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Simultaneous analysis of carbon oxides and hydrocarbons by gas chromatography-mass spectrometry

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ABSTRACT

The simultaneous determination of carbon monoxide, carbon oxide, and C_1–C_4 hydrocarbons is demonstrated by gas chromatography-mass spectrometry. The analysis utilizes room temperature trapping of carbon monoxide on a Molesieve PLOT column, while determination of other species is performed on a PoraPLOT Q column. Carbon monoxide is then eluted at an elevated temperature. Detection limits in the low $\mu g\,m^{-3}$ regime are reported with a linear dynamic range that permits analysis in the mg m^{-3} range. No interferences between analytes or with air components are reported.

INTRODUCTION

Concern over a variety of airborne pollutants has increased from the standpoint of social awareness as well as government regulations. Among the concerns are those pollutants that contain carbon, including the oxides of carbon and light hydrocarbons. To understand the total contribution of these impurities to the environment, it is important to be capable of determining the high (mg m^{-3}) concentration associated with combustion emissions as well as the lower ($\mu g\,m^{-3}$) concentration associated with ambient or indoor measurements. Often it is necessary to determine instantaneous pollutant concentration to correlate with specific events, as well as measurements that represent some time span.

Air sampling using traps for hydrocarbons such as **Tenax**, porous polymers, or other trapping material [1–5] is very common. However, the trapping efficiency for these materials is poor for hydrocarbons that are gases at room temperature, necessitating cryogenic cooling for this type of sampling [6]. Methane is not trapped at all, even at liquid oxygen temperature. These materials are also ineffective for sampling carbon monoxide and dioxide. Direct analysis of air using bombs or bags is therefore necessary. Gas chromatography has been used in many instances to determine individual components of interest [7–10], but the most universal stationary phase for this type of application is porous polymer material such as the Porapak series (Waters) and the Chromosorb "Century Series" (Johns-Manville) [11]. However, even this separation has severe drawbacks. First, at ambient temperature, carbon monoxide co-elutes with air, making quantitation with a universal detector extremely difficult even at subambient GC temperatures. While carbon monoxide and light hydrocarbons can be separated from air on molecular sieves, carbon dioxide is strongly adsorbed on this stationary phase, making it impractical for use in this determination. Furthermore, the most common universal detector, the thermal conductivity

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detector, lacks sufficient sensitivity to perform ambient air analysis where some components of interest may be present below 1 mg m^{-3} levels. A flame ionization detector in conjunction with a methanizer is capable of detecting hydrocarbons and carbon oxides at low levels. Unfortunately, the metal catalysts used in methanizers are poisoned by exposure to large quantities of oxygen, making them impractical for repeated air analysis. Also, percent level quantities of oxygen have been shown to produce positive responses with an FID [12], making quantitation of a co-eluting carbon monoxide impossible. Dynamic range may also be a problem, since carbon dioxide is usually present at considerably higher levels than the other components in most air samples.

Detection by mass spectrometry offers a possible solution to co-elution problems mentioned above. Operation of a mass spectrometer in the selective ion monitoring (SIM) mode may offer sufficient sensitivity for ambient air analysis. However, most gas analysis applications require relatively high carrier flow-rates necessary for packed columns and gas sampling valves. Typically, the pressure reduction required for the high vacuum of the mass spectrometer source is achieved by one of several interface types [13-27]. Unfortunately, none of these interfaces provide the desired sensitivity with low-molecular-mass compounds ($m/z < 50$), either due to poor discrimination or dilution in the interface. Direct interfacing of capillary columns to the ion source [28,29] was one of the first methods developed for sample introduction into the mass spectrometer, however smaller diameter columns are incompatible with typical sample volumes (> 0.1 ml) and flow-rates (cu. 10–30 ml min^{-1}) associated with the use of gas sampling valves, requiring sample splitting [30] and severely limiting sensitivity. Also the loss of column efficiency due to the so-called vacuum effect is well documented [31,32].

The advent of fused-silica porous layer open tubular (PLOT) columns [33] with the porous polymer and molecular sieve stationary phases typically used in the analysis of low-molecular-mass gases (including hydrocarbons) [34–37] offers a possible compromise to a number of these problems. Wide-bore (0.53-mm) PLOT columns operate well at carrier flows compatible with gas sampling valves. By using a deactivated fused-silica interface of sufficiently small internal diameter (0.2 mm) and sufficient length, the analytical column can be maintained at near atmospheric pressure, thereby preventing the loss of column efficiency mentioned above. This approach requires a differentially pumped mass spectrometer with sufficient pumping capacity to prevent high-pressure ionization effects such as chemical ionization. Two approaches that provide an appropriate combination of chromatography with mass selective detection to achieve this determination are described here.

EXPERIMENTAL

A Hewlett-Packard (Avondale, CA, USA) 5988A quadrupole mass spectrometer equipped with a 589OA gas chromatograph was used for this study. This mass spectrometer is differentially pumped with an electron impact (EI) ion source. While pumping capacity in this configuration is more than adequate for typical narrow-bore capillary carrier flows, it is marginal for a minimum carrier flow of cu. 10 ml min^{-1} necessary for flushing a sample loop of sufficient volume in a short enough time to prevent severe band broadening. By separating the forelines of the two diffusion pumps, and using a separate 400 l min^{-1} foreline pump (Fisher Scientific, Pittsburgh, PA, USA) for the source diffusion pump, pumping capacity was increased significantly. This modified vacuum system is capable of maintaining a nominal source vacuum pressure of $2 \cdot 10^{-5}$ Torr (1 Torr = 133.32 carrier flows of 10–15 min^{-1}. Carrier flows were calculated from averaged measurements and column volume, since actual

PoraPLOT 5A

m0.53 mm I.D. were utilized for this applica-

tion. Timing of valve switching was controlled by a digital valve sequence programmer combined with digital valve interfaces for each valve (Valco, Houston, TX, USA). The programmer also controlled the start of the mass spectrometer and chromatograph programs. A 5 m x 0.2 mm I.D. deactivated fused-silica capillary was used to directly interface the PLOT column to the mass spectrometer source and maintain the PLOT column at atmospheric pressure or above throughout the column, thereby avoiding loss of column efficiency. The direct connection was achieved with a zero dead volume union using special fused-silica adapter fittings (Valco). This configuration allows the use of up to a 0.2-ml sample loop. Sample loops with larger volumes were not used because of the resulting peak broadening, probably due to the limited capacity of the fused-silica restrictor or the sample loop not being flushed in a sufficiently short period of time. For the application using parallel columns, a 1:1 splitter (SGE, Austin, TX, USA) was used to divide the sample injections between the two columns. Carrier gas purified with a rare earth metal getter (SAES Getters, Colorado Springs, CO, USA) was used to lower the m/z = 28 background to improve detection limits for the molecular carbon monoxide ion.

Detection limit and linearity evaluations were conducted using a single-stage dynamic blender using mass flow controllers to dilute NIST (National Institute of Standards and Technology) traceable standards [15 ppm (v/v) methane, ethane, ethene, ethyne, propane, propene, propyne, and butane in nitrogen, 10 ppm carbon monoxide in nitrogen and 10 ppm carbon dioxide in nitrogen] (Scott Specialty Gas, Houston, TX, USA). The dilution gas was also nitrogen. Standards were also diluted in air without the carbon dioxide to compare response factors for the two balance gases, as well as identify any interferences or problems with dynamic range in the simultaneous determination of carbon dioxide and other components.

Mass tuning and signal optimization for the most common GC-EI-MS applications (organic mixture analysis) are typically performed with a compound such as perfluorotri-*n*-butylamine (PFTBA) [38], often utilizing a computerized optimization routine. These routines are typically designed to optimize performance at m/z values significantly larger than those of interest for this application. While mass calibration is usually still adequate, a significant gain in sensitivity was obtained by manually optimizing lens voltages using air components (m/z 18, 28, 32) to provide tuning masses. This is only possible with a system in which extreme care has been taken to maintain the air background at a sufficiently low level by minimizing leaks and maintaining sufficient carrier purity. A decrease in electron energy from 70 to 60 eV served to increase the molecular ion with respect to other fragments in all cases. Filament current was also increased from 300 to 400 μA to produce the maximum number of ions. Lens voltages were adjusted to attain maximum responses at these masses.

RESULTS AND DISCUSSION

The properties of molecular sieves when used as chromatographic stationary phases can be modified significantly by varying the water content of the media [39,40]. By modifying the conditioning temperature, carrier gas, and moisture content of the carrier gas, retention properties of the media can be drastically modified. It was determined empirically that 24 hours of conditioning at 200°C utilizing helium carrier gas with less than 1 ppb (v/v) moisture would result in a column that was capable of reversibly trapping carbon monoxide at room temperature. The carbon monoxide can then be eluted by raising the column temperature above 100°C.

Fig. 1 illustrates the first chromatographic approach utilizing the trapping of carbon monoxide on Molesieve PLOT. This configuration allows the Molesieve PLOT column to be removed from the flow path leading to the mass spectrometer. Fig. 2 illustrates SIM chromatograms for m/z 15, 26, 27, 28, and 44 representing carbon monoxide and carbon dioxide molecular ions and prominent ions for C_1–C_2 hydrocarbons using this approach. The m/z = 27 ion chromatogram is used to determine ethane and ethene to remove interference from the large nitrogen peak at m/z = 28. This chromatogram was gen-

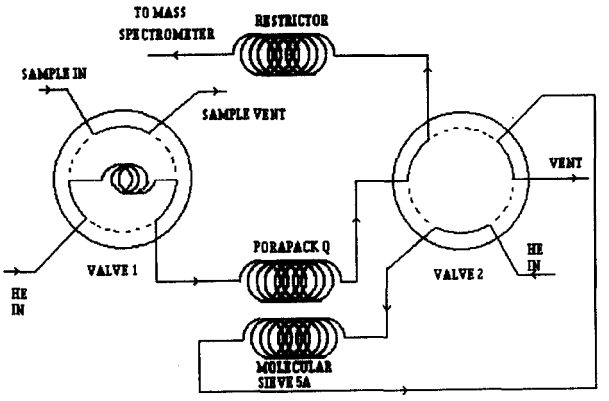

Fig. 1. Plumbing configuration allowing molecular sieve column to be inserted and removed from main chromatographic path. Path represented by solid line for each valve corresponds with position described as Inj in Table I. Dotted line represents Load position.

erated by the valve timing and GC oven temperature scheme shown in Table I. The analysis is begun with both the PoraPLOT and Molesieve PLOT columns in line with the mass spectrometer. After initial injection (valve 1 at *t = 0)* nitrogen, oxygen, carbon monoxide, and methane are allowed to pass through the PoraPLOT to the Molesieve PLOT column. At this low operating temperature, carbon monoxide is virtually immobilized and methane moves very slowly on the conditioned Molesieve PLOT column. Valve 2 is then switched and hydrocarbons and carbon dioxide are eluted to the mass spectrometer. The Molesieve PLOT

TABLE I

VALVE AND TEMPERATURE SEQUENCING

Time (min)	Valve 1	Valve 2	Temperature (°C)	Bate (°C/min)
Initial	Load	Load	30	0
0	Inj	Load	30	0
1.8	Inj	Inj	30	0
6.0	Inj	Load	30	25
10	Inj	Load	130	0
20			End run	

column is placed back in series with the mass spectrometer, the GC oven temperature elevated, and carbon monoxide is eluted. Using this scheme, all components can be separated by a combination of chromatography and mass selection. Nitrogen and carbon monoxide cannot be determined by molecular ions on the PoraPLOT alone because of inadequate mass or chromatographic resolution. Carbon monoxide could be determined at significantly higher (mg m^{-3}) concentrations using m/z 12, which may be of some benefit in evaluation of emission sources, but is inadequate for ambient samples. By separating carbon monoxide from nitrogen, the higher abundance molecular ion can be used, providing much greater sensitivity for carbon monoxide. This configuration prevents high levels of carbon dioxide and water from entering the Molesieve PLOT column, minimizing the

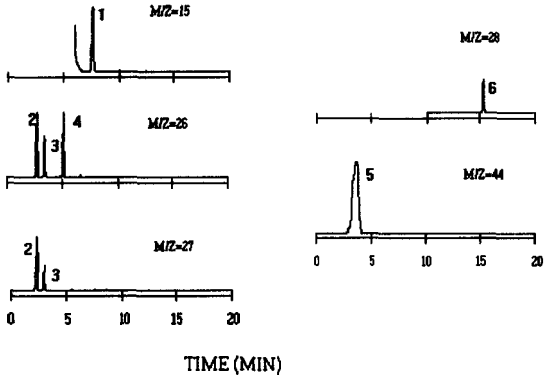

Fig. 2. Selected ion chromatograms of 0.2-ml injection for configuration in Fig. 1 for masses indicated. Components: 1 = methane, 2 = ethene, 3 = ethane, 4 = ethyne, 5 = carbon dioxide, 6 = carbon monoxide at approximately 1 mg ml-‘.

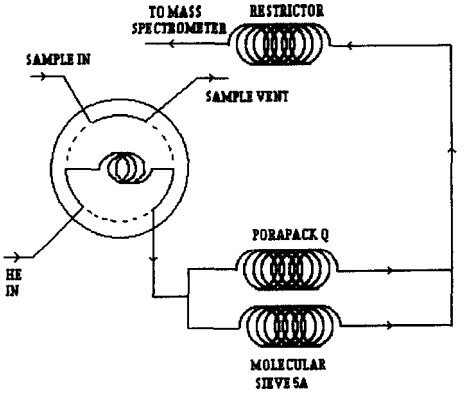

Fig. 3. Plumbing configuration with sample splitting between PoraPlot and molecular sieve columns. Path represented by solid line in injection valve represents sample injection position. Dashed line represents sample load position.

need for thermal reconditioning. However, hydrocarbons with more than two hydrocarbons require temperatures higher than ambient to elute them from the porous polymer column, preventing their determination with this configuration, if carbon monoxide is also to be determined. The possibility of extraneous peaks in future chromatograms also exists, as these hydrocarbons are eventually eluted from the Molesieve PLOT.

Fig. 3 illustrates the second chromatographic approach. This configuration allows samples to be split between the Molesieve PLOT column and the PoraPLOT column. Fig. 4 illustrates SIM chromatograms for m/z 15, 26, 27, 28, 29, 40, 41, and 44 representing carbon monoxide and carbon dioxide molecular ions and prominent ions for a number of C_1–C_4 hydrocarbons. This chromatogram was generated by a single valve event (injection) and GC oven temperature scheme similar to the one used in the two valve configuration used above. The analysis is begun with the sample being split between the PoraPLOT and Molesieve PLOT columns from the initial injection. Once again, carbon monoxide is virtually immobilized on the Molesieve PLOT column while hydrocarbons and carbon dioxide are detected by the mass spectrometer.

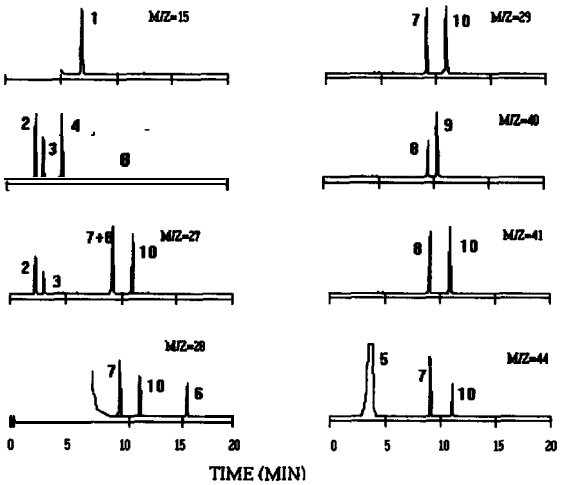

Fig. 4. Selected ion chromatograms of 0.2-ml injection for configuration in Fig. 3 for masses indicated. Components: 1 = methane, 2 = ethene, 3 = ethane, 4 = ethyne, 5 = carbon dioxide, 6 = carbon monoxide, 7 = propene, 8 = propane, 9 = propyne, 10 = butane at approximately 1 mg ml^{-1}.

The temperature is then elevated, and carbon monoxide is eluted to the mass spectrometer. While this configuration suffers from slightly poorer detection limits because of sample splitting, it is much simpler to operate. Unfortunately, it also requires the Molesieve PLOT column to be reconditioned after only a few injections of air. It does allow the direct determination of hydrocarbons with as many as four carbons as well as the carbon oxides in a single run.

Because of the trapping mechanism used in the determination of carbon monoxide, there was some concern about quantitation, especially at lower levels. A calibration curve generated over four orders of magnitude of concentration using the first configuration demonstrated linear response, indicating the trapping process is quantitative under these conditions. Similar results were obtained for carbon dioxide and the hydrocarbons considered here. From the calibration curves, it was possible to determine approximate detection limits for these analytes for this configuration using a response factor that would result in a signal-to-noise level of three to one. These approximate detection limits are listed in Table II. While frequent calibration is always a good practice, low variability in response factors is desirable as a confirmation of proper instrument operation. To evaluate the day-to-day

TABLE II

ANALYTE DETECTION LIMITS AND REPRODUCIBILITY

Analyte	m/z	Lower detection limit (μg m^{-3})	R.S.D. (at 1 mg m^{-3}) (%) (n = 5)
Methane	15	33	4.1
Ethane	27	31	3.9
Ethene	27	28	3.6
Ethyne	26	16	2.7
Propane	29	43	4.0
Propene	41	26	3.1
Propyne	40	24	2.9
Butane	29	59	4.5
Carbon monoxide	28	23	5.6
Carbon dioxide	44	1.8	2.0

variability of this method, response factors were measured daily for blends of all the components mentioned above at approximately 1 mg m^{-3} for seven days. The relative change of response factors as a percentage of the initial measurement demonstrated similar performance to those reported previously for nitrogen and sulfur oxides as determined by GC-MS [41], with relative variation over this period less than 10% for each component.

CONCLUSIONS

The results summarized here demonstrate that GC-MS offers a viable alternative technique to those presently used to determine carbon oxides and low-molecular-mass hydrocarbons. GC-MS offers the possibility of determining species simultaneously from a single whole air sample, often at sensitivities not available with other techniques. While cost and size may prevent replacing many analyzers presently used with this technique, GC-MS offers a new alternative where the characteristics mentioned above are important.

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