

Electron Capture Sulfur Detector: Reduced Sulfur Species Detection at the Femtomole Level

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We have developed a new technique to detect reduced sulfur compounds by fluorination with F_2 (at 200 ppm) on a heated Ag catalyst after GC separation. The excess F_2 is removed by conversion to HF by reaction with H_2 on a heated Pd catalyst. The fluorination product, presumably SF_6 , is then detected in an electron capture detector (ECD). The Pd catalyst also destroys the response from halocarbons making the system sulfur specific. This ECD sulfur detector has a calculated minimum detectable level (MDL) for H_2S , OCS , CH_3SH , DMS , and CS_2 of less than 2 fmol/s for each compound, 2 orders of magnitude lower than the best FPD systems. The ratio of the detected molar response of each of these sulfur compounds to the molar response of SF_6 ranges from 2% to 20% and increases with increasing AgF_2 temperature.

Two very desirable features of gas chromatographic detectors are high sensitivity and high selectivity toward a particular class of compounds. Sulfur compounds are vitally important in environmental, industrial, and medical fields and for these compounds the flame photometric detector (FPD), with its high selectivity for sulfur compounds, has generally been the detector of choice. Unfortunately, however, it suffers from a squared response which limits its ability to measure extremely low sulfur concentrations. Although there have been attempts to extend the minimum detectable range by doping the flame with a constant amount of sulfur (1, 2), the lowest reported MDL has been in the 70–300 fmol/s (femtomoles per second) range (3). Recently, two other sulfur detectors have been developed: the Hall electrolytic conductivity detector (4) and the fluorine-induced chemiluminescence detector (5). While the former can detect all sulfur compounds, the latter can detect only reduced sulfur compounds in which there is a H–C–S bond. Both of these recent detectors have reported minimum detectable peaks of about 300 fmol. For eluting peak widths of 5–10 s, this corresponds to an MDL similar to the best FPD systems.

The common electron capture detector can detect one sulfur compound, SF_6 , at extremely low levels with minimum detectable peaks lower than 0.2 fmol (6). Because of this ease of detection and because SF_6 is extremely inert in the natural environment, SF_6 has been used extensively as a tracer of atmospheric and oceanic mixing and diffusion (6–8). The ambient levels of SF_6 in the "clean" atmosphere, 1.5 pptv (parts per trillion by volume), are routinely measured (9, 10) and measurements of ambient SF_6 in the upper thermocline of the ocean have been reported with reliable quantification at concentrations of 0.2 fmol/L (7). The inertness and extreme electron capture detectability of SF_6 led us to begin work on a sulfur detector in which sulfur compounds are first separated on a gas chromatographic column and then fluorinated with AgF_2 with subsequent electron capture detection. Silver

difluoride has long been used as a solid phase fluorinating agent for the bulk preparation of fluorinated hydrocarbons and is recognized as a more powerful fluorinating agent than the less expensive but more commonly used CoF_3 (11). Although this technique was first proposed over a decade ago (12), we report here the first working system based on the original concept.

In our system, nitrogen carrier gas that elutes from a gas chromatographic column is mixed with a gas stream containing approximately 200 ppm F_2 in N_2 and then passed over heated silver wool. The silver surface, which is maintained as AgF_2 by the presence of the F_2 in the gas stream, fluorinates some of the sulfur in the analyte to an electron capturing species. SF_6 is the obvious candidate species for the fluorination product but we have not identified the fluorination products and so we cannot rule out other compounds such as SF_5 , S_2F_{10} , or $(CF_3)_2SF_4$. Although AgF_2 is the active fluorinating agent, it is continuously regenerated by the added F_2 so that the silver may be considered the catalyst for the fluorination reaction. Following the fluorination column, the excess F_2 in the carrier stream is removed by conversion to HF by reaction with H_2 on a heated palladium catalyst just prior to where the carrier stream enters the ECD.

EXPERIMENTAL SECTION

A schematic of the system is shown in Figure 1. From the sample loop to the O_2 switch-out valve the system resembles a conventional sulfur analysis system. Teflon sample loops (50 μ L to 2 mL) were placed on a six-way GC sampling valve (Valco). Nitrogen carrier gas at 40 mL/min carried the sample through a $1/16$ in. o.d. Teflon transfer line onto a column of 60/80 Carboxpack B/1% XE-60/1.5% H_3PO_4 (Supelco) packed into a 2 m long, $1/8$ in. o.d. FEP Teflon tube that was held at 65 °C in the oven of a Shimadzu Mini-2 gas chromatograph. A $1/16$ in. o.d. Teflon line transferred the carrier gas from the exit of the GC column to a four-port sampling valve (Valco) which was used to switch out interfering peaks such as O_2 . A third $1/16$ in. o.d. Teflon line transferred the carrier stream to a fluorinating column, which is shown in greater detail in Figure 2.

The fluorinating column was made from a 10 cm long, $1/8$ in. o.d. Monel tube which was packed with silver wool (Aldrich). The $1/16$ -in. PFA Teflon transfer line containing the carrier gas was inserted through a tee and extended several centimeters into the Monel tube. A low-level fluorine stream, about 200 ppm F_2 in N_2 , was connected to the third port of the inlet tee and a flow of 20 mL/min was continually maintained to keep the silver surface fully fluorinated to AgF_2 . The Monel tube and a thermocouple were wrapped with insulated nichrome heating wire which was further wrapped with three layers of fiberglass ribbon for thermal insulation. The fluorinating column was maintained at a temperature of 240 ± 5 °C with a temperature controller (LFE Corp.). The fluorinating column was preconditioned with a 1% F_2 in N_2 mixture which was passed through the fluorinating column, while the column was held at 240 °C, to fully convert the silver surface to the difluoride.

The low-level fluorine mixture was generated in a permeation cell, shown in Figure 3. The cell was made from a 3-L nickel-plated brass vessel with a stainless steel lid that was sealed with

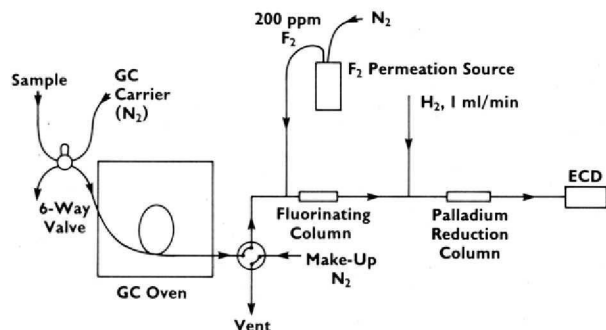


Figure 1. Schematic diagram of the analytical system.

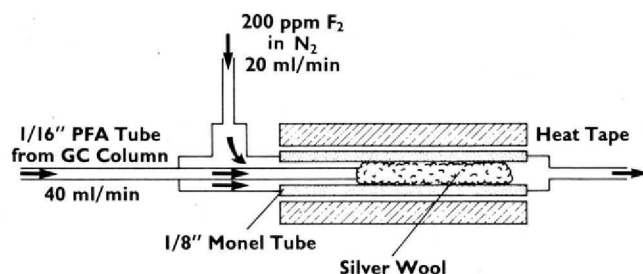


Figure 2. Schematic diagram of the fluorinating column.

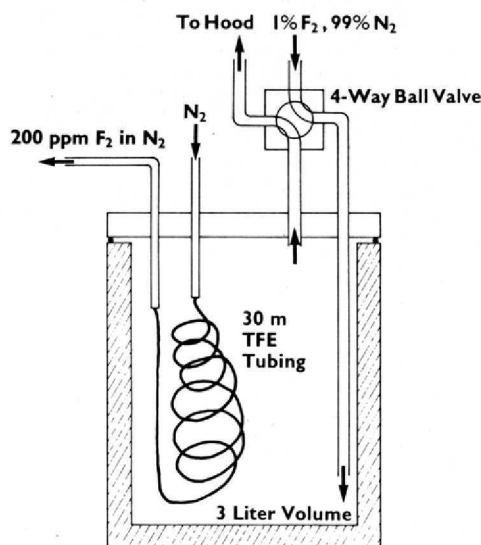


Figure 3. Schematic diagram of the low-concentration (200 ppm) F_2 permeation source.

a TFE O-ring. Thirty meters of TFE tubing, 0.066 in. o.d. 0.042 in. i.d. (Cole Parmer), was coiled inside the permeation cell and the ends were connected by $1/8$ to $1/16$ in. stainless steel unions to $1/8$ in. o.d. stainless steel tubes which extended through the vessel lid. The main volume of the vessel was filled with a 1% F_2 in N_2 mixture at room temperature and pressure and sealed by a four-way valve (Whitey, SS-43YF2). A flow of 20 mL/min of N_2 passed through the TFE tubing and the permeation of F_2 through the walls of the TFE tubing generated the low-level F_2 mixture. The F_2 permeation rate should be much greater than that of SF_6 , which is an impurity found in appreciable concentrations in almost all commercial F_2 mixtures. A single charge of the 1% F_2 mixture maintained the fluorinating ability of the silver catalyst for about 5 days, which was renewed by flushing 5–10 L of the 1% F_2 mixture through the permeation cell. During a typical 5-day period the overall detector response to injections of OCS or DMS gradually declined to 60% of its initial value. The fluorine concentration in the output stream (200 ppm) was estimated by assuming all of the initial F_2 in the vessel (30 mL, STP) permeated out at a constant rate over the 5-day period. In reality, the F_2 concentration must decay exponentially over this 5-day period and the value of 200 ppm is only a mean value over this period.

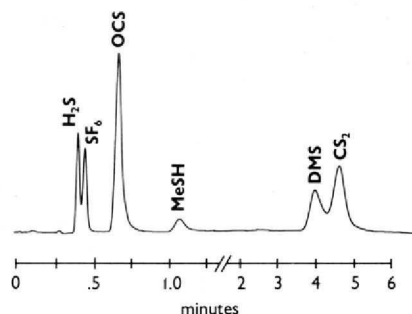


Figure 4. Chromatogram from the injection of 0.05 mL of air containing 140, 3.18, 43, 213, 29, and 160 fmol, respectively, of H_2S , SF_6 , OCS, MeSH (CH_3SH), DMS (CH_3SCH_3), and CS_2 .

Following the fluorinating column, the excess F_2 was removed from the carrier stream. A 3 mL/min flow of hydrogen from a hydrogen generator (GE Model 15EHG) was added to the carrier stream through a tee, and the combined flow then entered a palladium catalyst column where the F_2 was converted into HF. The Pd catalyst was made by placing 7.0 g of GC grade 60/80 mesh alumina (Supelco) in a beaker with 540 mg of $Pd(NO_3)_2$ hydrate (Aldrich) and 30 mL of distilled water. After evaporation the coated alumina particles were packed into a 10 cm long, $1/8$ in. o.d. stainless steel tube with $1/8$ to $1/16$ in. reducing unions on each end, each of which contained a stainless steel frit to hold the coated alumina in the tube. A heating wire, thermocouple, and temperature controller, similar to that used on the fluorinating column, were used to control the temperature of the Pd catalyst. The Pd catalyst was preconditioned for use by passing 10 mL/min of H_2 through it while it was held at 350 °C for 2 h. During use, unless otherwise stated, the Pd catalyst column was held at 230 ± 5 °C.

Scrubbed of residual F_2 , the carrier stream then entered the electron capture detector. This detector used 10 mCi of ^{63}Ni as the β source and was operated at 240 °C in the constant current/variable frequency mode with a current of 1 nA. The output signal from the detector/electrometer was fed into either a Hewlett-Packard 3380A or 3392 integrator/recorder.

The chromatographic base line was disrupted by a spiking noise when a new fluorination column was introduced into the system. The frequency of these spikes gradually decreased over time while the fluorinating column was held at 200–250 °C with the low-level F_2 in N_2 continually applied. After a 2-month period, the base-line spiking ended and the base line was clean. The following results were obtained after the 2-month conditioning period.

Mixtures of sulfur gases in air were made by using permeation tubes (Metronics) either in a commercial standard generator (Dynacal, Model 340) or in a lab-built standard generator consisting of a constant temperature chamber which used clean air from an Adco pure air generator for dilution. With the exception of the SF_6 tube and one DMS tube, the weight loss rates for the tubes were from 200 to 2000 ng of S/min. The maximum dilution flow that either system could accommodate was 10 L/min, so the minimum concentration that could be produced was from 15 to 150 ppbv (parts per billion by volume). The permeation rate of the low loss rate DMS tube was 1.4 ng of S/min and that of the SF_6 tube was 11 ng of S/min, allowing minimum concentrations of these gases of 100 and 800 pptv, respectively. The permeation rate of the low loss rate DMS tube was calculated after calibration with a higher loss rate tube (200 ng of S/min) which was calibrated by weight loss. The permeation rate of the SF_6 tube was determined by calibration with a 82 pptv bottled standard from Washington State University (WSU) which had been derived from a standard from the Scott-Marin Co. (8). The weight loss of this tube was also directly measured over a period of 129 days and although the change in weight was small (12 mg), the loss rate agreed to within 17% of the value calculated from the WSU standard.

RESULTS AND DISCUSSION

Response to Sulfur Compounds. Figure 4 is a chromatogram from the injection of subpicomole quantities of H_2S , SF_6 , OCS, MeSH (CH_3SH), DMS (CH_3SCH_3), and CS_2 in air

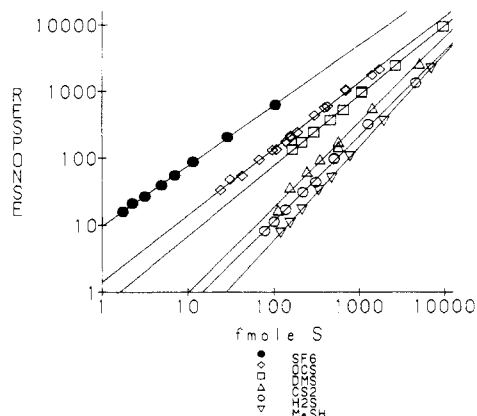


Figure 5. Calibration curves generated by injections of different dilutions of sulfur permeation standards using a 50- μ L sample loop. The response is the peak area from the HP 3392 integrator divided by 10 000.

Table I. Percent of SF_6 Response, and Calculated MDL for Each Compound in the Chromatogram in Figure 4

| compound | % of SF_6 response | MDL, fmol/s |
|----------------------|-----------------------------|-------------|
| SF_6 | | 0.03 |
| H_2S | 2.5 | 1.2 |
| OCS | 17.3 | 0.18 |
| MeSH | 1.8 | 1.7 |
| DMS | 11.7 | 0.26 |
| CS_2 | 6.6 | 0.46 |

from a 50- μ L sample loop. The column (Carbopack B/1% XE-60/1.5% H_3PO_4) was held at 65 $^\circ\text{C}$. The initial chart paper speed was 4 cm/s but was reduced to 1 cm/s after the MeSH peak. log-log calibration curves for each of the above compounds are shown in Figure 5. The slopes of the least-square linear fits for these log-log calibration points are as follows: SF_6 , 0.90; OCS, 0.99; DMS, 1.05; CS_2 , 1.27; H_2S , 1.27; and MeSH, 1.39. Although this detector is not strictly linear (except for OCS), it is considerably more linear than the FPD. It is interesting to note that the compounds with the lowest fluorination efficiencies have the greatest slopes in the log-log calibration curves, which may imply that for these compounds the fluorination efficiency is not independent of the concentration. Nonlinearities aside, however, these calibration curves are reproducible, allowing this technique to be quantitative.

A minimum detectable level for each sulfur compound in Figure 4 was calculated by measuring the noise in the base line and linearly extrapolating the sample size to where the peak would have a signal-to-noise ratio of 2 and dividing this amount by the peak width in seconds, defined as (peak area)/(peak height). The calculated MDL for all sulfur compounds in the chromatograms in Figure 4 was less than 2 fmol/s. A ratio of the peak area per femtomole of each sulfur compound to the peak area per femtomole of SF_6 (the percent of SF_6 response) was calculated. This ratio is the fluorination efficiency if SF_6 is the fluorination product and if compound losses between the sample loop and the fluorination column are zero. The calculated MDL and the percent of SF_6 response for these compounds are listed in Table I.

The response of the ECD sulfur detector (as measured by the percent of SF_6 response) increased with increasing temperature of the AgF_2 fluorination column (Figure 6). We are unsure of the mechanism by which sample response is lost at the cooler temperatures. We speculate, however, that it is due to either incomplete fluorination, fluorination to products other than SF_6 which are subsequently reduced in the H_2/Pd column, or the adsorption of sulfur gases on the Monel surface of the fluorinating column (which should be a nickel fluoride).

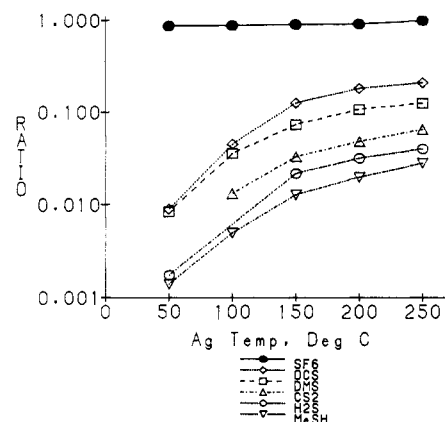


Figure 6. Ratio of the molar response of sulfur compounds to the molar response of SF_6 as a function of the fluorination column temperature.

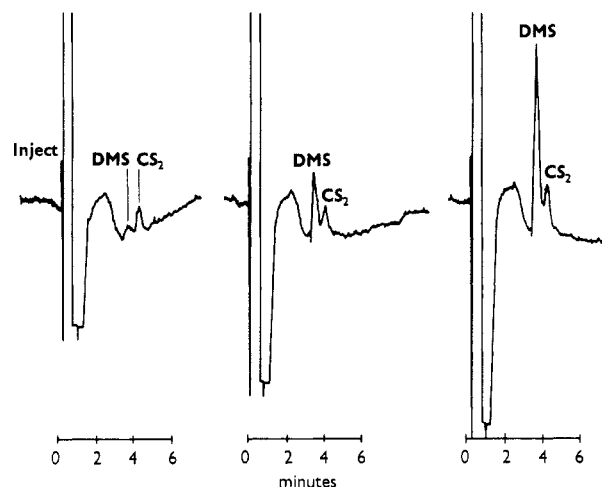


Figure 7. Chromatograms of DMS in air using a 1-mL sample loop: left, blank; middle, 0.7 ppbv DMS (28 fmol); right, 1.7 ppbv DMS (69 fmol). The CS_2 peaks are the blank amounts that arise from previous injections of much larger amounts.

The advantages of an extremely sensitive detector are that one can either analyze very small samples or one can analyze larger samples with a very low concentration of analyte. To demonstrate the sensitivity of this detector, we chose the former with the use of a 50- μ L sample loop because with the exception of DMS and SF_6 we could not generate reliable standards with our permeation tubes in the low to sub-part-per-billion-by-volume range. We could, however, inject larger samples of sub-part-per-billion-by-volume DMS mixtures. We first found that when more than a 200- μ L sample of air was injected, a broad hump appeared in the base line about 3 min into the run, coincident with the DMS peak. We theorized that the hump was due to water formed in the Pd/H_2 column from the O_2 in the larger sample, which then required several minutes to desorb from the stainless steel transfer line between the H_2/Pd column and the ECD. We added an additional four-port valve between the GC column and the fluorination column so that during the first 30 s of each run the column effluent could be vented. The hump disappeared when the O_2 in the sample was thus vented but the base line took about 2 min to recover, just allowing quantification of DMS, but not allowing measurements of any peaks with shorter retention times than DMS. Figure 7 shows the blank, 0.9, and 2.2 ppbv of DMS from an injection of 1 mL of air, with the GC column vented during the first 30 s of each run.

The dynamic range of SF_6 in an electron capture detector can be 5 orders of magnitude or more (13). For our detector

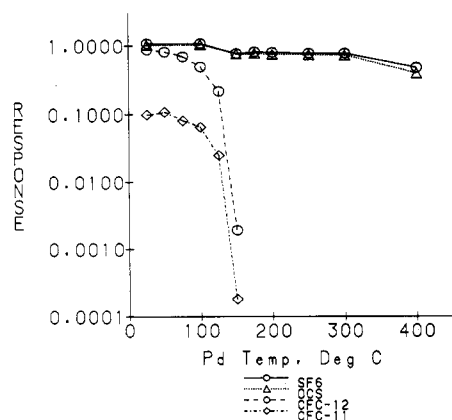


Figure 8. Effect of the Pd/H₂ column temperature on the response of CFCs, SF₆, and OCS. For SF₆ and the CFCs the plotted response was normalized to the response when the fluorination and Pd/H₂ columns were bypassed. For OCS the response was normalized to its response at 25 °C.

the dynamic range for sulfur compounds should be equal to that for SF₆ multiplied by the fluorination efficiency. The dynamic range for any practical sulfur system is, however, limited by the use of Teflon in sample loops, valves, columns, and tubing, which is necessitated by the surface reactive character of the sulfur gases. Sulfur compounds permeate into the Teflon from high concentration mixtures and bleed back out into low concentration mixtures, thus creating measurable blanks at low concentrations, limiting the dynamic range. We found that when a 120 ppbv OCS mixture was flowing through our 50- μ L sample loop for several hours, the OCS peak from a "zero air" blank became equal to 3 fmol. This is several times the MDL extrapolated from the signal to noise (S/N) ratio of the 120 ppbv mixture.

Selectivity. Along with its sensitivity for sulfur compounds this new detector also has a high degree of selectivity for sulfur compounds. This may seem surprising because the ECD is known as an extremely sensitive detector of halocarbons. The Pd/H₂ reduction column, however, along with converting the excess F₂ to HF, also efficiently destroys halocarbons, presumably by reducing them to hydrocarbons. We examined this process and found it to be a strong function of the temperature of the Pd/H₂ column.

Figure 8 displays the results of varying the temperature of the Pd/H₂ column to a series of injections of a mixture of 1.3 pmol of CFC-11 (trichlorofluoromethane), and 2.1 pmol of CFC-12 (dichlorodifluoromethane), and to a mixture of 0.6 and 8.5 pmol, respectively, of SF₆ and OCS. The other parameters such as the fluorination column temperature and the N₂ carrier flow rate were similar to that used for sulfur gases, except that a Deactegel column (deactivated silica gel, Altech) was used to improve the chromatography for the CFCs. The SF₆ and OCS were injected from a 50- μ L Teflon sample loop. The CFCs were injected from a 10- μ L stainless steel loop except for the run at 150 °C which was the same mixture injected from a 1-mL stainless steel sample loop. The plotted responses for SF₆, CFC-11, and CFC-12 were normalized to their measured responses when the fluorination column and the Pd/H₂ column were taken out of the carrier gas path. The OCS response was normalized to the response when the temperature of the Pd/H₂ column was 25 °C.

This simple experiment demonstrates several features of the system. First, with the Pd/H₂ column at 200–250 °C, 70% of the SF₆ which enters the Pd/H₂ column passes on through the detector. Second, at this temperature no measurable amount of CFC-11 and CFC-12 (and by inference, any halocarbon) survives in the Pd/H₂ column. Third, an alternative explanation for the lack of signal from CFC-11 and CFC-12, that being fluorination of these species to the non-electron-

capturing species CF₄, is discounted because this would be happening independently of the Pd column temperature. Finally, this experiment is evidence for SF₆ being the fluorination product of OCS because the loss in response to OCS parallels closely the loss in response of SF₆.

Hydrocarbons are most likely fluorinated in the fluorinating column followed by possible reduction back to hydrocarbons in the Pd/H₂ column. In either case the ECD signal from simple low molecular weight perfluorinated aliphatic compounds or from the hydrocarbons themselves is weak to nonexistent compared to the signal from SF₆. This was tested by injecting a simple mixture of C1–C5 alkanes and alkenes into the system, after first verifying the retention times of the hydrocarbons on an FID. Five hundred picomoles of ethane and propane produced negative peaks that were 6 times smaller than the positive peaks from 200 fmol of OCS, indicating a detector selectivity of OCS over ethane or propane of over 10 000.

The fluorination product of selenium compounds should be SeF₆ which is almost as inert as SF₆ and should give as large a signal in an ECD as SF₆, though we have not yet demonstrated this. Thus, the ECD sulfur detector may also be selective for Se. The major problem may be in getting SeF₆ through the Pd/H₂ column. This problem might be solved by lowering the temperature of the Pd/H₂ column with the only side effect being increased signals from halocarbons.

CONCLUSIONS

The ECD sulfur detector described herein has calculated MDLs for OCS, DMS, and CS₂ which are over 100 times less than that from an FPD. This new technique is only in its infancy. In the future we will be trying new approaches to further improve the MDL for sulfur compounds. As shown in Figure 8, the fluorination efficiency for all sulfur compounds increases with temperature. With the present fluorination column the upper temperature is limited to 250 °C by the presence of the Teflon tubing in the fluorinating column. We are presently working on using a metal tube, either nickel or stainless steel, to introduce the carrier gas to a high-temperature fluorinating column.

The extra volume in the two reaction columns between the chromatographic column and the ECD somewhat degrades the chromatographic resolution. However, this extra volume is less than 0.5 mL, and with a total flow rate of 60 mL/min through this volume, the maximum degradation is less than 0.5 s, provided there is no surface adsorption in the two heated reaction columns.

This study has focused on the detection system and for chromatographic separation has utilized an isothermal packed column due to its simplicity. Many chromatographic applications require capillary columns. Although we have yet to interface our detector with a capillary column, this should present no major problems. The sample entry to the fluorination column in Figure 2 will need to be from a capillary tube of a material which is inert to F₂, such as Teflon or nickel, and the N₂ flow through the F₂ permeation source will need to be increased to close to 60 mL/min to make up for the loss of the 40 mL/min N carrier flow in the packed column. Under these conditions the F₂ concentration in the fluorination column should be equal to its present value and the degradation in chromatographic resolution should continue to be less than 0.5 s.

The primary motivation for this new technique, from its first conception to its present form, has been to measure DMS in surface ocean waters. DMS has been shown to be the dominant volatile sulfur compound in the surface ocean waters, with concentrations ranging from 0.5 to 5 nM, and is believed to be the dominant source of sulfur to the remote marine atmosphere (14, 15). One method used on research

vessels to measure gases dissolved in seawater is to use a seawater equilibrator. The equilibrator, a variant of the headspace technique, sprays seawater through a fixed volume of air from which small samples can be periodically removed and analyzed. With typical ambient seawater concentrations and solubilities (16), the concentration of DMS in the equilibrated air is 1-5 ppbv. Until now all methods of analysis have employed sample preconcentration, either by a cryogenic freeze-out loop or by adsorption on gold wool. The ECD sulfur system in its present form is sufficiently sensitive to measure the equilibrated DMS concentrations by direct injection.

ACKNOWLEDGMENT

We thank Richard Gammon and Tim Bates for their support and John Birks and Brian Lamb for helpful discussions.

Registry No. H₂S, 7783-06-4; OCS, 463-58-1; CH₃SH, 75-18-3; DMS, 75-18-3; CS₂, 75-15-0.

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RECEIVED for review August 24, 1987. Accepted December 9, 1987. This work was funded by NOAA's National Acid Precipitation Assessment Program and by NOAA's Radiatively Important Trace Species (RITS) program. This work was done while J.E.J. held a National Research Council-NOAA Research Associateship. This is Contribution Number 923 from the NOAA/Pacific Marine Environmental Laboratory.

Gas Chromatographic Method for Measuring Nitrogen Dioxide and Peroxyacetyl Nitrate in Air without Compressed Gas Cylinders

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A gas chromatographic technique that measures atmospheric concentrations of peroxyacetyl nitrate (PAN) and NO₂ has been developed that uses luminol-based chemiluminescence for detection. The carrier gas is air that has been scrubbed by passing it over FeSO₄, which eliminates the need for any compressed gas cylinders. A novel gas sampling system and timer enable variable sample volumes of contaminated air to be injected. Ambient PAN and NO₂ measurements can be made every 40 s with detection limits of 0.12 ppb for PAN and 0.2 ppb for NO₂. Seven other atmospheric species, including ozone, gave no interference. Linear response was observed for NO₂ from 0.2 to 170 ppb and for PAN from 1 to 70 ppb.

Nitrogen oxides (NO_x) are an important component in the understanding and modeling of air pollution processes. NO_x (NO + NO₂) is a source of ozone in the troposphere (1) and NO_x reactions produce a variety of inorganic and organic nitrates (2). Nitrates of recent concern are nitric acid, and its role in acidic deposition (3, 4), and peroxyacetyl nitrate

(PAN), and its role in long-range transport (5-7). Definition of the atmospheric chemistry of NO_x requires a detector that can measure individual NO_x components and their secondary products and one that will allow no interference from any other atmospheric constituent (8).

A widely used NO_x monitoring approach employs the chemiluminescence monitor based on the NO + O₃ reaction (9, 10). A difficulty with this chemiluminescent method is that the monitor does not distinguish between NO₂ and interfering species such as HNO₃, HNO₂, and PAN (11-13). The reduction of NO₂ to NO on various catalysts is not specific for NO₂; that is, other nitrogen species can be reduced to NO. Gas chromatographic analysis of NO₂ has also been reported in the literature (14). This technique used cryogenic preconcentration and a thermal conductivity detector to measure ambient concentrations of NO₂. We report on the first gas chromatographic analysis of atmospheric concentrations of NO₂ which used neither compressed carrier gas nor cryogenic preconcentration. Other methods for the direct measurement of NO₂ include the photodissociation of NO₂ to NO and then reaction with O₃ (15), the absorption of infrared radiation for