



Project Summary

Totally Optical Technique for Monitoring Ambient Non-Methane Hydrocarbons

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A method for measuring ambient levels of nonmethane hydrocarbons (NMHCs) has been developed, and a prototype instrument based on that method has been fabricated. The instrument consists of a sample conditioner and an optical CO₂-CO analyzer. In the sample conditioner ambient air is selectively scrubbed of CO₂ and H₂O after which the sample stream is divided into two streams. In one, any NMHCs and CO are catalytically oxidized to CO₂ and then directed to one of two absorption cells in the optical analyzer. The other stream goes directly to the second absorption cell. The CO₂-CO optical analyzer measures two concentrations, that of the CO₂ resulting from conversion of NMHCs and CO as well as that of the CO present in the sample initially. Circuitry incorporated in the analyzer produces linearized output signals of the CO and CO₂ concentrations as well as their difference, the NMHC concentration. Unique optical designs using gas filter correlation, as well as the prospect of a combined CO and NMHC monitor requiring no consumable compressed gases for operation, make the prototype promising for ambient air monitoring.

This Project Summary was developed by EPA's Environmental Sciences Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Ambient nonmethane hydrocarbons and nitrogen oxides (NO_x) are primary precursors of ozone and other oxidants, which are key components of photochemical smog. Current strategies for controlling these photochemical oxidants depend primarily on nonmethane hydrocarbon (NMHC) abatement. EPA has identified the development of improved monitoring techniques for NMHC as a basic need for the agency. In particular, the problem of response variability that is inherent in the measurement of the many molecular species comprising NMHCs must be addressed.

The main goal of this work has been to develop and deliver a prototype instrument that measures NMHCs by optical absorption after converting each carbon atom in NMHCs to CO₂. A secondary goal was to provide a monitor that requires no compressed gases for operation. The effort was preceded by a feasibility test to prove a design of a conditioner suitable for eliminating CO₂ from an ambient air sample and for converting NMHC quantitatively to CO₂ in a catalytic oxidizer. After feasibility was shown, the prototype monitor was built. This summary provides information on the feasibility study results and on the design of the instrument. The detailed design of the optical CO₂-CO analyzer is described as Appendix A of the project report; the sample conditioner is described in a separate manual available from the EPA project officer.

Sample Conditioner

The schematic for the final design configuration for the NMHC analyzer is shown

in Figure 1. The sample air is pulled through a regenerative dryer made by Perma-Pure Products, Inc. The dryer was tested to show 100% transmission of both CO and a hydrocarbon mixture consisting of equal ppm concentrations of methane, ethane, ethylene, acetylene, propane, propylene, hexane, hexene, xylene and benzene, diluted with zero air and used in the concentration range 200 ppb-5 ppm with and without H₂O. The CO₂ scrubber was a 15 cm × 1.25 cm dia. column of ascarite maintained at approximately 300°K. Tests were performed to show an acceptable capacity for removal of ambient level concentrations of CO₂ with negligible breakthrough of CO₂. The ascarite scrubber was also tested to show 100% passage of CO for concentrations as low as 100 ppb.

The transmission of HC through the ascarite scrubber was tested. The signal due to the HC mixture did not change (100% ± 5%) over the range 150 ppb - 3.5 ppm after passing through ascarite held at 350°K for a residence time range 0.3 - 0.75s. Individual HCs, including ethane, propane, butane, butene, hexane, and benzene, were tested over a range of flows (3-100 ml (STP)s⁻¹) and concentrations (0.25-50 ppm). All were nearly quantitatively transmitted. It is known, however, that alcohols, aldehydes, and ketones will not be transmitted through alkaline materials such as ascarite. None of these compounds was tested.

The performance of ascarite is greatly impaired by the presence of high concentrations of water. The material channels quite readily when exposed to moist air (saturated at 293 K). A 20 g sample was completely destroyed, caking into a solid mass, by less than 4 h exposure at 80 ml (STP)s⁻¹ to such a moist air stream.

After passing through a particulate filter, the exit sample stream from the CO₂ scrubber is separated into two streams (19% and 81% of the total flow). The larger portion of the sample passes directly to a CO analyzer. The other stream passes into a "hopcalite" (a proprietary material of Mine Safety Appliances) catalytic converter that converts hydrocarbons into CO₂ and H₂O. Figure 2 shows the HC conversion efficiency to CO₂ using a 15 cm × 1.25 cm dia cylinder filled with "hopcalite."

Varying residence time, T, from 0.10 s to 3 s did not produce any measurable response from CH₄ at 525 K. All compounds that were 100% converted at T = 3s were also 100% converted at T = 0.1s. Ethane conversion was constant from T = 0.3 to 3 s but decreased by 2% as T was decreased from 0.3 to 0.10 s. This suggests that a residence time of ≈ 0.35 s should be used in designing an instrument. Examining the HCs individu-

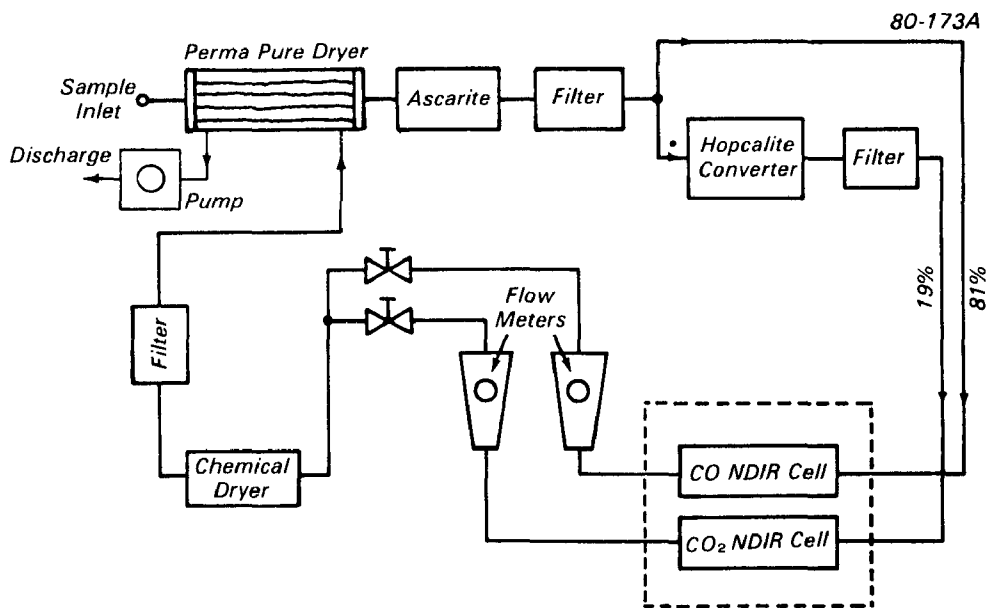


Figure 1. Schematic of NMHC analyzer.

ally, complete conversion was found to be independent of concentration over the entire range accessible to our experiments, i.e., up to 50 ppm. The possibility of synergistic effects among HCs at low concentration was also tested by analyzing the HC mixture referred to above. A linearity of response demonstrated response is in direct proportion to the amount of carbon in the sample.

Optical Absorption Analyzer

After the "hopcalite" converter, the sample stream passes through a filter and into the CO₂ analyzer. The difference between

the measured concentrations of CO₂ and CO is the concentration of carbon atoms in the NMHC. Two requirements for the CO₂-CO monitor played an important role in the design: (1) the minimum detectable concentration of each gas must be less than 0.02 ppm, and (2) the volumes of the sampling sections must be kept small. The second requirement results from the need to maintain a short sample "turnover" time without using an excessive amount of gas. The rate at which the NMHC can be oxidized to form CO₂ is a limiting factor; therefore, it is important that the CO₂ sample cell be small. Multiple-pass optics operated at 22 passes in the sample cells make it possible to achieve the required sensitivity in the relatively short sample cells. The approximate base lengths and volumes of the sample cells are, respectively: CO₂, 30 cm and 315 cm³; CO, 40 cm and 640 cm³.

The analysis section of the monitor consists of two basic assemblies, the optical assembly and the digital signal processor. The electrical outputs from the optical assembly are two analog signals; one signal is related non-linearly to the CO₂ concentration, the other to the CO concentration. These analog signals serve as inputs to the digital signal processor, the first stage of which is an analog-to-digital converter. The resulting digital signal for each channel is processed to account for the non-linearity in the relationships between gas concentrations and the output analog signals of the optics assembly. Three digital meters on the optics assembly give continuous readouts of (1) CO₂ concentration, (2) CO concentration,

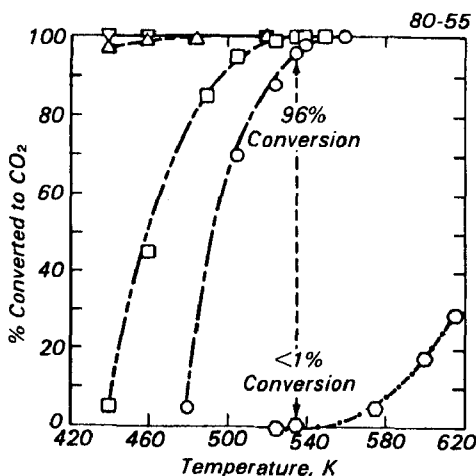


Figure 2. HC conversion efficiency to CO₂ over hopcalite. Residence time $\tau = 0.5$ s. O - methane; \diamond - ethane; \square - propane; \triangle - ethylene; ∇ - acetylene, butene, hexane.

and (3) the difference (1) - (2). The third reading is equal to the concentration of NMHC in the air being sampled.

The zero-setting of the monitor is quite stable although it should be checked 2 or 3 times per hour if the best possible accuracy is required. When using 10-second electronic time constants, the peak-to-peak noise equivalent concentrations are approximately 0.015 ppm of CO₂ and 0.04 ppm of CO. The minimum detectable concentrations are approximately one half the peak-to-peak noise-equivalent concentrations if the signal is observed for as long as 20-30 seconds.

Gas and Entrance Optics

The optical assembly contains two similar but separate channels, one for CO and one for CO₂. Figure 3 shows a perspective view of the entrance optics for both channels. Infrared energy from a hot source passes through window WC1 into the prism PC1; at the beveled surface of PC1, the beam is reflected through 90° to lens LC1 and into prism PC2. A beveled surface at the opposite end of prism PC2 reflects the beam out of the side of the prism and through the rotating gas-filter cell (GFC) to filter C and lens LC2. From there, the beam continues through prism PC3 to the CO sample cell discussed in the following sub-section. Lens LC1 images the source near filter C, which passes a narrow spectral band centered near 4.6 micrometers where CO absorbs strongly. Field lens LC2 forms an image of lens LC1 near the entrance window of the CO sample cell. The reflecting surfaces of CaF₂ prisms PC1, PC2, and PC3 are aluminized. Lenses LC1 and LC2 are also made of CaF₂. Sapphire window WC1 is anti-reflection coated for wavelengths near 4.6 micrometers and protects the brittle CaF₂ prism PC1 from heat shock due to the hot source.

Prisms PD1, PD2, etc., of the upper optical path are part of the CO₂ channel. This optical path is similar to the corresponding one for the CO channel except that filter D passes a narrow spectral interval near 4.3 micrometers where CO₂ absorbs strongly.

The prisms with reflecting surfaces are used instead of flat mirrors to reduce to optical path through air, and thus to reduce errors due to absorption by CO and/or CO₂ in the air. Variations in the amount of this absorption cause changes in the zero-settings. All of the components illustrated in Figure 3 are enclosed in a sealed aluminum box called the GFC enclosure. A Teflon O-ring seal fits around the motor shaft. The box is flushed with dry air that is free of CO and CO₂ to reduce further any error due to either of these gases in the optical path. The end of prism PD3 is within one mm of the entrance window of the CO₂ cell; prism PC3

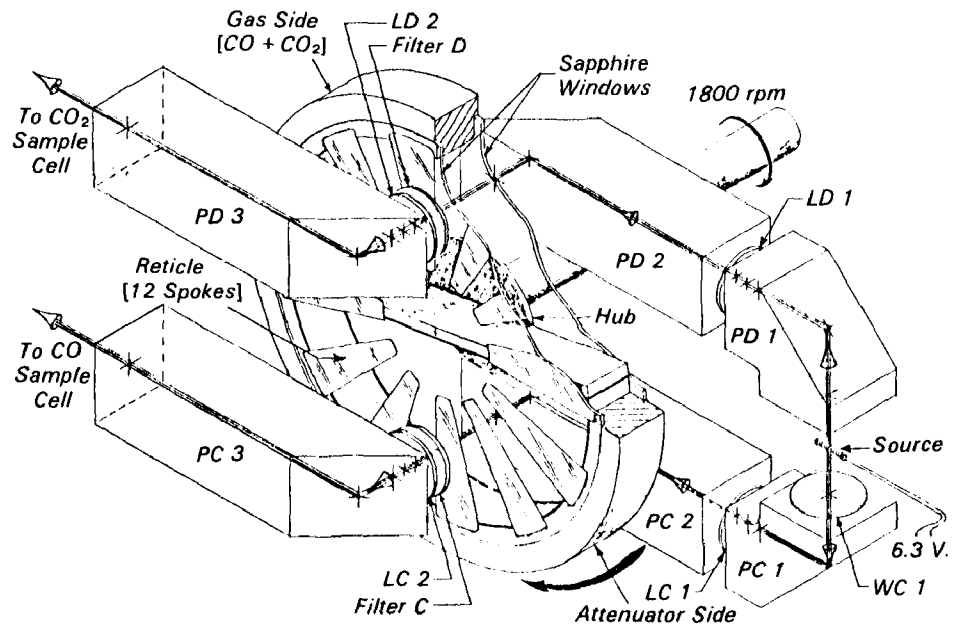


Figure 3. Optical diagram of the source optics. Infrared energy from an electrically heated source follows two different paths, one to each of the sample cells. All of the components shown are within an enclosure that is flushed with N₂ or Argon to reduce absorption by CO₂ in the air. The gas-filter cell [GFC] rotates at 1800 rpm.

is a similar distance from the CO cell. These air gaps are within the enclosure and are flushed. The total optical path through the air in the enclosure is less than one cm in each of the channels. Keeping air out of the optical path is more important for the CO₂ channel than for the CO channel because normal air contains more than one hundred times as much CO₂ as CO.

The sapphire windows of the GFC are 6.35 cm (2.5 inches) in diameter and are spaced 0.6 cm apart. One-half of the GFC is filled with a mixture of CO and CO₂; the other half contains a semi-circular piece of CaF₂ that fills the space between the windows. The hub is bonded concentrically to one window of the GFC. As the GFC rotates at 30 rps, each radiant energy beam passes alternately through the CO₂-CO mixture and the CaF₂. Twelve opaque reticles chop the beams at 360 Hz.

Sample Cells and Detectors

Figure 4 shows a top view of the optics in the multiple-pass cell that contains the CO₂ sample. Radiant energy from prism PD3 enters the sample cell through lens LD3, which serves as the entrance window and forms an image of the source near spherical mirror S2. This mirror forms an image of LD3 on spherical mirror S3, the first mirror of the multiple-pass optical system. After passing the length of the cell 22 times, the radiant energy is directed by flat mirror S6 through the exit lens LD4, which also serves as the

exit window and images mirror S3 on the 2 mm x 2 mm PbSe element of the detector. The distance from mirror S4 to either S3 or S5 is 30 cm, making the total optical path length in the cell approximately 665 cm.

The CO cell is similar to the CO₂ cell and is mounted directly beneath it. Mirrors S1, S2 and S6 are mounted identically in both cells, but the CO cell is longer and wider. The distance from mirror S4 to either S3 or S5 is 40 cm in the CO cell and 30 in the CO₂ cell. Thus, the optical path length in the CO cell, which is also adjusted to 22 passes, is approximately 885 cm. The internal width of the CO₂ cell is 4.8 cm, whereas the same dimension of the CO cell is 7.3 cm. The internal height of both cells is 2.2 cm.

Figure 5 shows the image patterns on mirrors S4 of both cells. The numbers adjacent to the images in the lower cell represent the number of passes made by the beam when the image is formed. Images 2, 6, 10, etc., are formed by mirror S3 and images 4, 8, 12, etc., are formed by mirror S5. Note that each radiant energy beam enters the upper portion of the cell and exits from the lower portion.

Each sample cell and its associated gas lines are designed so that each samples gas from a different source. The gas flows into one end of the cell and out the opposite end. The end flange contains several small holes (not shown in Figure 4) through which the gas enters the cell. Passing the gas through these holes reduces "jet streams" that would

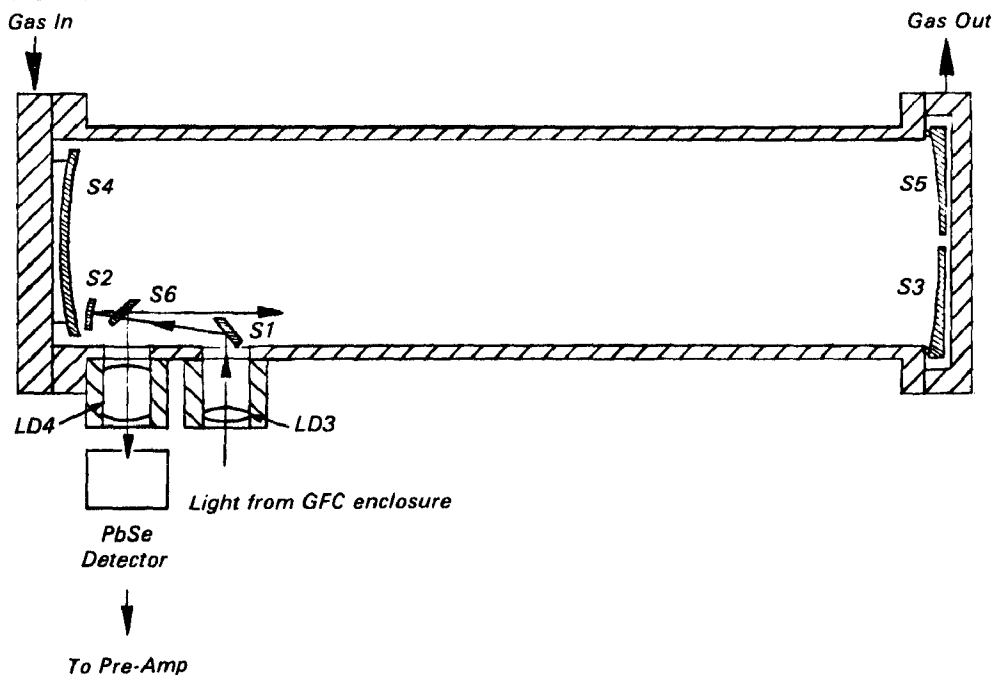


Figure 4. Top view of the optics in the multiple pass CO₂ cell. The CO cell is schematically the same but dimensionally longer and wider.

filled to 550 torr with a mixture of 97.2% CO and 2.8% CO₂. The attenuator side has a semi-circular piece of CaF₂ filling the gap between the sapphire windows so that there is no CO or CO₂ in the beam when it is passing through the attenuator side. The sapphire windows have anti-reflection coatings on the surfaces in the gas side. Reflection from the CaF₂ and sapphire surfaces in the attenuator side attenuate the beam so that the average transmittance is approximately the same as the transmittance through the gas side.

A reticle deposited on the surface of one of the GFC windows has 12 opaque strips and 12 openings to produce a high-frequency chopping rate of 360 Hz. When CO is added to the sample section, it absorbs a fraction of the chopped energy that passes through the attenuator side of the rotating GFC. However, when the gas side of the GFC is in the beam, the GFC absorbs most of the energy at wavelengths where the CO in the sample cell absorbs. Therefore, the addition of CO in the sample cell decreases the energy passing through the attenuator more than it reduces the energy through the gas side of the GFC. Thus, the 360-Hz chopped signal contains a modulation at 30 Hz, the rotational frequency of the GFC. The amount of modulation depends on the product of the

mix the incoming gas with the gas already in the cell. Thus, the gas travels in nearly a "plug flow," which is desirable to reduce the amount of gas required to completely flush out one sample and replace it with a new one.

Two important factors were considered in making the CO₂ cell smaller than the CO cell: (1) less CO₂ than CO is available from the scrubber/catalytic oxidizer to be used with the analyzer; (2) a longer optical path is required for CO than for CO₂ to obtain the desired sensitivity because the CO₂ absorption lines are much stronger than the CO lines. The concentrations of both CO and CO₂ can be monitored either while the gases flow continuously through the cells or when the gas flow is stopped. Zero-settings for both channels are adjusted with zero-gas flushing through the sample cells. High-purity N₂ is normally adequate as a zero-gas for CO₂, but the N₂ frequency contains a few hundred ppb of CO and can, therefore, not be used reliably as a zero-gas for the CO channel. High-purity argon is usually free of a significant amount of either CO or CO₂.

The 2 mm × 2 mm element of each PbSe detector is cooled thermo-electrically to approximately -25°C to increase the sensitivity. The sensitive element is slightly larger than the image formed on it.

Much of the good stability and high sensitivity of the instrument is due to the rotating GFC illustrated in Figure 3. The GFC consists of 2 semicircular compartments divided along a diameter. The gas side is

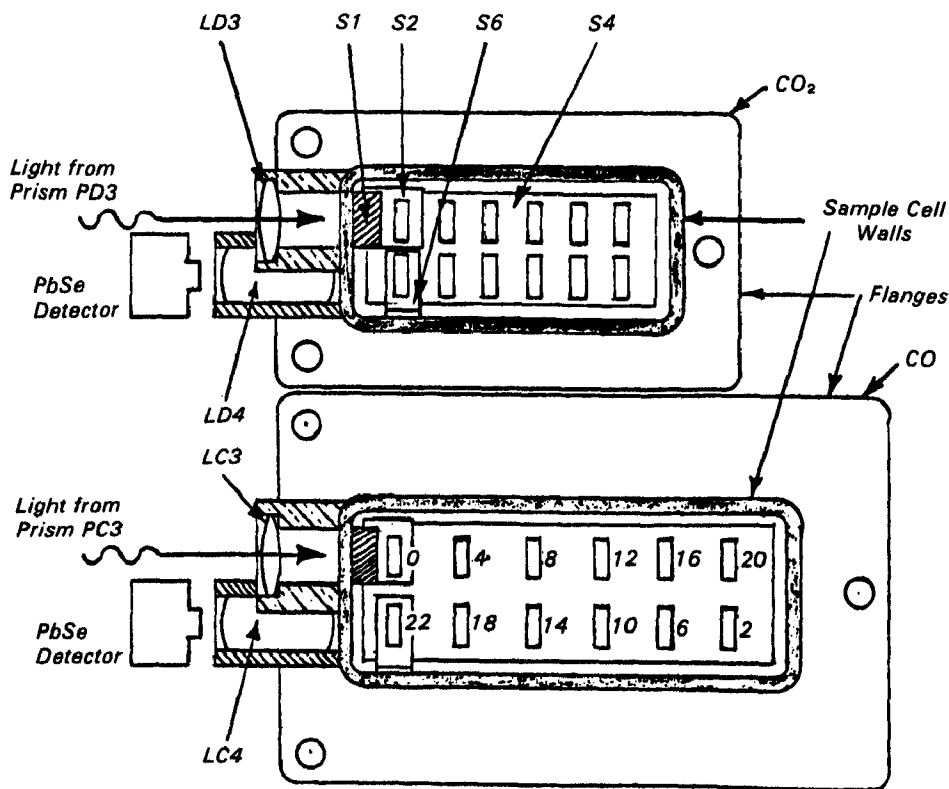


Figure 5. Image patterns on mirrors S4 of the CO₂ and CO sample cells. The relative positions of the two sample cells and detectors are as indicated.

CO concentration and optical path length in the sample cell. The detector signal is processed by the electronics to produce a dc output signal proportional to the fractional modulation of the energy incident on the detector, and thus to the concentration of CO in the sample cell.

Any absorbing gas species other than CO in the sample cell will not produce a 30-Hz modulation if there is no correlation between the spectral structures of the gas and the CO in the GFC. When there is no correlation between the spectral structures, the gas absorbs exactly the same fraction of the energy passing through the GFC as that passing through the attenuator. Thus, under this idealized condition, no 30-Hz modulation is produced and there is no interference in the output signal by the gas. Of course, the instrument cannot operate properly if the absorbing gas absorbs a large fraction of the radiant energy incident on it. Unfortunately, there is usually a small amount of correlation between the spectral structures of the gas species to be detected and another gas that absorbs in the same spectral region. There is a slight positive correlation between the spectral structures of CO and H₂O in the spectral bandpass of the CO channel. Thus, H₂O in the sample produces a small positive interference signal. This slight interference is negligible when the monitor is used for its intended purpose because most of the H₂O vapor is removed by the sample conditioner from the air being sampled.

Conclusions

A prototype non-methane hydrocarbon monitor has been designed and fabricated. The success of the unit in measuring NMHCs in the ambient air has yet to be demonstrated. However, the optical absorption analyzer is similar in design to previous instruments based on gas filter correlation, e.g., the optical absorption monitor for carbon monoxide, methane and water vapor, and should work as well. The unique design of the radiation source and correlation cell extends the usefulness of the gas filter correlation technique to multicomponent analysis. The sample conditioner subunit has three critical components: dryer, CO₂ scrubber and NMHC to CO₂ converter, each of which has been selected after reasonably exhaustive feasibility testing. Based on the feasibility testing, the prototype should be capable of monitoring NMHC and CO at a minimum detectable limit of approximately 0.02 ppm with a 30 second time constant for periods of up to three weeks using a total sample inlet flow rate of 200 cc/min. During the three week period no consumables should be required.

Recommendations

The prototype NMHC monitor should be evaluated using both simulated ambient air and ambient air to establish operational parameters such as the useful lifetime of the CO₂ scrubber, the stability of the "hopcalite" converter, and the noise equivalent concentration of the optical channels. Further testing with other new techniques such as cryogenic trapping followed by flame ionization detection should, if successful, provide the credibility needed to foster general acceptance and use of the technique.

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William McClenny is the EPA Project Officer (see below).

The complete report, entitled "Totally Optical Technique for Monitoring Ambient Non-Methane Hydrocarbons," (Order No. PB 84-152 800; Cost: \$11.50, subject to change) will be available only from:

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