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ASSESSMENT OF SCD-DP CALIBRATION TO QUANTIFY TRACES OF SULFUR COMPOUNDS IN GASEOUS STREAMS

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Abstract - This work describes the calibration of a gas chromatograph equipped with a sulfur chemiluminescent detector with dual plasma (GC-SCD-DP) for analysis of sulfur-containing petroleum refinery gaseous streams. A packed column in an inert tube (Sulfinert) and an inlet system resistant to reactive sulfur compounds were used. The behavior of the calibration procedure over time depended on the sulfur compound: hydrogen sulfide (H_2S), carbonyl sulfide (COS), methanethiol (MeSH) and dimethylsulfide (DMS) gave constant responses, whereas SO_2 presented a systematic increase and dimethyldisulfide (DMDS) showed a systematic decrease of their response factors. In all cases, the response factors were lower than the ones found in the ASTM D 5504-08 method. The GC-SCD-DP technique proved to be a suitable tool for quantification of sulfur compounds (including SO_2) at $\mu g.m^{-3}$ levels in several petroleum refinery gaseous streams.

Keywords: Sulfur compounds; Gas chromatography; Chemiluminescence; Dual plasma.

INTRODUCTION

In the petroleum refining process, the importance of selective and sensitive sulfur detection cannot be underestimated. Sulfur removal from gaseous streams produced in a petroleum refinery depends on the characterization of the sulfur compounds present. This is essential to monitor odor problems, prevent catalyst poisoning and reduce release of SO_2 when such streams are burned in flares. The presence of hydrogen sulfide (H_2S) in these streams in considerable amounts poses a health hazard. Its toxicity is a known risk for individuals working in the petroleum, sewer, maritime, and mining industries. It is a broad-spectrum toxicant because it affects most organ systems in the body. H_2S exhibits a very steep dose–response relationship with an LD_{50} of 15 mg/kg (rats), especially for the central nervous system and respiratory depression, which is the major cause of death in acute H_2S poisoning. Neurological and neuropsychiatric squeals have been observed. H_2S is a potent inhibitor of cytochrome oxidase (Yalamanchili and Smith, 2008; Lambert et al., 2006; Vale, 2007).

Identification and quantification of sulfur compounds require a suitable analytical procedure (Yan, 2006; Miller and Bruno, 2003). Gas chromatography (GC) is a very powerful technique to identify and quantify sulfur compounds present in gaseous streams. These data allow calculation of

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*To whom correspondence should be addressed properties like specific gravity and vapor pressure of such streams. In liquid streams, specific gravity data have been used to establish an empirical correlation for in-line estimation of their sulfur content (Pacheco et al., 2009). The on-line analyzer based on ultraviolet fluorescence (UVF) is an analytical technique conceived to determine total sulfur in gaseous streams (Blomberg et al., 2004; Pacheco et al., 2009). GC and the on-line analyzer have their weaknesses and strengths. The GC technique needs special recipients to collect samples and analyses must be performed as soon as possible. The on-line analyzers are subject to elemental sulfur deposition on the UVF system due to constant temperature and pressure changes, thus requiring frequent maintenance.

The main challenge to identify and quantify sulfur compounds in gaseous streams is to develop a reproducible and interference-free analytical method. This is possible by using gas chromatography with a double plasma chemiluminescent detector and a chemically inert system (Sulfinert) for sulfur compounds. Analysis with accuracy at the $\mu g.m^{-3}$ level for sulfur compounds is a critical issue. For instance, hydrogen sulfide and sulfur dioxide strongly absorb on metallic surfaces of the injection tubes, generating lower analytical results (Restek, 2005).

Extensive reviews of sulfur chemiluminescence detectors (SCD) for gas chromatography have been published (Gras et al., 2005; Yan, 1999, 2002, 2006; Johansen et al., 2005). There are relatively few reports on the use of SCD with dual plasma (DP) systems for analysis of sulfur compounds in gaseous streams from refineries (Gras et al., 2005). This system may use a packed column in a Sulfinert tube or a megabore column. The first one has two advantages: (i) the detector response is more stable, and (ii) it presents an excellent, accurate analysis at $\mu g.m^{-3}$ levels for light sulfur compounds. Comprehensive two-dimensional gas chromatography coupled with fast sulphur-chemiluminescence detection appears to be a useful technique to analyze liquid petroleum products (Blomberg et al., 2004, Yan, 2006), but apparently no studies using refinery gaseous streams have been reported.

This study reports calibration of a SCD-DP detector and comparison of the response factors obtained for some sulfur compounds (including sulfur dioxide, SO_2) with the ones available in the literature (ASTM, 2008). We are also interested in the application of the SCD-DP detector to determine the sulfur compounds present in several gaseous refinery streams. Physical and chemical properties of these compounds are very different. For this reason, two types of calibration mixture were considered: (a) commercially available calibration gas mixtures; (b) calibration gas mixtures obtained via passing a gas (at a known rate) through certified permeation devices.

EXPERIMENTAL

The high reactivity of sulfur compounds on non-inert metallic surfaces tends to reduce the detector response, thus giving lower peak areas than expected. Among the sulfur compounds, SO_2 stands out as the most reactive (Pereira, 2006). For this reason, the components in contact with samples must be made of inert materials (like aluminum), or chemically treated to become non-reactive towards sulfur compounds.

Chromatographic System

The detector used was a SCD-DP from Sievers Research, Inc. (Boulder, Colorado, USA). The injection system consisted of a PTFE (polytetrafluoroethylene) tubing up to the loop inlet, a 1 mL inert loop (Sulfinert) for sulfur compounds, a valve for automatic gas sampling (jacketed with aluminum) and a valve connection with the column inlet of inert material (Sulfinert) kept at 150°C. The combustion chamber contained ozone (65 cm^3) and hydrogen (45 cm^3). Flame temperature was 800°C. The detector probe pressure was 403 – 412 torr.

The packed column used (RT-XL sulfer) contains dimethylpolysiloxane as stationary phase (2.0 m x 0.75 mm i.d., 100-120 mesh particle size). According to the literature (Navas and Jiménez, 2000), this column was successful in analysing traces of sulfur compounds in light petroleum distillates using a detector based on the chemiluminescent reaction (SCLD) between hydrogen sulfide (H_2S) and ozone (O_3).

Standard Reference Materials

The performance of a calibrated SCD dual plasma was assessed using two types of standard reference material (SRM): (i) a certified compressed gas mixture (cgm) of methanethiol (MeSH) in butane (62.53 ± 3.13 $\mu g.m^{-3}$), from White Martins; (ii) certified permeation tubes (VICI Metronics Inc., Poulsbo, Washington, USA - ASTM, 2004, 2005). The device releases the specific sulfur compound through its permeable portion at a constant and known rate following its certificate at a constant temperature (30 or 40°C). The permeation tubes used are listed in Table 1.

Table 1: Types of permeation tubes used in the calibration tests

Sulfur compound and concentration range (μg.m^{-3})	Type of permeation tube
Hydrogen sulfide - H_2S (from 1802 to 6721) (from 57 to 71)	Extend life tube (ELT-30), 682 ng.min^{-1} ± 2%, 30°C Wafer device (WD-40), 28.5 ng.min^{-1} ± 5%, 40°C
Carbonyl sulfide – COS (from 1653 to 3359) (from 63 to 82)	Wafer device (WD-30), 641 ng.min^{-1} ± 5%, 30°C Wafer device (WD-40), 227 ng.min^{-1} ± 5%, 40°C
Sulfur dioxide - SO_2 (from 4121 to 6753) (from 87 to 91)	Low emission (LE-30), 1293 ng.min^{-1} ± 2%, 30°C Wafer device (WD-40), 19.2 ng.min^{-1} ± 5%, 40°C
Methanethiol – MeSH (from 3581 to 7770) (from 2025 to 2406)	High emission (HE-30), 1113 ng.min^{-1} ± 2%, 30°C Standard device (SD-40), 335 ng.min^{-1} ± 2%, 40°C
Dimethylsulfide – DMS From 1048 to 1324	Standard device (SD-30), 214 ng.min^{-1} ± 2%, 30°C
Dimethyldisulfide – DMDS From 1230 to 1825	High emission (HE-40), 469 ng.min^{-1} ± 5%, 40°C

Optimization of the Analytical System

We aimed at obtaining accurate and precise results at μg.m^{-3} concentration levels, as well as developing conditions to lower the minimum detectable quantity (MDQ) (Restek, 2005; Chawla and Di Sanzo, 2005; Seung-Wong et al., 1997). In this work, the following parameters were chosen.

H_2S and SO_2 Responses

The behavior of the SCD-DP detector was checked by generation of some gas flows containing H_2S or SO_2 in different concentrations (μg.m^{-3}). The correction factors (CF) were compared concerning area repeatability at an acceptable maximum difference of 5%.

Temperature Programming

Optimal temperature programming conditions must give the best resolution in the shortest analytical run time. The following parameters were investigated: (i) initial temperature (45-60°C); (ii) heating rate (1-15°C.min^{-1}). Final temperature was 190°C and helium (11.3 mL.min^{-1}) was the gas carrier.

Generation of Sulphur Compounds for Evaluation of the Response Factor

For sulfur pattern generation from certified permeation tubes, an automatic generation system - VICI Metronics Dynacalibrator, model 340 (VICI Metronics Inc., Poulsbo, Washington, USA) was used. Air is pumped though a glass chamber where the certified permeation tubes (from 1 to 6) are placed. A temperature control system sets the temperature mentioned in the tube certificate. According to the sulfur compound concentration desired, an air outflow controller sets the correct flow in a mix chamber. The concentration value (μg.m^{-3}) is calculated based on the air outflow used, chamber temperature, room temperature and pressure, molecular weight and sulfur percentage of each sulfur compound used (Asnin et al., 2005).

Calibration of SCD Response

The calibration method requires quantification by class of sulfur compounds, since the detector response is approximately equimolar for sulfur compounds with the same number of sulfur atoms in the molecule. The quantification was performed by standardizing the concentration of a sulfur compound for each class of interest: thiols, monosulfides, disulfides, H_2S, COS and SO_2. All tests were conducted for a range of permeation rate in order to obtain results from a minimum detectable concentration to the highest concentration possible in the permeation tube.

Evaluation of the Combination of Sulfur Compounds

In order to analyze changes in the SCD response through the correction factors calculated according to ASTM D 5504-08 (ASTM, 2008), calibration was performed using more than one permeation tube in the permeation chamber. Through the combined use of permeation tubes, it was possible to simulate some possible compositions expected in refinery samples, thus performing a calibration under conditions similar to the true samples studied in this work.

Sulfur Compounds in Refinery Samples

Seven samples were collected from a refinery sulfur treating plant: (a) residual gas from the sulfur recovery plant (SRP); (b) fuel and (c) residual gases from di-ethanol-amine (DEA) treatment; (d) propane after caustic soda treatment; (e) hydrogen from a hydrotreater (HDT) unit; and (f) natural gas from mono-ethanol-amine (MEA) treatment.

Propane, hydrogen and natural gas were collected using Sulfinert treated stainless steel high pressure sample cylinders (300 mL). The maximum storage time of these samples was 72 h to ensure a constant concentration of the sulfur compounds present (Pereira, 2006).

Fuel and residual gases were collected using 1 L PTFE bags with PTFE tubing. The samples were analyzed within 4 to 8 h because significant losses of sulfur compounds were observed during long-term storage (Pereira, 2006).

Many sulfur compounds like H_2S, methanethiol and ethanethiol adsorbed onto metal surfaces. To minimize adsorption phenomena in the sampling point, the samples were taken after purging the line during 30 min to passivate the metal. In the case of sampling residual gas from the sulfur recovery plant, a PTFE tubing inside the transfer line and a PTFE pump to increase the gas flow rate were used. The PTFE tubing inside the transfer lines was different for each sample taken in order to avoid contamination during sampling.

Besides the use of the six sulfur compounds for calibration of the SCD-DP detector, identification of peaks in the chromatograms was performed by using other standard sulfur compounds (1-propanethiol, 2-propanethiol and t-butanethiol) and the Kovats retention indexes published in the literature (Miller and Bruno, 2003; Seung-Woon et al., 1997; ASTM, 2008) for 21 sulfur compounds.

RESULTS AND DISCUSSION

Influence of Temperature on the Elution Sequence

Initial temperatures lower than 45ºC led to a broadening of the peakbase due to H_2S interaction with the column filling. The peaks corresponding to H_2S and carbonyl sulfide (COS) were not well resolved at 60ºC. In order to obtain a good resolution for dimethylsulfide (DMS) and SO_2 peaks, the highest possible temperature programming rate was 10°C.min^{-1}. Higher rates led to poor resolution of both peaks.

Calibration of the H_2S Response

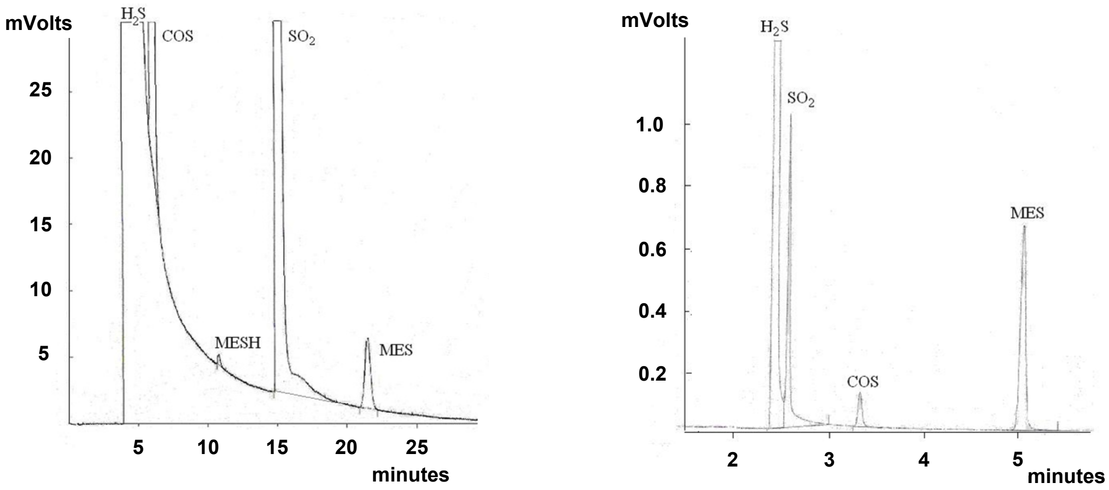
As shown in Table 2, the extended life tube (H_2S-30) presented a better repeatability than the gel mass one (H_2S-40). Discrepancies were not observed for the generation of H_2S SRM at either temperature, which is in accord with the frequent use of H_2S as reference sulfur compound in the quantitative analysis of other sulfur compounds. Therefore, the correction factor with the extended life tube (H_2S-30) was taken as the response of H_2S at μg.m^{-3} levels.

Calibration of the COS Response

The gel mass tube (COS-40) calibrated at 40°C presented the best repeatability (Table 2). Another gel mass tube (COS-30), calibrated at 30°C, presented a median slightly shifted to lower correction factor values. The calculated experimental correction factors were comparable to those published in the ADTM D 5504 standard method (ASTM, 2008), and are clearly different from those of the other sulfur compounds shown in Figure 1.

Table 2: Data set obtained for box-and-whisker plot of the correction factors obtained for H_2S, COS, MeSH, SO_2, DMS and DMDS

Sulfur compound	Data points	Lowest value (.10^{-5})	Lower quartile (.10^{-5})	CF Median (.10^{-5})	Upper quartile (.10^{-5})	Highest value (.10^{-5})
H_2S (ELT-30)	44	4.34	4.44	4.58	4.72	4.98
H_2S (WD-40)	39	3.97	4.27	4.45	4.67	4.92
COS (WD-30)	27	1.89	1.97	2.05	2.22	2.64
COS (WD-40)	63	1.96	2.14	2.21	2.29	2.49
MeSH (cgm)	18	3.32	3.34	3.67	3.90	4.09
MeSH (HE-30)	44	3.18	3.33	3.60	3.82	4.20
MeSH (SD-40)	62	3.26	3.94	4.43	4.59	4.89
SO_2 (WD-40)	28	2.24	2.84	3.52	3.92	4.49
DMS (SD-30)	40	3.18	3.35	3.40	3.62	4.02
DMDS (HE-40)	22	3.11	4.13	4.62	4.99	5.67



(a) (b)

Figure 1: Sulfur compounds in a SRP residual gas: (a) by SCD-DP with a RT-XL sulfur column in Sulfinert (initial temperature, 45°C; heating rate, $10°C.min^{-1}$; final temperature, 190°C for 24 min); (b) by SCD with a 60 m x 0.53 mm HP-1 megabore column (loop, 1 µL; combustion chamber pressure, 35 torr; flame temperature, 780°C. Initial temperature, 35°C; heating rate, $5°C.min^{-1}$; final temperature, 150°C for 10 min) (Pereira, 2006).

Calibration of the MeSH Response

The standard emission tube (MeSH-40) originally calibrated at 40°C presented a median slightly shifted to higher values and without outliners (Table 2). The high emission tube (MeSH-30) originally calibrated at 30°C presented a central median and no outliners. When the correction factors calculated for the two distinct types of tubes were compared, a significant difference was noted. This was not verified for the other sulfur compounds (generated by different types of permeation tubes). The variation between the calculated factors for high emission permeation tubes and the ones obtained by calibration with a certified pressurized gas mixture reference in the range of $mg.m^{-3}$ was lower than 5%. Thus, the correction factors from high emission permeation tubes were considered for the response of MeSH at the $\mu g.m^{-3}$ level, because it is known that the response is linear over at least three orders of magnitude of concentration (ASTM, 2008).

Calibration of DMS Response

The experimental correction factors of the standard emission tube (DMS-30) calibrated at 30°C, were reproducible and comparable to the values published in a standard method (Johansen et al., 2005). As shown in Table 2, the correction factors (CF) are very comparable to the calibration data for DMS generated at 30°C (CF = 3.40 10^{-5}), SO_2 generated at 40°C (CF = 3.52 10^{-5}) and MeSH generated at 30°C (CF = 3.60 10^{-5}).

Calibration of SO_2 and DMDS Responses

As shown in Table 2, the high emission tube of dimethyldisulfide (DMDS) (calibrated at 40°C) and the tube of low SO_2 emission (calibrated at 30 °C) presented the highest dispersions among the sulfur compounds examined. The median for DMDS was very close to the one for H_2S, whereas SO_2 showed a median near to DMS and MeSH.

From the data in Table 2, it is possible to see the differences among the calculated factors from different sulfur permeation tubes. The criterion applied for discrepancies considers that the variation between the calculated factors for each pair of permeation tubes for the same sulfur compound is not significant when it is less than 5% (Miller and Miller, 2000).

Calibration of sulfur compounds was performed over 4 months in order to evaluate the response stability of the SCD-DP system. For H_2S, COS, MeSH and DMDS, the detector presented repetitive responses (5% difference between areas) after 30 min for stabilization of the "flow-through system" without requiring previous passivation. However, a consecutive increase of the response area for SO_2 was observed during the first three hours, possibly due to passivation of the chromatographic system. Otherwise a consecutive decrease of the response area was observed for DMDS during the first 60 minutes, possibly due to retention by the adsorption column. Thus, SO_2 and DMDS SRM calibrations should be performed each time in order to verify whether the calibration factors maintain their previous values. It is advisable to make three preliminary injections before starting SO_2 analysis, and one injection in the case of DMDS.

Considering that the median of the SCD response factor for other monosulfur compounds in the calibration step is between 3.00 10^{-5} and 4.50 10^{-5}, it can be inferred that the system passivation and the adjustment of stabilization time in SO_2 pattern generation lead to experimental response factors close to the expected ones, thus confirming that the optimum working conditions were reached. It appears that the time of pattern generation for stabilization of flow and temperature is not as critical as the effect of previous passivation of the system (DMDS and SO_2). As a result, an increase in the detection signal was observed, thus improving sensibility and lowering the MDQ.

Significance Test for the Calibration Step

Table 3 shows the comparison of the correction factor calculated using data from the ASTM D 5504 standard method (ASTM, 2008). In virtually all cases, a significant difference was observed (Miller and Miller, 2000). The calculated correction factors were systematically lower than the published ones. The significance test suggests that the SCD-DP inert material column, the inert inlet system and the passivation procedure increased detector response, thus lowering the detection limit for sulfur compounds. In other words, the GC-SCD-DP system under optimized conditions for determination of sulfur compounds in gaseous streams showed higher responses and, consequently, smaller correction factors when compared with those published in the ASTM D 5504 method (ASTM, 2008).

Table 3: Calculated and tabulated correction factors (CF) for H_2S, COS, MeSH, SO_2, DMS and DMDS

Sulfur compound	Calculated CF (.10^{-5})	Tabulated CF (.10^{-5})
H_2S	4.60	5.96
COS	2.23	3.69
MeSH	3.61	5.01
DMS	3.49	4.90
DMDS	9.05	10.00

A comparative test demonstrated that the SCD-DP system with a packed column in a Sulfinert tube gives a better accurate analysis at the μg.m^{-3} level for light sulfur compounds than the traditional SCD system with a megabore column (Pereira, 2006). A typical residual gas sample from a sulfur recovery plant (SRP) was analyzed in the two chromatographic systems: (i) dual plasma with packed column (Figure 1a) and (ii) single plasma with megabore column (Figure 1b). In the first system, it was possible to detect 1 μg.m^{-3} of methanethiol.

Chromatographic data for six sulfur compounds are presented in Table 4. The determination of compound amounts (mg.m^{-3}) was carried out by using the following information in an electronic spreadsheet (Excel): peak name; area (counts); response factor; molecular weight and sulfur percent.

Table 4: Data set obtained for elution time (ET) for some sulfur compounds with helium as carrier gas (11.3 mL.min^{-1}) in a SCD-DP with a RT-XL sulfur column in Sulfinert

Sulfur compound	Mean (ET min)	Highest value (w½ min)	Upper value (ET min)	Lower value (ETmin)
H_2S (ELT-30)	4.143	0.198	4.190	4.075
H_2S (reference sample)	4.999	1.884	5.371	4.626
COS (WD-30)	5.998	0.230	6.048	5.944
MeSH (cgm)	10.057	0.403	10.097	10.008
MeSH (HE-30)	10.626	0.253	10.702	10.563
DMS (SD-30)	14.903	0.237	14.933	14.842
SO_2 (cgm)	13.806	4.780	14.107	13.372
SO_2 (WD-40)	16.180	2.045	16.656	15.970
DMDS (HE-40)	28.069	0.792	28.143	27.975

Sulfur Compounds in Selected Petroleum Refinery Streams

The analyses were performed under the following conditions: (i) initial temperature, 45°C; (ii) heating rate, 10°C.min^{-1}; (iii) final temperature, 190°C for 24 min.

Fuel Gas Samples

Figure 2 shows the chromatogram of a typical fuel gas sample from distillation of a Brazilian crude oil (Campos Basin) before desulfurization. Nine sulfur compounds were identified. Many of them are present in high concentrations. This leads to a poor resolution of two peaks: ETSH and DMS (peaks 4 and 5); t-butanethiol and s-butanethiol (peaks 7 and 8).

Figure 3 shows the chromatogram of a typical fuel gas sample from distillation of an Arabian crude oil before desulfurization. Fourteen sulfur compounds were found, including three disulfides: DMDS, methyl-ethyldisulfide (MEDS) and diethyldisulfide (DEDS). Only one co-elution was observed (peak 4): ETSH and SO_2.

Residual Gas Samples

Two residual gas samples were analyzed: a sample from FCC (Fluid Catalytic Cracking) after desulfurization using DEA (Figure 4) and after starting a sulfur recovery plant (SRP – Figure 5). In the first case, twelve sulfur compounds were found, H_2S and MESH being the major components. The sample from a SRP is much simpler; only five compounds were detected, being present at trace levels (μg.m^{-3}). Analysis of this sample is important to adjust the molar ratio between H_2S and SO_2 in the gas stream when entering the SRP to the best ratio (2:1) (Lieberman, 1991).

Propane Sample

Figure 6 shows the chromatogram of a typical propane stream after desulfurization with caustic soda. Seven sulfur compounds were identified. The major sulfur compound is DMDS.

Hydrogen and Gas Natural Samples

Four sulfur compounds were identified in each of these samples. Most of them are present at trace levels (μg.m^{-3}). Figure 7a shows the chromatogram of a typical hydrogen sample after naphtha catalytic reforming. During reforming, H_2S readily reacts with air, producing SO_2. This explains the higher amount of SO_2 found after reforming. The concentration of H_2S in the gas natural sample was very low (Figure 7b) because of the desulfurization process with MEA. The three thiols present were deliberately added to allow detection in case of leakage (odorization process). Their concentrations are very close to the amounts added to this sample.

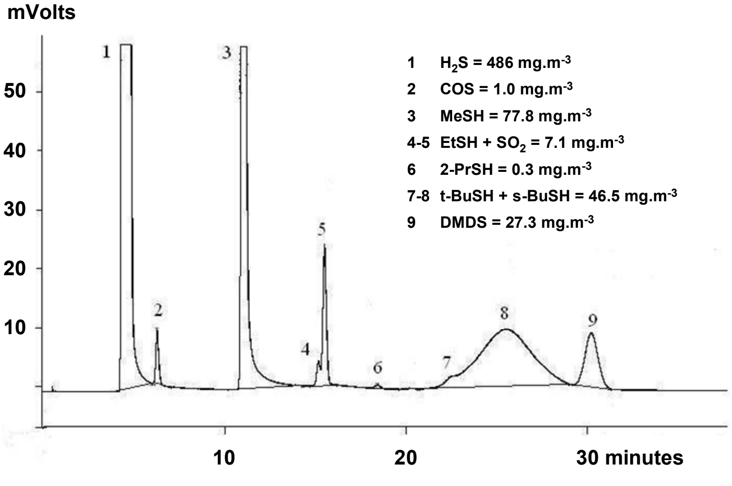


Figure 2: Sulfur compounds in a fuel gas sample from a Brazilian crude oil distillation before desulfurization by SCD-DP with a RT-XL sulfur column in Sulfinert.

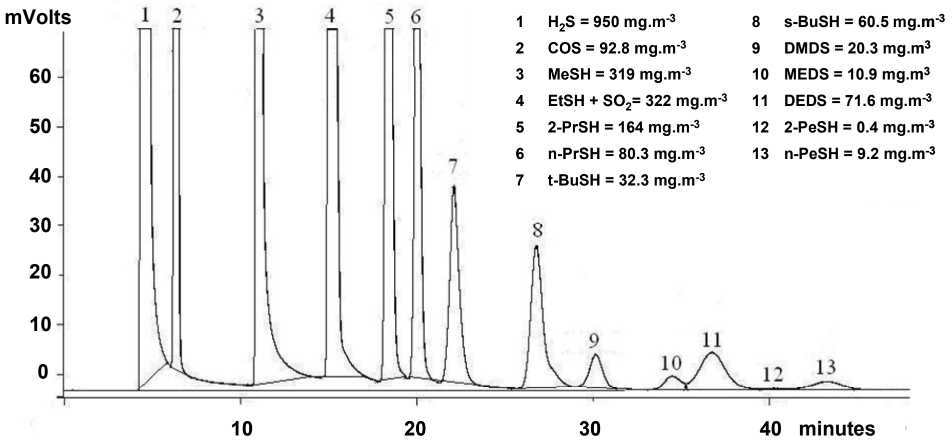


Figure 3: Sulfur compounds in fuel gas sample from an Arabian crude oil distillation before desulfurization, by SCD-DP with a RT-XL sulfur column in Sulfinert

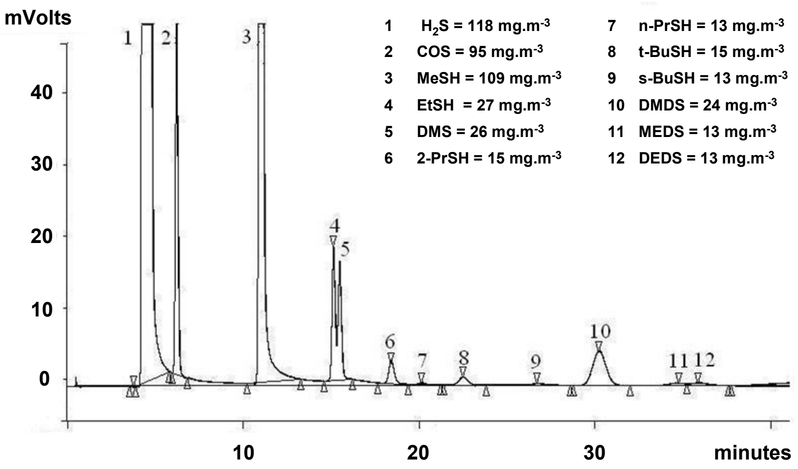


Figure 4: Sulfur compounds in residual gas sample from FCC after desulfurization, by SCD-DP with a RT-XL sulfur column in Sulfinert

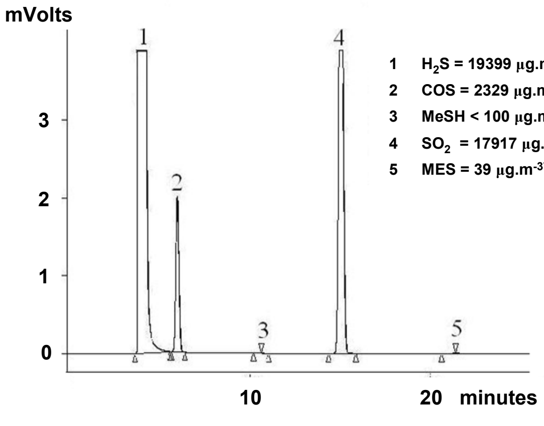


Figure 5: Sulfur compounds in a residual gas sample from SRP by SCD-DP with a RT-XL sulfur column in Sulfinert

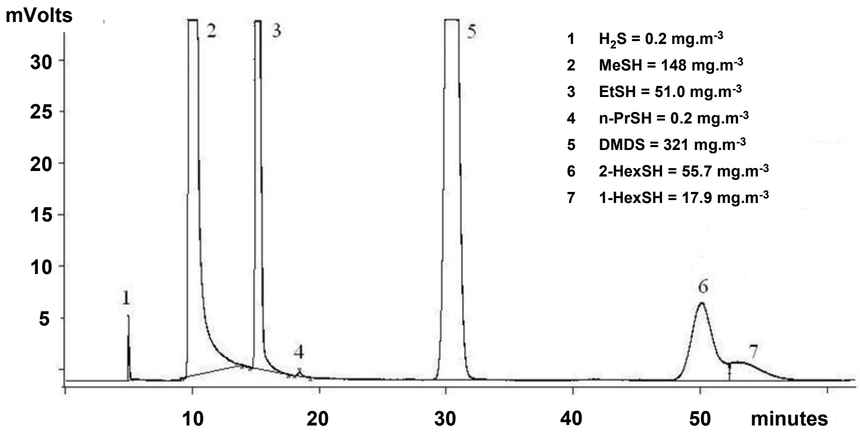
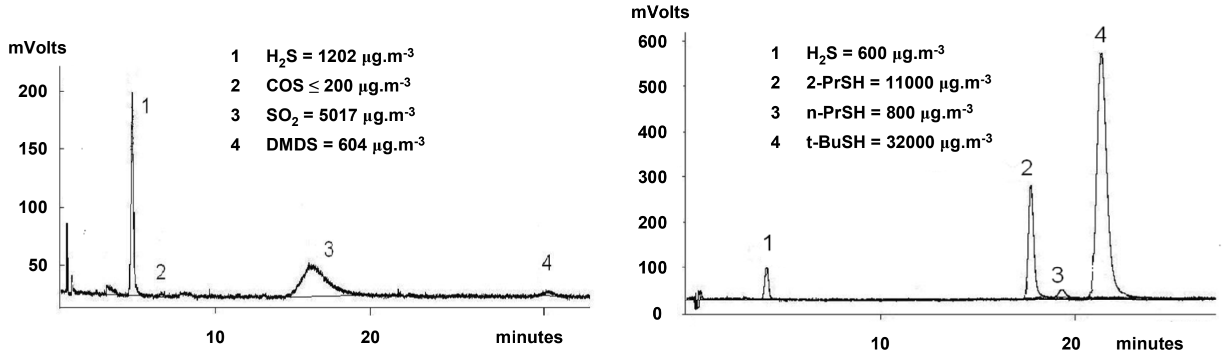


Figure 6: Sulfur compounds in a propane sample after caustic soda treatment, by SCD-DP with a RT-XL sulfur column in Sulfinert



(a) (b)

Figure 7: Sulfur compounds in (a) a hydrogen sample after naphtha catalytic reforming and (b) a natural gas sample after desulfurization with MEA and odorization process, by SCD-DP with a RT-XL sulfur column in Sulfinert.

CONCLUSIONS

Approximate equimolarity must be considered as a criterion for the analysis of H_2S, COS, thiols and sulfides by SCD-DP, since there are differences in the response at the µg.m^{-3} level. Different types of permeation tubes can lead to different calibration factors for the same sulfur compound, as seen for MeSH.

A critical analysis shows that: (i) there was a systematic difference between the factors calculated and published; (ii) the calculated factors were smaller than the tabulated ones, consequently the response areas of the SCD were higher. This indicates that the detector was optimized for quantification in µg.m^{-3} levels.

System passivation appears to be more critical than the time of pattern generation for flow stabilization and temperature in the pattern generator in the specific case of SO_2 and DMDS. Therefore, a good practice to minimize the analytical error during analysis of SO_2 and/or DMDS is to passivate the system with 3 injections of the generated pattern before injecting the sample to be analyzed.

The analytical procedure described in this work was able to quantify sulfur compounds present in a great variety of gaseous streams at µg.m^{-3} levels. This is of utmost importance for monitoring sulfur removal in the petroleum refinery processes and the quality of finished products.

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