

Comparison of commercially available atomic emission and chemiluminescence detectors for sulfur-selective gas chromatographic detection

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ABSTRACT

The determination of sulfur with sulfur chemiluminescence detection (SCD) and microwave-induced plasma atomic emission spectroscopic detection (AED) was compared for ten aliphatic and aromatic sulfur-containing organic compounds. Each detector was shown to be a sensitive and specific detector for sulfur present in different molecular forms. The linear dynamic range (LDR) for AED was independent of sulfur species at 10^5 , whereas the LDR for the SCD was generally 10^4 . The detection limit for both detectors was *ca.* 6–10 pg injected sulfur. Under conditions which optimized the SCD response for sulfur, the LDR for hydrocarbons using flame ionization detection (FID) (required for SCD operation) was similar to the 193-nm carbon emission line for the AED, but the sensitivities and reproducibilities with FID–SCD were poorer. The results of this study demonstrate that the selection of AED or SCD for sulfur detection is dependent on cost and whether the need is for a sulfur-only detector or a multi-element detector.

INTRODUCTION

The qualitative and quantitative determination of sulfur species in complex samples is becoming increasingly important to understand the sources of sulfur contamination and develop methods for removing them from the matrices of interest. For example, organic sulfur species are oxidized and released to the environment during combustion of fuels. These species are thought to exist in fuels as a mixture of thiols, sulfides, disulfides and thiophenes [1]. In addition to contributing to air pollution, many of these species are known to be mutagenic [2], affect the storage stability of petroleum products [3] and be detrimental to the catalysts used in processing hydrocarbon fuels [4].

One of the most frequently chosen methods for organic sulfur determination involves high-resolution gas chromatography (GC) with flame photometric detection (FPD). Although FPD is inexpensive and selective and sensitive to sulfur, it has sev-

eral disadvantages. The response is dependent on the environment of the sulfur atom and is subject to quenching by co-eluting hydrocarbons and water [5,6]. Two other sulfur-selective detection methods have recently become commercially available. Sulfur chemiluminescence detection (SCD) takes advantage of the fact that SO is produced during flame ionization detection (FID) when organic sulfur species are introduced by gas chromatography [4,7,8]. When SO reacts with ozone, a strong blue chemiluminescence signal is emitted by the resulting excited SO₂*. The signal is isolated from other radiation from the reaction chamber and detected by a photomultiplier tube [4]. Whereas SCD is specific for sulfur, atomic emission spectrometric detection (AED) is a multi-element method capable of detecting elements with atomic emission lines in the vacuum-UV, UV, visible and near-IR portions of the electromagnetic spectrum [9,10]. Radiation from the microwave-induced plasma is dispersed on a diode array spectrometer to monitor several ele-

ments at one time, including (but not limited to) C, H, S, N, O, P, halogens and many metals. The data are collected and manipulated by a computer.

Selectivity and sensitivity are minimum requirements for a useful sulfur detector for real, complex samples. Ideally, the detector will have a constant response per unit mass of sulfur regardless of the chemical form of the sulfur species that elutes from the gas chromatographic (GC) column. In addition, as sulfur components in real samples often co-elute with hydrocarbons present in much larger amounts (e.g., fuels), a useful sulfur detector should not show a change in sulfur response regardless of the presence of co-eluting hydrocarbons.

The aim of this work was to compare SCD and AED for a variety of sulfur-containing organics. In addition, the carbon response with AED is compared with the hydrocarbon response obtained with FID-SCD. The detectors were characterized using laboratory-prepared sulfur standards and chromatograms of real samples.

EXPERIMENTAL

Apparatus

The Model 350 sulfur chemiluminescence detector for SCD was provided by Sievers Research (Boulder, CO, USA). This detector was coupled in accordance with the manufacturer's specifications directly to a Hewlett-Packard (Avondale, PA, USA) Model 5890 gas chromatograph through a probe assembly attached to the FID flame ionization detector. The probe assembly was placed at a height of 6.0 mm above the flame of the flame ionization detector. The flow-rates of the hydrogen and oxygen in the flame ionization detector were measured to be 348 and 185 ml/min, respectively, for all analyses. The air pressure to the ozone generator in the sulfur chemiluminescence detector was maintained at 8 p.s.i. The flame ionization detector temperature was 350°C. The sulfur chemiluminescence detector allows smoothing of the millivolt output by an operator-selected integration time. An integration constant of 0.12 s was chosen to maximize the sulfur signal. The output was directed to a Hewlett-Packard Model 3393A integrator equipped with a Hewlett-Packard Model 9122 disk drive for data storage.

Detector gas flow-rates and probe placement for

the SCD instrument were optimized by maximizing the sulfur signal from 1- μ l injections of a 50 pg/ μ l solution of methyl ethyl sulfide in benzene. Interference from carbon signals can be seen on the SCD output when the hydrogen-to-air ratio is adjusted incorrectly, resulting in negative peaks when the flame ionization detector flame is hydrogen poor and positive peaks when the flame is hydrogen rich. The conditions were considered to be optimum when the maximum sulfur signal occurred with no response to carbon.

The AED system was a Hewlett-Packard Model 5921A microwave plasma emission detector coupled with a Hewlett-Packard Model 5890 series II gas chromatograph. Data acquisition and manipulation were performed through a ChemStation, a computer and software package provided by Hewlett-Packard. The instrumental design and data manipulation techniques are described elsewhere [9,10]. Sulfur and carbon were monitored on the AED system at the vacuum-UV wavelengths of 181.037 and 193.030 nm, respectively, using the manufacturer's recommended conditions. Helium supply gas for the plasma was maintained at 30 p.s.i. and the cavity pressure was 1.5 p.s.i. Unless noted otherwise, solvent was vented for the first 3.2 min of each chromatographic run to protect the plasma discharge tube from soot build-up.

The chromatographic conditions used with each detector were as identical as possible. All standard analyses were performed with 1- μ l splitless injections (1 min) using an HP 7673 autosampler. The same DB-5 (30 m \times 320 μ m I.D., film thickness 1.0 μ m) capillary column (J&W Scientific) was used for all SCD and AED standard analyses. The GC temperature programs for the sulfur standards were 60°C initially for 1 min with an increase at 8°C/min to 330°C. Both injection ports were at 300°C.

Preparation of standards and samples

Standard solutions were prepared using analytical-reagent grade chemicals (purity \geq 95%) as received. Approximately 0.2 g of each sulfur compound was dissolved in 100 ml of benzene to prepare a stock solution. Appropriate dilutions in benzene were made to obtain 22 standards with concentrations ranging from 5 pg to 0.9 μ g/ μ l of sulfur, corrected for the purity of the sulfur standard component. Each sulfur standard dilution was injected

on three different days using each detector system. This procedure was used to yield "worst case" results, as both detector systems were set up each day to run the series of standards.

RESULTS AND DISCUSSION

Sulfur response and reproducibility

Representative standard chromatograms obtained with SCD and AED are shown in Fig. 1. In

general, the peak shapes are comparable in each detector system, indicating no loss in chromatographic resolution due to the detectors. The cause of randomly occurring negative peaks on the SCD trace is unclear, but this interference has since been removed by installing a heated transfer line (now standard on this instrument) between the probe and detector. A comparison of methyl ethyl sulfide for each detector could not be made as this compound elutes near the solvent peak, and the solvent was

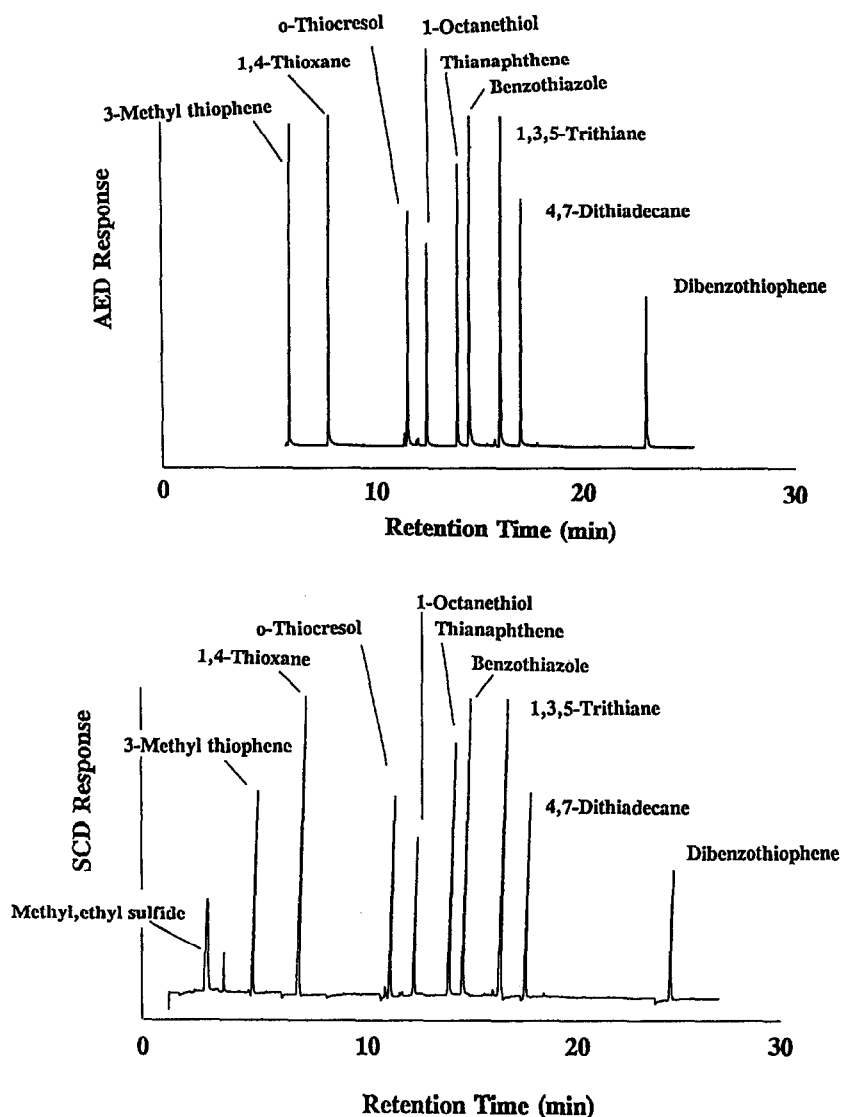


Fig. 1. Representative chromatograms for sulfur standards obtained using (top) AED and (bottom) SCD. Chromatographic oven program for both: 60°C for 1 min, increased at 8°C/min to 330°C.

TABLE I
SIGNAL-TO-NOISE RATIOS (S/N) FOR LOW-CONCENTRATION SULFUR STANDARDS

Component	Sulfur (pg) ^a	S/N ^b		Sulfur (pg)	S/N	
		SCD	AED		SCD	AED
Methyl ethyl sulfide	9.2	1.0	ND ^c	27.6	4.1	ND
3-Methylthiophene	6.7	3.9	5.1	20.1	7.6	23.0
1,4-Thioxane	9.1	2.1	5.4	27.4	10.7	8.9
<i>o</i> -Thiocresol	6.8	1.2	3.0	20.4	5.3	8.4
1-Octanethiol	4.9	1.0	2.4	14.7	3.5	14.8
Thianaphthene	5.9	1.2	3.5	17.6	7.3	27.8
Benzothiazole	8.9	2.8	11.0	26.7	8.9	35.1
1,3,5-Trithiane	14.1	2.5	10.0	42.2	12.7	12.7
4,7-Dithiadecane	5.7	1.3	3.2	17.1	6.1	9.0
Dibenzothiophene	3.7	1.1	3.0	11.0	4.3	14.8

^a Amount of S present for each species in the 1- μ l splitless injections.

^b Values are averages of three injections.

^c ND = Not determined. This species eluted during the solvent vent step using AED.

vented from the AED system to prevent soot build-up on the quartz emission tube.

Both detectors have sulfur detection limits in the low picogram range. Table I lists the signal-to-noise ratio (S/N) for the samples containing the two lowest concentrations of each sulfur-containing organic standard. The amount of sulfur injected was calculated from the mass of each standard in the 1- μ l splitless injections. Noise was determined as peak-to-peak baseline measurements collected over 60 s. As shown in Table I, the lowest standard used was at or below the detection limit for SCD, if the minimum detection limit for each sulfur component is defined as $S/N \geq 3$. Six of the ten sulfur responses are statistically indistinguishable from the noise. As can be seen from Table I, the S/N of these components from a more concentrated solution (sulfur amounts equaling three times those in the most dilute sample) range from 3.5 to 12.7, all above the detection limit. While the sensitivity of AED is slightly better, the S/N is generally less than four times that of SCD, indicating similar sensitivities for both detectors.

Because the standard dilutions were run as a set, and each set was run on a different day, each instrument was essentially set up on three separate occasions. Thianaphthene was arbitrarily chosen as the internal standard (sulfur response factor = 1.000), and response factors for the remaining sul-

fur compounds were calculated as peak areas per picogram of sulfur injected relative to thianaphthene (also corrected for the mass of sulfur). Both detectors show a relatively constant chromatographic mass response despite the different molecular forms of sulfur. Table II lists response factors for sulfur for four representative standard dilutions ranging from *ca.* 50 to *ca.* $4 \cdot 10^5$ pg/ μ l of sulfur injected. Peak areas are averages of the three replicate injections of the sulfur standard performed on three different days as described earlier. The sulfur response (determined chromatographically) increased with increasing retention time for both detectors (opposite from the trend expected from splitter discrimination). Similar changes in response with run time are also seen from the AED carbon response. The response factors for *o*-thiocresol and 1-octanethiol (species with weakly acidic hydrogens) are possibly low because of integration errors caused by chromatographic peak tailing associated with acids. The response factors for 1,3,5-trithiane determined with SCD were also low, whereas the AED response for this compound followed the trend of increased response with increasing retention time. The low SCD response may be due to inefficient SO production for this compound.

Table III lists the relative standard deviations (R.S.D.s) for both the raw peak areas (not relative to the internal standard) and the peak areas of each

TABLE II

RESPONSE FACTORS (RRF) PER UNIT MASS OF SULFUR RELATIVE TO THIANAPHTHENE FOR REPRESENTATIVE SULFUR STANDARDS

Component	Sulfur injected (pg) ^a	RRF ^b		Sulfur injected (pg)	RRF		Sulfur injected (pg)	RRF		Sulfur injected (ng)	RRF	
		SCD	AED		SCD	AED		SCD	AED		SCD	AED
Methyl ethyl sulfide	64.4	0.725	ND ^c	828	0.596	ND	8280	0.614	ND	449	0.973	ND
3-Methylthiophene	47.0	0.653	0.781	604	0.662	0.792	6040	0.702	0.755	365	0.683	0.768
1,4-Thioxane	63.8	0.928	0.876	820	0.806	0.931	8210	0.759	0.891	474	0.649	0.823
<i>o</i> -Thiocresol	47.5	0.614	0.557	611	0.659	0.634	6110	0.783	0.792	326	0.896	0.904
1-Octanethiol	34.3	0.645	0.731	442	0.679	0.783	4420	0.789	0.827	264	1.034	0.945
Benzothiazole	62.3	0.927	0.882	802	0.810	0.923	8020	0.804	0.855	432	0.750	0.912
1,3,5-Trithiane	98.5	0.671	0.999	1270	0.789	1.005	12 700	0.630	0.939	721	0.535	0.934
4,7-Dithiadecane	39.9	0.790	0.885	513	0.966	0.914	5130	0.938	0.915	310	0.957	1.124
Dibenzothiophene	25.8	0.990	0.996	332	0.914	1.013	3320	0.980	1.013	185	1.211	1.231

^a Amount of S present for each species in the 1- μ l splitless injections.^b RRF = Relative response factor. Values are averages of three runs performed on three days.^c ND = Not determined.

component relative to the thianaphthene internal standard for the same four standard dilutions shown in Table II. The R.S.D.s for raw peak areas for injections on three different days were higher (typically 5–15%) with SCD than with AED (typically 5%, with a few values as high as 15%). The R.S.D.s for injections on three different days relative to the internal standard were similar for both detectors, with nearly all the standards showing acceptable day-to-day reproducibility (< 5% R.S.D.).

The linear dynamic range (LDR) with AED is less compound dependent than that with SCD, and it consistently remains approximately one decade greater than that for the corresponding component determined with SCD. Typical calibration graphs [$\ln(\text{peak area})$ vs. $\ln(\text{mass of sulfur})$] are shown in Fig. 2 for 1,3,5-trithiane and dibenzothiophene. The calibration graphs for the remaining sulfur standards are very similar to those shown. As shown in Fig. 2, the AED calibration graphs for each species appear to be linear over the entire concentration range studied, but the SCD plots curve downward between the points corresponding to 10^3 and 10^4 pg of sulfur. Based on visual inspection, linear regression correlation coefficients (r^2) were calculated for each detector from their detection limits to be *ca.* $3 \cdot 10^4$ pg of sulfur injected (all but the highest three standard concentrations) and from detection limits to be *ca.* $6 \cdot 10^5$ pg of sulfur injected

(all standards) for each of the organic sulfur species. As can be seen in Table IV, all but 1,4-thioxane and 1,3,5-trithiane determined with SCD show $r^2 \geq 0.990$ at 10^4 pg of sulfur injected, but significantly lower correlation coefficients were obtained with SCD for each species calculated over the entire concentration range. In contrast, AED showed correlation coefficients > 0.990 for all of the test species over the entire concentration range. The LDRs determined are consistent with previously published data for both AED [9] and SCD [4]. The consistent LDRs for AED indicate that the compounds are stable over the chromatography portion of the analysis; hence the differences in LDRs are probably due to the detectors.

Hydrocarbon interference on sulfur response

To test the ability of SCD to determine sulfur in the presence of large amounts of co-eluting hydrocarbons, dilutions of 3-methylthiophene in toluene were injected into the SCD system at an oven temperature of 90°C so that the 3-methylthiophene eluted under the toluene solvent peak. A plot of picograms of sulfur, calculated as the mass of sulfur injected in a 1- μ l injection, *versus* the average peak areas for duplicate injections is shown in Fig. 3. The lowest amount of sulfur shown is *ca.* 8 pg, and this amount is easily integrated. As previously seen in Table I, the *S/N* for 6.7 pg of sulfur was 3.9; hence

TABLE III
REPRODUCIBILITIES OF RAW PEAK AREAS AND PEAK AREAS RELATIVE TO INTERNAL STANDARD FOR DETERMINATIONS OF THREE DIFFERENT DAYS

Component	Sulfur R.S.D. (%)			Sulfur R.S.D. (%)			Sulfur R.S.D. (%)			Sulfur R.S.D. (%)										
	(pg) ^a			(pg)			(pg)			(ng)										
	Raw ^b	Relative ^c		Raw	Relative		Raw	Relative		Raw	Relative									
	SCD	AED	SCD	AED	SCD	AED	SCD	AED	SCD	AED	SCD	AED								
Methyl ethyl sulfide	64.4	3.4	ND ^d	3.1	ND	828	14.8	ND	5.0	ND	8280	9.4	ND	449	12.6	ND	4.2	ND		
3-Methylthiophene	47.0	4.2	9.1	1.4	1.9	604	13.8	14.7	7.1	1.3	6040	14.5	3.5	3.5	0.6	365	5.4	4.5	3.5	0.9
1,4-Thioxane	63.8	8.3	3.7	1.9	1.3	820	13.1	5.2	4.1	3.7	8210	7.7	3.6	5.2	0.5	474	10.6	4.4	2.6	0.8
<i>o</i> -Thiocresol	47.5	1.6	5.4	0.5	2.7	611	2.9	7.5	2.0	6.4	6110	11.5	3.7	3.6	0.3	326	10.4	4.5	2.7	1.1
1-Octanethiol	34.3	12.3	9.9	2.2	1.8	442	9.1	4.7	5.3	2.1	4420	16.1	1.0	3.6	0.1	264	4.9	4.4	0.9	0.3
Benzothiazole	62.3	5.8	13.9	3.6	4.1	802	18.3	4.6	7.5	0.6	8020	11.6	2.1	4.7	0.5	432	3.8	4.0	1.1	0.5
1,3,5-Trithiane	98.5	18.7	2.9	1.8	0.8	1270	15.3	4.6	4.0	0.9	12700	15.5	4.5	5.2	0.4	721	3.0	4.2	0.9	0.2
4,7-Dithiadecane	39.9	9.8	9.9	2.7	2.9	513	9.1	4.0	3.0	3.9	5130	10.5	5.5	5.1	0.2	310	10.8	4.2	1.5	0.6
Dibenzothiophene	25.8	19.0	5.2	3.7	3.4	332	15.8	2.6	5.4	1.7	3320	9.5	3.9	3.6	0.1	185	10.9	4.4	0.5	3.1

^a Amount of S present for each species in the 1- μ l splitless injections.

^b R.S.D. in raw area counts for injections on three different days.

^c R.S.D. in area counts relative to the internal standard for injections on three different days.

^d ND = Not determined.

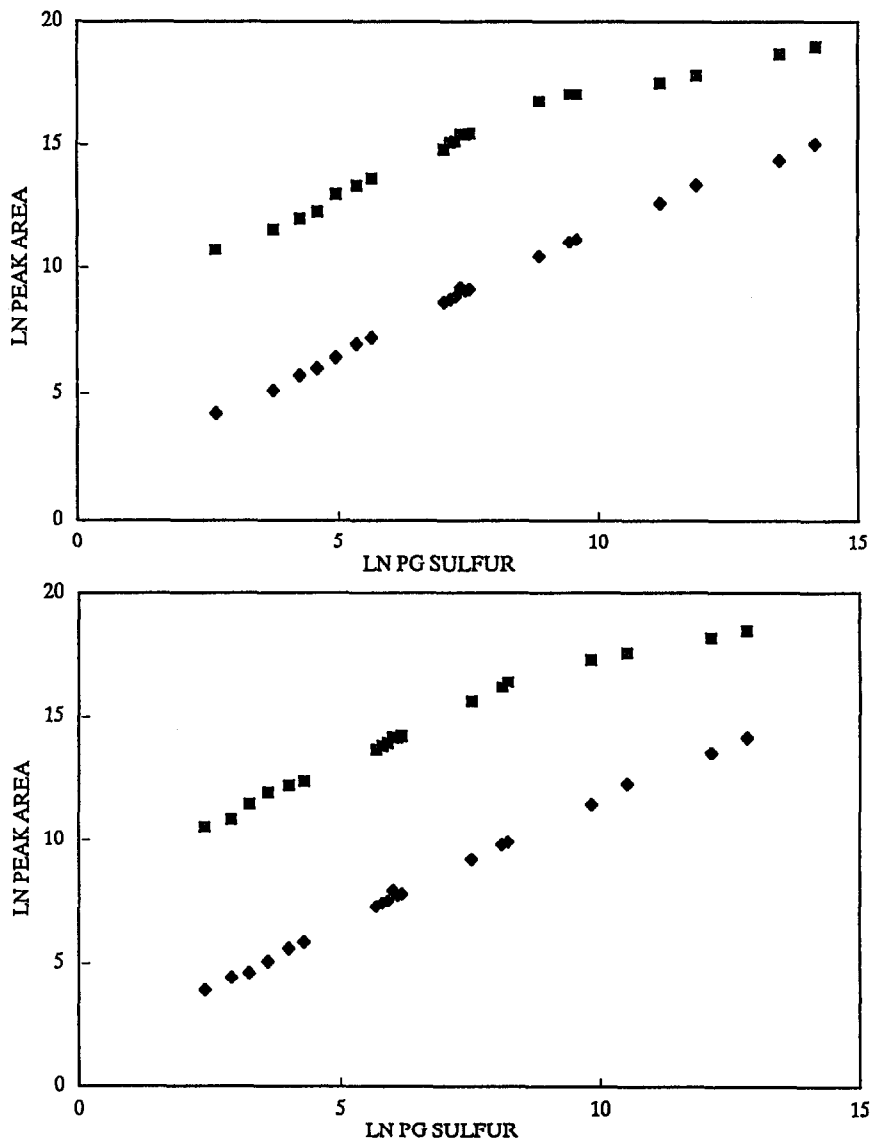


Fig. 2. Calibration graphs [ln (peak area) vs. (mass of sulfur)] for (top) 1,3,5-trithiane and (bottom) dibenzothiophene, determined using (◆) AED and (■) SCD.

one would not expect difficulty in integrating peaks at the 8-pg level if there were no interference from the large solvent peak. An additional sample containing *ca.* 0.8 pg of sulfur was injected but was not detected, as one would expect as this amount of sulfur is below the detection limit even without coelution of the toluene solvent peak. In addition, there was no detectable effect of toluene on a sam-

ple containing *ca.* 24 pg sulfur when compared with the sample injected at an oven temperature of 60°C, a temperature where 3-methylthiophene was resolved from the solvent. The calibration graph shown in Fig. 3 also shows good linearity ($r^2 = 0.999$) for the 3-methylthiophene, despite the coeluting toluene solvent peak.

Determining sulfur under a solvent peak as a

TABLE IV
LINEAR CORRELATION COEFFICIENTS (r^2) FOR SULFUR COMPONENT CALIBRATION GRAPHS

Component	r^2			
	SCD		AED	
	10-10 ⁵ pg S ^a	10-10 ⁴ pg S	10-10 ⁵ pg S	10-10 ⁴ pg S
Methyl ethyl sulfide	0.968	0.995	ND ^b	ND
3-Methylthiophene	0.952	0.991	0.993	0.998
1,4-Thioxane	0.942	0.984	0.992	0.997
<i>o</i> -Thiocresol	0.945	0.993	0.993	0.997
1-Octanethiol	0.952	0.994	0.995	0.998
Thianaphthene	0.953	0.994	0.994	0.998
Benzothiazole	0.942	0.990	0.993	0.998
1,3,5-Trithiane	0.953	0.985	0.994	0.997
4,7-Dithiadecane	0.938	0.992	0.994	0.998
Dibenzothiophene	0.971	0.997	0.996	0.997

^a Approximate amount of sulfur injected. See Table I for the exact amounts for the detection limits and Table III for the highest amount injected (*ca.* 10⁵ pg). The amount 10⁴ pg represents a 1:10 dilution of the highest concentration.

^b ND = Not determined.

strategy for detecting sulfur with large amounts of co-eluting hydrocarbon was not attempted with AED, because the solvent peak should be vented to reduce soot build-up and erosion of the discharge tube. However, the selectivity of one channel over

another (*i.e.*, sulfur over carbon) for the AED instrument can be determined by measuring the ratio of the peak response per mole of sulfur *versus* the peak response per mole of carbon for interfering signals [9-11]. Eicosane, used as a carbon source,

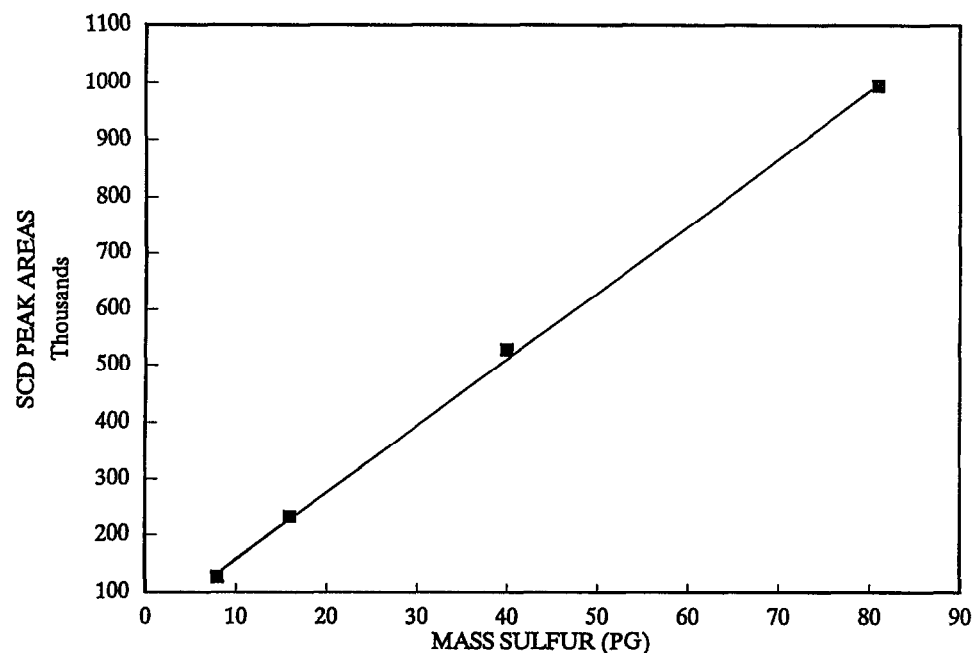


Fig. 3. Plot of SCD peak area *versus* mass of sulfur injected for 3-methylthiophene co-eluting with a toluene solvent peak.

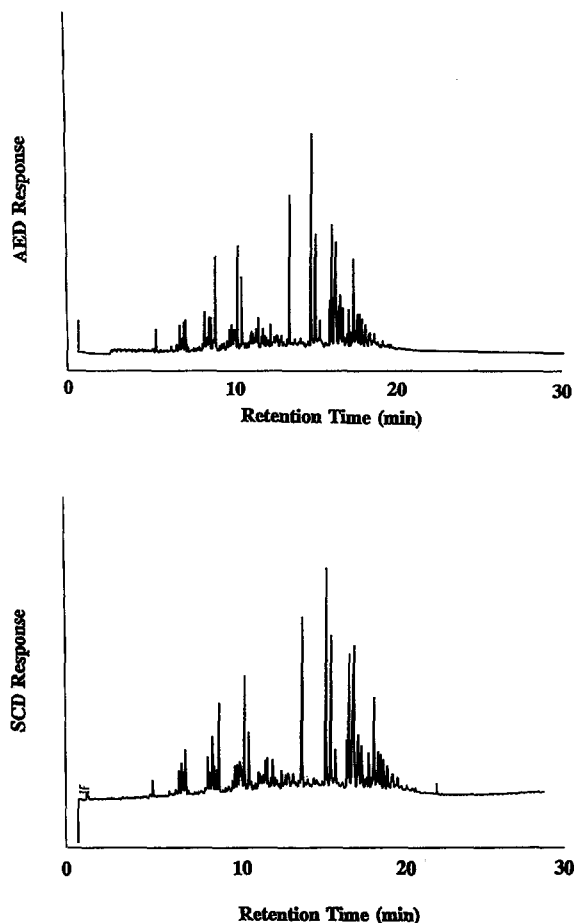


Fig. 4. Chromatograms for NIST 1624b standard for sulfur in diesel fuel obtained using (top) AED and (bottom) SCD. Injections of $1\ \mu\text{l}$ were made on an HP-5 capillary column ($25\ \text{m} \times 320\ \mu\text{m}$ I.D., film thickness $0.17\ \mu\text{m}$) (Hewlett-Packard) in the split mode (*ca.* 1:20). Chromatographic oven program for both: 70°C for 1 min, increased at $8^\circ\text{C}/\text{min}$ to 320°C .

was injected in the splitless mode and the 181-nm sulfur signal was monitored. Using the peak-to-peak noise as the sulfur signal (per mole), the selectivity for sulfur over carbon was calculated to be $> 10^4$. This is consistent with previous published reports of selectivity equalling $1.5 \cdot 10^5$ [9].

Fig. 4 shows sulfur responses from each of the detectors for a sample of diesel fuel (NIST 1624B standard reference materials for sulfur in diesel fuel). The chromatographic conditions were as identical as possible between the two detectors. The NIST standard, at *ca.* 0.33 wt.% total sulfur, was

injected neat as a $1\text{-}\mu\text{l}$ volume split *ca.* 1:20. As seen in Fig. 4, chromatograms with AED and SCD for the NIST standard agree fairly closely. Neither baseline exhibits drifting, despite the large amounts of hydrocarbons that are co-eluting with the sulfur species, and good resolution is evident within groups of closely-eluting sulfur species.

Carbon and hydrocarbon response

The sulfur chemiluminescence detector utilizes SO produced from sulfur-containing species in the flame ionization detector to determine sulfur. To prevent carbon species from interfering, the flame ionization detector gases are set at a level that produces a reducing flame, a condition not optimum for detecting hydrocarbons. To determine if the flame ionization detector (with the sulfur chemiluminescence detector probe attached) is useful for determining hydrocarbons, the former detector signals for the sulfur standards were recorded in tandem with the sulfur signals from the latter detector. The results were compared with those collected using AED with the same samples by simultaneously measuring the 181-nm sulfur line and the 193-nm carbon signal. Data acquisition and manipulation for each element were accomplished by using the appropriate "recipes" provided by the manufacturer, and no modifications were made to optimize AED further. The following data treatment for carbon (AED) and hydrocarbon (FID-SCD) was performed similarly to the data treatment for sulfur as discussed in the previous section.

Table V gives the *S/N* values for samples with the corresponding masses of carbon for the lowest concentration standards detected by each detector. The mass of carbon was calculated similarly to that previously described for sulfur, *i.e.*, the amount of carbon in a $1\text{-}\mu\text{l}$ injection using the splitless mode. Although both detection methods are partly compound dependent, the FID-SCD system is clearly less sensitive than the AED system for all the compounds. As reported previously [4], some reduction in sensitivity would be expected as the flame ionization detector was not optimized for hydrocarbon response. However, the FID-SCD method is still useful for hydrocarbon detection in many applications, as nanogram amounts were detected for each component.

Detector response reproducibilities were deter-

TABLE V
SIGNAL-TO-NOISE RATIOS (*S/N*) FOR CARBON (AED)
AND HYDROCARBON (FID-SCD) RESPONSES

Component	FID-SCD		AED	
	Carbon (pg) ^a	<i>S/N</i> ^b	Carbon (pg)	<i>S/N</i>
3-Methylthiophene	1110	10.4	139	30.1
1,4-Thioxane	1850	8.2	144	12.7
<i>o</i> -Thiocresol	1760	10.8	137	31.9
1-Octanethiol	1750	8.4	175	17.4
Thianaphthene	1510	13.6	132	14.4
Benzothiazole	2300	16.0	143	13.0
1,3,5-Trithiane	3120	8.9	44	15.8
4,7-Dithiadecane	1130	6.4	103	31.3
Dibenzothiophene	1410	8.2	176	10.9

^a Amount of C present for each species in the 1- μ l splitless injections.

^b Values are averages of three injections.

mined in the same manner as that described for sulfur using thianaphthene as the internal standard, and the R.S.D.s and the relative responses (corrected by mass of carbon) of the other components were determined relative to thianaphthene. Again, the triplicate sample runs were designed to test a "worst case", with three runs performed on three separate days. The R.S.D.s for the FID-SCD peak

areas are generally higher than the corresponding R.S.D.s for AED, and the R.S.D.s for raw peak areas and for peak areas relative to the internal standard were essentially identical with those in Table II for sulfur. The mass response for both detectors (listed in Table VI) also remained relatively constant, and both detectors showed an increase in chromatographic response with increasing retention time, similar to the trend seen for the sulfur signals. With the exception of 1,3,5-trithiane, both detectors showed good linearity ($r^2 > 0.990$) from their detection limits reported in Table V to the highest concentration tested (*ca.* 2 μ g of carbon injected). The LDR for 1,3,5-trithiane was only *ca.* 10^2 with FID-SCD and 10^4 with AED.

CONCLUSIONS

Both the AED and the SCD instruments are sensitive, selective detectors for organic sulfur and respond on a relatively constant mass basis independent of the source of the sulfur. The sulfur linear dynamic ranges and the detection limits with AED were slightly better than those with SCD, but these differences are small enough that they may not be significant for most applications. Both detectors were reliable during the course of this study and required only minimum routine maintenance by the operator. AED has the advantage of being a multi-

TABLE VI
RESPONSE FACTORS PER UNIT MASS OF CARBON RELATIVE TO THIANAPHTHENE FOR REPRESENTATIVE CARBON STANDARDS

Component	Carbon injected (pg) ^a	RRF ^b		Carbon injected (pg)	RRF		Carbon injected (ng)	RRF		Carbon injected (ng)	RRF	
		FID- SCD	AED		FID- SCD	AED		FID- SCD	AED		FID- SCD	AED
3-Methylthiophene	139	ND ^c	0.620	1530	0.685	0.587	12.5	0.725	0.702	75.5	0.802	0.756
1,4-Thioxane	206	ND	0.633	2260	0.558	0.590	18.5	0.502	0.645	107	0.494	0.668
<i>o</i> -Thiocresol	195	ND	0.857	2150	0.749	0.794	17.6	0.817	0.838	93.9	0.914	0.960
1-Octanethiol	175	ND	0.731	1920	0.821	0.750	15.7	0.718	0.772	94.1	0.832	0.947
Benzothiazole	287	ND	0.822	3160	0.850	0.776	25.8	0.751	0.773	139	0.823	0.845
1,3,5-Trithiane	62.3	ND	0.891	686	ND	0.820	5.61	0.831	0.896	31.9	0.950	1.322
4,7-Dithiadecane	103	ND	0.803	1130	0.928	0.845	9.27	0.854	0.862	56	0.899	1.128
Dibenzothiophene	176	ND	1.010	1940	0.898	1.004	15.8	1.035	1.035	88.5	1.099	1.180

^a Amount of C present for each species in the 1- μ l splitless injections.

^b Carbon response factor relative to internal standard. Values are averages of three runs performed on three days.

^c Hydrocarbon amounts were below the detection limit.

element detection method, allowing the detection of many different elements (although only a few combinations of elements can be obtained simultaneously), while SCD can only be used for sulfur and for hydrocarbon detection. However, AED instrumentation is more expensive (*ca.* four times) and requires more laboratory space than SCD instrumentation.

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