



ELSEVIER

Journal of Chromatography A, 670 (1994) 117–126

JOURNAL OF
CHROMATOGRAPHY A

Selective chemiluminescence detection of sulfur-containing compounds coupled with nitrogen–phosphorus detection for gas chromatography

Thomas B. Ryerson, Robert M. Barkley, Robert E. Sievers*

Department of Chemistry and Biochemistry, Cooperative Institute for Research in Environmental Sciences, and Global Change and Environmental Quality Program, University of Colorado, Boulder, CO 80309-0216, USA

(First received December 24th, 1993; revised manuscript received February 23rd, 1994)

Abstract

A new sulfur and nitrogen–phosphorus detector for gas chromatography is described. The detector is an integrated thermionic ionization–chemiluminescence device permitting simultaneous detection of sulfur-containing and nitrogen- or phosphorus-containing compounds. This new flameless detector utilizes a heated rubidium-doped ceramic bead in a thermionic ionization chamber to produce sulfur monoxide from sulfur compounds. The SO is mixed with O₃ and the resulting chemiluminescence is monitored with a photomultiplier tube, providing sulfur-selective detection. The thermionic ionization detector signal serves as an independent second response channel, affording simultaneous selective and sensitive nitrogen–phosphorus detection. Two chromatograms are obtained, one in which selectivity is exhibited for nitrogen and phosphorus compounds, and the other for sulfur compounds present in the sample.

1. Introduction

Gas chromatographic (GC) separation, combined with selective detection, is often used in the analysis of volatile S, N and P compounds in the complex matrices characteristic of environmental samples. Selective detection methods for GC determination of S, N and/or P compounds are flame photometric (FPD) [1–3], atomic emission (AED) [2,4,5], Hall electrolytic conductivity (ELCD) [2,6], thermionic ionization (TID) [2,7–9], and several chemiluminescence (CL) detec-

tion methods [2,10–13]. With the exception of AED, combined S, N and P detection requires the use of some combination of these detectors, repeat analyses, or splitting of the sample.

FPD is the most widely used GC detection method for sulfur and phosphorus; selective S and P detection is achieved by monitoring, in part, S₂* emission at 394 nm and HPO* emission at 526 nm. However, the FPD response to sulfur compounds is highly compound-dependent, varies non-linearly with sulfur concentration, and is affected by quenching and substantial interferences by co-eluting species. AED can detect S, N and P compounds simultaneously and is not as greatly affected by quenching and interferences, but this method is expensive and requires a skilled operator. ELCD can detect S and N

* Corresponding author. Address for correspondence: Department of Chemistry and Biochemistry, University of Colorado, Campus Box 215, Boulder, CO 80309-0215, USA.

compounds but is not widely used because it is difficult to set up and maintain and also exhibits quenching and interference problems from compounds that do not contain sulfur or nitrogen.

TID (also called nitrogen–phosphorus detection, NPD) is selective for N and P compounds [9]. Widespread use of TID has been hindered in part due to the poorly understood chemistry by which it operates and a perceived reproducibility problem as detector elements age. Nonetheless, TID designs offer sensitive detection for N and P compounds for GC, with detection limits in the picogram range.

A flame-based sulfur chemiluminescence detection (flame-SCD^a) system has been developed [12]. Flame-SCD monitors the chemiluminescence produced when SO, formed from S compounds combusted in a flame, is oxidized by added ozone. Flame-SCD exhibits a linear response to sulfur independent of sulfur atom functionality, is not affected by co-eluting hydrocarbons, and is sensitive to ppb concentrations of sulfur compounds in complex matrices.

The instrument described here integrates a unique form of a sulfur CL detector with a thermionic detector. While this new detector uses no flame to generate SO, it is similar in some respects to the SCD system; thus, a brief review of sulfur CL and TID will be presented in the Results and discussion section.

2. Experimental

2.1. Materials

Helium was used as the GC carrier gas and was purified by passing it through a molecular sieve and then a reducing catalyst trap. Molecular sieve (5 Å) from Fisher Scientific (Pittsburgh, PA, USA) was conditioned under vacuum at >400°C for 12 h prior to use. R3-11 Copper catalyst was obtained from Chemical Dynamics (South Plainfield, NJ, USA) and was conditioned under hydrogen gas at 160°C for 24 h

prior to use. Hopcalite (6–14 mesh, 1.41–3.36 mm), supplied by Mine Safety Appliances (Pittsburgh, PA, USA), was used to trap excess ozone upstream of the vacuum pump. Reagent-grade hexanes (*ca.* 50% *n*-hexane), acetone and dimethyl sulfoxide (DMSO) were purchased from Mallinckrodt Specialty Chemicals (Chesterfield, MO, USA). Malathion (95%), 3-methylpyridine and dimethyldisulfide (DMDS) were purchased from Pfalz & Bauer (Waterbury, CT, USA). The 1,4-thioxane, thiophene, 2,5-dimethylthiophene, dimethyl sulfate, tetramethylene sulfone, 4-*tert.*-butylpyridine and 2-bromochlorobenzene used to make standards were supplied by Aldrich. N-Dodecane and 1-tridecene standards were obtained from Polyscience (Niles, IL, USA). A test mixture of various mercaptans, sulfides and disulfides was supplied by Sievers Instruments (Boulder, CO, USA). The SO₂, SF₆ and H₂S gas standards were from Matheson (Secaucus, NJ, USA). All commercially supplied reagents were used as received without further purification. Thiirane-1-oxide was synthesized in our laboratory by the method of Hartzell and Paige [14].

2.2. Apparatus

A Hewlett-Packard Model 5730A gas chromatograph was modified with a Grob-type split/splitless injection port. Chromatographic separation was accomplished by use of a Hewlett-Packard HP-1 25 m × 0.2 mm I.D. fused-silica capillary column with a 0.33- μ m layer of cross-linked poly(dimethylsiloxane) stationary phase. GC conditions were 20 p.s.i.g. (1 p.s.i. = 6894.76 Pa) of helium head pressure (18 cm/s linear velocity) and a split ratio of 1:40. Helium was used as the carrier gas and was purified by passing it through molecular sieve and copper catalyst traps to remove carbon dioxide, water and oxygen. The gas chromatograph was equipped with unmodified flame ionization (FID) and TID detection systems. A digital multimeter (Fluke, Model 77) was used to measure the TID bead heating voltage. A Sievers Instruments Model 350A SCD system was used to measure sulfur monoxide CL; the new flame-

^a SCD is a registered trademark of Sievers Instrument Co., Boulder, CO, USA.

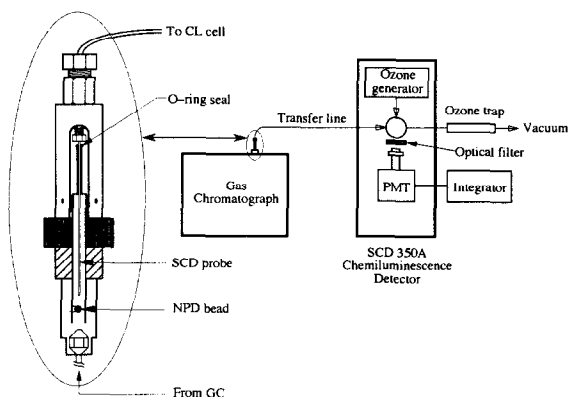


Fig. 1. Schematic of SNPD.

less method of SO generation was the only modification to the SCD design. The SCD ozone generator was supplied with pure industrial-grade air passed through a Drierite trap to remove water. Two Hewlett-Packard Model 3390A integrators were used to simultaneously monitor TID and SCD signals.

The sulfur and nitrogen–phosphorus detection (SNPD) system is shown schematically in Fig. 1. It consists of the following components: a gas chromatograph, a thermionic ionization detector and a sulfur chemiluminescence detector (without the flame interface) consisting of an alumina probe and transfer line, an ozone source, a CL reaction chamber, a photomultiplier tube (PMT) and a vacuum pump. An adapter was machined from an aluminum block to position the SCD probe (ordinarily located above a hydrogen-rich hydrogen–air flame) and was threaded to allow variable probe tip positioning from 1 to 35 mm above the thermionic ionization bead. Flow was maintained through the probe and CL chamber by the SCD vacuum pump, which served to maintain operating pressures in the chamber below 25 Torr (1 Torr = 133.322 Pa). A trap filled with Hopcalite catalyst on the vacuum pump inlet destroyed excess ozone before the pump exhaust was vented to a fume hood.

3. Results and discussion

Flame-SCD has been used for GC [10,12,15–23] supercritical fluid chromatography [19,24,25]

and capillary liquid chromatography [19,26]. It has been compared with FPD [15,17], with AED [5] and has been recently reviewed [18,22,27–29]. Briefly, flame-SCD is based on a two-step process described by Benner and Stedman [12]. Sulfur-containing compounds are combusted in a hydrogen-rich hydrogen–air flame to form SO. The SO is withdrawn under vacuum to a reaction chamber and O₃ is added. SO is oxidized to sulfur dioxide (SO₂^{*}) in an excited electronic state [30]. The SO₂^{*} decays by chemiluminescent emission of a photon, which is counted by a photomultiplier tube (reaction 2).



This chemiluminescence is highly selective for S compounds and affords excellent sensitivity due to the low background. Detection limits for the SCD are on the order of 0.5 pg S/s, or low ppb concentrations of sulfur. Detector response is linear over five orders of magnitude. The response to sulfur is independent of the configuration of sulfur atoms in the parent molecule. When gas flows are adjusted correctly, co-eluting hydrocarbons, including the large solvent peak, do not quench the sulfur CL signal. A patent has been granted for coupling flame-SCD with FID, the use of which permits simultaneous general and sulfur-selective chromatograms to be obtained [31].

Although generation of SO in a flame is a widely used sensitive and selective method of sulfur detection, there are several possible advantages to be realized by using other ways to produce SO from sulfur-containing compounds. Although the absolute conversion efficiency of sulfur compounds to SO in the flame is unknown, this efficiency has been estimated to be quite low, below 1% [20]. An increase in conversion efficiency has the potential to dramatically increase the sensitivity offered by SCD. Flame-SCD response to sulfur is dependent on a number of operating factors, especially those involving sampling of a flame for SO generated from S compounds.

Alternative methods to generate SO for sub-

sequent CL detection have been sought to avoid the use of an open flame. A flameless combustion chamber has been recently reported to convert sulfur compounds to SO for subsequent CL detection [32,33]. Our choice of the heated catalyst bead in a TID system was based on two reasons. First, coupling the two detectors in this manner offers the possibility of simultaneous S, N and P detection. Second, this technology was readily available from several manufacturers and was accessible to virtually any laboratory equipped with a GC system. Replacing the flame as the SO source has the potential to offer some operational advantages over flame-SCD. Less gas is consumed during SNPD operation, and less water is formed. The positioning of the sample probe is not as critical in SNPD as it is in flame-SCD.

The Hewlett-Packard TID system used in the present report collects positive ions, unlike most other commercial designs which collect negative ions. A recent theory, based on bead surface chemistry, proposes an explanation for the selective production of positive N and P ions in TID [34]. This theory describes the TID mechanism as one of purely surface decomposition and ionization. N and P analytes are first adsorbed onto the bead via lone pair interaction with a surface site. Analyte decomposition proceeds by loss of H or CH₃; ionization follows for those radicals with low ionization potentials, *i.e.*, those containing a N or P heteroatom. Mass spectral studies suggest that formation of reactive species residing on the bead surface, presumably H atoms, can account for the observed formation of both positive and negative N- and P-containing ions [34]. Thus, all steps involved in the production of charge carriers may occur on the bead surface. Subsequent discussion of the SO formation in the new SNPD system will be in terms of this surface decomposition and ionization theory. The TID system used in this study differs from other TID systems only in ion collection, not in fundamental ion formation chemistry. We expect that other TID systems may be successfully coupled to SCD, subject to the physical constraints of probe positioning inside the thermionic ionization source.

Sulfur CL detection can be coupled very easily to conventional TID; this coupling allows simultaneous selective measurement of S and N or P compounds in GC (see Fig. 1). A custom adapter was designed and fabricated to hold the SCD probe in the TID collector chimney. A 1/16-in. (1 in. = 2.54 cm) O.D. alumina SCD probe was inserted to within 2 mm of the TID bead. A solution of 50 ppm (w/w) DMSO in hexanes was injected into the GC system to determine whether any SO was produced by the reactive species on the surface of the heated TID bead. The resulting chromatogram is shown in Fig. 2a, with a comparison to the response obtained with a cool, inactive bead shown in Fig. 2b. There was no detectable response when the bead was not electrically heated, which demonstrated that the conversion depends upon processes that occur when TID is being operated. This rules out the possibility of cold catalytic formation of SO by the TID bead.

Fig. 2b also indicates DMSO does not exhibit reduced sulfur CL [13,35] upon direct ozone oxidation. Thus, S response is shown to be via production of SO by the heated TID bead. This novel method of S compound conversion to SO is highly selective. No response for solvent is

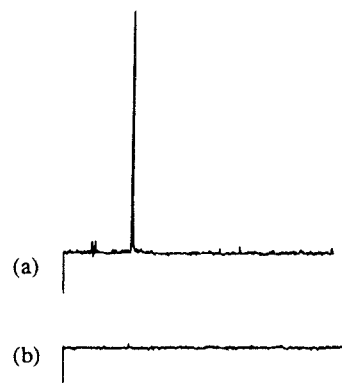


Fig. 2. Sulfur-selective detection by SNPD. (a) DMSO is converted to SO by a heated TID bead and detected by O₃-induced chemiluminescence. (b) This conversion is not accomplished until a minimum heating voltage is applied to the bead. GC conditions: 1.0 μ l of a 50 ppm DMSO in hexanes solution was injected, split 1:40; column and stationary phase as noted in the text. GC oven temperature 80°C. bead heating voltages (a) 26.00 V d.c.; (b) 0.00 V d.c.

noted under these conditions, indicating a SNPD S-channel selectivity over carbon-, hydrogen- and oxygen-containing compounds of $>10^6$.

Further experiments showed that SCD probe insertion does not disrupt normal TID processes. Chromatograms exhibiting selective, two-channel S and NP detection by the new SNPD system is shown in Fig. 3b and c. Neither S nor NP channel of the SNPD system exhibited detectable response to the non-S or -NP compounds, respectively, present at comparable or higher concentration levels. Examination of the NP trace in Fig. 3c reveals this SNPD channel behaves similarly to unmodified TID. A slight negative response for the large amount of solvent is noted and is characteristic of properly functioning TID. The large hydrocarbon plug

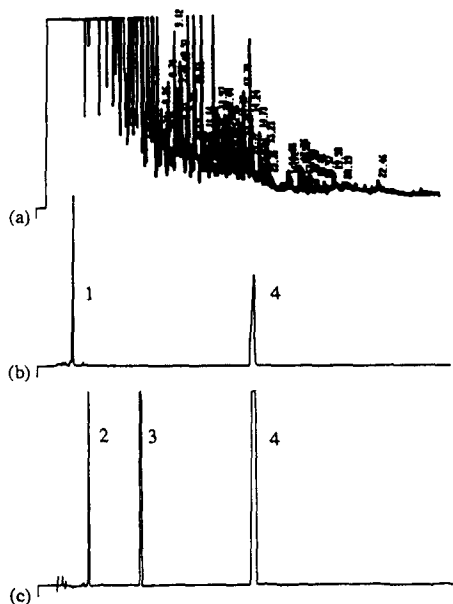


Fig. 3. Selective two-channel SNPD operation (b = S channel, c = NP channel), with comparison to FID (a). Only those compounds containing S, N or P are detected. These two chromatograms result from a single injection of a mixture of S/N/P compounds diluted in a complex mixture of hydrocarbons. Conditions were as follows: $1.0 \mu\text{l}$ of a solution of ca. 100 ppm of each S, N and P compound and 10% (v/v) gasoline in hexanes was injected, split 1:40; column and stationary phase as noted in the text. GC oven temperature program: 80°C for 2 min, increased at $8^\circ\text{C}/\text{min}$ to 160°C and held at 160°C for 2 min. Bead heating voltage 22.45 V d.c. Peaks: 1 = dimethyl sulfoxide; 2 = trimethylphosphate; 3 = 4-*tert.*-butylpyridine; 4 = dimethylthiourea.

tends to interfere with radical processes on the bead surface and thereby “cool” the bead. These processes are rapidly reestablished by continual external heating of the bead after passage of solvent.

SNPD response dependence on a number of operating parameters has been determined, and is presented below with a comparison to normal TID and SCD operation. In most cases, the NP channel response dependence is identical to that in normal TID. However, there are several differences between the S channel of the new SNPD and flame-SCD operation. These differences will be discussed in detail in section 3.1.

3.1. Detector optimization: bead heating voltage

Both the S and NP channel response dependence on TID bead heating voltage were investigated. DMSO and 3-methylpyridine were diluted in hexanes to form a stock solution containing $50 \text{ ng}/\mu\text{l}$ of each compound. Repetitive injections of this solution were made while varying the heating voltage to the bead from 0 to 25.50 V. The results are shown graphically in Fig. 4. No response was seen in either channel until the voltage exceeded ca. 22 V. Above this threshold, response increased rapidly with increased heating voltage. This is similar to normal TID behavior [9]. As with TID, the SNPD bead heating voltage was chosen to give a baseline deflection of 10% of full scale at attenuation 8 on the NP channel. This deflection signals the initiation of the radical processes at the surface of the bead. Increasing the voltage above this setting enhanced the S-channel response, but degraded reproducibility in both channels, increased NP-channel noise, and reduced the long-term stability of the SNPD system.

3.2. Probe positioning

Upon initial insertion of a flame-conditioned alumina SCD probe into the thermionic ionization chamber, an increased bead heating voltage (relative to conventional TID operation) was required to initiate and sustain TID chemical processes leading to selective N- and P-com-

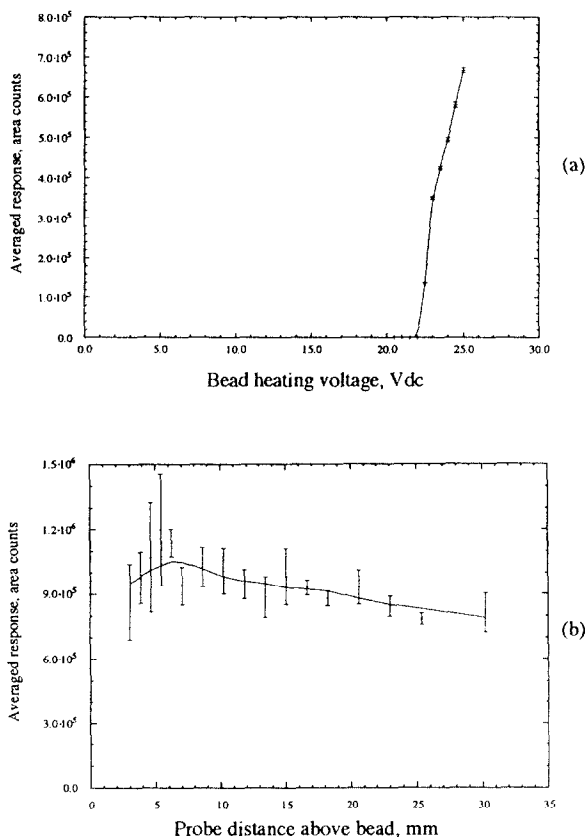


Fig. 4. SNP D Sulfur channel response dependence on (a) TID bead heating voltage and (b) SCD probe height above the bead. Plotted values represent average responses for five 1.0- μ l injections, of 50 ng/ μ l DMSO in hexanes, at each voltage/probe height; split ratio measured at 1:40. Error bars represent ± 1 standard deviation.

pound detection. The SCD vacuum pump creates a positive flow of over 600 ml/min through the probe, while TID gas flows total less than 100 ml/min into the chamber. A partial vacuum is created in the chamber, necessitating higher heating voltages to sustain the chemical processes leading to analyte decomposition and ionization [36].

Once the thermionic surface processes were initiated, injections of a solution of DMSO in hexanes were made while varying the probe height above the bead to ascertain the effect of probe positioning on the magnitude of the S channel response. The axial probe tip position was varied from 3 to 30 mm above the heated

bead. The results are shown in Fig. 4. A broad maximum is seen in the response, with the optimum at roughly 6 mm. Therefore, the S-channel response in SNP D is relatively independent of axial probe position.

This broad, forgiving maximum in SNP D S-channel dependence on axial probe position is markedly different than for flame-SCD. A sharply peaked maximum is exhibited when a flame is used to generate SO from S compounds [12]. Sulfur chemistry in flames is characterized by complex and rapid reactions between many different S species. These competing equilibria, and the relatively short lifetime in air of the SO diradical [37], give rise to a highly localized region within the flame in which the SO concentration is maximized. Thus, in flame-SCD, optimum sensitivity is highly dependent on the probe position. In practice, probe positioning has been a time-consuming step in the flame-SCD optimization process; recently, a new probe interface design has greatly reduced fluctuations arising from variations in the probe position.

The lessened dependence on probe position in the SNP D design does, however, facilitate S response optimization. The lessened dependence may be due to the lower pressures obtained in the thermionic ionization chamber. The lifetime of SO at reduced pressure is much longer than at atmospheric pressure [38,39]; therefore, SNP D may preserve SO longer than flame-SCD. At probe distances closer to the bead than optimum, the decreased sensitivity in the SNP D design may be due to interferences in bead surface chemistry. At short distances, the probe disturbs gas flows in the thermionic ionization chamber, thereby decreasing the S-channel sensitivity by interfering with radical processes at the bead surface. However, this decrease at short distances is still not as great as in conventional SCD.

3.3. Probe conditioning

The first alumina probe used in this study had been conditioned by heating for 12 h in a flame, as the manufacturer has suggested for flame-SCD operation. However, in SNP D, new, un-

conditioned probes used as replacements gave equivalent or slightly increased S-channel sensitivity. Therefore, the data in the present study were all obtained using an unconditioned probe.

3.4. Gas flows

Initial success in selective SNPDT was achieved at detector gas flow settings appropriate to unmodified TID, *i.e.*, 4 ml/min hydrogen, 50 ml/min air and 30 ml/min nitrogen makeup gas. The effects of changing both the absolute and relative amounts of these detector gases on both the S- and the NP-channel responses were investigated. A solution of DMDS and 3-methylpyridine in hexanes was repeatedly injected while simultaneously varying both hydro-

gen and air flows into the SNPDT thermionic ionization chamber. Optima for S- and NP-channel response were located by using a Simplex method. Data are presented as response surfaces in three dimensions in Fig. 5.

Examination of these surfaces indicates that S and NP responses are maximized under roughly similar conditions. However, two other criteria must be included in a determination of optimum gas flows. One is solvent response in the S channel, which becomes a significant factor at high total gas flow-rates. Another is the bead heating voltage required to sustain a given background signal in the NP channel. NP background is indicative of the "robustness" of the surface processes of the bead. The heating voltage required to sustain the reactions at the bead

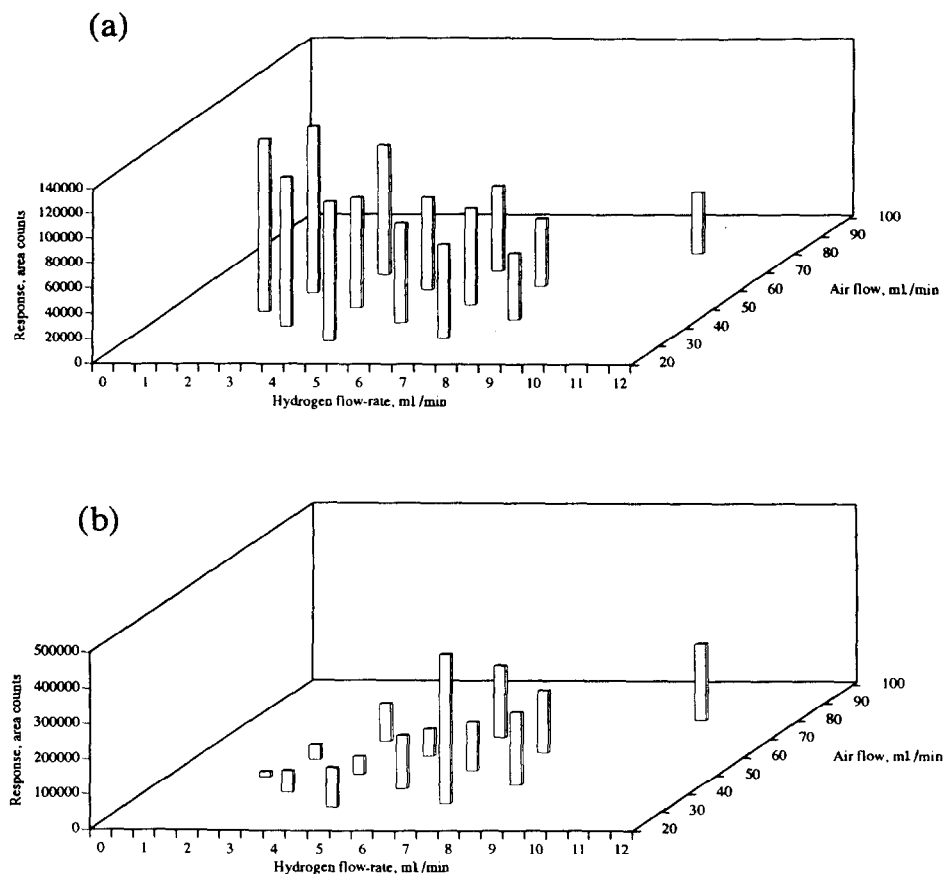


Fig. 5. Response surfaces in three dimensions obtained by varying hydrogen and air flows in SNPDT. (a) S-Channel response surface; (b) NP-channel response surface. Values are averages of five 1.0- μ l injections, split 1:40, of a 100 ppm solution of dimethyldisulfide (S channel) or 3-methylpyridine (NP channel) in hexanes.

Table 1
Comparison of detection limits of SNPD with other detection methods

	Sulfur, pg S/s (2,5-dimethylthiophene)	Nitrogen, pg N/s (4- <i>tert.</i> -butylpyridine)
NPD	N.D. ^a	0.23
SCD	0.73	N.D.
SNPD	1.5	1.1

Detection limits calculated based on $S/N_{pp} = 3.29$ (95% confidence), N_{pp} = peak-to-peak noise.

^a N.D. = Not detectable by this method.

surface increases rapidly at high gas flows. Therefore, the optimum gas mixture and the flow-rates must allow sensitive S and NP detection, with no response from the solvent in the S channel, at a reasonable heating voltage. These criteria are met at 4 ml/min hydrogen, 50 ml/min air and 30 ml/min of nitrogen makeup, which happen to be the flows recommended by the manufacturer for traditional TID operation. Apparently the conditions needed for effective NP detection also generate SO with virtually optimum efficiency.

Once the maximum SNPD response for simultaneous, selective two-channel S and NP detection was obtained, detector sensitivity, selectivity and linearity were determined. The detector response is linear over three orders of magnitude in concentration, from 0.3 to 375 ng/ μ l; the linear least-squares regression equation, detector response = $(18598 \pm 730) \times$ con-

centration + (15409 ± 15932) , yielded a correlation coefficient $r = 0.9996$ for the compound malathion. Malathion is an insecticide commonly used in formulations for pest control, and contains both S and P.

Detection limits were determined for this new detector and are presented in Table 1 and compared with unmodified TID and SCD operation. SNPD, when operated in the combined mode, is a factor of 5 less sensitive than TID for a test N compound, and a factor of 2 less sensitive than SCD for a test S compound. However, SNPD can selectively detect S and NP compounds at low ppm concentrations, and can do so virtually simultaneously without splitting of the sample.

A wide range of S and NP compounds has been detected by SNPD (see Table 2). The NP-channel response is equivalent in this respect to that of conventional TID [8,9]. The S-channel

Table 2
S-Containing compounds detected by SNPD

Sulfides	Carbon disulfide, hydrogen sulfide, methyl ethyl sulfide, dimethyl sulfide, diethyl sulfide, dimethyl disulfide, diethyl disulfide, dimethyl trisulfide, 1,4-thioxane, thiazole, thiourea, dimethylthiourea, diethylthiourea, 2-chloroethyl ethyl sulfide (half-mustard)
Mercaptans	Methyl, ethyl, 1-propyl, 2-propyl, 2-methylpropyl, 1-butyl, 2-butyl and <i>tert.</i> -butyl mercaptan
Aromatics	Thiophene, 2-methylthiophene, 2,5-dimethylthiophene
Oxides	Thiirane-1-oxide, dimethyl sulfoxide
Pesticides	Malathion, aldicarb, chlorpyrifos

response characteristics, however, are different than in flame-SCD. The flame-SCD design exhibits nearly equimolar responses to sulfur compounds regardless of the environment of the S atom in the analyte [12,23]. Although SNPD is sensitive to a wide range of sulfur compounds, the response is dependent on the S atom functionality. The chemiluminescence intensity decreased in the order sulfide > aromatic > mercaptan > sulfoxide; sensitivities of detection of these representative compounds are in the ratio 5.3:2.6:1.7:1.

While all reduced sulfur compounds tested were detected by SNPD, of those tested, only two of the oxidized sulfur compounds examined, DMSO and thiirane-1-oxide, gave a response. SO₂, SF₆, dimethyl sulfate and tetramethylene sulfone were not detected; the reason for this is not clear. We surmise that oxidizing conditions sufficient to convert reduced sulfur compounds to SO obtain at the surface of the bead. Oxidized sulfur compounds, with the two exceptions noted, do not appear to be reduced to SO under these conditions. Oxidized sulfur compounds are converted to SO by combustion in a hydrogen-rich flame in the conventional SCD design.

4. Conclusions

The new SNPD design offers the following advantages.

(a) *Simultaneous S and NP detection.* Information on S and NP compounds can now be obtained without duplicate analyses or splitting of sample. Many pharmaceuticals, pesticides and herbicides contain different combinations of S, N and P; therefore, a selective two-channel detector simplifies compound identification by providing an extra dimension of information. Detector response ratioing can assist in confirmation of the identities of unknown peaks.

(b) *High selectivity.* No solvent response is observed in the SNPD S channel under a wide range of operating conditions. In contrast, the SCD flame gas flows must be carefully adjusted to eliminate either positive or negative response from solvent.

(c) *Easy optimization.* The SNPD S channel can tolerate a wide range of variation in gas flows, probe positioning and bead heating voltage and still give sensitive, selective S and NP detection.

(d) *Low gas consumption.* Gas flows are identical to those in TID, and a tenth of that required for SCD. In contrast to conventional SCD, very little water is produced as a byproduct of SNPD operation. This prolongs pump oil and ozone trap lifetimes and permits more efficient pumping.

Applications for SNPD involve detection of S and NP compounds in complex matrices, especially those in which the constituents are so numerous that the resolving power of capillary GC is insufficient. These matrices include hydrocarbon feedstocks, petrochemical products and environmental samples. SNPD may also be useful for determining trace levels of drugs, medications and metabolites in complex biological matrices such as plasma and other bodily fluids. Many pesticides and almost all chemical warfare agents should be sensitively detected by this detector, since they contain sulfur, nitrogen and/or phosphorus.

5. Acknowledgements

Support from the NSF under grant ATM-9115295 is gratefully acknowledged. We would also like to thank Sievers Instruments Co. for the generous gift of a sulfur chemiluminescence detector, and Dr. R. Hutte for his insightful comments throughout the course of this research.

6. References

- [1] S.O. Farwell and C.J. Barinaga, *J. Chromatogr. Sci.*, 24 (1986) 483.
- [2] M. Dressler, *Selective Gas Chromatographic Detectors*, Elsevier, Amsterdam, New York, 1986.
- [3] S.S. Brody and J.E. Chaney, *J. Gas Chromatogr.*, 4 (1966) 44.
- [4] P.C. Uden, Y. Yoo, T. Wang and Z. Cheng, *J. Chromatogr.*, 468 (1989) 319.

- [5] S.E. Eckert-Tilotta, S.B. Hawthorne and D.J. Miller, *J. Chromatogr.*, 591 (1992) 313.
- [6] R.C. Hall, *J. Chromatogr. Sci.*, 12 (1974) 152.
- [7] B. Kolb and J. Bischoff, *J. Chromatogr. Sci.*, 12 (1974) 625.
- [8] C.A. Burgett, D.H. Smith and H.B. Bente, *J. Chromatogr.*, 134 (1977) 57.
- [9] P.L. Patterson, *DET Report 17*, DETector Engineering and Technology, Walnut Creek, CA, 1989.
- [10] J.K. Nelson, R.L. Getty and J.W. Birks, *Anal. Chem.*, 55 (1983) 1767.
- [11] S.A. Nyarady, R.M. Barkley and R.E. Sievers, *Anal. Chem.*, 57 (1985) 2074.
- [12] R.L. Benner and D.H. Stedman, *Anal. Chem.*, 61 (1989) 1268.
- [13] J.S. Gaffney, D.J. Spandau, T.J. Kelly and R.L. Tanner, *J. Chromatogr.*, 347 (1985) 121.
- [14] G.E. Hartzell and J.N. Paige, *J. Am. Chem. Soc.*, 88 (1966) 2616.
- [15] R.L. Benner and D.H. Stedman, *Environ. Sci. Technol.*, 24 (1990) 1592.
- [16] R.S. Hutte, N.G. Johansen and M.F. Legier, *J. High Resolut. Chromatogr.*, 13 (1990) 421.
- [17] K.K. Gaines, W.H. Chatham and S.O. Farwell, *J. High Resolut. Chromatogr.*, 13 (1990) 489.
- [18] A.L. Howard and L.T. Taylor, *J. High Resolut. Chromatogr.*, 14 (1991) 785.
- [19] N.G. Johansen and J.W. Birks, *Am. Lab.*, 23 (1991) 112.
- [20] R.L. Benner, *Ph. D. Thesis*, University of Denver, Denver, CO, 1991.
- [21] B. Chawla and F. Di Sanzo, *J. Chromatogr.*, 589 (1992) 271.
- [22] R.S. Hutte, R.E. Sievers and J.W. Birks, *J. Chromatogr. Sci.*, 24 (1986) 499.
- [23] R.L. Shearer, D.L. O'Neal, R. Rios and M.D. Baker, *J. Chromatogr. Sci.*, 28 (1990) 24.
- [24] H.-C.K. Chang and L.T. Taylor, *J. Chromatogr.*, 517 (1990) 491.
- [25] W.T. Foreman, C.L. Shellum, J.W. Birks and R.E. Sievers, *J. Chromatogr.*, 465 (1989) 23.
- [26] H.-C.K. Chang and L.T. Taylor, *Anal. Chem.*, 63 (1991) 486.
- [27] R.S. Hutte and J.D. Ray, in H.H. Hill and D.G. McMinn (Editors), *Detectors for Capillary Chromatography*, Wiley, New York, 1992, p. 193.
- [28] W. Wardencki and B. Zygmunt, *Anal. Chim. Acta*, 255 (1991) 1.
- [29] M. Dyson, *Anal. Proc.*, 30 (1993) 79.
- [30] C.J. Halstead and B.A. Thrush, *Photochem. Photobiol.*, 4 (1965) 1007.
- [31] R. Godec, N. Johansen and D.H. Stedman, *US Pat.*, 5 227 135 (July 13, 1993).
- [32] R.L. Shearer, *Anal. Chem.*, 64 (1992) 2192.
- [33] R.L. Shearer, E.B. Poole and J.B. Nowalk, *J. Chromatogr. Sci.*, 31 (1993) 82.
- [34] D.D. Bombick and J. Allison, *J. Chromatogr. Sci.*, 27 (1989) 612.
- [35] T.J. Kelly, J.S. Gaffney, M.F. Phillips and R.L. Tanner, *Anal. Chem.*, 55 (1983) 135.
- [36] L. Trelli and D. Bombick, presented at the 43rd Pittsburgh Conference on Analytical Spectroscopy, New Orleans, LA, 1992, poster 148P.
- [37] J.O. Sullivan and P. Warneck, *Ber. Bunsenges. Phys. Chem.*, 69 (1965) 7.
- [38] C.J. Halstead and B.A. Thrush, *Proc. Roy. Soc. A*, 295 (1966) 380.
- [39] M.A.A. Clyne, C.J. Halstead and B.A. Thrush, *Proc. Roy. Soc. A*, 295 (1966) 355.