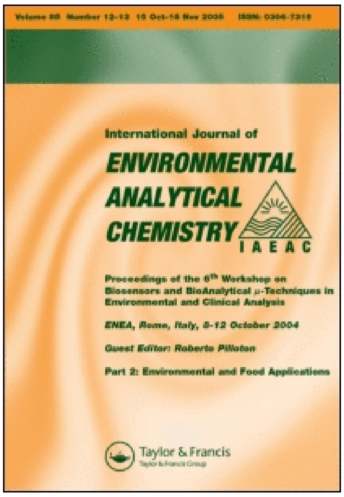

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A MULTIPURPOSE SAMPLING LOOP FOR ANALYSIS OF NANOGRAM TO MILLIGRAM PER CUBIC METER LEVELS OF SULFUR COMPOUNDS IN THE ATMOSPHERE, NATURAL GAS AND GASEOUS FUELS

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A multipurpose sampling loop coupled with a GC-sulfur chemiluminescence detector (SCD) for analysis of nanogram per cubic meter to milligram per cubic meter levels of sulfur compounds in the atmosphere, natural gas and gaseous fuels is reported in this paper. Samples with higher concentrations of sulfur compounds (> 70 μg/m^3) can be introduced to the GC-SCD by the sampling loop without cryogenic trapping. If the concentrations of sulfur compounds in the samples are lower than 70 μg/m^3, the sampling loop can be used as a cryogenic trap. This device is very useful for laboratories which handle different samples with a large range of concentrations of sulfur compounds.

KEY WORDS: Sampling loop, sulfur compounds, sulfur chemiluminescence detector, gas chromatography.

INTRODUCTION

In the past decades, the measurements of sulfur compounds in natural gas and gaseous fuels have been of continuous interest to both producers and marketers[1–4]. Also, the reliable assessment of sulfur compounds in the atmosphere is of the utmost importance to characterize global sulfur gas distributions and to understand their chemical fate[5–11]. The existing methods for directly introducing gaseous samples into GCs involve syringes or sampling loops[2–4]. The analysis of trace volatile sulfur compounds in the atmosphere involves a pre concentration step generally followed by gas chromatographic separation[12–16]. Those pre concentration devices include cryogenic trapping[13,14,16] and adsorption of sulfur compounds onto solid surfaces[12,15]. Because the concentrations of sulfur compounds in gaseous petroleum products and in the atmosphere range from nanogram (pg) to milligram (μg) per cubic meter, the normal sample introduction techniques are difficult to use. Many laboratories, especially commercial laboratories, need to analyze a variety of samples with a large concentration range of sulfur compounds. It is impractical to dedicate an additional instrument to analyze very low level of sulfur compounds. Although many new sulfur selective detectors with low detection limits have been developed, such as sulfur chemiluminescence detector (SCD) 350B[17], SCD 355B[18] and pulsed-flame photometric detector (PEPD)[19], they are still not sensitive enough to measure ng/m^3 level sulfur compounds without pre concentration. Therefore, it is necessary to develop a device to handle such a large range of concentrations of sulfur compounds.

In this paper, a multipurpose sampling loop (MPSL) is reported. This device is based on the use of a medium size sampling loop (100 μL) with cryogenic and heating facilities attached to the sampling loop. Thus, samples with higher concentrations of sulfur compounds (> 70 $\mu g/m^3$) can be introduced into a GC-SCD system directly by the sampling loop; for samples with lower concentrations (< 70 $\mu g/m^3$), the sampling loop was used as a cryogenic trap. Method precision, trapping efficiency, method detection limit and the properties of sampling loop materials were also reported.

EXPERIMENTAL

Multipurpose sampling loop (MPSL)

Figure 1 is the schematic view of the MPSL. A 0.50 mm i.d. stainless steel tubing (SSCS) coated with silica (Valco Instruments Co. Inc., Houston, TX, USA) was used as the sampling loop. The sampling loop was connected to a Valco four position P type valve (Valco Instruments Co. Inc. Houston, TX USA) and covered by a stainless steel tubing, which was used to carry liquid nitrogen. The stainless steel tubing was heated by a heating tape (BSD051060, Canlab, Toronto, ON Canada) and insulated with glass wool. The heating tape was controlled by a power input controller (Type 45500, Canlab, Toronto, ON Canada). The temperature of the sampling loop was monitored

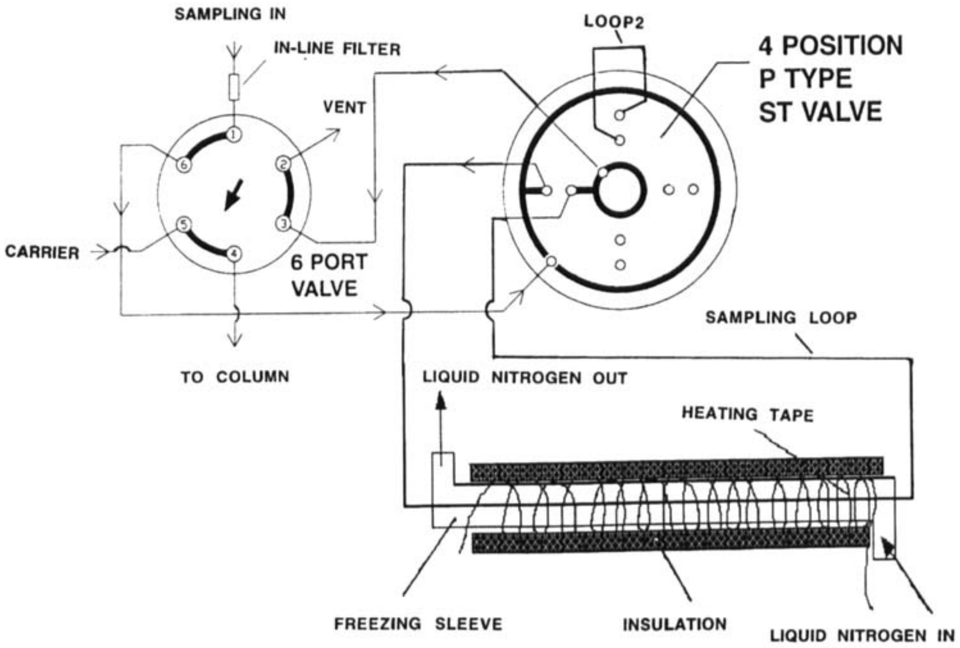

Figure 1 Schematic of the multipurpose sampling loop.

with an electronic thermometer (Hanna Instruments, Via Risorgimento, Italy). Gas samples were introduced to the sampling loop with a piece of SSCS tubing through a six port valve (Valco Instruments Co. Inc., Houston, TX, USA) and a vacuum pump connected to the sample out port in the six port valve. A flow meter was installed in front of the vacuum pump in order to monitor the sampling flow. A laboratory-made filter pack packed with a Teflon filter (pore size 5 µm, Gelman Sciences, Inc. Ann Arbon, MI) was installed in the sampling line (see Figure 1) in order to remove any particles in the samples. The MPSL was supported by a metal stand and could be easily installed on top of a GC.

Sampling loop material

Different megabore columns made from different materials were tested for use as the sampling loop. The materials tested included deactivated fused silica (FS) tubing (0.53 mm, J & W Scientific, CA, Folsom, USA), electropolished nickel tubing (EN) (Valco Instruments Co. Inc. Houston, TX USA) and SSCS tubing.

Instrumentation

A Shimadzu GC-9A (Shimadzu Corporation, Kyoto, Japan) and a Sievers Model 355 SCD (Sievers Instruments Inc., Boulder, Colorado, USA) were used. The data handling system was a Varian Star Work Station (Varian, Walnut Creek, CA, USA). The column used in this study was a J & W (J & W Scientific, Folsom, CA, USA) DB-1 megabore capillary column (30 m × 0.53 mm × 5 µm df.). The column was connected to the MPSL. Helium was used as the carrier gas; the flow rate was 7.0 mL/min. The burner of the detector was operated at the conditions suggested by the manufacturer, namely, air flow rate 40 std mL/min, H_2 flow rate 100 std mL/min, vacuum pressure 260 torr and temperature 780°C. The column temperature was held at 0°C for 1 min, then programmed to 200°C at a rate of 10°C/min. The column temperature was held at 200°C for 10 min.

Test sample preparation

H_2S, COS and CH_3SH (Matheson Gas Products Canada, Toronto, ON), CH_3SCH_3 (DMS) (BDH Chemicals LTD, Darmstadt, Germany) were used for preparing test samples. A 1 mL gastight syringe (Hamilton, Reno, Nevada, USA) was used in taking 1 mL pure gas phase of H_2S, COS and CH_3SH from their cylinders, respectively, and diluted into a Tedlar bag which had been previously filled with 10000 mL pure air to make a high concentration standard (HSD). The final concentrations of H_2S, COS and CH_3SH in the HSD, reported as sulfur (all concentrations of sulfur compounds are reported as sulfur in the following text), were 130 mg/m^3 at 25°C and 101 kpa. A 10 µL syringe (Hamilton, Reno, Nevada, USA) was used to inject 2 µL of DMS into the Tedlar bag. A certified 421 mg/m^3 gas mixture of DMS in nitrogen (Matheson Gas Products Canada, Toronto, ON) was used to determine the concentration of DMS in the Tedlar bag containing the HSD. Further dilutions of the HSD test sample were conducted in Tedlar bags. The concentrations were 65 mg/m^3 (STD-1), 32.5 mg/m^3 (STD-2), 6.5 mg/m^3 (STD-3), 0.13 mg/m^3 (STD-4), 65 µg/m^3 (STD-5) and 65 ng/m^3 (STD-6).

Test procedure

Two procedures were used for test samples with different concentrations of sufur compounds. Procedure 1: all test samples were introduced to the GC-SCD by the MPSL with a sampling flow rate of 50 mL/min and a sampling loop temperature of 150°C. Detection limits, method precision and calibration curves were determined. Procedure 2: the STD-4 and the STD-6 test samples were used for cryogenic trapping. At first, the STD-4 test sample was injected into the GC-CSD by the MPSL without cryogenic process at a sampling flow rate of 50 mL/min and the sampling loop temperature 150°C. The peak area of individual sulfur compounds and the peak area ratio of individual sulfur compounds to DMS were obtained. Secondly, the test sample was passed through the MPSL with liquid nitrogen on and heating tape off at the same sampling flow rate of 50 mL/min for different trapping periods (0.5 min, 1 min, 1.5 min, 2 min and 5 min). After turning the four position valve to loop-2 position (no gas flow in the sampling loop), the liquid nitrogen was turned off and the heating tape was turned on. When the temperature of the MPSL reached to 150°C, the six-port valve was turned to the injection position and the four position valve was turned to the sampling loop position at the same time (see Figure 1) The STD-6 test sample was test under 1.5 min and 5 min cryogenic trapping periods.

The peak area of different sulfur compounds during different cryogenic trapping periods and the peak area ratios of different sulfur compounds to DMS obtained at every cryogenic trapping period were compared to the value obtained without the cryogenic process in order to determine the cryogenic trapping efficiency for sulfur compounds.

Real sample study

Natural gases, liquefied petroleum gases (LPG) and an indoor air sample from a local restaurant were tested in our laboratory. Natural gas and LPG samples were collected in Telfon lined metal cylinders, and the indoor air from a restaurant was collected in a Tedlar bag. The natural gas and LPG samples were analyzed using the sampling loop without cryogenic trapping, and the indoor air sample was analyzed using the cryogenic process.

RESULTS AND DISCUSSION

Typical chromatograms of trace sulfur compounds are shown in Figure 2. Figure 2-A is a chromatogram from a standard sulfur compounds mixture. It can be seen that H_2S and COS are well resolved even when using a 30 m megabore column. Figures 2-B and 2-C are from a LPG and an indoor air samples. The concentrations of sulfur compounds measured in the LPG range from about μg/m^3 to mg/m^3; the concentrations of sulfur compounds in the indoor air range from ng/m^3 to μg/m^3.

Sampling loop

According to reference 20, the detection range of sulfur compounds with FD-SCD is from 0.01 mg/m^3 to 1000 mg/m^3 based on the analysis of 1 mL sample. The flameless SCD (Model 355) is approximately 10-times more sensitive than the FID-SCD (Model

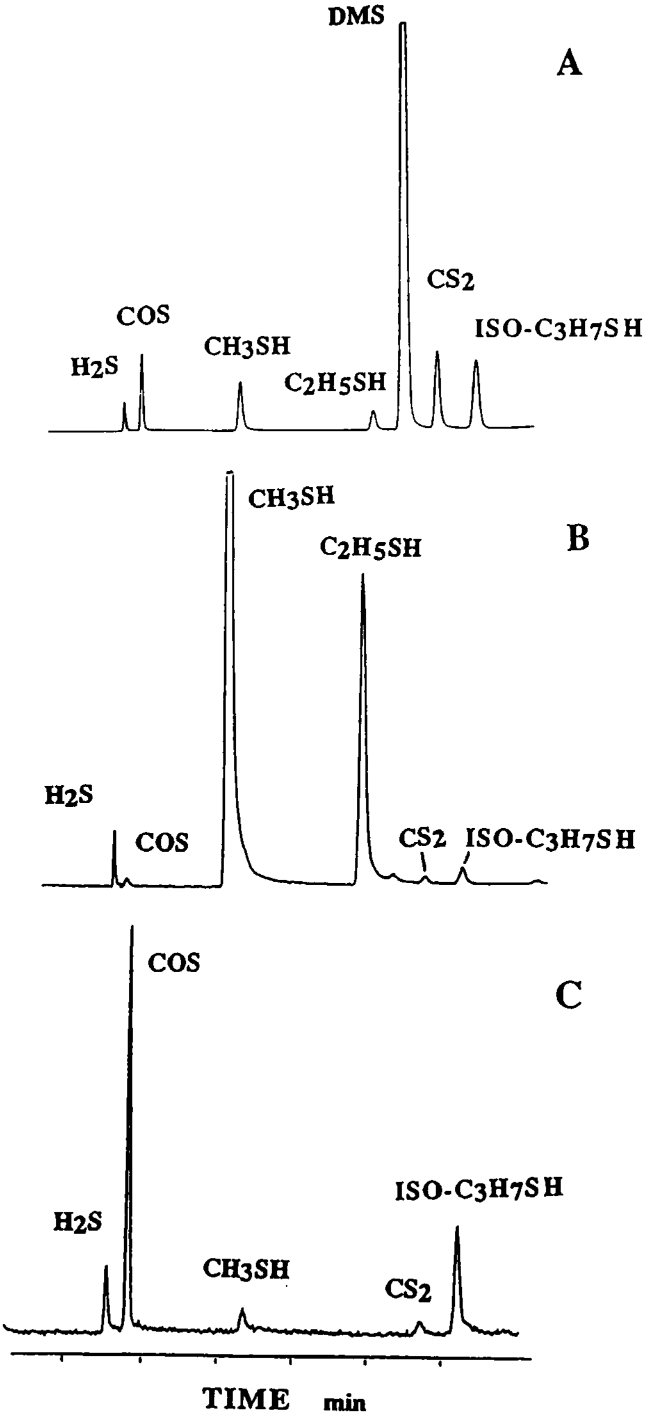

Figure 2 Chromatograms of a standard mixture of sulfur compounds (A), an LPG sample (B) and an indoor air (C).

350)[17,18]. Therefore, a 0.55 meter megabore tubing (0.5 min i.d.) with a volume of 0.11 mL was chosen as the sampling loop.

The analysis of gaseour sulfur compounds is difficult. Because sulfur compounds are polar, they may be lost to active sites in the analytical instrumentation and the sample vessel. The surface properties of different materials used for making capillary columns can strongly affect compound analysis.

Capillary columns commercially available are made from many different materials, such as stainless steel (SS), fused silica (FS), nickel and stainless steel coated with silica (SSCS) etc. Shearer *et al.*[4] reported that FEP Teflon tubing and eletropolished nickel tubing could be used to transfer of LPG from its sample vessel to the GC column without altering the composition of the sample.

In our laboratory, three different megabore columns made from FS, electropolished nickel (EN) and SSCS were tested using these as the sampling loop. Peak areas of H_2S, COS and CH_3SH obtained from those sampling loops were shown in Figure 2. It can be seen that FS tubing is the best material; the nickel tubing absorbed some sulfur compounds; the SSCS tubing is very similar to, although less satisfactory than, the FS tubing.

Although the FS tubing in less active, it is easily broken, which causes a significant maintenance problem. Therefore, SSCS tubing was finally chosen as the sampling loop and the sampling inlet line (Figure 1). SSCS tubing has another advantage compared to FS tubing, in that it has a better thermal conductivity. Experiments showed that when

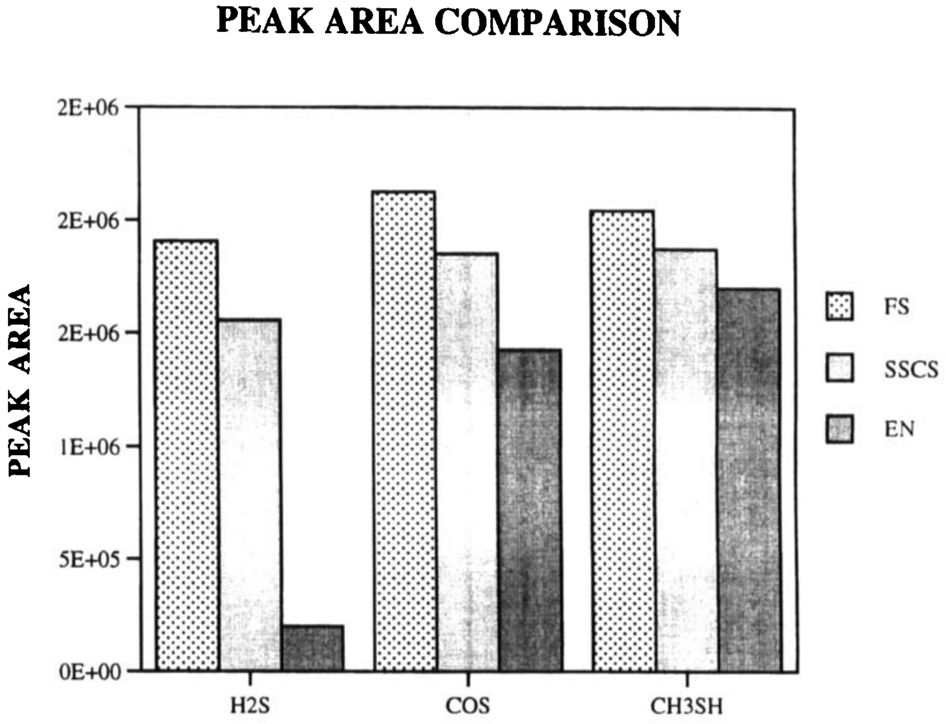

Figure 3 Peak area comparison from a fused silica tubing (FS), a stainless steel tubing coated with silica (SSCS) and an electropolished nickel tubing (EN).

operating at the same conditions, the cryogenic trapping efficiency of the SSCS sampling loop for H_2S, COS and CH_3SH was about 5 to 40 times higher than that of the FS sampling loop (Table 1) despite the surface activity of the SSCS is slightly higher than that of the FS.

Cryogenic trapping efficiency

The trapping efficiency of the MPSL for sulfur compounds was determined by comparing the peak area obtained with and without cryogenic process at different trapping periods.

In the test samples, DMS has a boiling point of 38°C and is a relatively stable sulfur compound. It is reasonable to choose the trapping efficiency of DMS as 100% when using liquid nitrogen. Therefore comparing the peak area of H_2S, COS and CH_3SH to DMS can provide useful information for the determination of trapping efficiency.

Table 2 lists the comparison of relative peak areas of different sulfur compounds obtained by cryogenic trapping processes to the non-cryogenic process. It can be found that the cryogenic trapping efficiencies are above 70% within 1.5 min. The trapping efficiency of H_2S decreased very fast along with increasing trapping time. That may be due to the thermal conductivity of the SSCS decreases when more compounds are condensed on the inside SSCS tubing wall. This conclusion is further proved by the ng/m^3 level of the test sample. Table 3 lists the trapping efficiencies for STD-6 with a 1.5 min and 5 min trapping periods. The relative standard deviations range from 4 to 8%, and the H_2S trapping efficiencies are almost the same in the two different trapping periods.

Table 1 Comparison of relative cryogenic trapping efficiency of H_2S, COS and CH_3SH to DMS in stainless steel coated with silica (SSCS) tubing and fused silica (FS) tubing.

	H_2S	*COS*	*CH_3SH*	*DMS*
FS	0.02 ± 0.00	0.23 ± 0.02	0.21 ± 0.02	1.00 ± 0.01
SSCS	0.80 ± 0.03	1.02 ± 0.02	0.94 ± 0.03	1.00 ± 0.01

Table 2 Comparison of relative peak area of cryogenic trapping to the non-cryogenic process and cryogenic trapping efficiency.

Cryogenic time (min)	*H_2S*	*COS*	*CH_3SH*	*DMS*	*Calculated* value*
		(Relative peak area)			
0.5	196 (86)	205 (90)	218 (96)	220 (96**)	228
1	356 (80)	408 (88)	431 (95)	429 (95)	455
1.5	478 (70)	587 (86)	618 (89)	629 (92)	683
2	442 (49)	773 (85)	810 (89)	835 (92)	910
5	721 (32)	1706 (75)	1900 (84)	2047 (90)	2275

* Calculated value
= flow rate (50 mL/min) × cryogenic time/0.11 mL
0.11 mL is the sampling loop volume. Cryogenic time > 0.
** The values in parentheses are the trapping efficiency (TE)
TE% = Relative peak area × 100/Calculation value.

Table 3 Recoveries of the selected sulfur compounds in STD-6 test standard by cryogenic trappling.

Trapping time (min)	*H_2S*	*COS*	*CH_3SH (%)*	*DMS*
1.5	75 ± 8	82 ± 7	85 ± 6	90 ± 5
5.0	73 ± 6	85 ± 6	91 ± 4	93 ± 5

Method detection limits

The method detection limits for different sulfur compounds were obtained following the approach given in Massard *et al.*[21]. Detectability equals to 3N/S. The results of none-cryogenic trapping are reported in Table 4. The method detection limits with cryogenic trapping depend on trapping times. In order to avoid the clogging problem and remain trapping efficiencies higher than 70% for the selected sulfur compounds, a 5 min trapping period was chosen.

Method precision

The method precision was determined by repeated injections of test samples (3 replicates) without cryogenic trapping and with cryogenic trapping for STD-6 test sample at 5 min trapping time. The resulting standard deviations are shown in Table 5. It can be seen that minimal relative standard deviations were obtained at higher concentrations of sulfur compounds without cryogenic trapping. In carefully checking the chromatograms, it can be found that one source for the larger standard deviation at low concentrations might be from the integrator. Due to the instrument noise, the computer cannot set the base line properly, which causes the peak area to change from run to run. The relative standard deviations for cryogenic trapping range from 4 to 6%.

Quantitation

External standards were used for quantitation. It is reported that the response factors of all sulfur compounds are essentially equivalent in the flameless SCD on a molar basis[4]. According to our experiments[22] and other literature references[2,3,20], the relative molar

Table 4 Method detection limit (without cryogenic trapping).

Compound	*Detection limit ($\mu g/m^3$)* *None-cryogenic*	*cryogenic*
H_2S	39	52×10^{-3}
COS	26	11×10^{-3}
CH_3SH	39	17×10^{-3}
DMS	39	17×10^{-3}

Table 5 Method precision (standard deviation).

Without cryogenic trapping

Concentration (min)	*H_2S*	*COS*	*CH_3SH (%)*	*DMS*
0.065	34.3	32.3	32.1	33.3
0.13	17.2	4.0	4.7	12.7
130	0.8	0.3	0.4	0.5

With cryogenic trapping (STD-6)

Trapping time (min)	*H_2S*	*COS*	*CH_3SH (%)*	*DMS*
5	6.3	6.4	3.9	5.3

response factors of H_2S, COS and CH_3SH are different from other sulfur compounds (Table 6). Therefore, in this study, four calibration curves were measured. H_2S, COS and CH_3SH have their own calibration curves. The calibration curve of DMS was used for DMS and the other sulfur compounds. The calibration curves are shown in Figure 4.

Moisture in samples

Moisture in samples can create plugging problems in cryogenic sampling systems. Hygroscopic salts[23,24] and Nafion driers[25] have been reported to remove moisture from samples. According to Henatsch and Juttner[12] and Hoffmann *et al.*[25], the methods used might cause losses of sulfur compounds at low concentrations. Dryers were not used by Simo *et al.*[16]; the clogging problem was avoided by optimization of the sampling flow rate and the depth of the sampling loop in liquid argon.

In this study, no drier was used. Experiments found that by using a megabore column as the sampling loop, employing relatively low trapping flow rate and a short period of sampling time, the clogging problem could be avoided. A Teflon filter must be used, however, to filer particles from samples in order to protect the MPSL from being clogged by particles.

Table 6 Comparison of relative RFs to methyl mercaptan.

Compounds	*RFs*	
	ASTM (19)	*Hines (2)*
H_2S	1.17	0.94
COS	0.73	1.30
CH_3SH	*1.00*	*1.00*
DMS	0.98	/

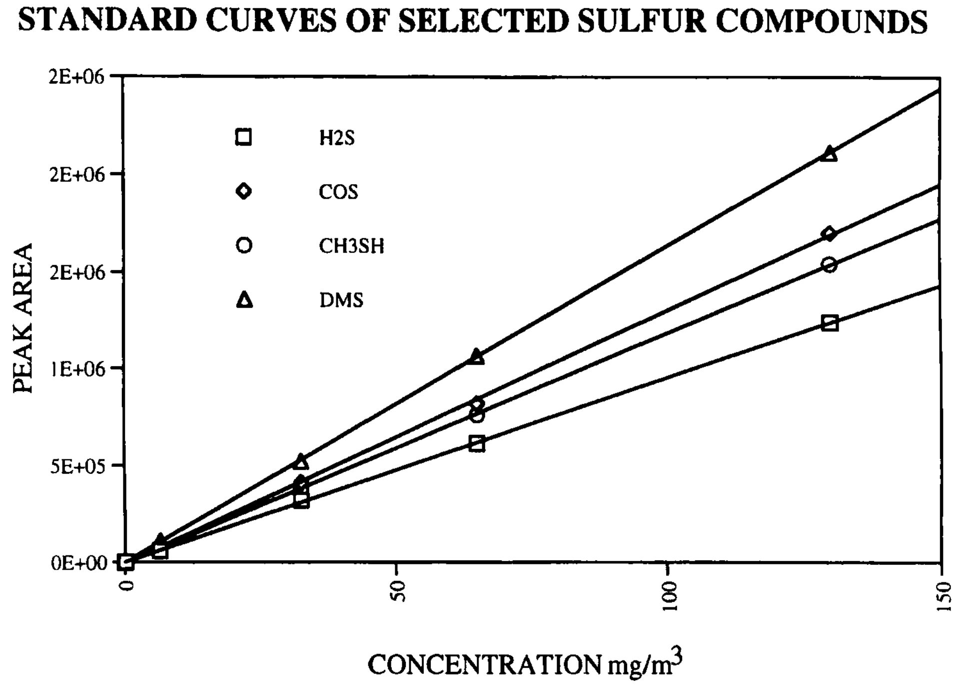

Figure 4 Calibration curves of selected sulfur compounds.

CONCLUSIONS

The MPSL reported here is useful for the measurement of a large concentration ranges of sulfur compounds in different sample matrices. The system is easy to install onto a GC. The SSCS tubing is the best choice for making the sampling loop. For field study, this device can be used to introduce ng to mg/m^3 levels of samples to a GC, thus minimizing storage time, possible contamination, and losses or degradation of sulfur compounds. Another reasonable conclusion is that this device can be used for measurement of compounds other than sulfur compounds when coupled with other detectors such as using FID to measure hydrocarbons.

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