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Project Summary

Ambient Air Non-Methane Hydrocarbon Monitor

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A real-time monitor has been developed for measuring non-methane hydrocarbons (NMHC) in ambient air. The monitor consists of two basic instruments, a methane monitor and a flame-ionization detector (FID). The methane monitor, which is based on gas-filter correlation techniques, makes use of the infrared absorption characteristics of methane to measure its concentration. A slight interference in the measurement of methane by H_2O vapor in the sample air is minimized using an electronic correction derived from a simultaneous measurement of the H_2O concentration. The flame-ion ization detector measures the concentration of the total hydrocarbons (THC), including methane. The concentration of non-methane hydrocarbons is obtained by subtracting the methane concentration from the THC concentration. The noise-equivalent concentrations (peak-to-peak) of the methane monitor and the FID are approximately 50 ppb and 5 ppb of carbon, respectively. The estimated uncertainty in the measurement of a typical low-level NMHC concentration is between 20 ppb and 50 ppb. Concentrations as high as 70 ppm can be measured.

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

Hydrocarbons in the atmosphere play an important role in the production of photochemical smog and are of great interest to atmospheric chemists and to those concerned with air quality. Methane, the most abundant atmospheric hydrocarbon, is essentially non-reactive at the normal ambient concentrations of a few ppm; thus, this gas does not contribute significantly to atmospheric photochemistry. It follows that the quantity of most interest is the concentration of the other hydrocarbons, commonly called non-methane hydrocarbons (NMHC). For some detailed studies, it may be desirable to know the concentration of certain hydrocarbon species, but for many purposes, it is sufficient to know the sum of the concentrations of all the NMHC's.

No convenient and reliable method has yet been developed for routine monitoring of NMHC's. One widely used instrument, the flame-ionization detector (FID), is capable of measuring the concentrations of all the hydrocarbons, frequently called total hydrocarbons (THC). However, this quantity is not the one of most interest because it includes the inert methane, which may constitute from 30 to 90% of the THC.

The Ford Aerospace and Communications Corporation-Aeronutronic Division of Newport Beach, California, with the support of the Atmospheric Chemistry and Physics Division of the Environmental Sciences Research Laboratory, Research Triangle Park, North Carolina, has developed a system for measuring the concentration of non-methane hydrocarbons in an air sample. This program involves coupling a commercially available FID to measure the THC concentration with a custom-designed methane monitor. The NMHC concentration is equal to the difference between the concentrations measured by the two instruments. The methane monitor uses gas-filter correlation techniques and contains a set of multiple-pass optics to give an 845 cm absorption path. Water vapor in the air sample interfers with the methane measurement, giving a false reading that depends on the partial pressure of the H_2O vapor. An infrared H_2O monitor built as an integral part of the methane monitor measures the H_2O concentration; this measurement is used to correct the apparent methane concentration. A diaphragm pump circulates either sample air, bottled zero-gas or bottle span gas through the monitors. The span calibrations of both the methane monitor and the FID are quite stable. Slight drifts in the zero settings of both instruments make it necessary to flush the sample chambers with zero-gas approximately once each hour if the most accurate results are required. The estimated uncertainty in a measurement of a typical NMHC concentration below 1 ppm (parts per million of carbon) is between 20 and 50 ppb (parts per billion of carbon).

Tests and Performance

Results of a few of the tests performed on the entire instrument with the methane monitor and FID coupled together are listed below. Output signals were recorded separately for each monitor and are expressed in terms of ppm of methane. The sample cell of the methane monitor was operated at 2-atm pressure and 50°C.

Performance of Methane Monitor Plus FID

Sensitivity and Noise

(Peak-to-peak noise level with 3 sec electronic time constant)

Methane Monitor: 0.05 ppm
FID: 0.005 ppm

Linearity

Methane Monitor: Linear for concentrations less than 10 ppm, only a slight deviation from linearity for concentrations between 10 to 20 ppm.

FID: Not checked carefully, probably linear to beyond 20 ppm.

Interferences

Methane Monitor: (Without automatic correction) 2.5 percent H_2O produces interference corresponding to approximately +2.4 ppm. (With automatic correction) No interference for 1 percent H_2O. Less than +0.1 ppm for lower H_2O concentrations; approximately 0.2 ppm at 3 percent H_2O.

FID: No significant interferences by normal atmospheric constituents.

Additional topics covered in the main report include: (1) the use of a Perma-Pure Dryer as a means to reduce H_2O interference in methane measurement; (2) the modification of an FID to increase stability; and (3) the electrical and optical designs used in instrument fabrication.

Conclusions

An instrument consisting of a methane monitor combined with a FID can be designed and built with adequate sensitivity and accuracy to monitor ambient NMHC concentrations under most conditions of interest. The low concentrations of hydrocarbons make it necessary that both of the instruments be very sensitive and stable. It is desirable that the instruments be kept in a temperature controlled room and the sample air be drawn in from the outside through a heated line. Care must be exercised to avoid contaminating air samples and calibration gases or losing hydrocarbons on the walls of the gas handling system. Activated charcoal filters in the fuel line and combustion-air line of the FID remove any residual hydrocarbons in these gases and lead to greatly improved instrument stability. A single pump of the proper design can circulate the air sample through both the methane monitor and the FID. No changes in the hydrocarbon concentration of an air sample appear to take place when it passes through a diaphragm pump with the interior Teflon coated and properly cleaned copper tubing heated to approximately 50°C.

A standard sensor (combustion chamber plus electronics) for a FID provides adequate sensitivity when operated with a convenient fuel mixture of 40% H_2 + 60% He. The short-term peak-to-peak noise (period less than 10 sec) can be made less than the equivalent of 5 ppb of methane for the FID and less than 50 ppb of methane for the methane monitor. Longer-term drift of the zero-settings of the instruments normally leads to uncertainties in the measurements that are somewhat larger than those imposed by noise unless the drift is accounted for by flushing the sample chambers once every few minutes with zero-gas. Stability of the methane monitor is improved greatly by controlling the temperatures of the sample cell, band-pass filter, and gas-filter cell of the methane monitor.

Interference by H_2O in the air limits the accuracy of the methane monitor unless most of this gas is removed from the air before it enters the methane sample cell. One acceptable method of accomplishing this is to pump the air through a Perma-Pure Dryer before it enters the methane sample cell. Air going to the FID should by-pass the dryer to avoid possible adsorption of some of the complex hydrocarbons on the walls of the dryer. The H_2O interference can also be accounted for by measuring the H_2O concentration in the methane sample cell and applying a correction based on interference data obtained previously with samples of H_2O plus clean air.

Recommendations

Additional tests should be carried out with the instrument under a variety of laboratory and field conditions to gain more information about the detailed performance. After these tests have been completed, a prototype instrument should be designed and built to operate on the same basic principles as the present instrument. This instrument should include a FID to measure THC concentrations and a methane monitor that employs gas-filter correlation techniques.

The following features and procedures are recommended for the prototype instrument. Many of these features are included in the present instrument and have proven to be desirable; others are recommended as a result of knowledge gained while assembling and testing the present instrument. Important features of the present instrument that are not mentioned below should be included.

1. Package both the FID and methane monitor into a single unit.

2. Use the combustion chamber from a commercially available FID with combustion fuel of 40% H_2 and 60% He.
3. Pump sample air through heated lines to both the methane monitor and the FID with a single diaphragm pump capable of producing pressures up to 5 atm. Split the gas flow so that the gas to the FID does not pass through the methane sample cell. Include in the line to the FID a small "delay tank" so that at a given time the FID is sampling air that entered the inlet line over the same period of time as the air in the methane sample cell.
4. Pass the air to the methane sample cell through a dryer such as a Perma-Pure Dryer to remove most of the H_2O vapor and thus reduce the interference by this gas in the measurement of methane concentration.
5. Employ activated charcoal filters, or some substitute, in the lines for the combustion-air and fuel.
6. Operate the sample cell of the methane monitor between 3 atm and 5 atm to increase sensitivity and reduce interference due to residual H_2O. This also improves the efficiency of a dryer similar to the Perma-Pure Dryer.
7. Decrease the volume of the methane sample cell and use multiple-pass optics in the cell to obtain a sample path length between approximately 8m and 15m.
8. Shape the sample cell to reduce the volume while passing approximately the same amount of radiation in the monitoring beam as the present instrument.
9. Control the temperatures of: (a) methane gas-filter cell, (b) spectral bandpass filter for methane monitor, (c) methane sample cell, and (d) regulators, valves, tubing, etc., that are parts of the FID. Heat gas lines, including the dryer, to approximately 50°C; it is not necessary to control the temperature of these lines.
10. Include electronics to measure directly the difference between the output signals of the FID and methane monitor; this voltage is proportional to the NMHC concentration.

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The complete report, entitled "Ambient Air Non-Methane Hydrocarbon Monitor," (Order No. PB 81 120-008; Cost: $6.50, subject to change) will be available only from:
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650
The EPA Project Officer can be contacted at:
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