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TECHNICAL REPORT NO. 11940

TRANSFER OF THERMAL ENERGY TO SELECTED VIBRATIONAL BANDS IN THE INFRARED

September 1974

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by Edgar B. Singleton

Department of Physics
Bowling Green State University
Bowling Green, Ohio 43403

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ABSTRACT

Molecular gases are considered as possible additives to the exhaust stream of internal combustion engines with the purpose of transferring thermal energy of the exhaust gases to vibrational energy of the additives in order to reduce the temperature of the exhaust gases and the manifold system.

The gases considered are carbon dioxide (CO_2), bromotrifluoromethane (Halon 1301, $CBrF_3$), vapor from ethylene glycol coolant solutions, and in some cases air and nitrogen. These gases are introduced into the exhaust stream of a hydrocarbon burner specially constructed for use in the laboratory. Emission spectra in the infrared region from 2μm to 16μm are presented for the heated exhaust gases and parts of the exhaust port. $CBrF_3$ is the only additive, of those presented, which produces a sufficient effect within the criteria established to warrent further study.

FOREWARD

The work presented here was carried out at Bowling Green State University, Department of Physics, between 22 April 1974 and 30 September 1974, under the supervision of the Engineering Science Division, Army Tank-Automotive Command, under Contract No. DAAE07-74-C-0153.

This work is under the general category of Vehicle Countersurveillance Studies and in particular aims at supression of the infrared signature characteristics of exhaust gas-manifold systems.

Recommendations are made concerning the continuation of certain parts of the work.

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NARRATIVE

Objective

The over-all objective of the research reported here is to reduce the infrared signature characteristics of vehicles powered by internal combustion engines.

Specifically, we want to transfer thermal energy from the exhaust gas-manifold system to energy associated with the vibrational modes of selective additive gases. The vibrationally excited additives are subsequently exhausted into the atmosphere where they emit radiation characteristic of the vibrational modes of the molecules. The additive gases are chosen on the basis of the following criteria:

1. The excited vibrational modes must be in a wavelength region which is difficult to detect, for either of two reasons: low detector sensitivity or atmospheric absorption. Low detector sensitivity is considered to be wavelengths longer than $5.0\mu m$. High atmospheric absorption is considered only in the $4.3\mu m$ CO_2 band and the $6.3\mu m$ water vapor band.

2. The additive gases must be readily available and preferably already carried aboard the vehicle for other purposes.

3. The excitation of the molecules must produce no toxic effects.

Physics Background

The thermal energy of gases on a simple kinetic theory basis is thought of as the kinetic energy associated with the random violent translational motion of the molecules as they collide with one another and the walls of the container. As energy is added to or taken from this system the average kinetic energy per molecule (or per mole) increases or decreases. It can be shown that, for a monatomic gas, the average kinetic energy per atom is $\frac{3}{2}kT$ where k is Boltzmann's constant (1.38×10^{-23} joule/K^o) and T is the absolute temperature. The average kinetic energy of the gas is thus proportional to the absolute temperature.

Diatomic and polyatomic gases have vibrational and rotational motions which contribute to the internal energy of the molecule in addition to any kinetic energy associated with random translational motion. The vibrational-rotational modes are quantized and represent a deparure from simple kinetic theory. The vibration-rotation mode can be excited by collision under certain conditions; the quantum condition being that sufficient energy is available in the collision to excite the quantized energy transition associated with the vibration-rotation mode. Even if this minimum energy condition is met, not all collisions result in energy transfer to the vibrational mode. For instance, the time in which the collision takes place must be short compared to the period of vibration. This implies that high speed collisions (thus, high kinetic energy and high temperatures) are more efficient in energy transfer to vibrational modes.

If the temperature of the gas is such that the average kinetic energy per molecule ($\frac{3}{2}kT$) is equal to the energy required by the quantized vibrational transition, a significant number of transitions may take place. For instance at 527°C (800°K), $\frac{3}{2}kT$ is 0.1 eV which corresponds to a wavelength of 10.4 μm in the infrared region of the spectrum. Many molecules have vibration-rotation bands in this spectral region which may be excited by temperatures of this order of magnitude.

Experimental Procedures and Results

The experimental work was divided into three sections, described briefly here and in more detail to follow.

Section I	Selection of possible gases to be used as additives.
Section II	Recording emission spectra of the selected gases when heated alone and mixed with air.
Section III	Recording emission spectra of the selected gases when heated by exhaust gas-manifold system.

Section I

Selection of possible gases to be used was based primarily on the criterion of availability aboard the vehicle. The following substances have been considered. Carbon dioxide (CO_2), bromotrifluoromethane ($CBrF_3$), liquid coolant solutions (ethylene glycol plus water), pure water and air.

Carbon dioxide was chosen because it is a common fire extinguisher and at the same time its primary vibration band of interest is strongly absorbed by carbon dioxide in the atmosphere.

Bromotrifluoromethane is the chemical name for Freon 13B1, a refrigerant and Halon 1301, used as a fire extinguishing agent. The Halon 1301 is simply a more purified form of $CBrF_3$ than Freon 13B1.

Liquid coolant solutions of ethylene glycol and water (plus anti-rust additives, etc.) are standard solutions used in most liquid cooled engines.

Pure water is considered because its emission bands would be strongly absorbed by atmospheric water vapor.

Air is considered only because of its thermodynamic cooling effect. The concentration of molecules with suitable vibration bands is very small in air.

Figure 1 is for identification purposes. It shows laboratory absorption spectra of CO_2, $CBrF_3$, ethylene glycol liquid and, for reference purposes, a solar spectrum which shows the large water vapor absorption in the $6.3\mu m$ region. Two strong absorption bands in $CBrF_3$ are noted at $8.3\mu m$ and $9.2\mu m$ and one weaker band at $7.7\mu m$. These particular bands are noted here for future reference.

Section II

Emission spectra of the selected gases were obtained using two procedures. The gases were heated in a 10 cm cell with a rock salt window in one end and a blackened disc in the other end. The blackened disc serves as an approximation to a perfect black-body

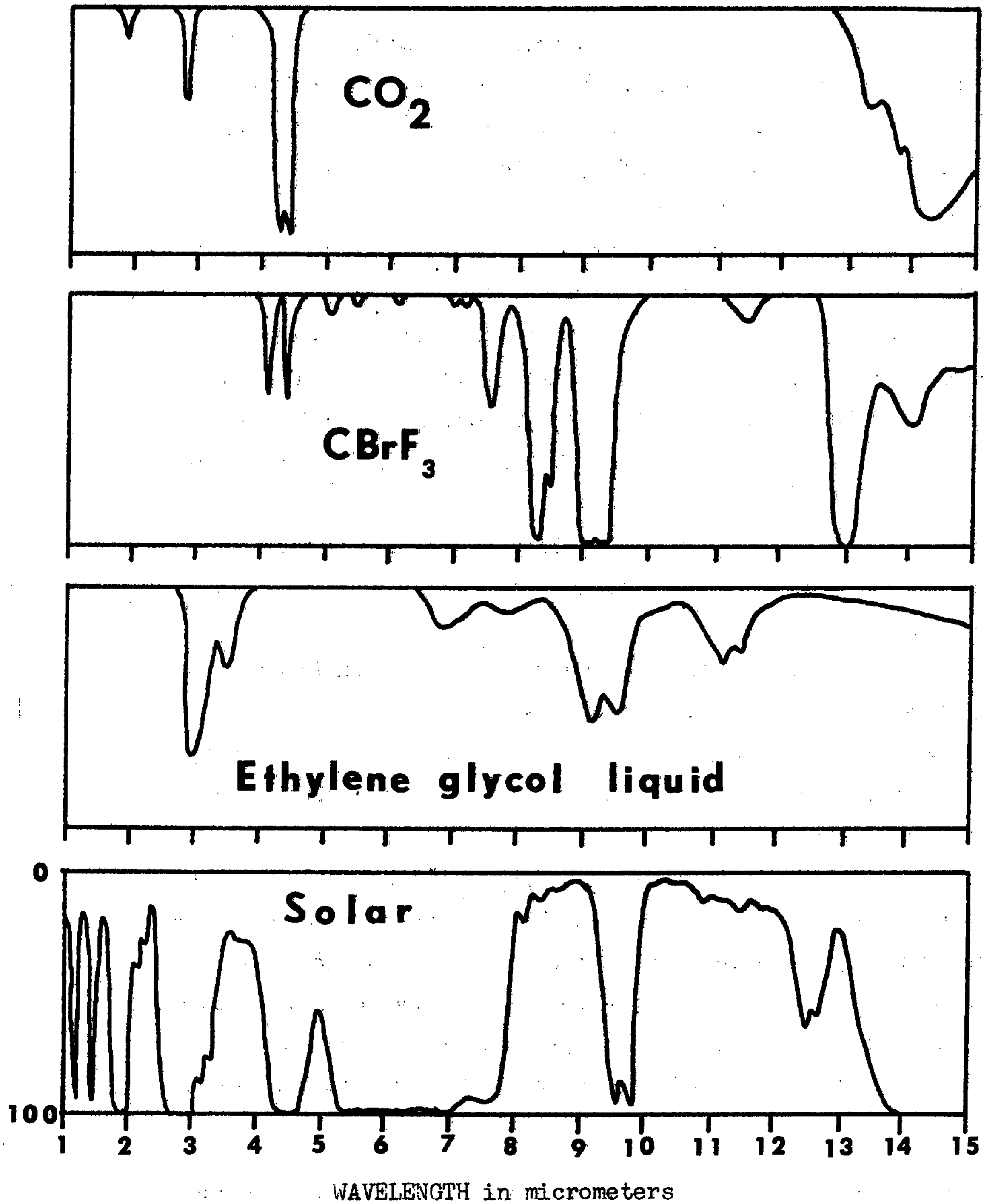

Figure 1

Absorption Spectra of Selected Gases and a Solar Spectrum radiator at the temperature of the gas. The maximum practical temperature available in this cell is 200°C (473°K). The second method of obtaining emission spectra was to allow the selected gases to pass through a heated and baffled flue pipe. The gases were heated as they passed around the baffles and exited at the top of the flue pipe into the atmosphere to be observed by the spectrometer. The temperature of the gas at the top of the flue pipe was measured by an iron-constantan thermocouple.

Figure 2 shows schematic diagrams of the two emission cells. Figure 3A shows a background emission spectrum from the evacuated 10 cm cell with radiation from the blackened end being absorbed by atmospheric molecules. Superposed on the background spectrum is the emission spectrum of $CBrF_3$. In Figure 3B these spectra are reduced to emission of $CBrF_3$ as a percentage of the background. Note that emission predominates in the wings of the bands where absorption is weak. At the center of the bands (approximately $8.3\mu m$ and $9.2\mu m$), where absorption is strong, absorption predominates, even when the $CBrF_3$ is heated to 200°C.

Figure 4 is a representation of emission spectra from $CBrF_3$ at the top of the heated flue pipe. The several superposed spectra represent several flow rates. Again, the centers of the strong absorption bands at $8.3\mu m$ and $9.2\mu m$ show a net absorption while the relatively weak absorbing wings of these bands show a net emission. A relatively weak band at $7.7\mu m$ shows net emission even at the band center. At the highest flow rate shown, the net emission from the entire group of bands begins to decrease as the relative number of non-excited molecules increases at the exit port of the flue pipe.

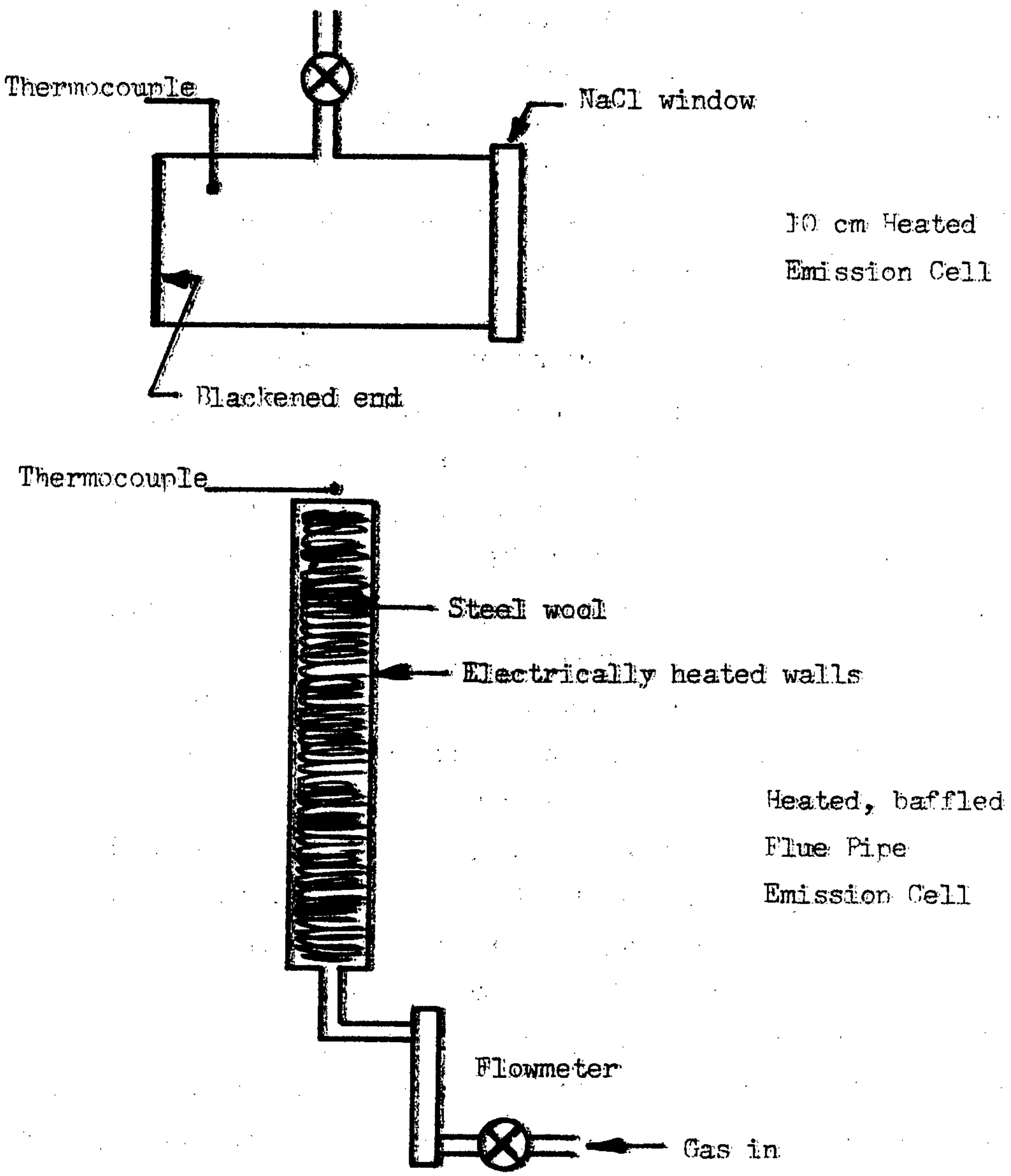

Figure 2

Schematic Diagrams of Emission Cells

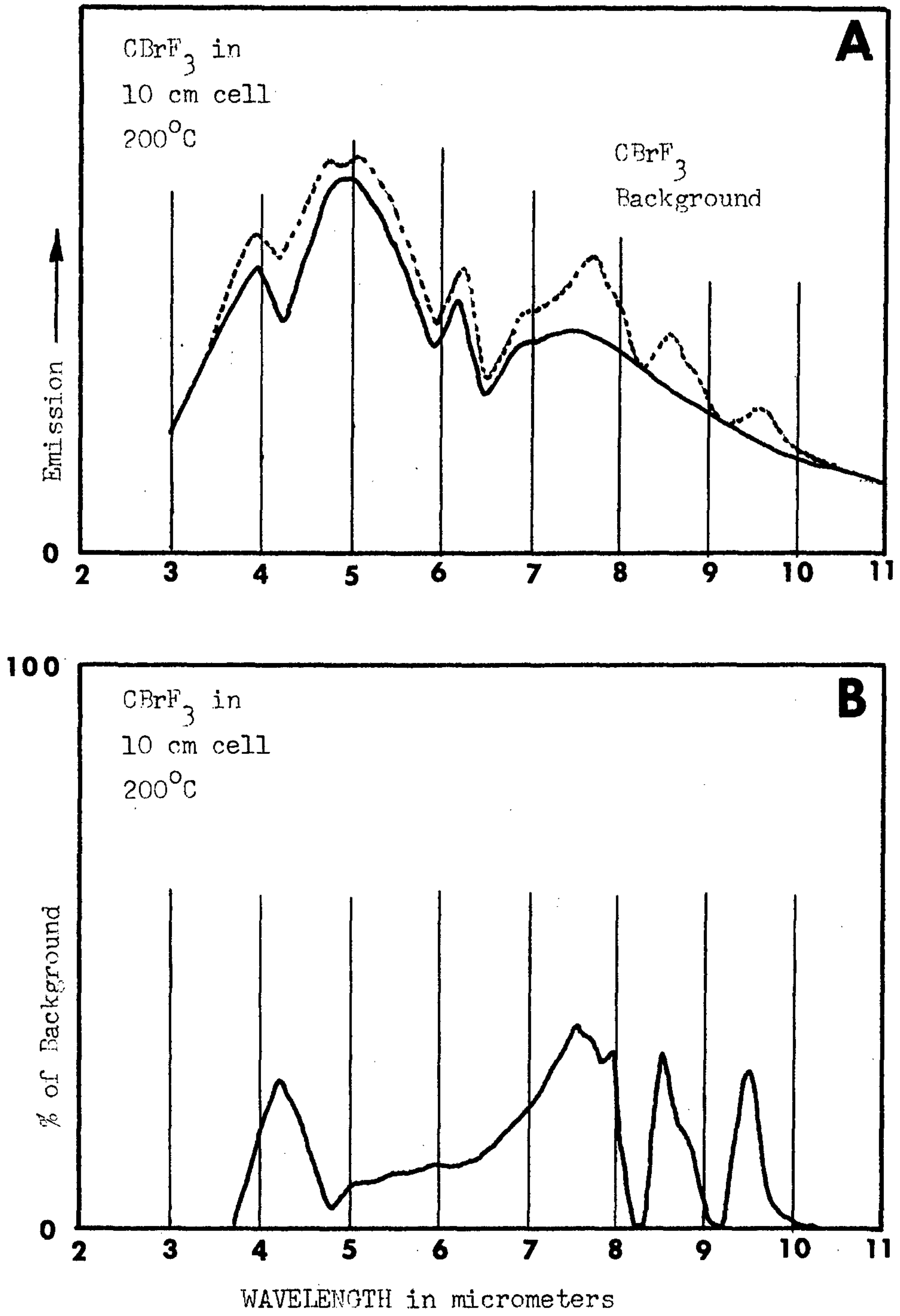

Figure 3

Emission Spectra of $CBrF_3$ in 10 cm Cell at 200°C

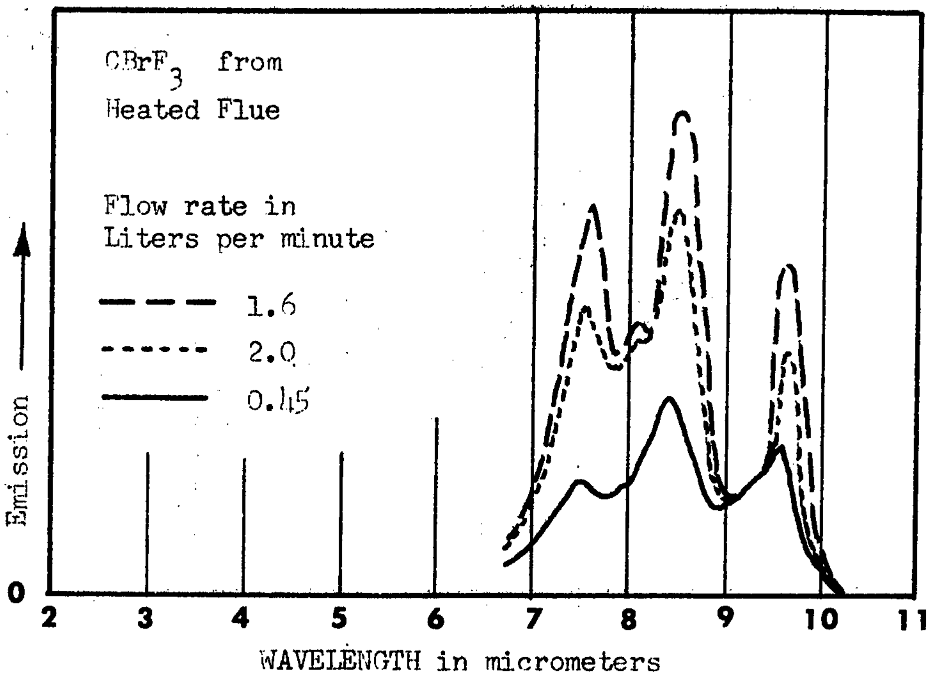

Figure 4

Emission Spectra of $CBrF_3$ from Heated Flue

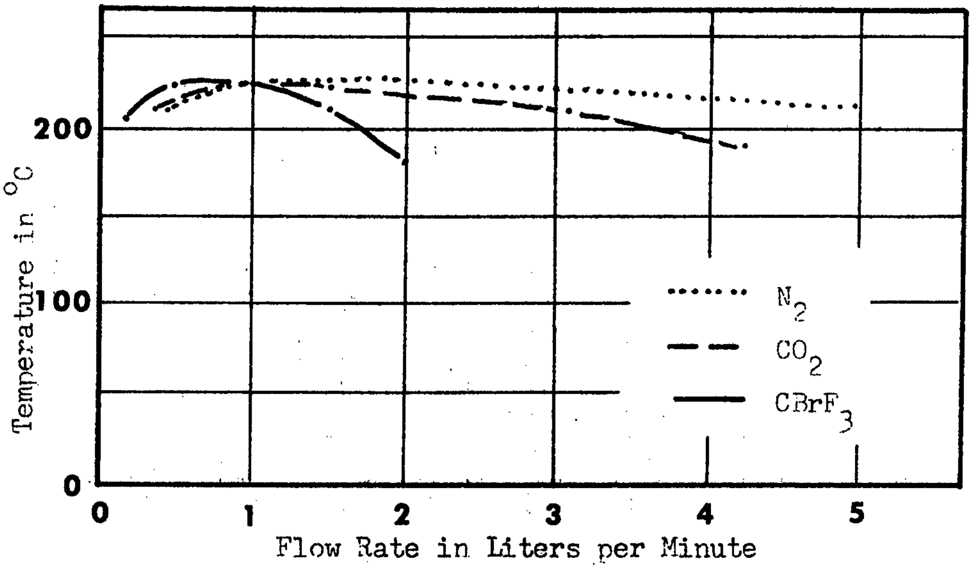

Figure 5

Temperature of Gas at Top of Baffled Flue Pipe versus Flow Rate of Gas Through the Pipe

Figure 5 is a plot of the temperature of the heated gases at the exit port of the flue pipe versus flow rate. Figure 5 shows temperatures for $CBrF_3$, CO_2 (the emission spectra of which will be discussed next) and nitrogen as a molecular gas with no infrared active bands. At low flow rates the temperature data are inconclusive because it is difficult to attach a meaning to temperature as measured by the thermocouple when, at low flow rates, the interaction between the thermocouple and its steady state surroundings is probably more significant to the measured temperature than the interaction between the thermocouple and the heated gases at low flow rates. Two other points should be mentioned in connection with Figure 5. The relatively low flow rate shown for $CBrF_3$ is simply the result of the flow meter available being unable to register a higher flow rate for $CBrF_3$ than that indicated. The flow rates for all the gases are measured on the same flow meter but the relatively high molecular weight of $CBrF_3$ (149) reduced the range of the flow meter for this gas. A second point is that the relative temperatures for a constant flow rate can be understood on the basis of heat flow. Molecular weight times specific heat at constant pressure is a measure of heat required to raise the temperature of a given volume of gas one degree. At a constant flow rate (say, 2 liters per minute) a constant volume of gas passes through the heater in unit time. Molecular weight times specific heat for the three gases shown in Figure 5 have the following (approximate) values: N_2-7 , CO_2-9 , $CBrF_3$-16.

Figure 6A shows a background emission spectrum from the evacuated 10 cm cell and superposed on this background spectrum are emission spectra of CO_2 near the $4.3\mu m$ region of the infrared spectrum. In figure 6B these spectra are reduced to emission of CO_2 as a percentage of the background. Unlike the strong absorption bands of $CBrF_3$, this "strong" CO_2 band shows a predominate emission at all wavelenghts over the band.

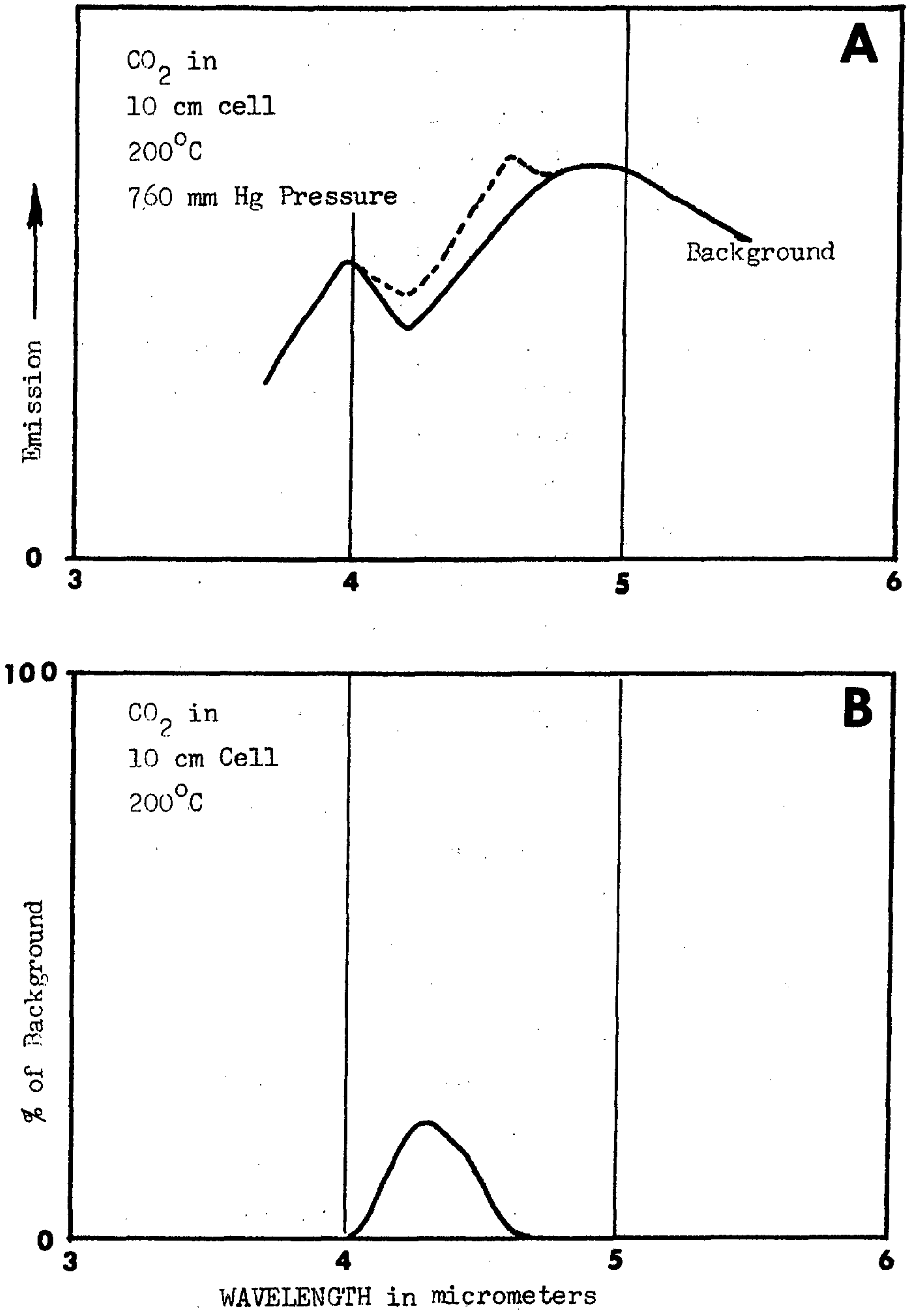

Figure 6

Emission Spectra of CO_2 in 10 cm Cell at 200°C

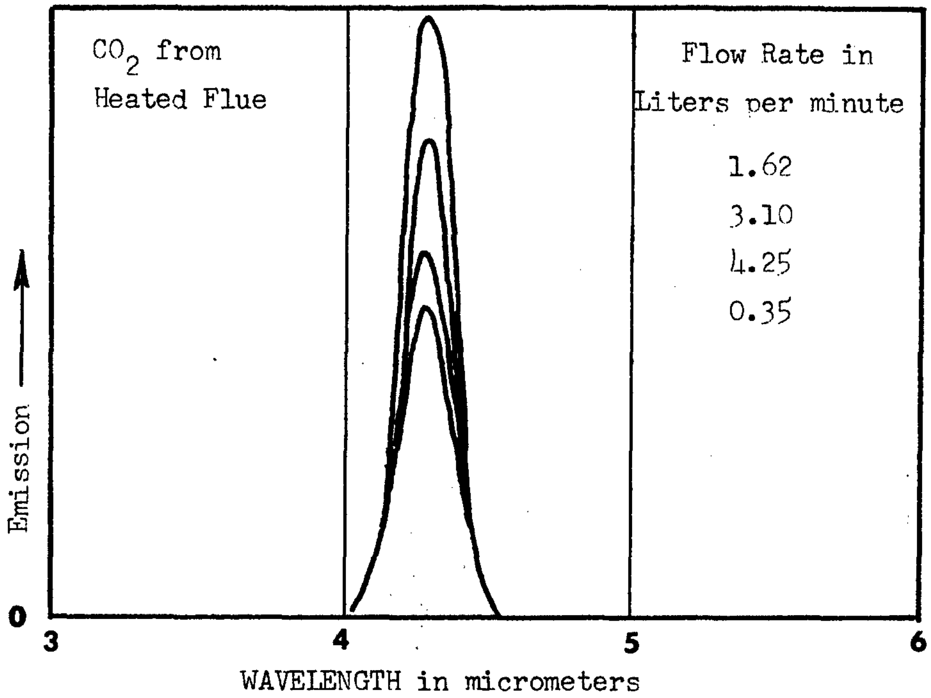

Figure 7

Emission Spectra of CO_2 at Top of Heated Flue

Figure 7 is a representation of emission spectra from CO_2 at the top of the heated flue pipe. The several superposed spectra represent several flow rates. At the highest flow rate shown the net emission from the band begins to decrease as the relative number of unexcited molecules increases at the exit port of the flue pipe.

No emission spectra could be obtained from the vapor of the ethylene glycol cooling solution. The vapor pressure of the solution was about 2 mm Hg at room temperature. When heated to 200°C no emission spectra were observed from this vapor. Efforts to raise the vapor pressure by heating the solution were abandoned because regions of the apparatus could not be heated and the vapor pressure would be limited to the coldest point in the apparatus. Ethylene glycol was introduced into the heated flue pipe as a liquid with nitrogen used to carry the heated vapors out of the exit port. Emission spectra were difficult to observe and an objectionable smoke was observed as the solution was vaporized in this manner.

Section III

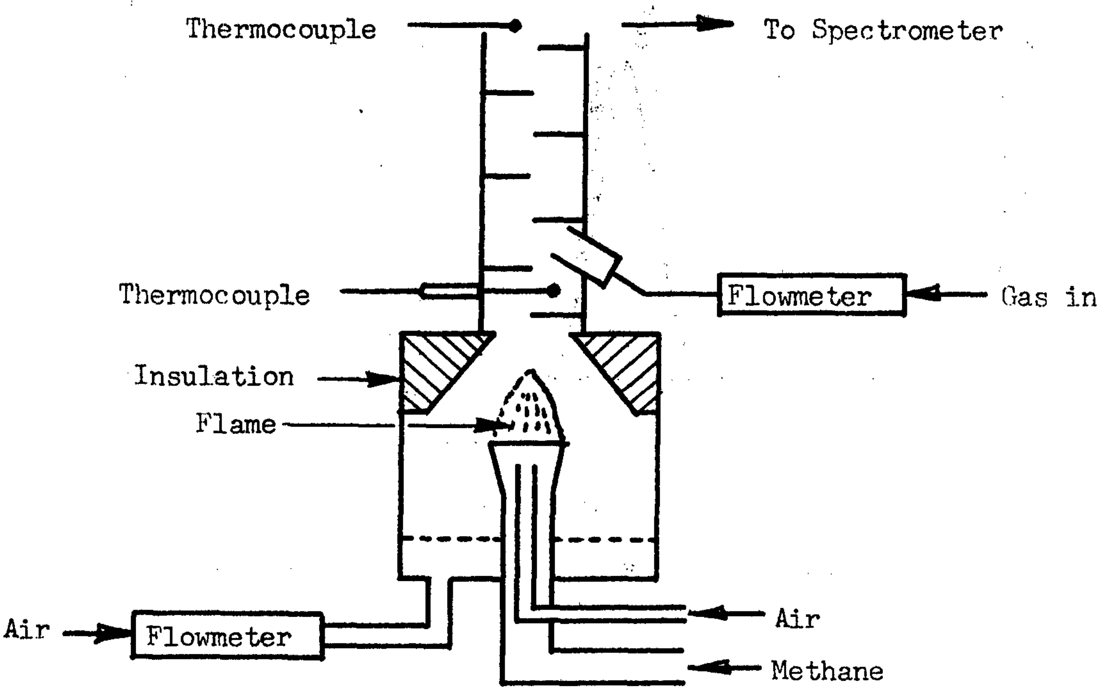

Figure 8

Schematic Diagram of Closed Burner System and Baffled Muffler

Figure 8 is a schematic diagram of the closed hydrocarbon burner used in the present work. The products of combustion yield an exhaust stream which then passes through a baffled manifold-muffler system into the atmosphere. Selected gases are introduced into the exhaust stream to be heated by the molecules of the products of combustion of the burner and the manifold-muffler system. The heated gases at the exit port of the muffler can be examined with an infrared spectrometer and the exit port itself can be observed as a background with the heated gases superposed on the background spectrum.

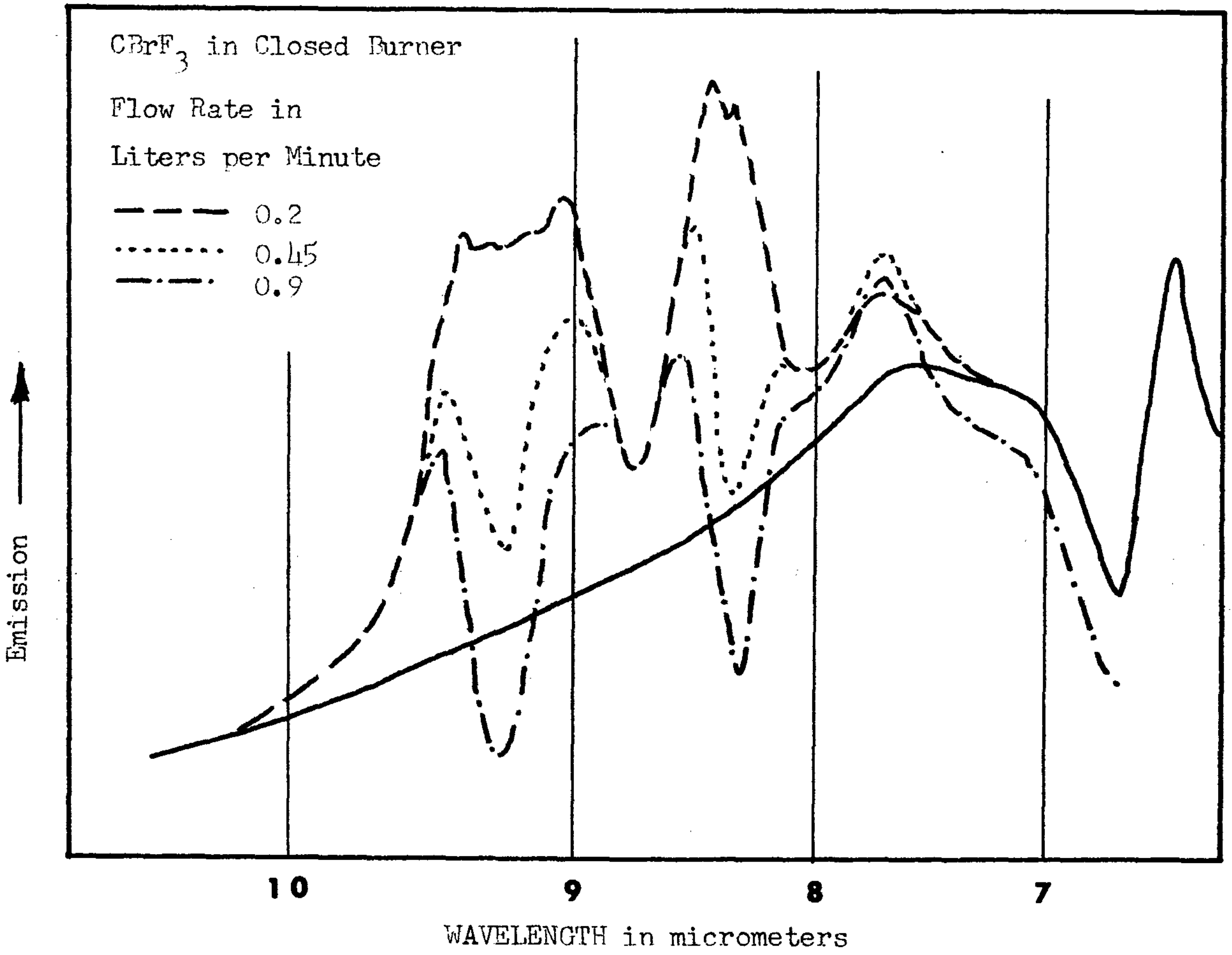

Figure 9

Emission Spectra of $CBrF_3$ from Closed Burner System

Figure 9 shows a background spectrum of the exit port of the muffler. Atmospheric water vapor and CO_2 in the optical path of the spectrometer appear as absorption on this background spectrum. The wavelength of the maximum emission of a black-body curve as estimated from this background spectrum yields an approximate temperature of the exit port as 200°C. The temperature of the exhaust stream as it enters the muffler is measured as 525°C.

Superposed on the background spectrum is the emission spectrum of $CBrF_3$ at several flow rates. The data (spectra) are consistant with the following description: at low flow rates the discharged gases are relatively hot and even the centers of the strong absorption bands show a net emission. As the flow rate increases, the discharged gases become cooler and the center of the bands begin to absorb. Emission over the background now occurs only in the wings where absorption is weak. As the flow rate increases further, absorption at the band center now occurs even below the original background level of emission and cooling of the exit port is evident by the lower background level outside the limits of the $CBrF_3$ bands.

Figure 10 is similar to Figure 9. It covers a wider range of wavelengths and shows spectra of $CBrF_3$ and CO_2. Figure 10 shows a background spectrum which includes the heated exit port of the closed burner system and the normal products of combustion. The temperature of the exhaust gases for the background spectrum is 150°C. Superposed on this background spectrum are spectra which occur as a result of adding $CBrF_3$ and, separately, CO_2 to the exhaust stream at identical flow rates. The temperature of the exhaust stream with CO_2 added is 134°C. With $CBrF_3$ added the temperature of the exhaust stream is 107°C. The lower temperature produced by the addition of $CBrF_3$ is evidenced in the spectra of Figure 10 by the lower general level of emission at all wavelengths except in the very strong $CBrF_3$ bands where some net emission occurs in the wings of the bands.

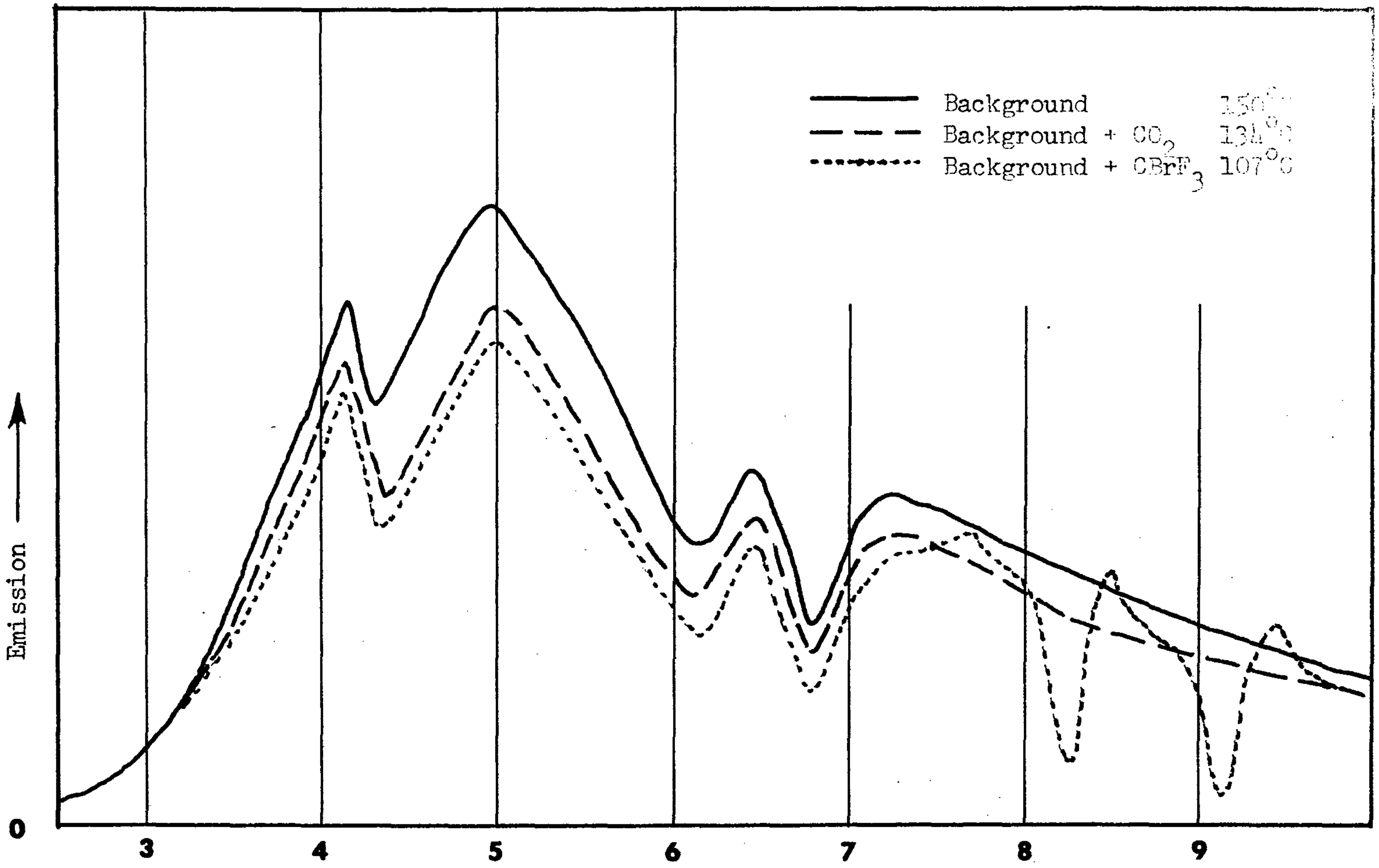

Figure 10

Emission Spectra with $CBrF_3$ and CO_2 added at the Same Flow Rate to Exhaust Stream of Closed Burner System

No emission spectra from aspirating ethylene glycol cooling solutions into the exhaust stream from the closed burner could be obtained. As previously described in Section II (page 11) objectionable smoke issues from the exit port and no further efforts were made to understand the origin of the smoke or possible methods of eliminating it.

Conclusions and Recommendations

On the basis of the data presented in this report it is apparent that $CBrF_3$, of the substances considered, is most efficient at reducing the temperature of exhaust gases. This is partially due to the high heat capacity of $CBrF_3$ and partially due to excited vibrational energy levels. The data do not separate the relative effectiveness of the two processes.

It is recommended that further laboratory work be done to refine the data presented in this report. Specifically, only $CBrF_3$ and CO_2 should be considered, along with N_2 as a non-infrared active gas. More precise thermometry should be employed and differently designed laboratory mufflers should be used to study and evaluate thermal equilibrium conditions existing within the muffler.

At the same time, actual vehicle exhaust systems should be instrumented to make preliminary evaluations of temperature reduction under field conditions along with flow rates necessary to produce these reductions. It is possible that under actual conditions the flow rate required to produce the desired temperature reduction will be prohibitively high.

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The gases considered are carbon dioxide (CO_2), bromotrifluoromethane (Halon 1301, $CBrF_3$), vapor from ethylene glycol coolant

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