which allowed placing the tip of the ceramic sampling probe exactly 4 mm above the FID jet tip. The SCD vacuum system had a pumping speed of approximately 500 mL/min. If the total flow of FID gases is under this value, air from outside will be drawn into the system thereby reducing the signal of the sulfur compounds.

The SCD performance was found to be strongly dependent on the ratio of the FID air and hydrogen flow rates. Figure 3 shows the effects of the air/hydrogen flow-rate ratio on the experimental response factors (A) and the signal-to-noise ratios (B) of 11 investigated sulfur compounds. In general the SCD signal was found to be less compound dependent at higher air/hydrogen ratios. Unfortunately, however, at these flow ratios the sensitivity is lower. The maximum sensitivity, in terms of the highest signal-to-noise ratio (S/N), was achieved with an air/hydrogen ratio of one. Under these conditions an adequate compound independent sulfur response was observed.

Another aspect that should be taken into consideration is the lifetime of the ceramic sampling probe. The flame temperature increases significantly at higher air/hydrogen ratios and, hence, considerably shortens the lifetime of the probe. At gas flow settings of 150 mL/min for hydrogen, 250 mL/min for air and 100 mL/min for nitrogen (make-up gas) the tip of the probe was totally destroyed after approximately 4 weeks of continuous operation. With flow rates of 350 mL/min for hydrogen and 150 mL/min for air the ceramic probe was still fully functional after 12 weeks of continuous operation. To achieve these high hydrogen flow rates the make-up gas line was connected to the fuel gas line.

J. High Resol. Chromatogr.
Universal and Selective Detectors for Sulfur Determination in Natural Gas

From the experimental results discussed above it is evident that the optimum SCD performance is a compromise between the sensitivity (in terms of signal and signal-to-noise ratio), the compound independence of the sulfur response, and the lifetime of the ceramic probe tip. All further experiments were performed at an air-to-hydrogen flow-rate ratio of one (air flow = hydrogen flow = 250 mL/min). Under these conditions a good sensitivity was obtained and the SCD signal was virtually independent of the molecular structure of the sulfur compounds.

Figure 4 shows SCD calibration graphs for 11 sulfur compounds on a log-log scale. From Figure 4 a number of interesting conclusions can be drawn. First of all it can be seen that the SCD response is compound independent. The slopes of the calibration graphs for the various sulfur compounds range from 0.95 to 1.02. The linear dynamic range is over five orders of magnitude. The reproducibility, based on areas of three subsequent injections, is generally in the range of 5% relative standard deviation (RSD). The detection limit, based on S/n = 3, is approximately 2 pg S/l. An SCD chromatogram of 11 sulfur compounds at concentrations near the detection limits is given in Figure 5. Under the SCD settings used in the present study, large amounts of hydrocarbons give negative signals. For example the baseline drop at the end of the chromatogram in Figure 5 is caused by the elution of n-nonane, which was used as the solvent.

The long-term stability of the SCD was established by measuring the slopes of the calibration graphs of the 11 sulfur compounds on three different days. The RSD of the absolute sensitivities was below 6%.

A first series of experiments to investigate the quenching behavior of the SCD upon coelution of sulfur compounds with large quantities of sulfur-free species was carried out by measuring the sulfur signal on a hydrocarbon background and comparing this with the signal in a system free of hydrocarbons. These experiments were performed at the optimum flow settings identified above, i.e., air = hydrogen = 250 mL/min. The ozone generator was operated using air as the oxygen source. A simple dynamic headspace sampling device was used to introduce pentane, hexane, or heptane vapors, respectively, into the air supply of the FID in this way mimicking the elution of sulfur compounds on a hydrocarbon background. No significant quenching was observed with C/S ratio up to 10³. This result is in accordance with statements of the manufacturer claiming that the SCD is completely free of quenching. The loss of the sulfur signal when sulfur species coeluted with a hydrocarbon solvent such as cyclohexane
Universal and Selective Detectors for Sulfur Determination in Natural Gas

Figure 3. Influence of air/hydrogen flow-rate ratio on SCD performance: A) response factor = area/concentration; B) S/N = (peak height/concentration)/noise.

Figure 4. Calibration graph of sulfur compounds on the SCD. Chromatographic conditions: see Experimental.

in Figure 2B, however, indicates that the quenching effect on the SCD should be studied in more detail.

Quenching effects in the SCD signal are generally thought to be caused by incomplete combustion of coeluted hydrocarbons in the FID flame as well as by competitive reactions of combustion products of hydrocarbons and sulfur compounds for ozone in the reaction chamber [14]. At low air-to-hydrogen flow-rate ratios coeluting hydrocarbons will not be completely burnt in the FID flame. If now insufficient oxygen is fed into the ozone generator, the reaction of sulfur monoxide (combustion product of sulfur species) with ozone to form the electronically excited sulfur dioxide will be incomplete as hydrocarbon combustion products compete with the SO for the ozone. Furthermore, if the total flow is not high enough, ambient air is likely to be drawn into the SCD reaction chamber which in turn could also result in signal quenching. Summarizing, the parameters that could cause the SCD to show quenching, if not carefully optimized, are: i) air-to-hydrogen flow-rate ratio; ii) amount of oxygen fed into the SCD ozone generator; and iii) total FID combustion flow rate.

In further experiments on SCD quenching, first the minimum required FID combustion flow (air + hydrogen) was established by observing the SCD signal while injecting a gas mixture containing sulfur components directly into the FID flame housing. If a sulfur signal is observed immediately after the injection, the total flow of air and hydrogen is still too low and ambient air is drawn into the SCD. A total flow of 550 mL/min was found to be the minimum flow rate needed to prevent ambient air from entering the SCD.

To investigate the magnitude of the SCD quenching effect under non-optimized settings, chromatographic conditions were selected to create a situation in which a sulfur compound (i-BuSH) coeluted with a non-sulfur containing species (cyclohexane). A small amount of cyclohexane was added to a solution containing the investigated sulfur compounds in n-nonane. To obtain true coelution of cyclohexane and i-BuSH the oven temperature program was changed to 30 °C (3 min) to 150 °C at 30 °C/min. The calculated carbon-to-sulfur ratio, in case of complete coelution, was approximately 100.

Using the sample described above, the influence of the air-to-hydrogen flow-rate ratio was studied. In these experiments the hydrogen flow rate was held constant at 250 mL/min while the
air flow rate was gradually increased from 300 mL/min to 500 mL/min. Air was used for ozone generation in the ozone generator. The difference in response factors (peak areas divided by concentration) of i-BUSH and that of three other sulfur compounds eluting close to the i-BUSH peak (s-BUSH, DES, and n-BUSH) was found to decrease with increasing air/hydrogen ratio. Unfortunately, however, even at the highest air/hydrogen ratio quenching of the i-BUSH signal was not fully absent. Further increasing the air/hydrogen ratio is not recommendable because of the deleterious effects of flame temperature on the lifetime of the ceramic probe.

To investigate the influence of the amount of ozone generated in the ozone generator on the quenching behavior of the SCD the amount of oxygen fed to the ozone generator was increased by applying a higher inlet pressure in the air supply line. No significant improvement was achieved. In a second series of experiments the air cylinder was replaced by an oxygen one and the experiments described in the previous paragraph were repeated. When pure oxygen was used quenching was found to be less at all investigated FID air/hydrogen ratios. Quenching free chromatograms were obtained at an air/hydrogen ratio of two or higher. Representative chromatograms are shown in Figure 6.

From Figure 6 it can be seen that although equal response factors are obtained for the four sulfur components mentioned above at an air/hydrogen of two with oxygen as the ozone generator feed gas, the heights of s-BUSH and i-BUSH peaks are significantly lower than that of the DES and n-BUSH peaks. This is most likely caused by the band broadening that occurs in the column as the sulfur compounds elute together with a much larger amount of cyclohexane. Increasing amounts of cyclohexane injected into the chromatographic column will cause the column to become overloaded which will eventually affect the separation of coeluting sulfur compounds. The resolution will decrease which will result in incorrect peak integration. This conclusion is evident from Figure 7, where the response factors of the four sulfur compounds investigated are plotted vs. the carbon-to-sulfur ratios. Up to carbon-to-sulfur ratios of approximately $2 \times 10^4$, no errors in peak area integration are observed, although the peaks clearly show severe band broadening and peak distortion. Carbon-to-sulfur ratios exceeding $2 \times 10^4$ lead to errors in integration of the individual peak areas, but the average of the peak response factors from these four sulfur compounds remains identical.

From the study described above it can be concluded that for optimum sensitivity of the SCD air-to-hydrogen flow-rate ratio
of one should be used. However, for quenching free operation, which is of utmost importance in natural gas analysis, a higher air-to-hydrogen flow-rate ratio is beneficial. A value of two is an optimum compromise between quenching free operation and lifetime of the ceramic probe. Moreover, pure oxygen instead of air should be used for the SCD ozone generator.

4.2 Flame Photometric Detector

Flame photometric detection is based on measuring emission light from $S_2^*$ species which are formed when sulfur compounds are burnt in a hydrogen rich flame. The optimization of the FPD performance was carried out in the same manner as with the SCD, i.e., the influence of the air-to-hydrogen flow-rate ratio and the nitrogen make-up flow rate on the response factor and the signal-to-noise ratio of all 11 sulfur compounds was studied. Figure 8 shows that the optimum FPD performance is obtained at an air/hydrogen ratio of approximately 0.6 (air 25 mL/min, hydrogen 40 mL/min). From this figure it is also evident that the FPD signal exhibits a much stronger compound dependency than the SCD signal. The make-up gas flow rate was found to have only a marginal effect on the FPD performance. In all further experiments a make-up flow of 30 mL/min was used. The detector temperature was set at 250 °C.

Calibration graphs of the 11 sulfur compounds present in the sample are shown in Figure 9. From this figure it is clear that the FPD signal shows a square dependence on the concentration of the sulfur species. The slopes of the calibration graphs for the various sulfur compounds range from 1.8 to 2.2 on a log-log scale. The “linear dynamic” range of the square FPD response after linearization (log-log scale) is limited to two orders of magnitude. The reproducibility of absolute peak areas, based on three subsequent measurements, is generally in the range of 6% RSD. The detection limit ($S/N = 3$) was 0.15 ng S/s and was hence about 100 times higher than that achieved with the SCD. The carbon-to-sulfur selectivity is in the range of $5 \times 10^4$ to $1 \times 10^5$. The long-term stability of the FPD was somewhat better than that of the SCD. The FPD can be left on overnight, whereas the FID flame of the SCD must be shut off because of the high consumption of...
flame gases. Moreover, the ceramic sampling probe of the SCD had to be taken out overnight to vent the water accumulated in the vacuum pump during operation. These two factors result in a slightly poorer long-term stability for the SCD. The slopes of the FPD calibration graphs, measured on three different days, have RSDs of less than 3%.

The quantitative study of the quenching effect of the FPD was performed in the same manner as with the SCD in the first series of quenching effect experiments. Now, however, the hydrocarbons were fed into the make-up gas supply line. Figure 10 shows a plot of the response factors of the sulfur compounds for various carbon-to-sulfur ratios. It was found that the sulfur signal was reduced by 50% when sulfur species coelute with a 20 fold excess of hydrocarbons. Natural gas contains numerous higher hydrocarbons that elute in the elution range of the sulfur species of interest. Although the concentrations of these hydrocarbons are low, they still vastly exceed the concentration levels of the sulfur species. Hence, there is a serious risk of quantitation errors unless the detection is (almost) completely free of quenching.

Figure 10. Results of quenching effect study on the FPD.

![Figure 10](image)

**Table 2.** Conditions set on the mass spectrometric detector:

<table>
<thead>
<tr>
<th>Mode</th>
<th>Amplifier Voltage</th>
<th>Scan Range</th>
<th>Scan Speed</th>
<th>Start Time (min)</th>
<th>Selected Ions (amu)</th>
<th>Dwell Time (ms/ion)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCAN</td>
<td>3600 V</td>
<td>10-100 amu</td>
<td>2 scans/s</td>
<td></td>
<td></td>
<td>100</td>
</tr>
<tr>
<td>SIM</td>
<td>1800 V</td>
<td>10-100 amu</td>
<td>2 scans/s</td>
<td></td>
<td></td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>150</td>
</tr>
</tbody>
</table>

From Figure 12 it can be seen that the linear dynamic range of the MSD in the SIM mode is over five orders of magnitude. The detection limit (based on S/N = 3) varies from 1.5 pg S/s for THT to 9.5 pg S/s for EtSH. In the full scan mode the detection limit
Universal and Selective Detectors for Sulfur Determination in Natural Gas

is approximately 100 times higher. The reproducibility, based on three measurements, was very good with RSDs in the range of 1–3%. The “long-term” stability, based on slopes of three calibration graphs measured on three different days, was also very good. Here values of 1.5 to 3.5% were obtained.

4.4 Thermal Conductivity Detector

This detection technique is based on the change of the thermal conductivity of the gas stream through the detector cell when a compound elutes from the chromatographic column. As a universal detector the TCD responds to all compounds that elute from the chromatographic column. In general, its response depends on the molecular weight of the eluting compounds, i.e., the detector is generally more sensitive for the heavier species. Proof of this principle is to be seen in Figure 14, which shows calibration graphs for the 11 sulfur compounds used in this study. The minimum detectable amounts for this detector are around 30 ng S. Figure 15 shows a representative chromatogram of the sulfur compounds near the detection limits. The linear dynamic range of this TCD is over 3 orders of magnitude. Here it is important to emphasize that the upper limit of this range is not dictated by the detector but by overloading of the chromatographic column. The reproducibility was in the range of 10% RSD, which is poor in comparison with other detectors. This is caused by fluctuations in the make-up flow rate. The long-term stability was in the range of 1–6% RSD.

Table 3. Summarized parameters of several investigated universal and sulfur selective detectors.

<table>
<thead>
<tr>
<th>Detector</th>
<th>MDA (g S)</th>
<th>DL (g S/sI)</th>
<th>LDR</th>
<th>Reprod. Stability (RSD%)</th>
<th>Select.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCD</td>
<td>$5 \times 10^{-12}$</td>
<td>$2 \times 10^{-12}$</td>
<td>$&gt;10^6$</td>
<td>5</td>
<td>3–6</td>
</tr>
<tr>
<td>FPD</td>
<td>$3 \times 10^{-10}$</td>
<td>$1.5 \times 10^{-10}$</td>
<td>$&lt;10^2$</td>
<td>6</td>
<td>$&lt;3$</td>
</tr>
<tr>
<td>MSD</td>
<td>$4-14 \times 10^{-12}$</td>
<td>$2-11 \times 10^{-12}$</td>
<td>$&gt;10^3$</td>
<td>1–3</td>
<td>2–4</td>
</tr>
<tr>
<td>TCD</td>
<td>$1-4 \times 10^{-6}$</td>
<td>$1-4 \times 10^{-2}$ (b)</td>
<td>$&gt;10^1$</td>
<td>10</td>
<td>1–6</td>
</tr>
</tbody>
</table>

(a) Linear section on the calibration graph in the log-log scale.
(b) Only for mass flow sensitive detectors. For the TCD the unit was mg S/m³.
(c) Hydrocarbons give negative response under the experimental conditions used in this study.
(d) In the selected ion monitoring mode.
(e) The range is limited by column overloading.

4.5 Other Possible Detection Techniques

Apart from the detection techniques mentioned above, there are several other universal as well as “sulfur-selective” detectors available. These include, for example, the electron capture detector (ECD) and the flame ionization detector (FID). The ECD, sensitive to electronegative elements, has been quoted as very sensitive for sulfur species [23,24]. One of the disadvantages of this detector, however, is the strong compound dependence of its response. Figure 16 shows a representative chromatogram of sulfur compounds recorded on an ECD. An example of flame ionization detection of sulfur compounds is shown in Figure 17.

5 Conclusion

From the comparative experiments described above it is obvious that for the selective determination of sulfur in a complex matrix as natural gas, the SCD is the best choice. This detector offers the highest selectivity and sensitivity, has a large linear dynamic range, and its response is largely compound independent and free...
Universal and Selective Detectors for Sulfur Determination in Natural Gas

![Chromatogram of sulfur compounds obtained on an ECD in a high-speed GC instrument with hot split injection.](image)

Figure 16. Chromatogram of sulfur compounds obtained on a ECD in a high-speed GC instrument with hot split injection.

![Chromatogram of sulfur compounds on an FID. Chromatographic condition: see Experimental.](image)

Figure 17. Chromatogram of sulfur compounds on an FID. Chromatographic condition: see Experimental.

of quenching over a wide concentration range. The SCD to a large extent lowers the demands posed on sample pretreatment and chromatographic separation, which would be very stringent in case a TCD or a FID is used as the system detector.

References


Ms received: September 28, 1994; Accepted: April 20, 1995