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Analysis of carbon monoxide by molecular sieve trapping

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ABSTRACT

The determination of carbon monoxide is demonstrated trapping CO on preconditioned molecular sieve and thermal desorption. Analysis in this case is performed by gas chromatography–mass spectrometry, although the trapping technique is applicable to other suitable GC techniques. Storage of the trapped sample for an indefinite time is possible with no degradation, even at several tenths of mg m^{-3}. Detection limits of 100 μg m^{-3} are reported with a linear dynamic range that permits analysis in the mg m^{-3} range. Balance gas interferences are reduced, but not eliminated.

INTRODUCTION

Carbon monoxide is one of many common pollutants that has come under increasing scrutiny in the last several years [1,2]. Carbon monoxide is most often produced from incomplete combustion of carbonaceous fuels such as coal, natural gas, and gasoline. Carbon monoxide is also suspected of contributing to ozone production [3]. To understand the total contribution of carbon monoxide 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 (μg 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 an average measurement over a defined time period.

Carbon monoxide is often determined in source sampling using remote optical sensing [4], but this method is inconvenient for ambient or indoor sampling. Fourier transform infrared spectroscopy has been used to determine carbon monoxide concentrations in air [5], as well as CO-specific sensors of SnO_2 and other materials [6–10], but these usually require a continuous sample stream. Direct analysis of air using bombs or bags is often used to determine carbon monoxide in air. Gas chromatography has been used in many instances to determine carbon monoxide [11–14], but the most universal stationary phases for this type application are porous polymer materials such as the Porapak series (Waters Assoc.) and the Chromosorb "Century Series" (Johns-Manville) [15]. This separation technique cannot be used directly for air samples since at ambient temperature, carbon monoxide coelutes with air, making quantitation with a universal detector extremely difficult even at subambient GC temperatures. Carbon monoxide can be separated from air on molecular sieves, but the carbon dioxide and water content of most air samples makes frequent thermal conditioning necessary. A flame ionization detector in conjunction with a methanizer is capable of detecting carbon monoxide at low levels. Unfortunately, the metal catalysts used in methanizers are poisoned by exposure to large

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quantities of oxygen, making them impractical for repeated air analysis. Also, percent level quantities of oxygen have been known to produce positive responses with a flame ionization detector, making quantitation of a coeluting carbon monoxide impossible. Carbon monoxide is also reactive with many materials including metals and plastics, making the storage of air samples with trace amounts of carbon monoxide in any container suspect.

Trapping of carbon monoxide may offer a solution to chromatographic interferences mentioned above, as well as potentially offering a stable method of storing samples while in transit to the laboratory for analysis. A passive sampler utilizing the trapping of carbon monoxide on specially treated zeolites has demonstrated quantitative recoveries [16]. Short-term immobilization has also been demonstrated on a molecular sieve porous-layer open tubular (PLOT) column [17]. It is possible that a suitable trap could be constructed to allow remote sampling by trapping, and subsequent laboratory analysis.

Detection by mass spectrometry offers a possible solution to coelution 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 [18–32]. 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 [33,34] 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 (*ca.* 10–30 ml min^{-1}) associated with the use of gas sampling valves, requiring sample splitting [35] and severely limiting sensitivity. Also the loss of column efficiency due to the "vacuum effect" is well documented [36,37].

The advent of fused-silica PLOT columns [38] with the porous polymer and molecular sieve stationary phases typically used in the analysis of low-molecular-mass gases [39–42] 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 5890A 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 *ca.* 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 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 = 133.322 Pa) at carrier flows of 10–15 ml min^{-1}. Carrier flows were calculated from averaged linear velocity measurements and column volume, since actual flow-rates are expected to be significantly different with the column end at atmospheric pressure and high vacuum. Average linear velocity was determined from the retention time of neon,

which is virtually unretained on these column materials.

A PoraPLOT Q (Chrompack, Raritan, NJ, USA) column 25 m × 0.53 mm was utilized for this application. A 5 m × 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 butt connection was achieved with a zero dead volume union using special fused-silica adapter fittings (Valco Instruments). The typical chromatographic configuration used for gas samples was modified by inserting an additional 4-port valve between the injection valve and the column (Fig. 1). This configuration allows the trap to be inserted in the chromatographic flow, purged with carrier gas, heated independently of the gas chromatograph to desorb the carbon monoxide, and injected onto the column through appropriate sequencing of valves and heaters. Timing of valve switching was controlled by a digital valve sequence programmer combined with digital valve interfaces for each valve (Valco Instruments, Houston, TX, USA). The programmer also controlled the start of the mass spectrometer and chromatograph programs. Carrier gas was purified with a rare earth metal getter (SAES Getters, Colorado Springs, CO, USA) to reduce air impurities below detectable levels.

The trap was constructed from a Valco 4-port valve and fittings, and 1/16 in. O.D. × 0.03 in. I.D. (1 in. = 2.54 cm) 316L stainless-steel tubing. The empty trap volume in each case was approximately 1 ml. The tubing was packed with 180–220-mesh molecular sieves 3A, 4A, 5A and 13X (Alltech, Deerfield, IL, USA), and wrapped around a temperature-controlled column mandrel (Valco). Air samples were drawn through the sampler with a PAS-3000 battery-operated variable volume sampling personal air sampler (Supelco, Bellefonte, PA, USA). Fig. 2 schematically illustrates the trapping device.

Detection limit and linearity evaluations were conducted using a single stage dynamic blender using mass flow controllers to dilute NIST traceable standards [100 ppm (v/v) CO in nitrogen] (Scott Specialty Gas, Houston, TX, USA). The dilution gas was air.

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), 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 tuning parameters using molecular ions of air components (m/z

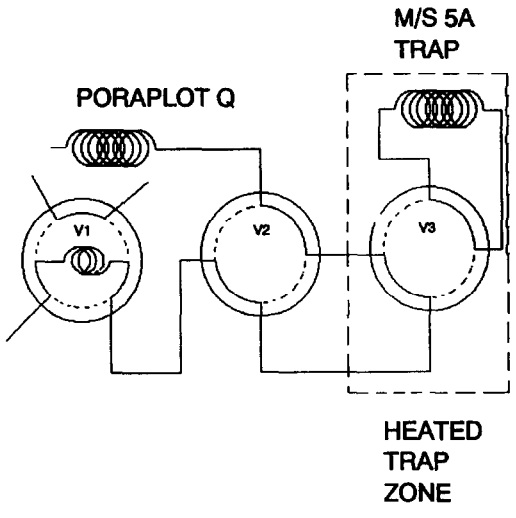

Fig. 1. Plumbing configuration for chromatographic utilization of molecular sieve (M/S) trap.

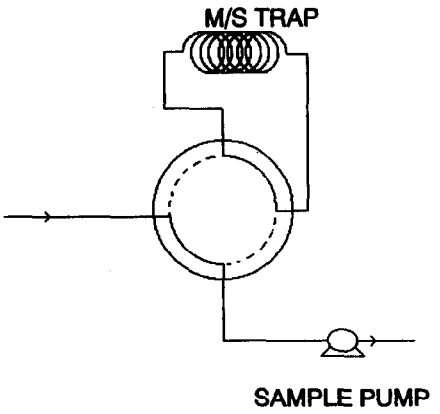

Fig. 2. Molecular sieve trap.

18, 28, 32). 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 [43,44]. By modifying the conditioning temperature, carrier gas, and moisture content of the carrier gas, water content and therefore retention properties of the media can be drastically modified. Similar effects would be expected when molecular sieve is being used as a trapping media. Trapping efficiencies were evaluated for molecular sieves 3A, 4A, 5A and 13X. All materials were conditioned under flowing gettered helium for 24 h at 350°C to remove as much water as possible without affecting the molecular sieve structure. Recoveries were determined for each trap as a function of desorption temperature for a 1 mg m^{-3} concentration of carbon monoxide flowed over the trap for 1 min at 10 ml min^{-1}. Analysis was performed using the chromatographic configuration described earlier, and the timing sequence shown in Table I. The results are shown in Fig. 3. Both 3A and 13X show little propensity to act as effective trapping media. This was not unexpected, since carbon monoxide (3.12 Å molecular diameter) is larger than the effective diameter of 3A, and much smaller than 13X. Molecular sieve 4A shows a definite tendency to trap carbon monoxide, however adequate recoveries are never reached, indicating that perhaps carbon monoxide is too strongly bound. Only molecular sieve 5A shows reasonable recovery, therefore it was selected as the trapping media.

One of the improvements desired from this method is the elimination of the matrix gas (air in the case of environmental samples) from the trapped sample. Fig. 4 shows the SIM chromatograms at m/z 12, 28 and 32 for the molecular sieve 5A sample at 200°C from the above evaluation. Unfortunately, significant levels of oxygen and nitrogen apparently remain adsorbed to the trapping material. While the matrix is drastically reduced, it is not eliminated, thereby precluding the use of this method with universal detectors without adequate chromatographic separation. Also, m/z 28 (the molecular ion for CO, which occurs in the mass spectra at higher abundance than any other ion) cannot be used for quantitation by GC–MS, limiting the sensitivity of the

TABLE I

VALVE SEQUENCE AND TEMPERATURE PROGRAM FOR DESORPTION AND ANALYSIS FOR PLUMBING CONFIGURATION IN FIG. 1

Time (min)	Trap temperature	Valve position		
		V1	V2	V3
0.0	Ambient	1	2	1
0.1	Ambient	1	1	1
0.5	Ambient	1	1	2
2.0	Ambient	1	1	1
10.0	200°C	1	1	1
10.1	200°C	1	1	2
15	200°C	1	1	1
30	Ambient	1	1	1

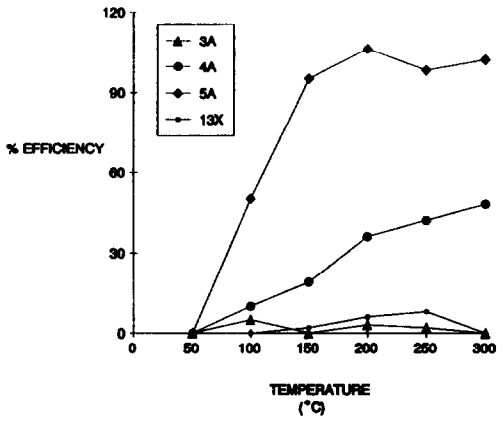

Fig. 3. Trapping performance for several common molecular sieves.

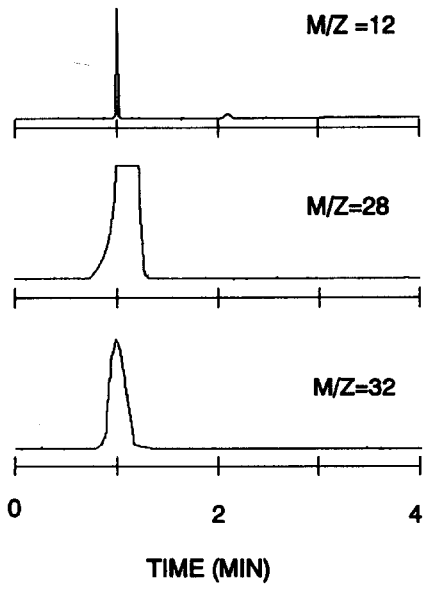

Fig. 4. Selected ion chromatograms for m/z 12, 28 and 32.

technique. The technique still provides acceptable results by monitoring m/z 12, and provides approximately a 100-fold improvement over direct analysis of CO in air using m/z 12. Other selective detectors, such as flame ionization detector–methanizer, should be applicable, although this was not evaluated here.

Since it was suspected that the trapping process was not totally irreversible at ambient temperature, the trapping efficiency was studied

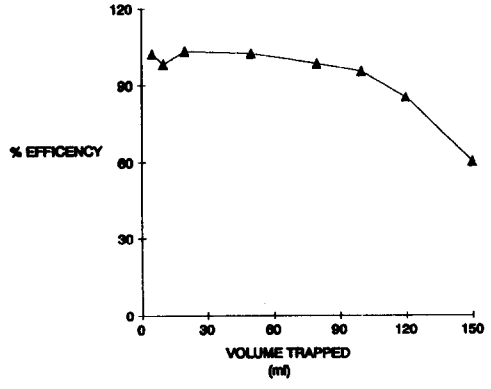

Fig. 5. Trapping efficiency *vs.* sample volume for molecular sieve 5A trap.

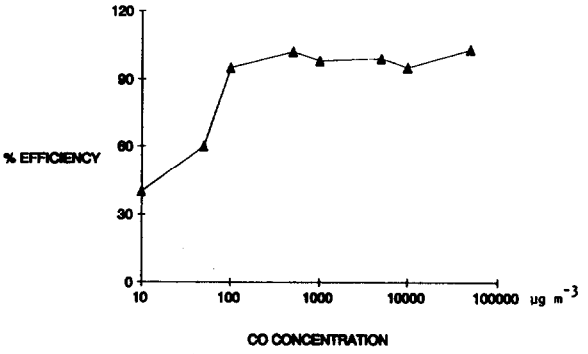

Fig. 6. Trapping efficiency *vs.* carbon monoxide concentration for molecular sieve 5A trap.

as a function of total air volume passed through the trap. The results are shown in Fig. 5. Non-linearity was observed at approximately 100 times the volume of the trapping material for 180–220-mesh 5A at ambient temperature. Mesh size, flow-rate and temperature are all expected to affect maximum trapping volume, but were not explored further. An evaluation of efficiency over four orders of magnitude of concentration of carbon monoxide using a constant volume of air demonstrated linear response with a negative deviation observed below about 100 $\mu g\ m^{-3}$ as shown in Fig. 6. Sample stability over time was also a concern. To evaluated the stability of trapped samples, 1 mg m^{-3} of carbon monoxide in air was sampled with the 5A trap for 1 min and allowed to sit for 1–7 days. The trap was desorbed and analyzed by GC–MS. All results were found to be within 10% of the mean of the group.

CONCLUSIONS

The results summarized here demonstrate that trapping carbon monoxide on molecular sieve allows the collection of the analyte with elimination of most of the sample matrix, in the case of air. Carbon monoxide can be concentrated on the molecular sieve to achieve approximately a 100-fold increase in sensitivity with compatible techniques. Samples can be collected remotely and stored for an adequate period of time to allow transportation to a laboratory.

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