

DOT/FAA/AM-94/18

Office of Aviation Medicine
Washington, D.C. 20591

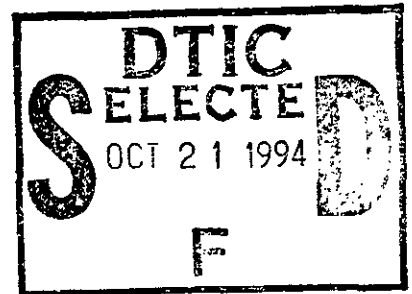
AD-A285 666



Simultaneous Gas-Chromatographic Determination of Four Toxic Gases Generally Present in Combustion Atmospheres

1

Boyd R. Endecott
Donald C. Sanders
Arvind K. Chaturvedi



Civil Aeromedical Institute
Federal Aviation Administration
Oklahoma City, Oklahoma 73125

This document has been approved
for public release and sale, its
distribution is unlimited

September 1994

Final Report

This document is available to the public
through the National Technical Information
Service, Springfield, Virginia 22161.



U.S. Department
of Transportation
**Federal Aviation
Administration**

94-32729

9 4 1 0 01 21

NOTICE

This document is disseminated under the sponsorship of the U.S. Department of Transportation in the interest of information exchange. The United States Government assumes no liability for the contents or use thereof.

1. Report No. DOT/FAA/AM-94/18		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle Simultaneous Gas-Chromatographic Determination of Four Toxic Gases Generally Present in Combustion Atmospheres				5. Report Date September 1994	
				6. Performing Organization Code	
7. Author(s) Boyd R. Endecott, Donald C. Sanders, and Arvind K. Chaturvedi				8. Performing Organization Report No.	
9. Performing Organization Name and Address FAA Civil Aeromedical Institute P. O. Box 25082 Oklahoma City, OK 73125-5066				10. Work Unit No. (TRAIS)	
				11. Contract or Grant No.	
				13. Type of Report and Period Covered	
12. Sponsoring Agency Name and Address Office of Aviation Medicine Federal Aviation Administration 800 Independence Avenue, SW Washington, DC 20591				14. Sponsoring Agency Code	
15. Supplementary Notes This work was performed under task AM-B-93-TOX-65.					
16. Abstract Measurement of combustion gases produced by burning aircraft cabin materials poses a continuing limitation for smoke toxicity research. Since toxic effects of gases depend on both their concentrations and duration of exposures, frequent atmosphere sampling is necessary to define the concentration-time curve. A gas chromatographic method was developed for the simultaneous analyses of carbon monoxide (CO), hydrogen sulfide (H ₂ S), sulfur dioxide (SO ₂), and hydrogen cyanide (HCN). The method utilized an MTI M200 dual-column gas chromatograph (GC) equipped with 4-m molecular sieve-5A and 8-m PoraPlot-U capillary columns and two low-volume, high-sensitivity thermal conductivity detectors. Detectability (ppm)/retention times (seconds) for the gases were: CO (100/28); H ₂ S (50/26); SO ₂ (125/76); HCN (60/108). The method was effective for determining these gases in mixtures and in the combustion atmospheres generated by burning wool (CO, HCN, and H ₂ S) and modacrylic (CO and HCN) fabrics. Common atmospheric gaseous or combustion products (oxygen, carbon dioxide, nitrogen, water vapor, and other volatiles) did not interfere with the analyses. However, filtration of the combustion atmospheres was necessary to prevent restriction of the GC sampling inlet by smoke particulates. The speed, sensitivity, and selectivity of this method make it suitable for smoke toxicity research and for evaluating performance of passenger protective breathing equipment.					
17. Key Words Inhalation toxicology; combustion gases; carbon monoxide; hydrogen sulfide; sulfur dioxide; hydrogen cyanide; wool; modacrylic fabric			18. Distribution Statement Document is available to the public through the National Technical Information Service, Springfield, VA 22161		
19. Security Classif. (of this report) Unclassified		20. Security Classif. (of this page) Unclassified		21. No. of Pages 12	
				22. Price	

SIMULTANEOUS GAS-CHROMATOGRAPHIC DETERMINATION OF FOUR TOXIC GASES GENERALLY PRESENT IN COMBUSTION ATMOSPHERES

INTRODUCTION

Rapid, precise, and simultaneous measurements of combustion gases pose a continuing limitation for evaluating the resultant toxicity of gas mixtures. Toxic effects of individual gases depend on both their concentrations and durations of exposure. Thus, analyzing changing combustion atmospheres at frequent intervals becomes a necessity to accurately define the gas concentration-exposure time (C-t) curve for each gas and to quantitate the total combined effects of gas mixtures on an observed animal response (Alexeeff and Packham, 1989; Tsuchiya and Nakaya, 1989).

Besides carbon monoxide (CO) and hydrogen cyanide (HCN), hydrogen sulfide (H_2S) and sulfur dioxide (SO_2) are toxic gases present in fires (Hilado and Machado, 1977; Spurgeon, et al., 1977; Spurgeon, 1978; Anderson, et al., 1981). Methods for the determination of these gases individually are described in the literature, but H_2S (Blanchette and Cooper, 1976; Rath and Wimmer, 1980), SO_2 (West and Gaeke, 1956; Margeson, et al., 1985), and HCN (Chaturvedi, et al., 1993) quantitation methods are generally cumbersome and/or time consuming and lack sensitivity and/or selectivity. Most quantitation methods are not suitable for simultaneous determinations of these gases in mixtures at frequent time intervals on a continuous basis; they are primarily limited to the quantitation of only one gas at a time.

This study describes development of a sensitive and selective gas-chromatographic method suitable for the analyses of CO, H_2S , SO_2 , and/or HCN, singly, in mixtures, and in combustion atmospheres at 2-minute intervals.

MATERIALS AND METHODS

Materials

Compressed air, CO (99.5%), HCN (2000 ppm in air), and helium (99.999%) were purchased locally in

cylinders; H_2S (99.5%) and SO_2 (99.98%) lecture bottles were obtained from MG Industries, Valley Forge, PA.

Instrumentation

The analytical instrument used was an MTI M200 gas chromatograph (GC; Microsensor Technology, Inc., Fremont, CA) configured specifically for the analysis of gases (Siemers, et al., 1991). The instrument was equipped with 2 independent modules, each containing its own sample injection system, analytical and reference columns, heater, temperature sensor, and low-volume, high-sensitivity thermal conductivity detector. Module #1 (Channel A) contained a 4-m molecular sieve-5A capillary column (0.32 mm i.d.) for CO determination. Module #2 (Channel 2) contained an 8-m PoraPlot-U capillary column (0.32 mm i.d.) for the separation and determination of H_2S , SO_2 , and HCN. Helium was the selected carrier gas for both columns. The GC was interfaced with a 386/40 computer. The EZChrom 200 Chromatography Data System software (version 3.3; Microsensor Technology, Inc., Fremont, CA) was used to collect and analyze the data.

Analytical Procedures and Parameters

Standard samples of each of the 4 pure gases were prepared by making syringe dilutions of CO, H_2S , SO_2 , or HCN and injecting the requisite volumes of the gases and air into evacuated Saran gas bags through a rubber septum; purity of these gases is given in the "Materials" subsection. The bags were kneaded for about 1 min to ensure the mixing of the gaseous components. Using the GC's internal vacuum pump, gas samples were drawn from the sample bag through a metal capillary sampling tube to the GC sample injection loops. The gas sampling time from the Saran bags was 20 seconds, and the GC injection time was 250 milliseconds; the actual volume of the injected gas sample was not determined. Like single gases,

Dist	Avail and/or Special
A-1	

Table 1
Comparison of Analytical Results of Pure Gases Analyzed Individually and Simultaneously with the Known Concentrations

Gas	Single Gas (ppm)		Gases in Mixture (ppm)	
	Known Concentration	Analyzed Value*	Known Concentration	Analyzed Value*
CO	400	412 ± 7.0	500	514 ± 9.5
H ₂ S	218	209 ± 2.6	250	235 ± 0.5
SO ₂	218	242 ± 1.7	250	281 ± 26
HCN	240	243 ± 6.6	180	192 ± 7.1

*Represents the mean (± Standard Deviation) of 3 individual gas sample preparations, each analyzed in triplicate.

Table 2
Analyses of Combustion Atmospheres from the Pyrolysis of 2 Fabrics

Gas	Concentration (ppm)*			
	0.5-g Fabric Sample		1.0-g Fabric Sample	
	3-min	10-min	3-min	10-min
WOOL FABRIC				
CO	1072 ± 36	2790 ± 68	1603 ± 239	5009 ± 147
H ₂ S	67 ± 11	0	139 ± 24	0
HCN	237 ± 30	150 ± 34	445 ± 200	259 ± 97
MODACRYLIC FABRIC				
CO	2593 ± 199	3228 ± 582	3446 ± 159	5486 ± 1132
HCN	1047 ± 107	796 ± 219	1721 ± 282	1209 ± 401

*Mean (± Standard Deviation) of 5 pyrolyses of each weight of each fabric at 3- and 10-min intervals.

mixtures of all 4 pure gases were prepared in Saran bags. The final concentrations of gases, singly and in mixtures, are given in Table 1.

Optimal chromatographic conditions were established for the simultaneous analyses of the 4 gases. For each gas, retention times were established and standard curves were prepared. Analytical parameters for CO were 95°C column temperature, 20 psi column head pressure, and a medium instrument gain setting. Parameters for H₂S, SO₂, and HCN were 80°C column temperature, 30 psi column head pressure, and a high instrument gain. All 4 gases chromatographed within 120 seconds. Standard single gases and gas mixtures were analyzed, and their experimental values were compared with the known values (Table 1).

Analyses of Gases in Combustion Atmospheres

To evaluate the method's effectiveness for analyzing actual combustion atmospheres, 2 fabrics were pyrolyzed in a 12.6-L combustion/animal exposure assembly (Crane, et al., 1985), and the resultant atmospheres were analyzed for the 4 gases. Briefly, the assembly consisted of a 50-mm quartz combustion tube encircled by two 425-watt semicylindrical heating units to provide radiant and conductive heat for decomposition of the material sample. The combustion tube is part of a closed system wherein a recirculating blower forces air from an animal exposure chamber through the combustion tube and back into the chamber.

Wool fabric was chosen to produce CO, HCN, and one or more of the sulfur gases (Spurgeon, et al., 1977), and modacrylic fabric was selected as a known producer of CO and HCN. The weighed fabric sample was placed in the center of the pre-heated combustion tube, the system was sealed, and the recirculating blower was activated. Temperature at the sample position was 600°C for all tests; sampling time of the combustion atmosphere was at 3 and 10 minutes after the fabric sample insertion. Combustion atmosphere samples were drawn from a port in the exposure chamber through a 25-mm diameter, 0.45 μ m Millipore filter into a 100-mL glass syringe; the combustion atmosphere sample was immediately injected into an evacuated Saran gas bag, sampled as described

for the prepared pure gas samples, and analyzed. Five replicate pyrolyses of each fabric were performed at each of the 0.5- and 1.0-g fabric sample weights. Results of the combustion atmosphere gas analyses are summarized in Table 2.

RESULTS AND DISCUSSION

The developed analytical method was effective for the individual and simultaneous analyses of 4 common toxic combustion gases. Under the described chromatographic conditions, the 4 gases can be easily separated and quantitated (Fig. 1). Retention times were 28 seconds for CO on the molecular sieve-5A column (Channel A) and were respectively 26, 76, and 108 seconds for H₂S, SO₂, and HCN on the Poraplot-U column (Channel B). Therefore, the presence of H₂S, SO₂, and/or HCN in a sample did not compromise the CO analysis and *vice versa*. Oxygen, carbon dioxide, nitrogen, and water vapor did not interfere with the analyses. However, water chromatographed close to SO₂, limiting accurate peak area integration.

Standard curves of these gases plotted from 10 analyses of each gas at each of the concentrations are exhibited in Fig. 2. Although the absolute minimum detectable concentration for each gas was not determined, the lowest concentration (100 ppm CO, 50 ppm H₂S, 125 ppm SO₂, 60 ppm HCN) on each curve appeared to be a practical lower limit for the described analytical conditions. Some changes in gas concentrations in air were observed as a function of time. The change in the detector response was negligible with CO and H₂S analyses through 10 successive samplings during about a 50-min period, but the detector response gradually decreased with the HCN analyses; the decrease was approximately 6% between the first and last 5 analyses from the same bag sample. The widest spread of values was observed with the SO₂ analyses, with a relative standard deviation of 7.4% for the 10 samplings of the 500 ppm sample; this deviation could be associated with the incomplete separation from the trailing edge of the water peak (Fig. 1). Using the regression equations obtained from the standard curves, analyses of triplicate preparations of the individual gases and their mixtures, at

identical concentrations, revealed an excellent agreement with the known concentrations (Table 1). The mean analytical values were accurate within $\pm 3\%$ of the respective known concentrations, and the coefficients of variation of mean analytical values were $< 10\%$.

Under the chromatographic conditions developed for the pure gases in air, analyses of combustion atmospheres generated from wool and modacrylic fabrics pyrolyses revealed that (i) wool produced CO and HCN as expected, and moderate levels of H_2S and (ii) modacrylic generated relatively high levels of CO and HCN. No SO_2 was detected in the combustion atmospheres from either material. Other volatiles present in the combustion atmospheres did not appear to interfere with the analyses. Representative chromatograms are exhibited in Figs. 3 and 4. Peaks were well separated and defined, and the gases were present in amounts that could be easily determined. However, the analysis of combustion atmospheres initially caused some difficulty because particulate matter in the smoke progressively restricted the GC sampling tube; cleaning the sampling tube and adding a filter assembly to the sampling syringe alleviated this difficulty. Gas concentrations of the combustion atmospheres were calculated utilizing the pure gas standard curves; their mean values are given in Table 2. In comparison to individual and simultaneous analytical values of 4 pure gases (Table 1), variations were higher with combustion atmosphere analyses (Table 2). Out of 18 mean gas concentration values, 6 values had coefficient of variations more than 20%; 5 of the 6 values were of HCN. These variations could be attributed to (i) the generation of gases in the combustion atmosphere at levels exceeding the upper limit of the standard curves (which may not be linear at those levels) and/or (ii) the solubility of HCN in water produced during pyrolysis. So, fluctuation in water-vapor content can affect the HCN levels. In general, however, the variation in gas concentrations produced from 5 replicate pyrolyses is believed to be primarily due to variations in combustion rates in this system. Although the 1.0-g fabric samples always produced higher gas concentrations than the 0.5-g fabric samples in the same time frame, the gas production was not directly proportional to weight of fabric

burned. A possible explanation is that the heavier sample decomposed at a slower rate, so that the gas concentrations for the 1.0-g samples did not show a 2-fold increase (at the fixed sampling intervals) over the 0.5-g samples. The selected 3- and 10-minute sampling intervals do not define the gas generation curve adequately, but they depict the progression of the pyrolysis within the realm of the study. For analyzing combustion atmospheres as a function of time, the gas standard curves should encompass the gas concentration range anticipated from the burn process. Of course, the gas concentration range will be dependent on the amount and the chemical nature of the polymeric material used in the experiments.

Efficiency of the combustion atmosphere sampling could be increased by utilizing the GC's internal pump to sample directly from the exposure chamber, using intermediate particulate filtration. This would allow more frequent sampling of the changing gas concentrations and thus, would provide better definition of the C-t curve (Alexeeff and Packham, 1989; Tsuchiya and Nakaya, 1989). For the limited scope of this study, we chose to use the syringe/bag sampling technique instead of relocating the analytical instrumentation. This method may have applicability for evaluating the passenger protective breathing equipment for compliance with international performance standards (EUROCAE, 1991). This method is also suitable for inhalation/combustion toxicology research.

SUMMARY AND CONCLUSIONS

A dual-column gas chromatograph was utilized to simultaneously measure CO, HCN, SO_2 , and H_2S ; the method was also effective for detecting and quantitating CO, HCN, and H_2S in the "smoke" from burning polymers. Common atmospheric gases and combustion volatiles did not interfere with the analysis, but tailing of the water vapor peak caused some variation in the integrated values for the SO_2 peak.

The speed, sensitivity, and selectivity of this method make it suitable for analyzing combustion gas mixtures for the 4 gases studied. The method may be useful for testing passenger protective breathing equipment and for inhalation/combustion toxicology research.

identical concentrations, revealed an excellent agreement with the known concentrations (Table 1). The mean analytical values were accurate within $\pm 13\%$ of the respective known concentrations, and the coefficients of variation of mean analytical values were $< 10\%$.

Under the chromatographic conditions developed for the pure gases in air, analyses of combustion atmospheres generated from wool and modacrylic fabrics pyrolyses revealed that (i) wool produced CO and HCN as expected, and moderate levels of H_2S and (ii) modacrylic generated relatively high levels of CO and HCN. No SO_2 was detected in the combustion atmospheres from either material. Other volatiles present in the combustion atmospheres did not appear to interfere with the analyses. Representative chromatograms are exhibited in Figs. 3 and 4. Peaks were well separated and defined, and the gases were present in amounts that could be easily determined. However, the analysis of combustion atmospheres initially caused some difficulty because particulate matter in the smoke progressively restricted the GC sampling tube; cleaning the sampling tube and adding a filter assembly to the sampling syringe alleviated this difficulty. Gas concentrations of the combustion atmospheres were calculated utilizing the pure gas standard curves; their mean values are given in Table 2. In comparison to individual and simultaneous analytical values of 4 pure gases (Table 1), variations were higher with combustion atmosphere analyses (Table 2). Out of 18 mean gas concentration values, 6 values had coefficient of variations more than 20%; 5 of the 6 values were of HCN. These variations could be attributed to (i) the generation of gases in the combustion atmosphere at levels exceeding the upper limit of the standard curves (which may not be linear at those levels) and/or (ii) the solubility of HCN in water produced during pyrolysis. So, fluctuation in water-vapor content can affect the HCN levels. In general, however, the variation in gas concentrations produced from 5 replicate pyrolyses is believed to be primarily due to variations in combustion rates in this system. Although the 1.0-g fabric samples always produced higher gas concentrations than the 0.5-g fabric samples in the same time frame, the gas production was not directly proportional to weight of fabric

burned. A possible explanation is that the heavier sample decomposed at a slower rate, so that the gas concentrations for the 1.0-g samples did not show a 2-fold increase (at the fixed sampling intervals) over the 0.5-g samples. The selected 3- and 10-minute sampling intervals do not define the gas generation curve adequately, but they depict the progression of the pyrolysis within the realm of the study. For analyzing combustion atmospheres as a function of time, the gas standard curves should encompass the gas concentration range anticipated from the burn process. Of course, the gas concentration range will be dependent on the amount and the chemical nature of the polymeric material used in the experiments.

Efficiency of the combustion atmosphere sampling could be increased by utilizing the GC's internal pump to sample directly from the exposure chamber, using intermediate particulate filtration. This would allow more frequent sampling of the changing gas concentrations and thus, would provide better definition of the C-t curve (Alexeeff and Packham, 1989; Tsuchiya and Nakaya, 1989). For the limited scope of this study, we chose to use the syringe/bag sampling technique instead of relocating the analytical instrumentation. This method may have applicability for evaluating the passenger protective breathing equipment for compliance with international performance standards (EUROCAE, 1991). This method is also suitable for inhalation/combustion toxicology research.

SUMMARY AND CONCLUSIONS

A dual-column gas chromatograph was utilized to simultaneously measure CO, HCN, SO_2 , and H_2S ; the method was also effective for detecting and quantitating CO, HCN, and H_2S in the "smoke" from burning polymers. Common atmospheric gases and combustion volatiles did not interfere with the analysis, but tailing of the water vapor peak caused some variation in the integrated values for the SO_2 peak.

The speed, sensitivity, and selectivity of this method make it suitable for analyzing combustion gas mixtures for the 4 gases studied. The method may be useful for testing passenger protective breathing equipment and for inhalation/combustion toxicology research.

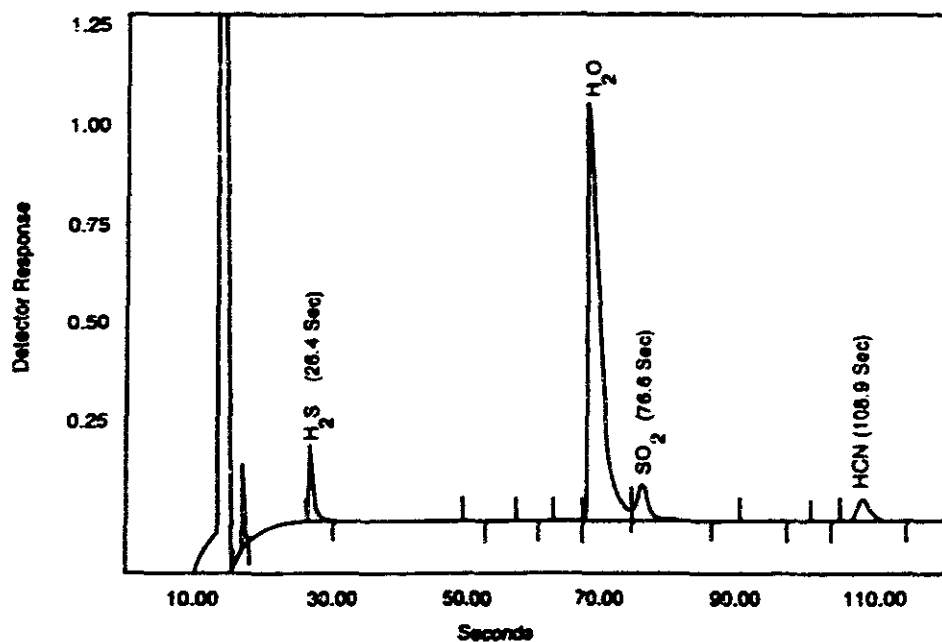
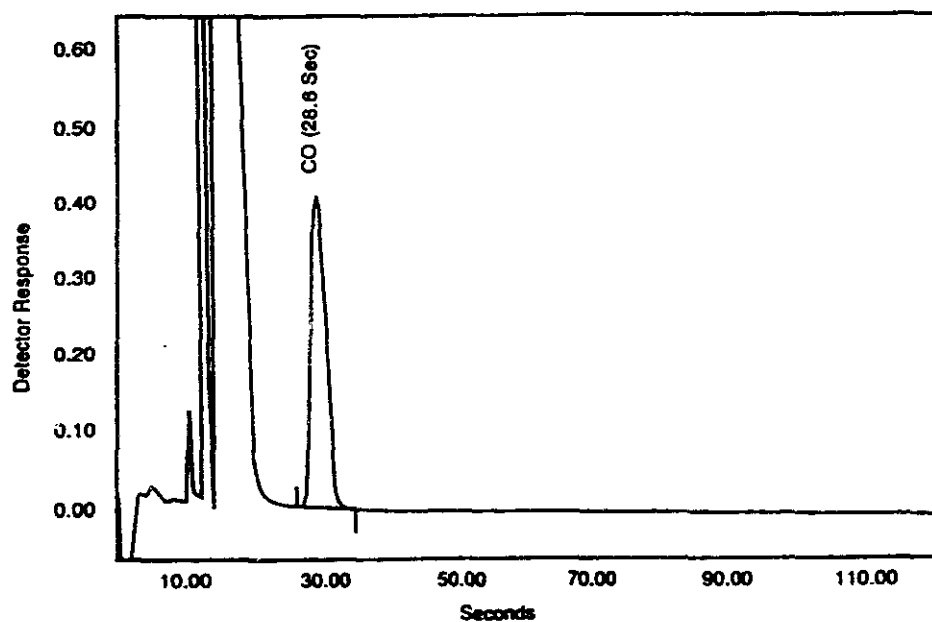


Figure 1. Chromatograms of CO, H₂S, SO₂, and HCN in a Mixture Sample of Pure Gases. Retention times of respective gases are given in seconds. Panel A (Top panel): Module #1 for CO using a 4-m molecular sieve-5A capillary column. Panel B (Bottom panel): Module #2 for H₂S, SO₂, and HCN utilizing an 8-m PoraPlot-U capillary column.

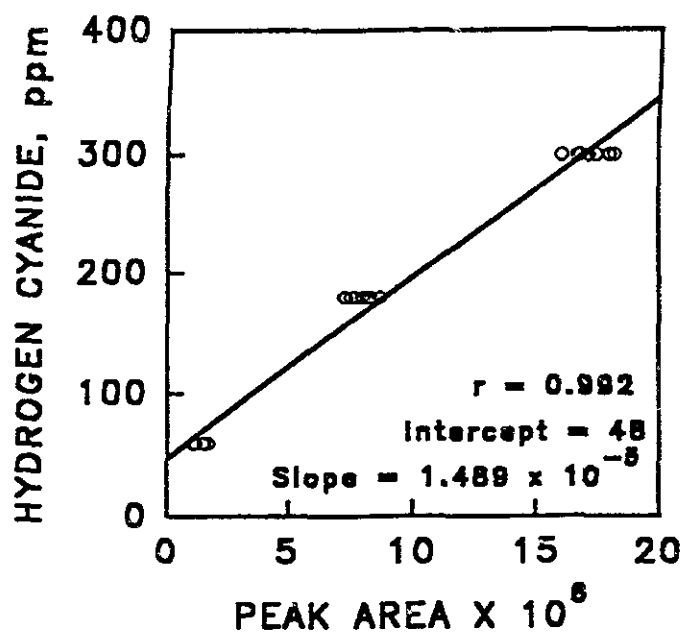
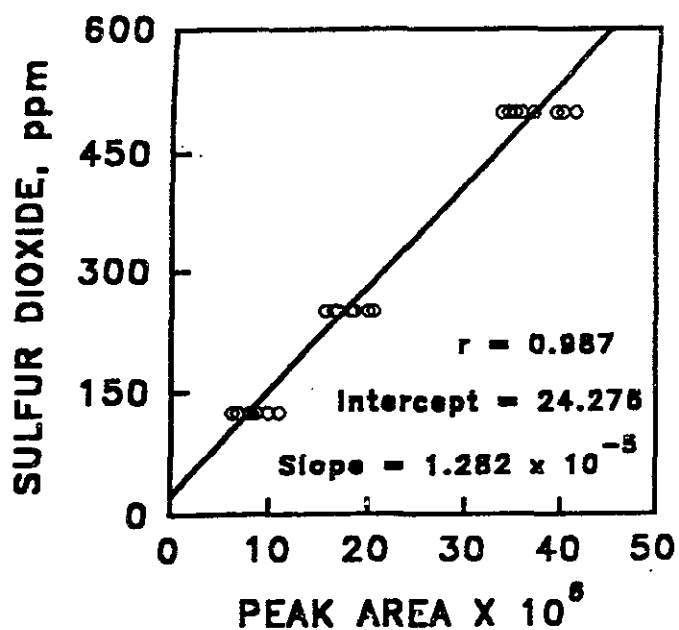
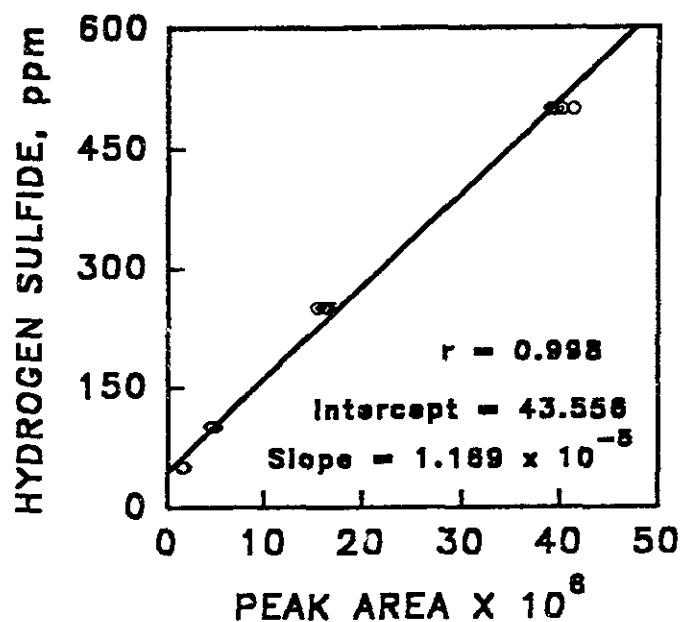
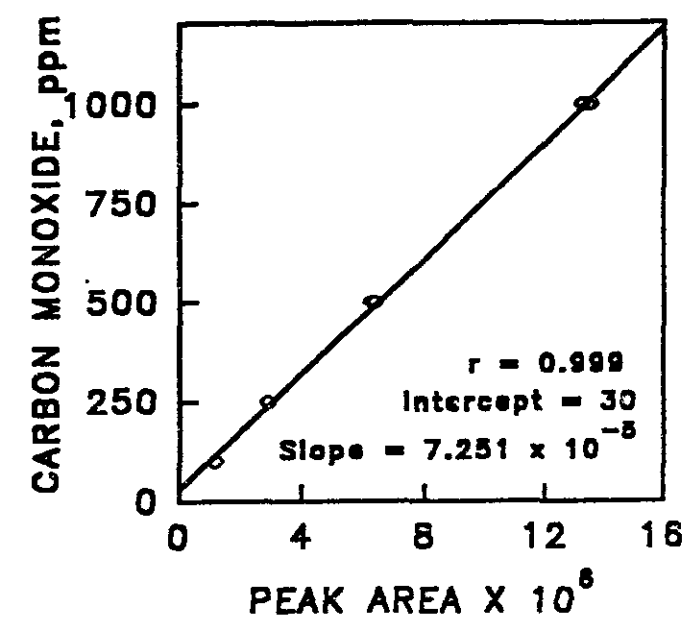


Figure 2. Standard Curves for CO , H_2S , SO_2 , and HCN . Each curve was constructed from 10 replicate samplings at each concentration. The lowest concentration on each curve represents the practical lower detection limit under the described experimental conditions.

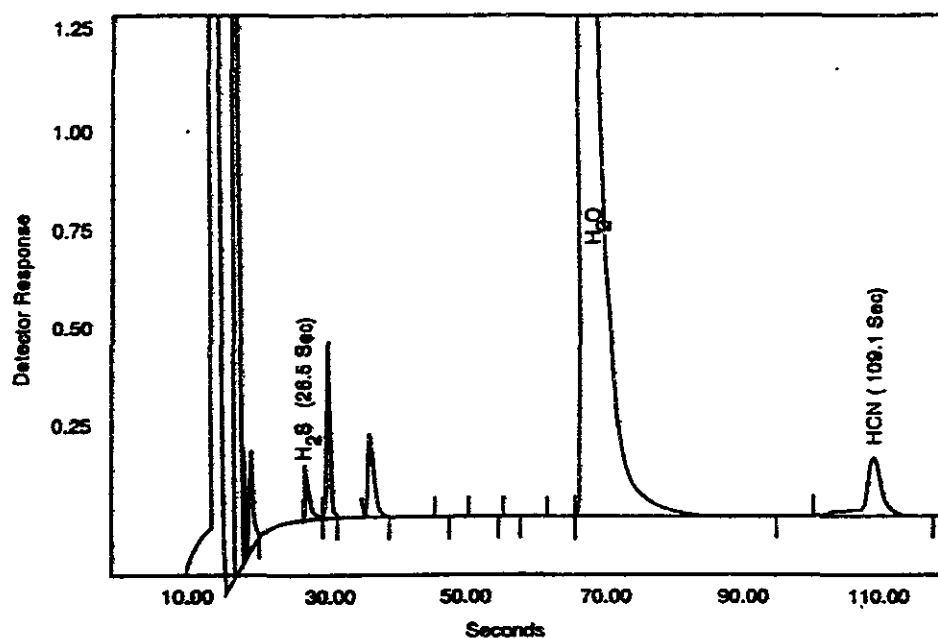
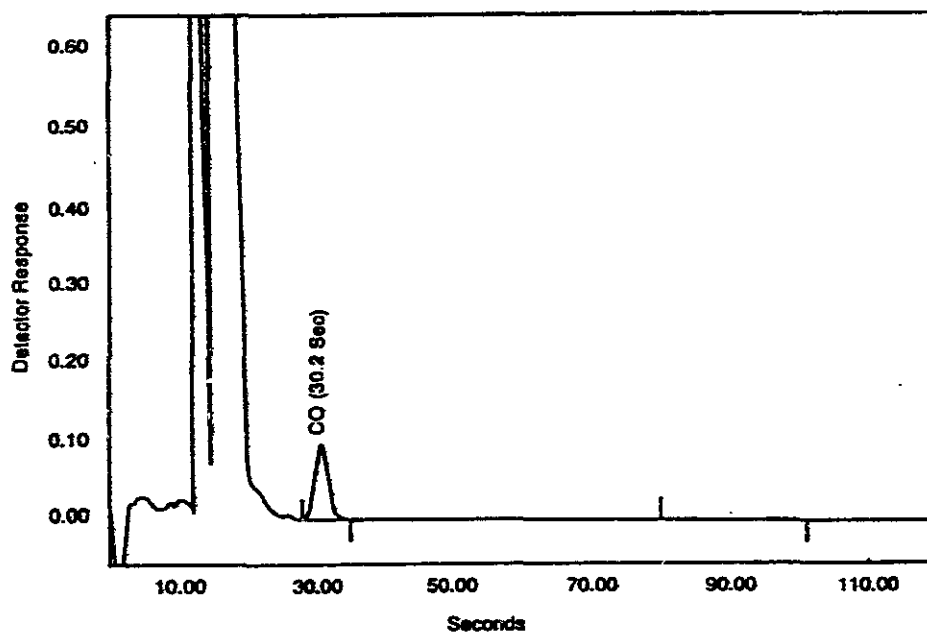


Figure 3. Identification of CO, H₂S, and HCN in the Combustion Atmosphere Generated by the Pyrolysis of Wool Fabric. These chromatograms depict the simultaneous analyses of the combustion gases from 1.0 g of wool fabric pyrolyzed at 600°C in a 12.6-L combustion/exposure assembly and are for a representative atmosphere sample taken at 10 min following insertion of the wool sample into the combustion tube. Panel A (Top panel): Module #1 using a 4-m molecular sieve-5A capillary column. Panel B (Bottom panel): Module #2 utilizing an 8-m PoraPlot-U capillary column.

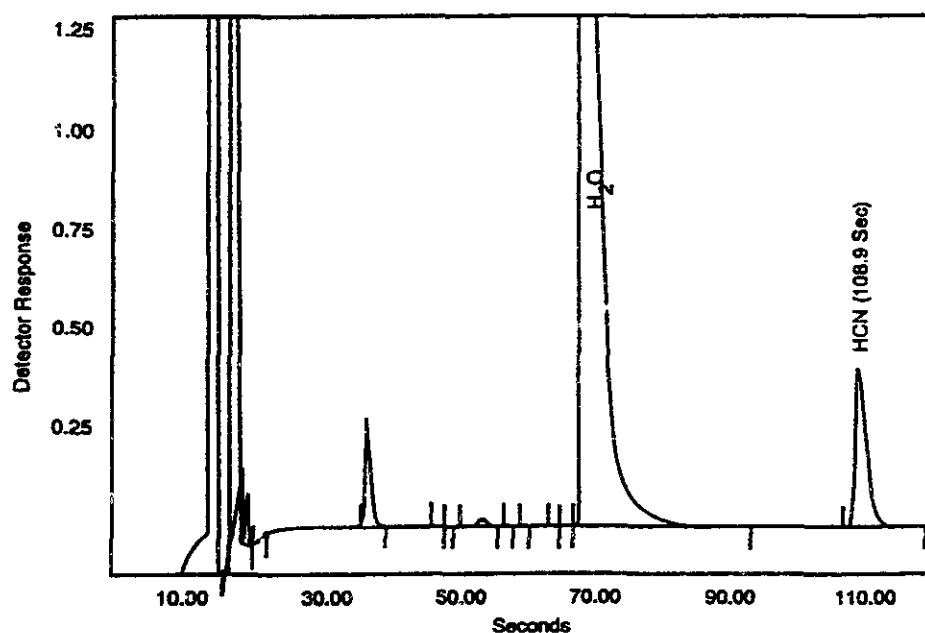
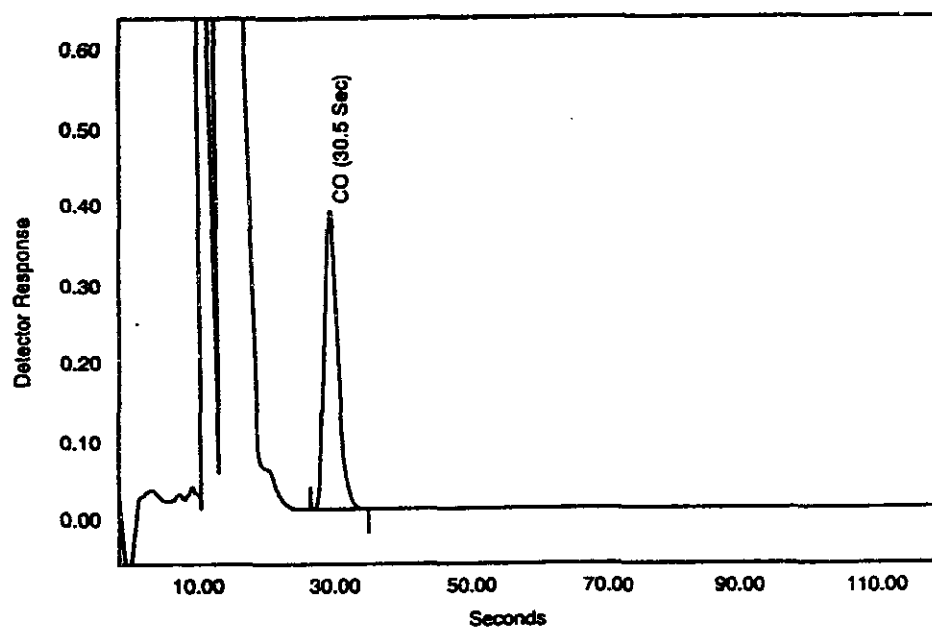


Figure 4. Characterization of CO and HCN in Combustion Atmosphere from Modacrylic Fabric. These chromatograms exhibit separation of CO [Panel A (Top panel): Module #1, 4-m molecular sieve-5A column] and of HCN [Panel B (Bottom panel): Module #2, an 8-m PoraPlot-U column] from a sample collected at 3 min from an atmosphere generated by pyrolyzing 1.0 g of modacrylic fabric. The fabric was pyrolyzed at 600°C in a 12.6-L combustion/exposure assembly.

REFERENCES

- Alexeeff GV, Packham SC (1989). Evaluation of smoke toxicity using concentration-time products. In: *Advances in Combustion Toxicology*, Vol. 1, GE Hartzell, ed., pp 202-19. Technomic Publishing Co., Inc., Lancaster, PA.
- Anderson RA, Watson AA, Harland WA (1981). Fire deaths in the Glasgow area: II The role of carbon monoxide. *Med. Sci. Law*, 21, 288-94.
- Blanchette AR, Cooper AD (1976). Determination of hydrogen sulfide and methyl mercaptan in air at the parts-per-billion level by gas chromatography. *Anal. Chem.*, 48, 729-31.
- Chaturvedi AK, Endecott BR, Ritter RM, Sanders DC (1993). Variations in time-to-incapacitation and blood cyanide values for rats exposed to two hydrogen cyanide gas concentrations. Department of Transportation/Federal Aviation Administration, Washington, DC. Publication No. DOT/FAA/AM-93/8. Available from National Technical Information Service, Springfield, VA 22161.
- Crane CR, Sanders DC, Endecott BR, Abbott JK (1983). Combustibility of electrical wire and cable for rail rapid transit systems, Vol. II: Toxicity. Department of Transportation/Urban Mass Transportation Administration, Washington, DC. Report No. UMTA-MA-06-0025-83-7. Available from National Technical Information Service, Springfield, VA 22161.
- EUROCAE (1991). Minimum operational performance specification for passenger protective breathing equipment. EUROCAE Document No. ED-65. The European Organisation for Civil Aviation Equipment, Paris, France.
- Hilado CJ, Machado AM (1977). Effect of sulfur dioxide on Swiss albino mice. *J. Combustion Toxicol.*, 4, 236-45.
- Margeson JH, Knoll JE, Midgett MR, Oldaker GB III, Reynolds WE (1985). Determination of sulfur dioxide, nitrogen oxides, and carbon dioxide in emissions from electric utility plants by alkaline permanganate sampling and ion chromatography. *Anal. Chem.*, 57, 1586-90.
- Rath HJ, Wimmer J (1980). Gas chromatographic analysis of traces of hydrogen sulfide in hydrogen. *Chromatographia*, 13, 513-4.
- Siemers R, Heigel D, Spilkin A (1991). Rapid micro-GC analysis of permanent gases. *American Laboratory*, March 1991.
- Spurgeon JC, Speitel LC, Feher RE (1977). Thermal decomposition products of aircraft interior materials. Department of Transportation/Federal Aviation Administration, Washington, DC. Publication No. FAA-RD-77-20. Available from National Technical Information Service, Springfield, VA 22161.
- Spurgeon JC (1978). The correlation of animal response data with the yields of selected thermal decomposition products for typical aircraft interior materials. Department of Transportation/Federal Aviation Administration, Washington, DC. Publication No. FAA-RD-78-131. Available from National Technical Information Service, Springfield, VA 22161.
- Tsuchiya Y, Nakaya I (1989). Numerical analysis of fire gas toxicity: Mathematical predictions and experimental results. In: *Advances in Combustion Toxicology*, Vol. 2, GE Hartzell, ed., pp 61-9. Technomic Publishing Co., Inc., Lancaster, PA.
- West PW, Gaeke GC (1956). Fixation of sulfur dioxide as disulfitomercurate (II) and subsequent colorimetric estimation. *Anal. Chem.*, 28, 1816-19.