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

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

Toxicology and Accident Research Laboratory (AAM-610), Aeromedical Research Division, Civil Aeromedical Institute, Federal Aviation Administration, U.S. Department of Transportation, P.O. Box 25082, Oklahoma City, OK 73125-5066

Abstract

The measurement of combustion gases produced by burning aircraft cabin materials poses a continuing limitation for smoke toxicity research. Because toxic effects of gases depend on both their concentrations and the duration of exposure, frequent atmosphere sampling is necessary to define the gas concentration–exposure time curve. A gas chromatographic (GC) method was developed for the simultaneous analyses of carbon monoxide (CO), hydrogen sulfide (H₂S), sulfur dioxide (SO₂), and hydrogen cyanide (HCN). The method used an MTI M200 dual-column gas chromatograph equipped with 4-m molecular sieve-5A and 8-m PoraPlot-U wall-coated capillary columns and two low-volume, high-sensitivity thermal conductivity detectors. Detectability (in parts per million [ppm]) and retention times (in seconds) for the gases were as follows: CO, 100 ppm, 28 s; H₂S, 50 ppm, 26 s; SO₂, 125 ppm, 76 s; and HCN, 60 ppm, 108 s. The method was effective for determining these gases in mixtures and in the combustion atmospheres generated by burning wool (CO, HCN, and H₂S) and modacrylic fabrics (CO and HCN). 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. Also, this method can potentially be modified to analyze these gases when they are liberated from biosamples.

Introduction

Rapid, precise, and simultaneous measurement of combustion gases poses a continuing limitation for evaluating the resultant toxicity of gas mixtures. Toxic effects of individual gases depend on both their concentrations and duration of exposure. Thus, analyzing changing combustion atmospheres at frequent intervals becomes a necessity to accurately define the gas concentration–exposure time curve for each gas and to quantitate the total combined effects of gas mixtures on an observed animal response (1,2).

In addition to carbon monoxide (CO) and hydrogen cyanide (HCN), hydrogen sulfide (H₂S) and sulfur dioxide (SO₂) are toxic gases present in fires (3–6). Methods for the individual determination of these gases are described in the literature, but H₂S (7,8), SO₂ (9,10), and HCN (11) quantitation methods are generally cumbersome and time consuming and lack sensitivity and selectivity. Most quantitation methods are not suitable for the simultaneous determination of these gases in mixtures at frequent time intervals on a continuous basis; they are primarily limited to the quantitation of one gas at a time.

This study describes the development of a sensitive and selective gas chromatographic (GC) method suitable for the analyses of CO, H₂S, SO₂, and HCN singly, in mixtures, and in combustion atmospheres at 2-min intervals.

Materials and Methods

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

<table>
<thead>
<tr>
<th></th>
<th>Single gas (ppm)*</th>
<th>Gases in mixtures (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>known concentration</td>
<td>analyzed value*</td>
</tr>
<tr>
<td>CO</td>
<td>400</td>
<td>412 ± 7.0</td>
</tr>
<tr>
<td>H₂S</td>
<td>218</td>
<td>209 ± 2.6</td>
</tr>
<tr>
<td>SO₂</td>
<td>218</td>
<td>242 ± 1.7</td>
</tr>
<tr>
<td>HCN</td>
<td>240</td>
<td>243 ± 6.6</td>
</tr>
</tbody>
</table>

* ppm = Parts per million.  
† Mean plus or minus one standard deviation of three individual gas sample preparations, each analyzed in triplicate.

* Presented at the 63rd Annual Scientific Meeting of the Aerospace Medical Association, San Antonio, TX, May 8–12, 1994; this article was also produced as the U.S. Department of Transportation, Federal Aviation Administration, Office of Aviation Medicine technical report DOT/FAA/AM-94/18.
† Author to whom correspondence should be addressed.
Table II. Analyses of Combustion Atmospheres from the Pyrolysis of Two Fabrics

<table>
<thead>
<tr>
<th>Gas</th>
<th>Concentration (ppm)*</th>
<th>0.5-g fabric sample</th>
<th>1.0-g fabric sample</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>3 min</td>
<td>10 min</td>
</tr>
<tr>
<td>Wool fabric</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>1072 ± 36</td>
<td>2790 ± 68</td>
<td>1603 ± 239</td>
</tr>
<tr>
<td>H₂S</td>
<td>67 ± 11</td>
<td>0</td>
<td>139 ± 24</td>
</tr>
<tr>
<td>HCN</td>
<td>237 ± 30</td>
<td>150 ± 34</td>
<td>445 ± 200</td>
</tr>
<tr>
<td>Modacrylic fabric</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>2593 ± 199</td>
<td>3228 ± 582</td>
<td>3446 ± 159</td>
</tr>
<tr>
<td>HCN</td>
<td>1047 ± 107</td>
<td>796 ± 219</td>
<td>1721 ± 282</td>
</tr>
</tbody>
</table>

* Mean plus or minus one standard deviation of five pyrolyses of each weight of each fabric at 3- and 10-min intervals.

Instrumentation

The analytical instrument used was an MTI M200 gas chromatograph (Microsensor Technology, Inc., Fremont, CA) configured specifically for the analysis of gases (12). The instrument was equipped with two independent modules, each of which contained its own sample injection system, analytical and reference columns, a heater, a temperature sensor, and a low-volume, high-sensitivity thermal conductivity detector. Module 1 (channel A) contained a 4-m molecular sieve-5A wall-coated capillary column (0.32-mm i.d.) for CO determination. Module 2 (channel B) contained an 8-m PoraPlot-U wall-coated capillary column (0.32-mm i.d.) for the separation and determination of H₂S, SO₂, and HCN. Helium was the selected carrier gas for both columns. The GC was interfaced with a 386/40 personal computer. The EZChrom 200 chromatography data system software (version 3.3; Microsensor Technology) was used to collect and analyze the data.

Analytical procedures and parameters

Standard samples of each of the four pure gases were prepared by making syringe dilutions of CO, H₂S, SO₂, and HCN and injecting the requisite volumes of the gases and air into evacuated Saran gas bags through a rubber septum installed on each bag. The bags were kneaded for approximately 1 min to ensure the mixing of the gaseous components. Following the mixing, a metal capillary sampling tube that was attached to the GC sample injection loop system was inserted into the gas sample Saran bags through their rubber septa to obtain a sample. Gas samples were drawn from the bags through the sampling tube into the GC injection loops with the GC's internal vacuum pump. The gas sampling time from the Saran bags was 20 s, and the GC injection time was 250 ms; the actual volume of the injected gas sample was not determined. Like the single gases, mixtures of all four pure gases were prepared in Saran bags. The final concentrations of gases, singly and in mixtures, are given in Table I.

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

Analyses of gases in combustion atmospheres
To evaluate the method's effectiveness for analyzing actual combustion atmospheres, two fabrics were pyrolyzed in a 12.6-L combustion—animal-exposure assembly (13), and the resultant atmospheres were analyzed for the four gases. Briefly, the assembly consisted of a 50-mm quartz combustion tube encircled by two 425-W semicylindrical heating units, which provided radiant and conductive heat for decomposition of the material sample. The combustion tube was part of a closed system wherein a recirculating blower forced air from an animal exposure chamber through the combustion tube and back into the chamber.

Wool fabric was selected to produce CO, HCN, and one or more of the sulfur gases (4), and modacrylic fabric was selected as a known producer of CO and HCN. The weighed fabric sample was placed in the center of the preheated combustion tube, the system was sealed, and the recirculating blower was activated. The temperature at the sample position was 600°C for all tests; the sampling time of the combustion atmosphere was at 3 and 10 min after fabric sample insertion. Each combustion atmosphere sample was drawn from a port in the exposure chamber through a filter (25-mm diameter, 0.45-μm pore size) into a 100-ml glass syringe. The filters used were Acrodisc CR PTFE filters with female luer-lock inlets and standard male luer outlets (Gelman Sciences, Inc., Ann Arbor, MI). The combustion atmosphere sample was immediately injected into an evacuated Saran gas bag, sampled as previously described for the prepared pure gas samples, and analyzed. Five replicate pyrolyses of each fabric were performed at the 0.5- and 1.0-g fabric sample weights. The results of the combustion atmosphere gas analyses are summarized in Table II.

Results and Discussion

The developed analytical method was effective for the individual and simultaneous analyses of four common toxic combustion gases. Under the described chromatographic conditions, the four gases could be easily separated and quantitated (Figure 1). The use of a two-column/two-detector system permitted the simultaneous analysis of the four gases using a single injection sample split onto two columns. The molecular sieve-5A column separated CO from the air peak, and the PoraPlot-U column separated the other gases, H₂S, SO₂, and HCN. The CO gas eluted from the PoraPlot-U column with the air peak. The presence of H₂S, SO₂, or HCN in a sample did not compromise the CO analysis and vice versa. The retention time was 28.6 s for CO on the molecular sieve-5A column (channel A), and the retention times were 26.4, 76.6, and 108.9 s for H₂S, SO₂, and HCN, respectively, on the PoraPlot-U column (channel B). Oxygen, carbon dioxide, nitrogen, and water vapor did not interfere with the analyses. However, water peaked close to SO₂, which limited accurate peak-area integration.

The standard curves of these gases were plotted from 10 analyses of each gas at each of the concentrations, as shown in Figure 2. Although the absolute minimum detectable concentration for each gas was not determined, the lowest concentration (CO, 100 ppm; H₂S, 50 ppm; SO₂, 125 ppm; and HCN, 60 ppm) 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 approximately a 50-min period. However, the detector response gradually decreased in the HCN analyses; the decrease was approximately 6% between the first and the last five analyses from the same bag sample. The widest spread of values was observed with the SO₂ analyses, and there was 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.

Figure 2. Standard curves for (A) CO, (B) SO₂, (C) H₂S, and (D) HCN.
from the trailing edge of the water peak (Figure 1). By using the regression equations obtained from the standard curves, analyses of triplicate preparations of the individual gases and their mixtures at identical concentrations revealed excellent agreement with the known concentrations (Table I). The mean analytical values were accurate within plus or minus 13% of the respective known concentrations, and the coefficients of variation of mean analytical values were less than 10%.

Under the chromatographic conditions developed for the pure gases in air, analyses of combustion atmospheres generated from wool and modacrylic fabrics pyrolyses revealed the following: wool produced CO and HCN, as expected, as well as moderate concentrations of H2S; and modacrylic fabric generated relatively high concentrations of CO and HCN. No SO2 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 shown in Figures 3 and 4. The 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 using the pure gas standard curves; their mean values are given in Table II. In comparison with individual and simultaneous analytical values of four pure gases (Table I), variations were higher with combustion atmosphere analyses (Table II). Out of 18 mean gas concentration values, six concentrations had coefficients of variation that were more than 20%; five of these six concentrations were HCN. These variations could be attributed to the generation of gases in the combustion atmosphere at concentrations exceeding the upper limit of the standard curves (which may not be linear at those concentrations), to the solubility of HCN in water, which was produced during pyrolysis, or to both. Fluctuation in water vapor content can affect HCN concentration. In general, however, the variation in gas concentrations produced from five 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 the 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 twofold increase (at the fixed sampling intervals) over the 0.5-g samples. The selected 3- and 10-min sampling intervals did not define the gas generation curve adequately, but they depicted the progression of the pyrolysis within the realm of the study. When 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.

The efficiency of the combustion atmosphere sampling could be increased by using 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 gas concentration–exposure time curve (1,2). For the limited scope of this study, we chose to use the

![Figure 3](https://academic.oup.com/jat/article-abstract/20/3/189/757926/192)
Figure 4. Characterization of CO and HCN in a combustion atmosphere sample produced by modacrylic fabric collected after 3 min. (A) Separation of CO using module 1 and (B) separation of HCN using module 2.

Acknowledgment

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

Conclusion

A dual-column gas chromatograph was used to simultaneously measure CO, H$_2$S, SO$_2$, and HCN; the method was also effective for detecting and quantitating CO, H$_2$S, and HCN 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 of the four gases studied. The method may be useful for testing passenger protective breathing equipment and for inhalation/combustion toxicology research. After modification, this method can be applied for the analysis of these gases in biological specimens.

References


Manuscript received May 15, 1995; revision received October 10, 1995.