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Analysis of Both Sulfur and Non-Sulfur Compounds Using a Single Gas Chromatograph with Parallel Sulfur Chemiluminescence and Thermal Conductivity Detectors

Hui Wang, Qinglin Zhang, Ivo G. Dalla Lana, and **Karl T. Chuang**
Department of Chemical and Materials Engineering, University of Alberta, Edmonton, AB T6G 2G6, Canada

Abstract

Sulfur chemiluminescence detectoion (SCD) allows precise measurements of sulfur-containing molecules down to ppb levels. Because SCD ignores the presence of compounds other than those containing sulfur, a complete analysis of such gas mixtures is not possible using SCD alone. This paper describes how the coupling of sulfur chemiluminescence and thermal conductivity detectors in parallel within a single gas chromatograph enables the determination of concentrations of both sulfur-containing and other gaseous compounds through simultaneous sampling, separation, and detection. The method extends the range of a single instrument for detecting sulfur-containing compounds from percentage to ppb levels.

Introduction

The work of Benner and Stedman (1), the systematic studies on the design of sulfur chemiluminescence detectors and possible influencing factors, started sulfur detection by chemiluminescence. The underlying chemistry remains contentious, but one view as stated by Shearer (2) suggests that it is the formation of sulfur monoxide from sulfur-containing compounds being eluted from a gas chromatograph (GC) separation column to a reducing hydrogen–air flame, and that the sulfur monoxide that is formed is subsequently detected because of its chemiluminescent reaction with ozone. Following this early work, many improvements in its application have popularized the use of sulfur chemiluminescence detectors (SCD). Shearer et al. (3) coupled SCD to a GC and evaluated its performance and operating features, initiating a commercially available means of sulfur-selective detection. They modified SCD using an externally heated ceramic combustion assembly that allowed it to operate at low pressure and under fuel-rich conditions outside of the flammability limits of hydrogen in air (2). This flameless SCD, as it was termed, improved the ease of use, reliability, and detectability of the commercially available equipment. In addition, they extended the use of SCD to the examination of sulfur compounds in liquefied petroleum products by adding an inert sample inlet assembly to the flameless SCD and GC system (4). Their work played a very important role in developing and extending the applications of SCD.

Hines (5) measured specific sulfur compounds in liquefied petroleum gases and natural gasoline streams, and Harryman and Smith (6) determined the sulfur species distribution of streams at Texaco's NGL Fractionation Plant. The results of the latter indicated that higher concentrations than those predicted by using the Soave Redlish-Kwong (SRK) or the Peng-Robinson (PR) equations of state were present. Chawla and Sanzo (7) also studied the optimization and operational characteristics such as linear response, sensitivity, and stability of SCD coupled to a GC. Tang et al. (8) developed a multi-purpose sampling loop with a cryogenic trap that, when coupled to a GC-SCD, permitted analysis from nanogram-per-cubic-meter to milligram-per-cubic-meter levels of sulfur compounds in the atmosphere, natural gas, and gaseous fuels.

The major advantage of SCD as a selective detector, as pointed out by Shearer et al. (2), resulted from its ability to measure components of interest, whereas other co-eluting species were not sensed. However, this apparent advantage becomes a disadvantage when the composition of what is not sensed also needs to be known. To date, no SCD-related literature is available that describes the simultaneous analysis of both sulfur- and non-sulfur-containing compounds. To deal with the wide concentration ranges, Lechner-Fish (9) used two separate chromatographs with different detectors; one for measuring the components of higher concentration, and the other for those of lower concentration. In research and commercial practice, one frequently encounters situations where not only the concentrations of both sulfur and non-sulfur containing components but also both high concentrations (percentage level) and low concentrations (ppm and ppb levels) of sulfur-containing species must be determined. To meet this requirement, a single GC instrument with parallel SC and thermal conductivity (TC) detectors was configured, enabling the simultaneous sampling and determination of the compositions of both sulfur-containing and other species. This method also extended the measurement range for sulfur-containing compounds from percentage to ppb levels.

This article describes the design considerations for a parallel SCD-TCD GC and gives an example of its use.

Experimental

Design considerations

SCD can precisely measure sulfur-containing molecular species down to ppb levels. Coupled with GC separation using an appropriate column, SCD can detect all sulfur compounds present. However, this detector is insensitive to compounds lacking sulfur atoms. Although TCD can theoretically detect components whose thermal capacities differ from that of the carrier gas, it can not detect those components present at several-hundred-ppm levels because of its limited sensitivity. Combining these two detectors enables the measurement of compositions of both sulfur and non-sulfur species, a situation often encountered in research and industrial applications.

Two options are available for combining SCD and TCD within a single GC. The first option is to place them in series after a single GC column, and the other option is to arrange them in parallel (each of the detectors senses an effluent from separate GC columns). The large difference in intrinsic sensitivity between TCD and SCD renders the consecutive combination impractical. For example, if the TCD and SCD series monitors the effluent from a single packed column, when the TCD obtains a suitable response, the SCD may be overloaded. On the other hand, if the series combination comes after a capillary column with a split sample injection, SCD may get an appropriate response, but the response of TCD will be very poor. Both situations will result in overall unsatisfactory quantitative analysis. In addition, the connection between TCD and SCD can also lead to GC peaks with tails that adversely influence the precision of the measurement. The parallel combination acts like two separate GCs, except that the two columns share the same oven; each detector has its own sampling loop, GC column, and carrier gas stream. It is difficult to optimize a common oven temperature or a temperature program for both columns so that the best separation results. One can only adjust the flow rate of the

Table I. Composition of Gas Samples

Component	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
CH_4 (%)	8.70	13.8	9.11	7.47	5.89
CO_2 (%)	8.07	13.0	8.59	7.05	5.55
C_2H_4 (%)	5.98	0	0	0	0
H_2S (ppm)	1300	2090	1370	1130	890
COS (ppm)	1440	2320	1530	1260	991
SO_2 (ppm)	991	1540	1020	835	658
CS_2 (ppm)	139	224	148	121	95.4
Thiophene (ppm)	69.4	112	73.8	60.6	47.7
C_3H_7SH (ppm)	69.4	112	73.8	60.6	47.7
Balance	N_2	N_2	N_2	N_2	N_2

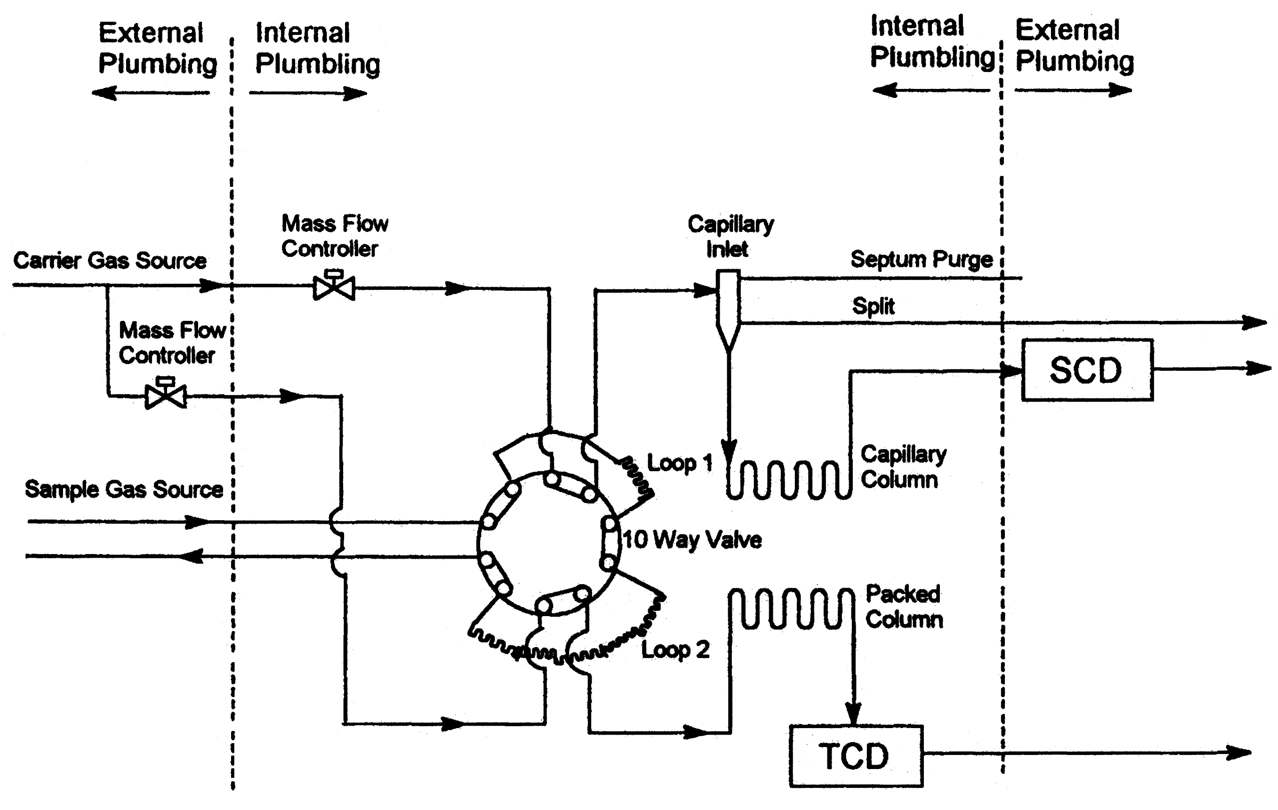

Figure 1. Schematic drawing of parallel sulfur chemiluminescence and thermal conductivity detectors within one GC.

carrier gas, the length of the column, and different kinds of packing for the two GC columns in order to obtain the best separation. The response, resolution, and sensitivity are also affected by the size of the sampling loops and by setting the appropriate split flow rate of the capillary column.

As mentioned previously, the size of sampling loop is very important to the sensitivity of the equipment. Two different loop sizes were chosen for the SCD and TCD independently, depending on their different intrinsic sensitivity. Of course, the smaller loop (38.5 µL) was used for the more sensitive SCD, and the bigger loop (146 µL) was used for the less sensitive TCD. The two loops were connected by a 10-way valve that was controlled automatically with a timer, so that simultaneous sampling was realized.

Figure 1 shows a schematic drawing of the GC with parallel SCD and TCD. the original carrier gas stream of the HP 5890 II GC (Hewlett-Packard, Palo Alto, CA) was retained for the capillary column-SCD, and another carrier gas stream was added for the packed column-TCD, the gas flow rate of the latter being controlled by a separate mass flow controller. A 10-way valve was used to connect the sampling lines, the two sample loops, and the two carrier gas lines. To obtain the best separation performance, a satisfactory temperature program for the capillary column was determined, and the packed column was adjusted by changing its specifications until it worked well at the same temperature program.

Instrumentation

A Hewlett-Packard model 5890 II GC fitted with a TCD and a Sievers model 350B SCD (Sievers Instruments, Boulder, CO) was used in this study. Hewlett-Packard ChemStation software was used for data acquisition and chromatogram analysis. This software enables the data processing of two simultaneous detector signals. A CP-Sil 5CB capillary column (50 m × 0.32 mm × 0.5 µm, fused-silica WCOT) was purchased from Chrompack (Middelburg, the Netherlands). The packed column was made from a stainless steel tube (4 m × 3.2-mm o.d.), and the packing was Porapak Q (Waters Associates, Milford, MA). Helium (Praxair Products, Edmonton, Alberta, Canada) was used as the carrier gas. The thermal conductivity detector was maintained at 200°C. Meanwhile, the burner of the SCD was operated at the conditions that the manufacturer suggested: 40 mL/min of air (Praxair Products), 100 mL/min of hydrogen (Praxair Products), 34.6 kPa, and 800°C. The oven temperature was held at 75°C for 3 min, programmed to 120°C at 20°C/min, and held at 120°C for the duration of the separation.

Gas sample preparation

The following mixtures were used: 1.49% H_2S (balance: methane; Praxair Products), 3% SO_2 (balance: nitrogen; Union Carbide, Quebec, Canada) and 5% COS (balance: nitrogen; Matheson Gas Products, Toronto, Ontario, Canada). Liquid reagents (R grade) such as carbon disulfide (Fisher Scientific, NJ), 1-propyl mercaptan (Eastman Kodak Company, Rochester, NY), thiophene (Aldrich Chemical Company, WI) and 1-propanol (Fisher Scientific) were used to prepare additional sulfur-containing gas samples. Non-sulfur-containing gases

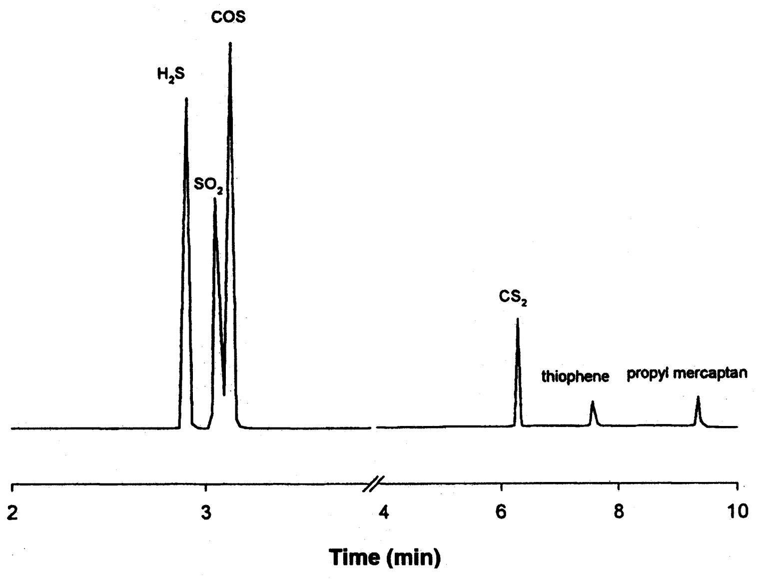

Figure 2. SCD chromatogram of typical sulfur-containing compounds separated using a CP-Sil PCB capillary column at a chosen temperature program. Oven temperature: 75°C for 3 min to 120°C at 20°C/min and held for 10 min.

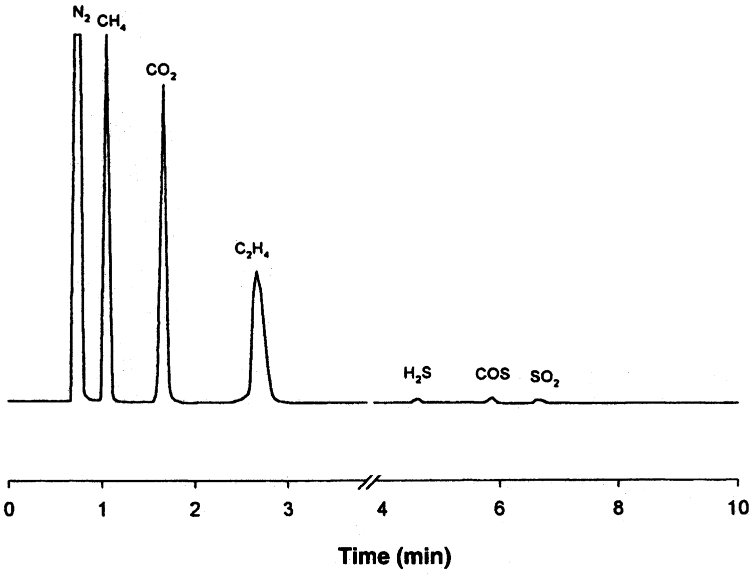

Figure 3. TCD chromatogram of sulfur and non-sulfur-containing gas mixtures separated using a packed column at a chosen temperature program. Oven temperature: 75°C for 3 min to 120°C at 20°C/min and held for 10 min.

included nitrogen (Praxair Products), carbon dioxide (Union Carbide Canada), and ethylene (Union Carbide Canada). Mass flow controllers (Sierra Instruments, Monterey, CA) were used to control the gas flow rates. The amount of each liquid component (CS_2, thiophene, or C_3H_7SH) was introduced by bubbling nitrogen through a propanol solution of the liquid sulfur-containing compounds. Because the amount of solution is as large as 500 mL and the concentrations of the sulfur compounds were relatively low, it was assumed that their concentrations remained constant during the bubbling. The content of these compounds in the gas stream was estimated using Raoult's law. Table I lists the compositions of the sample gases used in this study. The compositions were determined by the flow rate of each gas component and the concentration of each sulfur species in the solution. Therefore, the precision of the composition data in Table I depends on the accuracy of the mass flow controllers and the preparation of the solution. It was estimated to be ± 1%.

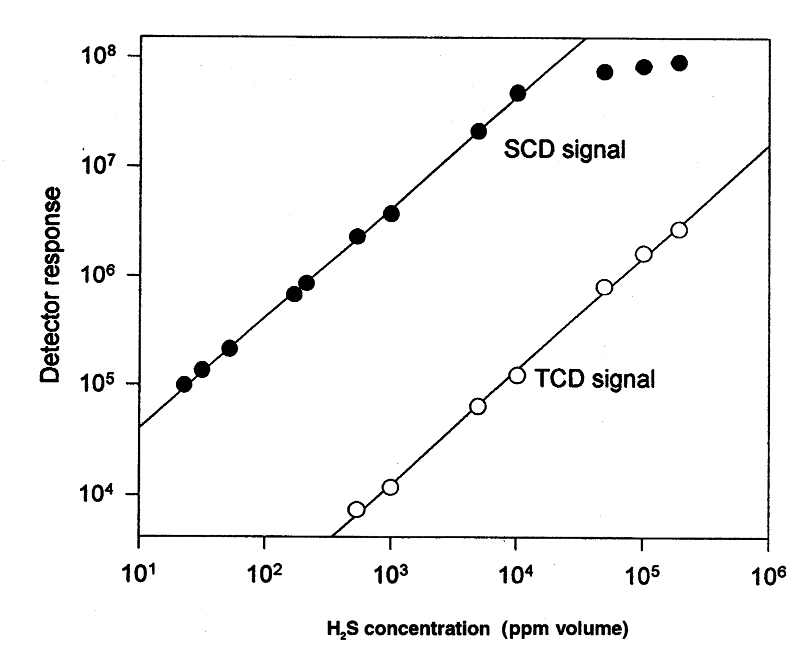

Figure 4. Detector linearity and measuring range.

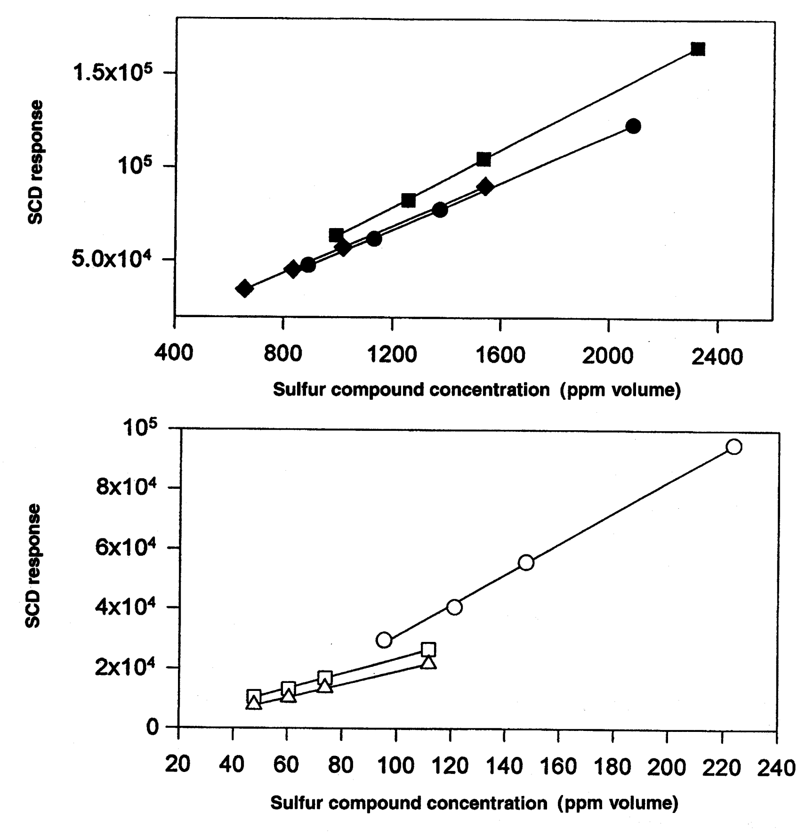

Figure 5. SCD calibration curves for selected sulfur compounds. ●, H_2S; ■, COS; ◆, SO_2; ○, CS_2; □, thiophene; △, propyl mercaptan.

Results and Discussion

Separation test

A CP-Sil 5CB capillary column was designed to separate the sulfur species. However, the separation of SO_2 and COS was very sensitive to the oven temperature, the temperature for the first 3 min being very important. Therefore, using sample gas 1, a temperature or temperature program at which the capillary column separated COS and SO_2 as well as possible was first sought. Figure 2 shows the SCD responses for typical sulfur compounds at the optimum temperature program. The separation was satisfactory, enabling the quantitative analysis of COS and SO_2.

Once this oven temperature or temperature program was determined, a packed column had to be chosen for the system with the thermal conductivity detector. A commercial packed column (HayseSep DB SS column, 100/120 mesh, 3 m × 3.2-mm o.d.) did not perform well at the temperature or temperature program selected for the capillary column. A packed column was fabricated to separate the common non-sulfur gases, such as N_2, CO_2, CH_4, and ethylene, and higher concentration sulfur species, such as H_2S, COS, and SO_2, satisfactorily at the previously determined temperature. Based on the work of Wilhite and Hollis (10), several types of Porapak packing that are related to sulfur species separation, such as R, Q, and QS, were tested, and then the length of the column was optimized. Although the flow rate of carrier gas could be adjusted to improve the separation performance, flows not much beyond the suggested value were used. The packed column performed well with the following specifications: packing type, Porapak Q; column length and diameter, 3 m × 3.2-mm o.d.; carrier gas flow rate, 30 mL/min. Figure 3 shows the TCD chromatogram for certain sulfur species of higher concentration and for the non-sulfur containing species.

Using the combination of SCD and TCD in parallel within the single GC oven, the sample was injected into two loops at the same time, and sulfur and non-sulfur compounds were analyzed simultaneously. It should be mentioned that the selection of both the hardware (each column and its specifications) and the software (the optimum temperature and carrier gas flow rates) is specific to the analytical problem encountered.

Linearity and measuring range

A variety of concentrations of H_2S (20 ppm, 20%, etc.) were used to determine the linearity of the signals and the measuring range. Figure 4 shows the various responses plotted against the H_2S concentrations. The SCD signals show good linearity from 20 to 10,000 ppm (1%) and a large response factor (4000 response/ppm). Being limited by the source of H_2S, concentrations lower than 20 ppm were not measured. However, a response factor as large as 4000 indicates that SCD should easily detect ppb levels of sulfur. Even though it was successful with sulfur concentrations up to 10,000 ppm (0.1%), SCD was designed to measure sulfur compounds at low concentrations (11). Using samples with high concentrations of sulfur leads to overloading, which adversely influences the precision, resolution, sensitivity, and linearity of the responses. Frequent exposure to high sulfur contents would also reduce the life span of the equipment. Therefore, higher concentrations should be avoided when using SCD. It was observed that when using TCD, the linear range of H_2S concentration was from 500 ppm to 20%. The linearity of the TCD over a broad range of higher H_2S concentrations made it suitable for the present application. Therefore, coupling SCD and TCD greatly extended the measuring range of sulfur components using a single GC instrument.

Calibration curves

Gas samples 2–5 were used for calibrations. The results shown in Figure 5 clearly illustrate that the linear calibration curves for H_2S, COS, and SO_2 and CS_2, propyl mercaptan, and thiophene do not coincide. Shearer (4) reported that SCD produced a linear response to sulfur, and that all sulfur species were equivalent on a molar basis. In other words, the SCD signals of all sulfur species should fall on the same straight line in the plot of response versus

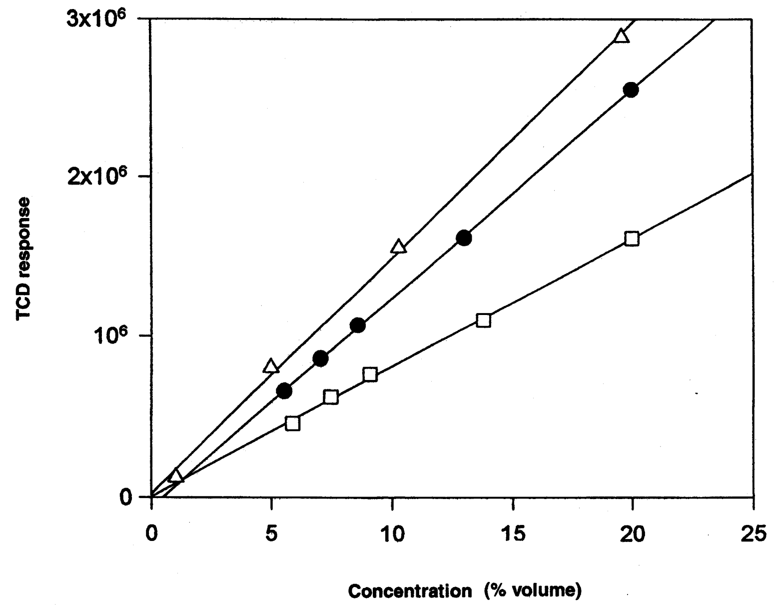

Figure 6. TCD calibration curves for selected compounds. ●, CO_2; □, CH_4; △, H_2S.

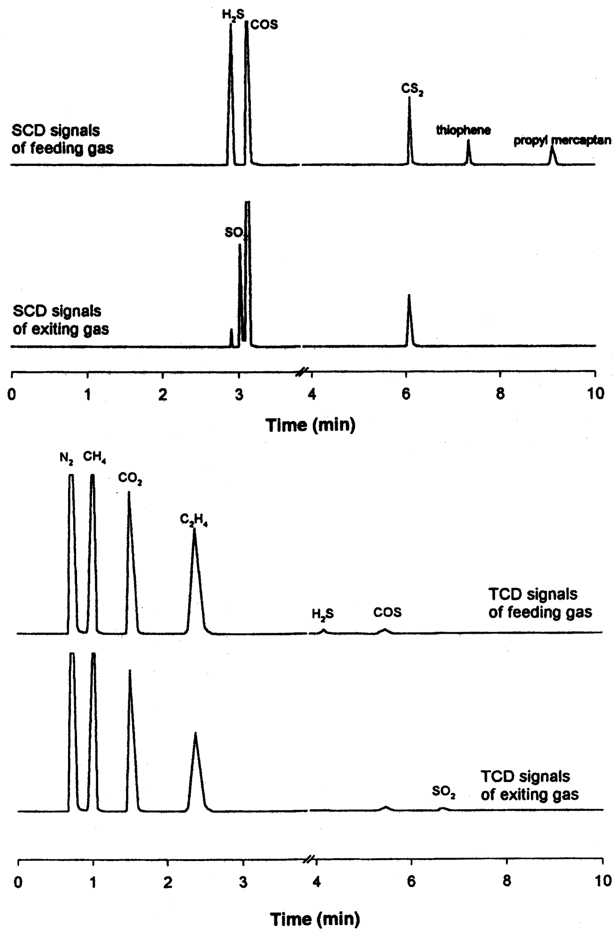

Figure 7. Chromatograms of application example. Oven temperature: 75°C for 3 min to 120°C at 20°C/min and held for 5 min.

concentration. However, in the present work as well as in that of others (5,6,8,12,13), different response factors were observed for the various species.

Different authors offer different explanations as to why various sulfur species show different response factors. Tang et al. (13) recently studied the response factors of sulfur compounds using SCD coupled with GC and pointed out that many factors may contribute to the differences in responses. These factors included those relating to SCD, such as the ceramic probe position and H_2/air ratio for the flame ionization detector (FID), and those relating to the GC, such as initial and final oven temperatures, sample states and concentrations, etc. Based on our results, we tend to believe that the differences in conversion for the sulfur species in the SCD burner are the main cause of the different responses. The capacity of the burner converting the effluent sulfur species into SO is certainly limited by conditions such as the H_2/air ratio to the FID, burner temperature, the ceramic probe position, and even the amount of sulfur that is fed. The lower response at higher H_2S concentration (Figure 4) probably suggests that when the sulfur content in the effluent is high, the burner is unable to convert the sulfur species completely to SO. Moreover, as a chemical reaction, its conversion also depends on the properties of the reactants and the reaction conditions determined by the burner. Therefore, different concentrations could result in different conversions, as observed for the various species. Relative to the reaction converting sulfides to SO, the reaction $2SO + O_3 \rightarrow 2SO_2$ that takes place in the chemiluminescence reaction cell does not seem to be the major factor in accounting for the differences in response factors. The calibration result of TCD, shown in Figure 6, is as normal as that obtained using TCD alone.

Application example

This method was used to evaluate the performance during the development of a new gas-sweetening process in our laboratory. One group of experimental data are used to illustrate the advantage of this method. Figure 7 shows two sets of SCD and TCD chromatograms, one for a sour gas sample and the other for the gas after being treated with the process. The TCD and SCD chromatograms for the same gas sample were recorded simultaneously. Quantitative calculation of the chromatograms before and after treatment (Table II) gave the following results: most of the H_2S was removed, approximately 20% of CS2 was removed, 24.4% of ethylene disappeared or was converted into some other non-sulfur containing products, nearly 100% of the mercaptan and thiophene was converted, COS and CH_4 concentrations did not change, and SO_2 was produced.

In summary, the information tells us that ths process can remove H_2S, thiophene, mercaptan, and part of CS_2. It does not affect CO_2 and saturated hydrocarbons such as methane in the gas, but some part of the olefins may be converted into other products. The application example clearly illustrates the advantage of this method: simultaneous analysis of sulfur- and non-sulfur-containing gases for either high- or low-concentration sulfur species.

Conclusion

The results obtained led to several conclusions. First, the single GC coupled with parallel SCD and TCD is able to analyze sulfur and non-sulfur containing species simultaneously. Second, the combination of SCD and TCD within a GC extends the sulfur measurement range from ppb levels to percentage levels. Third, in addition to allowing the measurement of both low and high concentrations of sulfur species, the simultaneous sampling and analysis of sulfur- and non-sulfur-containing gases eliminates errors arising from multiple sample injections. This method is particularly useful in real-time analyses. Finally, the parallel combination of SCD and TCD in a single GC exhibited high reliability and ease of operation and required little or no maintenance.

Acknowledgments

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Table II. Data Obtained by Quantitative Analysis of Chromatograms in Figure 7

Component	CH_4 (%)	CO_2 (%)	C_2H_4 (%)	H_2S (ppm)	COS (ppm)	SO_2 (ppm)	CS_2 (ppm)	Thiophene (ppm)	RSH (ppm)
Feed	8.92	8.28	6.13	1320	1630	0	519	81.0	129
Exit	8.87	8.46	4.63	190	1740	620	414	0	0

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