Journal of Chromatography, 465 (1989) 23–33
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROMSYMP. 1554

SUPERCRITICAL FLUID CHROMATOGRAPHY WITH SULFUR CHEMILUMINESCENCE DETECTION

WILLIAM T. FOREMAN[a], CURTIS L. SHELLUM[b], JOHN W. BIRKS* and ROBERT E. SIEVERS
Cooperative Institute for Research in Environmental Sciences (CIRES), and Department of Chemistry and Biochemistry, Campus Box 215, University of Colorado, Boulder, CO 80309 (U.S.A.)

SUMMARY

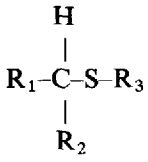
The newly commercialized sulfur chemiluminescence detector, originally designed for gas chromatography, has been successfully interfaced to a capillary-column supercritical fluid chromatograph used with carbon dioxide as the mobile phase. Interfacing was accomplished by inserting the capillary column through a heated (100–125°C) interface tube, and carefully positioning the integral restrictor end of the column within the chemiluminescence reaction chamber. This coupling resulted in direct transfer of the column effluent into the chamber, which minimized the dead volume and provided acceptable sensitivity and peak shape. Example chromatograms are presented to demonstrate the feasibility of this new separation–detection scheme, in which sulfur compounds are detected by the chemiluminescence emitted upon reaction with molecular fluorine. Some observed detection limits and linearity of response are also presented.

INTRODUCTION

The chemiluminescence reaction that occurs when certain sulfur-containing organic compounds react with molecular fluorine forms the basis of detection by the sulfur chemiluminescence detector (SCD)[1]

$$R_1\text{–}S\text{–}R_2 + F_2 \rightarrow \text{products} + h\nu$$

This detector typically exhibits a strong response to organosulfur compounds when the R group bonded to the sulfur is either hydrogen (except for H_2S) or an alkyl group containing hydrogen. Reduced organosulfur compounds having the general structure



[a] Present address: U.S. Geological Survey, National Water Quality Laboratory, 5293 Ward Road, Arvada, CO 80002, U.S.A.

[b] Present address: University of Graz, Institute for Pharmaceutical Chemistry, Universitätsplatz 1, Graz, Austria.

0021-9673/89/$03.50

and containing hydrogen in the alpha position relative to the sulfur have displayed particularly strong responses, especially when the R groups are short-chain alkyl groups[1–3]. Nelson *et al.*[1] proposed that addition of fluorine gas to an organosulfur compound having the general structure shown above could result in a hydrogen abstraction reaction to form vibrationally excited $HF^{\dagger}$ ($v' < 6$), which provides a chemiluminescence signal at wavelengths higher than 450 nm. Spectroscopic investigations of the chemiluminescent products formed upon reaction of F_2 with the low-molecular-weight hydrogen-bearing organosulfur compounds studied revealed the formation of excited $HF^{\dagger}$ and HCF* as emitting species[4]. Phosphorescent emission from electronically excited thioformaldehyde was observed when at least one of the R groups was $-CH_3$[4,5]. Emissions from a species ascribed to FCS* were also observed for many analytes[4]. In addition to organosulfur compounds, some organoselenium species have been found to respond in the SCD, although their response is about an order of magnitude less than the corresponding sulfur compound[1]. For dimethyl-diselenide the principal emitting species was identified as selenoformaldehyde[6]. Some olefins also show a fairly strong response[1–3].

The SCD was first developed for packed-column gas chromatography (GC), and in that apparatus a short, heated section of PTFE-lined 1/8 in. stainless-steel tubing was utilized as an interface between the GC column and the SCD. This GC–SCD was found to be very sensitive to alkyl sulfides, disulfides, and thiols[1,2]. Subsequently, the SCD was successfully interfaced to a capillary-column system by inserting the column through a section of 1/16 in. I.D. × 1/8 in. O.D. stainless-steel interface tube and up into the chemiluminescence chamber[7]. The interface was heated to temperatures typically in excess of 200°C to maintain analyte volatility in the transfer from the column into the SCD. Detection limits of < 10 pg for methanethiol, ethanethiol, 1- and 2-propanethiol, dimethyl sulfide, and dimethyl disulfide have been determined recently[8], using capillary-column GC–SCD. This combination is at least one order of magnitude more sensitive than the same GC system used with a flame-photometric detector.

While GC can provide excellent separation of analytes, it is not applicable to a large number of organosulfur compounds that are relatively polar, non-volatile, and/or thermally unstable. Several attempts have been made to extend the utility of the SCD to these analytes by interfacing the detector to a high-performance liquid chromatography (HPLC) system[3,9]. These HPLC–SCD systems have provided the necessary liquid-phase separation, but they rely on a heated (typically 300°C or higher) transfer line to introduce the mobile phase and analytes into the chemiluminescence chamber in the vapor phase. While HPLC–SCD systems have been shown to work well, even for some thermally unstable compounds, the development of new interface designs which do not require excessive heating is desirable.

Supercritical fluid chromatography (SFC), a technique complementary to GC and HPLC, shows the potential of separating a variety of thermally labile and higher-molecular-weight organosulfur compounds, and has been found to be relatively easy to interface to a number of detectors used in GC and/or HPLC[10–12]. Recently, Foreman *et al.*[13] succesfully interfaced a capillary-column supercritical fluid chromatograph to the redox chemiluminescence detector and demonstrated some potential applications of the system. Those findings suggested that a supercritical fluid chromatograph might also be directly coupled to other chemiluminescence-based

detectors. This paper describes our successful efforts in interfacing a supercritical fluid chromatograph with the SCD.

EXPERIMENTAL

The SFC system was assembled in-house from commercially available components. Liquid CO_2 was supplied to the chromatograph pump from a siphon tank pressurized to 100 atm with He. A Brownlee Labs. microgradient system syringe pump (Applied Biosystems, Santa Clara Analytical Div., Santa Clara, CA, U.S.A.) with pressure programming capability, was used to deliver the CO_2 mobile phase. All separations were carried out in a 3.5 m × 0.10 mm I.D. DB-5 fused-silica capillary column with a 0.4-μm film thickness (J & W Scientific, Folsom, CA, U.S.A.). The mobile phase was maintained at supercritical temperatures (typically 80–125°C) by housing the column inside the oven of a Model 5890 GC (Hewlett-Packard, Avondale, PA, U.S.A.). Direct injections of 60 nl of sample were made with an unheated Model C2I4W valve (Valco Instrument, Houston, TX, U.S.A.). The column pressure was maintained through use of an integral restrictor[14] at the detector end of the column. CO_2 flow-rates, measured at the column outlet, ranged from *ca.* 0.75 ml/min at 100 atm to 2 ml/min at 300 atm.

A Model 300 SCD (Sievers Research, Boulder, CO, U.S.A.) was connected to the chromatograph oven by an insulated 42.5-cm-long section of a 1/8 in. O.D. × 1/16 in. I.D. stainless-steel tubing which housed part of the chromatograph's capillary column. The detector end of the capillary column was first inserted through a 1/16-in.–1/8-in. stainless-steel reducing union fitting, attached to the supercritical-fluid chromatograph oven end of the interface tube. The restrictor end of the column was carfully positioned to extend 2 mm beyond the detector end of the interface tube, and the reducing union fitting with graphite ferrule was tightened to maintain the column position. The detector end of the tube was then inserted through the 3.2-cm-thick wall of the chemiluminescence chamber and into the chamber another 0.5 cm, and connected to the chamber wall with a 1/8-in. stainless-steel nut and ferrule (see Fig. 1). This nut plus about 2 cm of interface tubing outside the chamber were wrapped

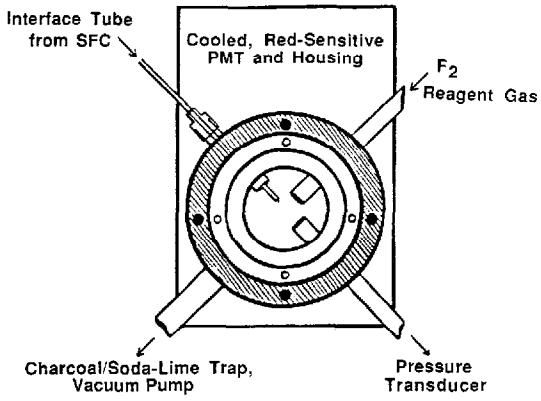


Fig. 1. Diagram of the chemiluminescence reaction chamber of the SCD, showing the positioning of the interface tube within the chamber. The restrictor end of the capillary column extends 2 mm beyond the end of the interface tube (not to scale).

with heating tape and heated to 100–125°C to maintain the column restrictor in the chamber above the critical temperature of CO_2. The remainder of the transfer line was not heated, since heat from the chromatographic oven and the heating tape was enough to maintain the insulated transfer line at or above 40°C.

The column effluent from the supercritical fluid chromatograph was mixed with F_2 reagent gas in the chemiluminescence chamber, the pressure of which was maintained at 1 Torr using a vacuum pump and monitored with a pressure transducer. The F_2 was generated *in situ* prior to entering the chamber by passing SF_6 at 0.5 ml/min through a high-voltage electrical discharge. Light resulting from the chemiluminescent reaction of the reagent gas with each analyte was monitored by photon counting with a red-sensitive photomultiplier tube, cooled to −15°C. A trap, containing charcoal and soda-lime, was positioned between the chamber and the vacuum pump to remove residual organics, HF and F_2. As an additional safety measure, the vacuum pump exhaust was vented to a hood. Additional SCD operational procedures are detailed in refs. 1–3 and 15.

All solvents were of chromatography grade obtained from various commercial sources. Other reagents were benzyl sulfide, benzyl disulfide, and polycyclic aromatic hydrocarbons from Chem Service (West Chester, PA, U.S.A.), and Malathion Insect Control formulation from Dexol Industries (Torrance, CA, U.S.A.). All other pesticide standards were obtained from the Environmental Protection Agency's Pesticides and Industrial Chemicals Repository (Research Triangle Park, NC, U.S.A.). The carbon-black extract and the other anti-oxidant standards were gifts from various researchers.

RESULTS AND DISCUSSION

The coupling of capillary-column GC with the SCD[7,16] requires the use of a transfer line, into which the column is inserted, that is commonly heated to at least 225°C to maintain analyte volatility until it reaches the chemiluminescence chamber. Since SFC relies on analyte solubility in the mobile phase and not on intrinsic analyte volatility we assumed that the interface tube would only need to be heated enough to maintain the mobile phase above its critical temperature (above 32°C for CO_2). Experimental evidence has confirmed that this assumption is warranted.

As shown in Fig. 1, the interface tube extended through the chemiluminescence chamber wall 3.2 cm and into the chamber another 0.5 cm, and the restrictor end of the capillary column was carefully positioned to extend 2 mm beyond the end of this tube. When CO_2 expands through the restrictor into the chamber, maintained at reduced pressure, the Joule-Thomson effect[17] can cause the CO_2 to freeze at the end of the column. The resulting freeze–thaw of CO_2 leads to spiking of analyte peaks. Therefore, it was necessary to supply enough heat to the restrictor end of the column to eliminate the freezing effect. To accomplish this, the nut connecting the interface tube to the chamber plus an additional 2 cm of the tube outside the chamber were wrapped and heated to 100–125°C with heating tape. This heat source provided an adequate heat transfer along the tube into the chamber to maintain the restrictor above the critical temperature of CO_2. With this interface tube design, positioning of the column end within the chamber was found to be critical for the achievement of acceptable chromatograms. If the column end extended more than *ca.* 2 mm past the end of the

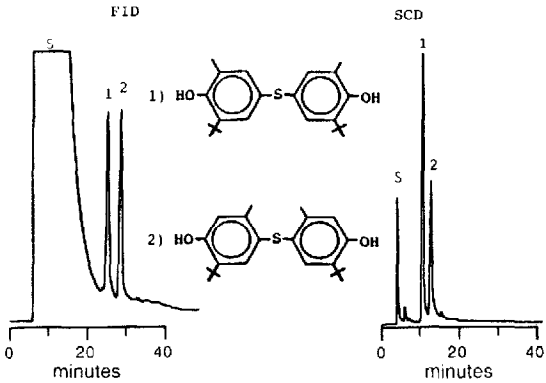


Fig. 2. SFC with flame ionization detection (FID) and sulfur chemiluminescence detection (SCD) of two anti-oxidant isomers: 125 ng of 4,4'-thiobis(*tert.*-butyl-*o*-cresol) (1) and 151 ng of 4,4'-thiobis(*tert.*-butyl-*m*-cresol) (2) in toluene (S). Linear pressure program from 150 atm to 250 atm in 40 min for both chromatograms. FID at 250°C and capillary column at 100°C. SCD at 100°C and capillary column at 80°C. All other conditions as described in the Experimental section.

tube, heat transfer to the restrictor at the end of the column was limited, and spiking and poor peak shape resulted. However, the column had to extend at least beyond the end of the interface tube or else analyte deposition would occur inside the tube, again resulting in poor peak shape. While correct positioning of the column within the chamber was critical, this was easily accomplished, as described in the experimental section.

The responses observed for two sulfur-containing phenolic anti-oxidant isomers analyzed using SFC with a flame ionization detector (FID) and SFC–SCD are compared in Fig. 2. The FID shows a typical, large response to the toluene solvent, whereas the SCD response to toluene was much smaller. This lower response to the solvent allowed chromatographic conditions to be changed to provide faster elution of the analytes by SCD without overlap with the tail of the solvent peak. For the separation in Fig. 2, faster elution was accomplished by increasing the fluid density through reduction of the column temperature to 80°C for the SCD chromatogram (compared with 100°C for the FID). All other conditions for obtaining these two chromatograms were identical, although column flow-rates probably varied slightly due to differences in temperatures at the restrictor (FID at 250°C and SCD heated to 100°C outside the chamber, as described above.) The molar responses in the FID to the two anti-oxidant isomers, which differed only in the position of their two methyl groups [both methyl groups in the *ortho*-position (1) or both in the *meta*-position (2)], were approximately equivalent and typical of this detector. However, in the SCD the molar response of the *ortho*-isomer was about twice that of the *meta*-isomer. The dissimilar SCD responses are likely due to differences between the two isomers in their reactivity with F_2.

In Fig. 3 is shown a chromatogram obtained by SFC–SCD of thermally labile benzyl sulfide and benzyl disulfide. Again, the SCD response to the toluene solvent was relatively small, and due to the complete separation of the two analytes under the conditions of Fig. 3, the chromatographic conditions could be altered to allow

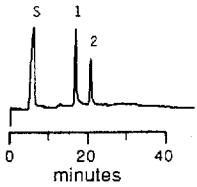


Fig. 3. SFC–SCD of 3.1 ng of benzyl sulfide (1) and 4.5 ng of benzyl disulfide in toluene (S). Linear pressure program from 100 atm to 200 atm in 40 min. SFC column at 80°C. All other conditions as described in the Experimental section.

somewhat faster analysis, while maintaining complete resolution of the analytes. These two analytes possess an alpha hydrogen relative to the sulfur atom, and this renders them reasonably sensitive to detection by the SCD[1–4].

An example analysis of three thermally labile sulfur-containing anti-oxidants by SFC–SCD is shown in Fig. 4. The chloroform used to dissolve these compounds was nearly undetected by the SCD. Of particular interest are the varying responses observed for the three anti-oxidants. Compound **3** (see Fig. 4), while possessing the greatest number of sulfur atoms, gave the least response, exemplifying that the chemiluminescence reactions in the SCD are largely based on hydrogen abstraction reactions, which form vibrationally excited $HF^{\dagger}$ (refs. 1–4), and not on reactions that are specifically related to the number of sulfur atoms. The strongest response was exhibited by compound **2**. This was an unexpected observation since compound **1** contains a hydrogen which is in the alpha position relative to a sulfur atom (but attached to a N atom instead of a C atom), and organosulfur compounds having an alpha-hydrogen configuration (with the H attached to a C atom) have been reported to be very responsive in the SCD[1,3,16]. However, compound **2** does not contain an alpha hydrogen relative to a sulfur atom, and compound **1** was expected to give a greater response than compound **2**, but this is not the case. Since all three of the anti-oxidants in Fig. 4 contain hydrogen atoms, the formation of vibrationally excited $HF^{\dagger}$ is likely for the reactions of these analytes with F_2. In addition, electronically excited HCF* and FCS* reaction products, which have been previously observed in reactions

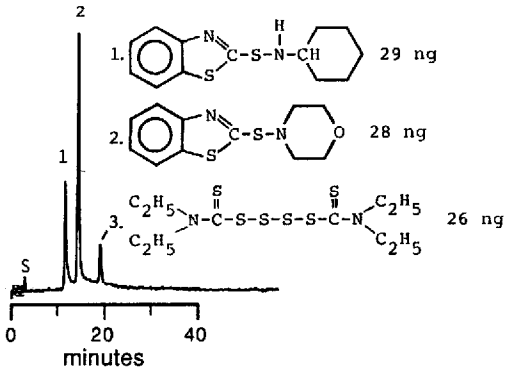


Fig. 4. SFC–SCD of three sulfur-containing anti-oxidants in $CHCl_3$ (S). Linear pressure program from 110 atm to 250 atm in 40 min. All other conditions same as for Fig. 3.

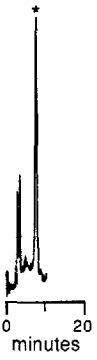


Fig. 5. Isoconfertic SFC–SCD of 28 ng of malathion (*) from a dilution in toluene of a commercial malathion formulation. Pressure at 115 atm, SFC column at 100°C. All other conditions as described in the Experimental section.

between F_2 and organosulfur compounds[4], may be contributing to the chemiluminesc ence signal. The examples in Fig. 2–4 reemphasize that the molar response in the SCD is compound-dependent[1,3,16], and the use of compound-specific standards would be required to do accurate quantitative work with the SCD.

A number of sulfur-containing organophosphate pesticides are thermally unstable, which renders it difficult to determine them by GC; therefore, analysis by SFC–SCD could be of benefit. An isoconfertic analysis of malathion is shown in Fig. 5. This sample was prepared by dilution of a commercial malathion insecticide formulation with toluene. Other inert ingredients besides the xylene solvent were reported to be in this formulation. The two early peaks in the chromatogram are responses to the toluene and xylene solvents and possibly to another ingredient. This SFC–SCD analysis is comparable to a previously reported HPLC–SCD analysis of this formulation[3]. Five other sulfur-containing organophosphate pesticides, carbophenothion, dioxathion, fenitrothion, and methyl and ethyl parathion, were successfully chromatographed and detected by SFC–SCD.

In Table I are shown the detection limits observed in this study for malathion,

TABLE I

DETECTION LIMITS BY SCD[a]

	SFC–SCD		
	ng	*pg/s*	*pg S/s*
1-Octanethiol	1.3	27	6
1-Dodecanethiol	5.0	89	14
Malathion	4.5	77	15
Methyl parathion	39	65	72
Anti-oxidant 1[b]	1.0	26	6
Anti-oxidant 2[b]	0.45	11	3
Anti-oxidant 3[b]	5.0	170	90

[a] Detection limits determined at a 3:1 signal-to-noise ratio as described in the Discussion section.
[b] Structures of anti-oxidants are shown in Fig. 4.

methyl parathion, and a number of other compounds by SFC–SCD. These detection limits were all determined at a 3:1 signal-to-noise (S/N) ratio using the following equation:

$$\text{detection limit} = \frac{3N}{S_i/m_i}$$

where N is the peak-to-peak noise, S_i is the peak signal obtained from the chromatogram for species *i*, and m_i is the mass of species *i* injected. The detection limits were calculated from chromatograms in which the analyte signals were *ca.* 5 times greater than the baseline peak-to-peak signal. This detection limit calculation method is identical to that previously described[3]. The detection limits are reported in nanograms of compound injected, picograms of compound per peak width (pg/s), and picograms of sulfur per second (pg S/s). As noted above, however, the number of sulfur atoms present in the analyte does not appear as important as the overall structural configuration to the reactivity of F_2 with analytes. As a result, the pg S/s values likely provide less useful information than the ng compound injected and pg compound injected/s data presented in Table I, but they are included to allow comparison with previous work. The SCD response appears to be compound specific, probably due to different activation energies for the reaction between the analytes and F_2 and due to the formation of a number of different excited-state products that produce distinct chemiluminescence emission spectra. The latter results in a varied response when monitored by the photomultiplier tube in the SCD[4]. Calculated SFC–SCD detection limits were typically in the high-picogram to low-nanogram range of analyte injected.

Using a capillary-column SFC system with dual-flame photometric detector (FPD), Markides *et al.*[19] reported a detection limit of 0.5 ng (S/N = 2) for ethyl parathion in the phosphorous mode. While no detection limit was reported specifically for ethyl parathion in the sulfur mode, they found that the FPD in the sulfur mode was less sensitive (detection limit of 25 ng for benzo[*b*]thiophene) and more noisy than when operated in the phosphorus mode and exhibited a baseline rise during pressure programming, requiring baseline correction procedures. In comparison, the sulfur chemiluminescence detector exhibited no additional noise and only minimal baseline drift during pressure programming, and was found to have a detection limit of 39 ng (S/N = 3) for methyl parathion.

The SFC–SCD detection limits of several analytes reported here can be compared to detection limits previously determined using GC–SCD or HPLC–SCD systems. Compared to the 1-dodecanethiol detection limits determined by SFC–SCD (Table I), a capillary GC–SCD system[18] with a He mobile phase was two orders of magnitude more sensitive, based on the absolute amount of analyte injected (0.06 ng) and one order of magnitude more sensitive when the amount per peak width values (9.5 pg/s) were used to compensate for chromatographic differences between capillary GC and SFC. Signal quenching by CO_2 in the SFC–SCD may account for some of these differences, since triatomic CO_2 is generally a much more effective quencher of chemiluminescence signals than monoatomic He[20,21]. The use of packed-column SFC with SCD was not investigated here. However, outlet flow-rates in packed-column SFC are typically >20 ml/min, and in earlier studies of SFC with another chemiluminescence-based detector, the redox chemiluminescence detector, these

higher mobile phase flow-rates were found to cause substantial signal quenching[13,22]. Whether a similar reduction in response by the SCD will be observed under packed-column SFC mobile phase flow-rates remains to be determined. In 1986, Mishalanie and Birks[3] reported a detection limit of 77 pg/s for 1-octanethiol using a HPLC–SCD system. Their value is *ca.* three times higher than the 27 pg/s value observed in SFC–SCD. This difference may be due in part to instrumental improvements in the new Model 300 SCD over their earlier SCD design. More recently, Legier and Birks[9] reported a detection limit of 390 pg/s of malathion by HPLC when using the Model 300 SCD. Their value is *ca.* five times higher than that found with the SFC–SCD system (77 pg/s). Additional signal quenching from the volatilized mobile phase may account for the slightly lower detection limits observed with HPLC–SCD using acetonitrile–water or methanol–water mobile phases, compared to SFC–SCD with CO_2.

A plot of response (peak area) *versus* amount of 1-octanethiol injected into the SFC–SCD system shows linearity (r^2 = 0.999) over the one order of magnitude variation in amount injected. This finding is consistent with calibration curves obtained in the GC–SCD system, which exhibits excellent linearity over approximately four orders of magnitude down to the detection limit for a variety of analytes[2,16]. Linear response up to three orders of magnitude has also been observed recently by another research group, which used an SFC–SCD system similar to the one described here[23].

A number of industrial and environmentally relevant materials contain organosulfur compounds, many at trace levels. One example is carbon black, which has been reported to contain trace quantities of sulfur-containing polycyclic aromatic heterocycles[24,25]. In Fig. 6 is shown an SFC–SCD chromatogram of a dichloromethane extract of carbon black, prepared according to the procedure of Lee and Hites[24]. Again, the minimal response by the SCD to the dichloromethane solvent should be noted. Some of the peaks obtained may be sulfur-containing heterocyclic species. However, the SCD has been found to be not as responsive to sulfur heterocyclic compounds as it is to alkyl sulfur compounds[2,26]. Since carbon black is reported[27] to contain up to nearly 1 part per thousand of individual polycyclic aromatic hydrocarbons (PAHs), we suspected that these hydrocarbons in the carbon black

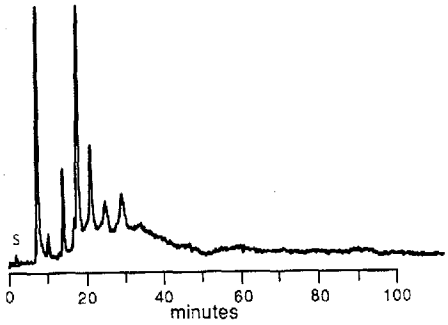


Fig. 6. SFC–SCD of a dichloromethane (S) extract of carbon black. Pressure held for 2 min at 136 atm, then linearly programmed at 4.1 atm/min to a final hold of 374 atm. SFC column at 100°C. All other conditions as described in the Experimental section.

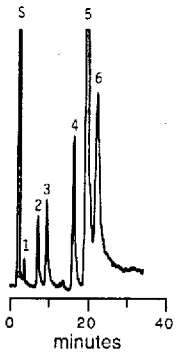


Fig. 7. SFC–SCD of a standard containing six polycyclic aromatic hydrocarbons in toluene (S). Linear pressure program from 100 atm. to 300 atm in 40 min. SFC column at 100°C. All other conditions as described in the Experimental section. Peaks: 1 = naphthalene, 77.4 ng; 2 = fluorene, 95.4 ng; 3 = phenanthrene, 59.4 ng; 4 = chrysene, 58.8 ng; 5 = benzo[*a*]pyrene, 57.0 ng; and 6 = 1,2,5,6-dibenzanthracene, 69.0 ng.

extract might be producing most of the peaks in this chromatogram. In Fig. 7 is shown an SFC–SCD chromatogram of a mixed standard of six PAHs in toluene, run under different chromatographic conditions than Fig. 6. All the PAHs responded with an overall increase in response with increasing number of aromatic rings. The differences in response observed between PAHs of equivalent number of aromatic rings is probably due to varying levels of reactivity of the PAHs with F_2. The substantial response to PAHs, especially those of higher molecular weight, coupled with the reported high concentrations of PAHs in carbon black extracts, suggests that the peaks in Fig. 6 were likely due principally to response by the SCD to PAHs. Potential interferences from olefins and PAHs may therefore present a problem when attempting to determine organosulfur compounds in some matrices. However, the fairly high degree of sensitivity to olefins and some PAHs may be advantageous in some selected analyses.

CONCLUSIONS

The examples shown in this study demonstrate the feasibility and potential applicability of supercritical fluid chromatography coupled with sulfur chemiluminescence detection to the analysis of many thermally labile, polar, and/or high-molecular-weight organosulfur compounds in a variety of fields. Continued refinements of the new SCD will likely further improve detector selectivity and sensitivity, and additional developments and applications using SFC–SCD by another research group are reportedly forthcoming[23].

ACKNOWLEDGEMENTS

The loan of a Model 300 sulfur chemiluminescence detector from Sievers Research, Boulder, CO, U.S.A., and partial financial support is gratefully acknowledged. We thank Applied Biosystems, Santa Clara Analytical Division, Santa Clara,

CA, U.S.A., for a loan of their microgradient system pump. Special thanks also to Steve Montzka for technical assistance and to Herb Schwartz and Randy Shearer for supplying some of the analytes. W.T.F. gratefully acknowledges the support of the Cooperative Institute for Research in Environmental Sciences for a visiting scientist fellowship. Support of the National Science Foundation under Grant ATM-8618793 to the University of Colorado is gratefully acknowledged.

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