

CHROM. 18 046

GAS CHROMATOGRAPHIC DETECTION OF REDUCED SULFUR COMPOUNDS USING OZONE CHEMILUMINESCENCE

JEFFREY S. GAFFNEY*, DANIEL J. SPANAU*, THOMAS J. KELLY and ROGER L. TANNER
Environmental Chemistry Division, Department of Applied Science, Brookhaven National Laboratory, Upton, Long Island, NY 11973 (U.S.A.)

(Received July 16th, 1985)

SUMMARY

The use of ozone chemiluminescent reactions with reduced sulfur compounds as a gas chromatographic detector is described. Flow and temperature dependence of the detection system have been investigated, as well as the use of air *versus* oxygen in the ozonizer. Present detection limits for a number of reduced sulfur compounds range from sub-nanogram to low tens of nanograms of analyte. Selectivity of this detection system for sulfur compounds over most other compounds investigated was found to be greater than seven orders of magnitude. The only significant interference observed was that from olefins, with selectivity on the order of a thousand to one. This detection system is compared to other detection systems for monitoring reduced sulfur compounds by gas chromatography.

INTRODUCTION

A number of gas-phase chemiluminescent reactions have found applications in analytical chemistry. A prime example is the ozone chemiluminescent reaction with nitric oxide¹, which is a highly sensitive real-time analytical tool in atmospheric science, environmental monitoring, and industrial hygiene. A number of other chemiluminescent reactions are also well established. For example the reaction of ozone with olefins (in particular, ethylene) has led to a number of commercial ozone monitors based on this chemistry^{2,3}. In addition, we recently described a potential real-time monitor for reduced sulfur gases⁴, based on the chemiluminescent reaction with ozone^{5,6}.

The sensitivity, selectivity, and simplicity of this type of mass flow detection system make them readily amenable to chromatographic application. For example, ozone chemiluminescent reactions with organics have been employed as detectors in liquid chromatography⁷ and in gas chromatography (GC)^{8,9}.

Selective detection of reduced sulfur compounds is of importance in a number

* Present address: P.O. Box 1663, Group INC-7, MS-J514, Los Alamos National Laboratory, Los Alamos, NM 87545, U.S.A.

of research fields, including geochemical exploration, environmental monitoring, industrial hygiene, and atmospheric science. In particular, the natural gas industry has need for simple, reliable techniques for the analysis of organic sulfides and mercaptans used as odorants.

Of the analytical methods available for reduced sulfur analysis, many suffer from inadequate sensitivity or selectivity, and/or are too expensive for wide spread usage^{4,10,11}. Reported here is a novel GC detector for reduced sulfur compounds based on the ozone-reduced sulfur chemiluminescence. The selectivity of the detector for reduced sulfur compounds over other classes of organic compounds has been examined, and the relative advantages and disadvantages of this detector are compared to recently reported detection methods which use chlorine dioxide¹⁰ or fluorine¹¹ chemiluminescent reactions. Direct comparison to previous GC detection of thiophene using ozone chemiluminescence⁹ without use of optical filters to distinguish the chemiluminescent species is also discussed.

EXPERIMENTAL

Apparatus

The instrumentation used in this study was similar to that previously reported⁴, with the following modifications for GC analysis. A Varian Model 3700 gas chromatograph was interfaced to a modified nitrogen oxides analyzer (Monitor Labs Model 8440) used as the ozone chemiluminescence reduced sulfur detector. An ultraviolet transmitting-visible absorbing glass filter (Corning CS-7-60) was used in place of the normal red filter in the reaction cell. The photomultiplier tube used (Hamamatsu R-268) was that originally present in the nitrogen oxides detector, as this tube has extended response in the ultraviolet as well as in the red. The reaction chamber and column interface were wrapped with heating tape (Clayborn Labs, type K-16-2 pressure sensitive heating tape) in order to keep the GC interface and chemiluminescence detection cell at the desired temperatures. Chromel-alumel thermocouples were used to monitor the interface and detector temperatures. An electrical discharge source using dried lab air or tank oxygen was used to produce the ozone needed for the chemiluminescence detector. No changes were made to the detector electronics or to the reaction chamber design. A 5-s time constant was used for this work unless otherwise stated. The photomultiplier high voltage was adjusted to optimize the signal-to-noise ratio (*ca.* 1000 V).

Upon exiting the reaction cell, the chromatographic effluent-ozone mixture passed through a charcoal or hopcalite trap, which destroyed the ozone and collected noxious exhaust gases upstream of the rubber-diaphragm sampling pump.

Column and chromatographic conditions

A 40 × 1/8 in. O.D. PTFE column was packed with acetone-washed Porapak QS (Altech Stock No. 2719 80-100 mesh)¹², and operated using the following conditions: column temperature, 109°C (isothermal); injection port, 190°C; interface, 170°C; carrier gas, helium at 25 ml/min; ozone-air or ozone-oxygen flow-rate 280 ml/min.

Standards

Standards for determination of GC detection sensitivity were prepared using reagent grade materials and high purity solvents. The compound to be studied was diluted to an appropriate level (1–100 μM) using volumetric flasks and calibrated microsyringes. Samples were made up fresh each day; precision of replicate analyses from day to day was better than 5% (0.5–5- μl injections). Compounds studied included dimethyl sulfoxide, dimethyl sulfide, carbon disulfide, and mercaptoethanol. Solvents used were carbon tetrachloride, cyclohexane, decane, nonane, and hexane.

A Dasibi Gas Calibrator (Model 1005-C2) was used to prepare gas mixtures for the initial detector response studies. These studies, which used a steady state level of reduced sulfur gas in air or other carrier gas, were useful in determining the best ozone reagent (air or oxygen) and also allowed the temperature and flow dependence of the detector to be examined. Compressed tank air, filtered through charcoal and dried, was used as makeup gas and as a zero air source in these studies. Permeation tubes for dimethyl sulfide, methyl mercaptan, hydrogen sulfide, 1-butene, and propane were supplied by AID, Inc. Carbon disulfide and carbonyl sulfide tubes were supplied by Vici Metronics.

RESULTS AND DISCUSSION

Initial tests were made using the detector as a real-time gas-phase sulfur monitor. In these tests the limits of detection for a number of reduced sulfur gases were reexamined as a function of cell temperature, identity of the ozonizer gas, and ozone-sample flow-rates. It was observed, as previously reported⁴, that increased sensitivity could be obtained if air was used instead of oxygen in the ozone source. This increase was found to be approximately a factor of five for some reduced sulfur gases (*i.e.* mercaptans, organic sulfides, etc.) and approximately a factor of two for others (*i.e.* hydrogen sulfide or carbon disulfide).

A strong temperature dependence was observed in the detection sensitivity for

TABLE I

SENSITIVITY OF THE OZONE-REDUCED SULFUR CHEMILUMINESCENCE DETECTOR AS A FUNCTION OF DETECTOR OPERATING CONDITIONS (STEADY STATE FLOW OF GAS STANDARDS FROM PERMEATION TUBES AND GAS CALIBRATOR)

	Ref. 4	This work		
<i>Operating conditions</i>				
Ozone flow (ml/min)	100	130	50	50
Sample flow (ml/min)	100	130	200	200
Cell temperature (°C)	25	70	100	100
Ozonizer gas	air	air	air	O ₂
<i>Detection limit for reduced sulfur compound (ppb, v/v)</i>				
Methyl mercaptan	0.1	0.07	0.2	1
Dimethyl sulfide	0.3	0.1	0.4	2
Hydrogen sulfide	4	6	1	2
Carbon disulfide	—	6	1	2

a number of the reduced sulfur gases, especially for the less reactive compounds. In Table I detection limits for methyl mercaptan, dimethyl sulfide, hydrogen sulfide, and carbon disulfide are given for a variety of conditions. These results indicate that this detector can be adjusted to increase selectively the sensitivity for individual classes of reduced sulfur compounds, or to give approximately equal detection sensitivities for all classes, depending on the operating conditions. These data also suggest that heating the ozone chemiluminescence detector may increase the sensitivity in GC applications, consistent with previous observations^{8,9}. For the GC data presented below, a detection cell temperature of 80°C was used. This temperature could have been increased if the reaction cell had been modified to prevent excessive noise caused by transfer of heat to the photomultiplier tube. One possible design in this regard has been described^{8,9}.

The ozone chemiluminescence detector was coupled to the gas chromatograph as described above for testing as a GC detector. The results of one test illustrate the capabilities of the ozone chemiluminescence detector. In this test the effluent flow from a capillary GC column (25 m OV-101) was split (50/50) and analyzed simultaneously by the ozone chemiluminescence detector and by flame ionization detection (FID). Fig. 1 shows the chart traces obtained from injection of 0.1 μ l of 10 μ M

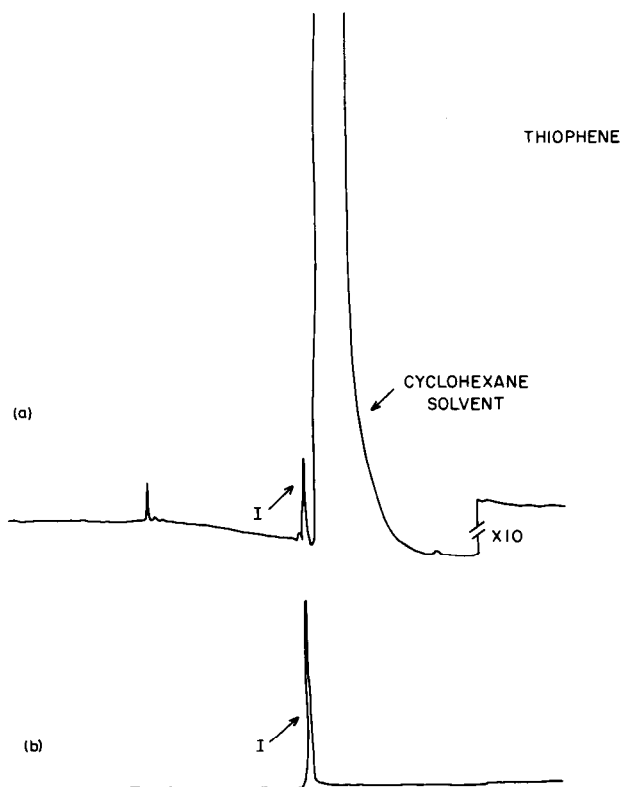


Fig. 1. Comparison of ozone-reduced sulfur detector with flame ionization detector (splitter ratio 50/50, glass capillary column). I = thiophene peak; (a) flame ionization detector; (b) ozone-reduced sulfur chemiluminescence detector.

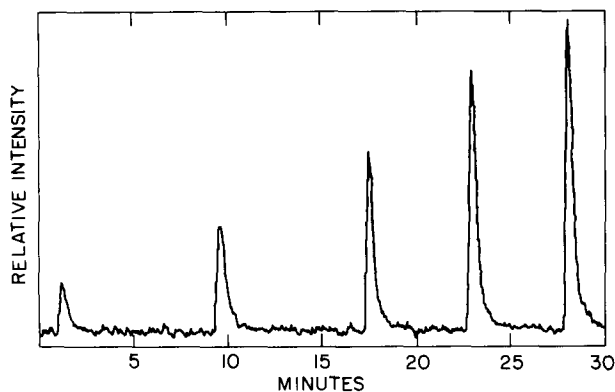


Fig. 2. Ozone-reduced sulfur response to a series of injections of thiophene in cyclohexane (0.5–2.5- μ l injections).

thiophene in cyclohexane, as measured by FID (Fig. 1a) and the ozone chemiluminescence detector (Fig. 1b). Note that comparable sensitivity was obtained for thiophene in both detectors in good agreement with previous work^{8,9}, but that the solvent peak was absent from the chemiluminescence detector trace. The insensitivity of the chemiluminescence detector to the solvent results from the spectral filtering of the detected light, an improvement on previous work without such filtering^{8,9}. Fig. 2 shows the response of the chemiluminescence detector to successive injections of 190 μ M thiophene in cyclohexane (packed column); injected volumes were 0.5, 1, 1.5, 2, and 2.5 μ l, respectively. The calibration plot resulting from these analyses is shown in Fig. 3, which illustrates sensitivity and linearity of the detector. The linearity of the response is noteworthy, since it indicates no significant effect on the chemiluminescence response from the presence of varying amounts of co-eluting solvent. The response of the detector to a number of reduced sulfur compounds was determined. Observed limits of detection for a number of compounds are given in Table II. At the detector temperature of 80°C, response was linear for the compounds studied over at least three orders of magnitude in concentration. Detector stability was found to be excellent with replicate analyses within 5% of each other during a single day, and within 10% over a months operation time.

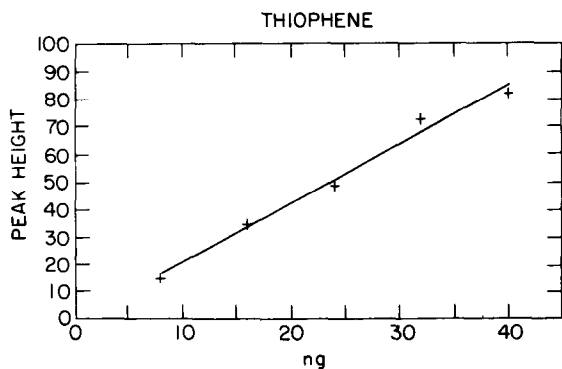


Fig. 3. Plot of peak height versus nanograms thiophene injected for data given in Fig. 2. Note there is no measurable effect due to co-eluting cyclohexane solvent on the thiophene response.

TABLE II

CURRENT LIMITS OF DETECTION FOR OZONE-REDUCED SULFUR GAS CHROMATOGRAPHIC DETECTOR

Conditions: packed column; GC detector operated at 80°C; detection limits determined at a signal-to-noise ratio of 2.

<i>Reduced sulfur compound</i>	<i>Detection limit (ng injected)</i>
Dimethyl sulfide	2
Carbon disulfide	2
Thiophene	6
Dimethyl sulfoxide	35
Mercaptoethanol	50

Greater than seven orders of magnitude selectivity toward reduced sulfur compounds was found relative to aromatics, alkanes, aldehydes, and halocarbons used as solvents (*i.e.* no response to these compounds detected). Olefins were the only class of compounds observed to interfere with selectivity toward reduced sulfur compounds of approximately three orders of magnitude (*i.e.* response to 1-hexene is one thousandth the response to equal amount of thiophene). This selectivity is comparable to that reported for the fluorine chemiluminescence detection method¹¹ for reduced sulfur species. The selectivity of the present device could be improved by use of an ultraviolet filter with a slightly shorter wavelength cutoff (the present filter cuts off at 400 nm), since the ozone-olefin reaction is known to produce excited formaldehyde as the dominant emitting species at atmospheric pressure, and this species emits a broad band emission peaking at 440 nm^{3,5}.

The limit of detection of the present detector is approximately one order of magnitude higher than that of the fluorine chemiluminescence detector¹¹ for comparable reduced sulfur compounds. However, the former has the advantage of using scrubbed lab air to generate the ozone source, which in turn can easily be destroyed downstream of the detector. In contrast, the fluorine chemiluminescence detector requires frequent replenishment of its supply of the extremely hazardous fluorine reagent. Increases in sensitivity for the ozone chemiluminescence reduced sulfur GC detection system are expected from (1) reaction cell modification^{8,9}, (2) photomultiplier cooling and use of photon counting, and (3) increased ozonizer output. Furthermore, the increase in sensitivity for a number of reduced sulfur gases when air is used in the ozonizer instead of oxygen indicates that addition of trace levels of nitrogen oxides may accelerate the chemiluminescent reaction⁴. Future studies investigating these possibilities are planned.

The present detection system has comparable sensitivity to a flame photometric detector for the reduced sulfur compounds studied. State of the art flame photometric detection of dimethyl sulfide is approximately one order of magnitude more sensitive than the ozone chemiluminescence method, but has the disadvantages that it is sensitive to sulfur dioxide and other oxidized sulfur species, requires hydrogen for the flame, is inherently non-linear in its response, and may exhibit variable sensitivity during long-term operation^{13,14}. Recent work has indicated that chlorine dioxide can also be used as an on-line chemiluminescence detector for hydrogen sulfide and meth-

yl mercaptan¹⁰. This method has shown good sensitivity for hydrogen sulfide (3 ppb, v/v). However, the chlorine dioxide chemiluminescent reaction is very specific, yielding an order of magnitude lower response for methyl mercaptan, and negligible response to other inorganic and organic reduced sulfur compounds. This behavior makes it a much less versatile GC detector for most applications. In addition, this technique also requires the production and use of the chlorine dioxide reagent, which like the fluorine system must be replenished.

ACKNOWLEDGEMENTS

We thank Dr. Gunnar Senum for helpful discussions. The help of Dawnita Robinson, Thomas Orlando, Stacy Ellis, Susan Matzdorf, and Mary Phillips is also greatly appreciated.

This work was supported by the Division of Chemical Sciences, U.S. Department of Energy, Washington, DC, under Contract No. DE-AC02-76CH00016.

REFERENCES

- 1 A. Fontijn, A. J. Sabadell and R. J. Ronco, *Anal. Chem.*, 42 (1970) 575.
- 2 C. W. Nederbragt, A. van der Horst and T. van Duijn, *Nature (London)*, 206 (1965) 87.
- 3 B. J. Finlayson, J. N. Pitts, Jr. and R. Atkinson, *J. Chem. Soc.*, 96 (1974) 5356.
- 4 T. J. Kelly, J. S. Gaffney, M. F. Phillips and R. L. Tanner, *Anal. Chem.*, 55 (1983) 135.
- 5 W. A. Kummur, J. N. Pitts, Jr. and R. P. Steer, *Environ. Sci. Technol.*, 5 (1971) 1045.
- 6 H. Akimoto, B. J. Finlayson and J. N. Pitts, Jr., *Chem. Phys. Lett.*, (1971) 199.
- 7 J. W. Birks and M. C. Kuge, *Anal. Chem.*, 52 (1980) 897.
- 8 W. Bruening and F. J. M. Concha, *J. Chromatogr.*, 112 (1975) 253.
- 9 W. Bruening and F. J. M. Concha, *J. Chromatogr.*, 142 (1977) 191.
- 10 S. R. Spurlin and E. S. Yeung, *Anal. Chem.*, 54 (1982) 320.
- 11 J. K. Nelson, R. H. Getty and J. W. Birks, *Anal. Chem.*, 55 (1983) 1767.
- 12 T. L. C. deSouza, D. C. Lane and S. P. Bhatia, *Anal. Chem.*, 47 (1975) 543.
- 13 M. O. Andreae, *Anal. Chem.*, 52 (1980) 150.
- 14 M. O. Andreae and W. R. Barnard, *Anal. Chem.*, 55 (1983) 608.