Interferences with Measurements of CO, CO_2, and O_2 in Woodstove Flue Gases

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(ABSTRACT)

Concentrations of CO, CO_2, and O_2 in woodstove flue gases are some of the measured inputs required by algorithms used to calculate woodstove efficiency by the stack loss method. Since these algorithms have been shown to be very sensitive to small errors in these input values, it was necessary to determine whether measurements of these compounds are subject to interference.

Concentrations of CO, CO_2, and O_2 in a series of flue gas samples were measured using a variety of independent measurement techniques for each compound. The concentrations indicated by each of the measurement techniques for each compound and sample were compared to check for agreement. Disagreement among the measurement techniques for a given compound could indicate interference if some trend could be established. Tests were conducted on four samples taken randomly during each of three stove firings.

Since flue gases contain a large number of hydrocarbons, some of these compounds might absorb IR radiation at wavelengths coincident with CO_2 or CO, which would cause interference with infrared gas analyzers used to monitor these compounds. Therefore, IR absorption spectra were generated to identify constituents of the flue gas stream.

No evidence of interference with O_2 measurements was found. CO and CO_2 measurements showed considerable disagreement among the techniques used to monitor these compounds, but offered no clear evidence of interference. Interpretation of IR absorption spectra showed only CO, CO_2, CH_4, and C_2H_4 were present in sufficient quantities to be identified by IR spectroscopy.

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I. Introduction

The recent resurgence in the popularity of woodstoves as residential heat sources has enhanced the need for a standard test method for efficiency measurements on these devices. The determination of woodstove efficiency using the stack-loss method is preferable to the calorimeter room method because the stack loss method is relatively simple and has the ability to provide more information about the combustion process (1). However, it has been observed that the algorithm (proposed ASHRAE standard 106P) used to calculate woodstove efficiency by the stack-loss method can be very sensitive to small errors in input values for concentrations of CO, CO_2, and O_2 (2,3). These investigations show tha deviations in the input values for concentrations of CO, CO_2, and O_2 (with nominal concentrations of 0.4%, 5.0%, and 15.2%, respectively) of just 0.2 mole percent can cause deviations in the calculated efficiency of more than 10% (with nominal efficiency of 68.5%). Thus even small errors (less than 0.2 mole percent) in the measured concentrations of these compounds can cause considerable error in calculated efficiencies. For this reason it is desired to ascertain the accuracy with which measurements of these compounds can be made.

One possible cause of systematic errors in the measurements of CO, CO_2, and O_2 in woodstove flue gases is the presence of interfering compounds. The objective of this investigation is to determine whether these measurements are subject to interference.

If the analyzers used to measure CO, CO_2, and O_2 concentrations in flue gases report the actual concentrations of these compounds, no interference is indicated (assuming the absence of random error). Differences between the actual and reported concentrations, however, could indicate interferences if some trend in these differences could be established. But the actual concentrations of CO, CO_2, and O_2 in woodstove flue gases cannot be known without uncertainty, so such a comparison is not possible.

The fact that each of these compounds can be measured by a variety of techniques presents a means by which any interferences might be exposed. Since it is unlikely that each method would be susceptible to interference to the same degree, comparison of the readings obtained from a variety of measurement techniques for each of the three compounds of interest might yield evidence which could confirm the presence or absence of interferences with these measurements. Therefore, concentrations of CO, CO_2, and O_2 in woodstove flue gases were each measured by various methods and compared to check for indications of measurement interferences.

Due to the unsteady nature of wood combustion, the compositions of both fuel and exhaust products change continuously throughout the burn cycle. Thus if interfering compounds are present at any time during the burn cycle, their presence may be dependent upon the point during the burn cycle being examined, or even the burn rate of the fuel. For this reason samples of flue gas were drawn from the stack at four points during each of three burn cycles. Each burn cycle was conducted at a different burn rate.

Carbon monoxide was measured using a nondispersive infrared gas analyzer, a gas chromatograph, and an orsat apparatus. Oxygen was measured using a paramagnetic analyzer and an orsat apparatus. Carbon dioxide was measured using two types of nondispersive infrared analyzers, a gas chromatograph and an orsat apparatus. The readings obtained from these instruments for the twelve samples drawn were converted into indicated concentrations of CO, CO_2, and O_2 using a set of carefully-prepared calibration curves. The resulting indicated concentrations were then examined for agreement or disagreement among the various analyzers for each sample drawn.

The use of nondispersive infrared analyzers for measurements of CO and CO_2 suggested the possibility of interference with these measurements by hydrocarbons in the flue gases, since all hydrocarbons absorb energy in the infrared region. Therefore IR absorption spectra of the flue gases were generated and used to identify constituents of the flue gases which could interfere with the NDIR analyzers.

This thesis begins with a review of the literature concerning various types of instrumentation for the analysis of CO, CO_2, and O_2, sample conditioning considerations, and interpretation of infrared absorption spectra. The literature review is followed by an explanation of the instrumentation used, its arrangement for carrying out the stack gas tests, and the procedures followed to calibrate the instruments and perform the stack gas tests. It also describes the method and reasoning behind the reduction and interpretation of the test results. The last three sections present and discuss the results of these tests in detail, present the conclusions of this work, and offer some recommendations.

II. Literature Review

2.1 Measurement Techniques and Interferences

Several techniques are available for the measurement of CO, CO_2, and O_2 in gas mixtures. This section is a review of the most common methods and discuss their respective suitabilities for use in the analysis of woodstove flue gases.

Verdin (4) has compiled an extensive survey of gas analysis instrumentation, and suggests a number of methods for CO, CO_2, and O_2 determination. These methods include catalytic filament methods for CO and O_2 measurement, paramagnetic analysis for O_2 measurement, infrared absorption for CO and CO_2 measurement, interferometry for CO_2 measurement, and mass spectrometry and gas chromatography for measurements of all three compounds of interest here. Unless otherwise noted, the discussion of each of these measurement techniques (which will occur in the order shown above) is based on information supplied by Verdin's text.

Carbon monoxide can be measured using a catalytic filament placed in a flowing sample gas stream. The combustible compounds are oxidized, and the heat of combustion causes an increase in the temperature, and therefore the resistance, of the filament which can be monitored and correlated to the concentration of combustibles in the sample. Unfortunately, this device measures total gaseous combustibles, of which CO is but a part in woodstove exhausts, and interference with this method is assured.

Catalytic filaments can also be used to measure oxygen content. Low O_2 and high combustibles levels create a situation in which the output of a filament will depend on the quantity of oxygen present, the combustion being oxygen-limited. However, this low O_2/combustibles ratio does not typically exist in woodstove flue gases. A continuous flow of a combustible gas, such as hydrogen, could be mixed with the sample gas to lower the O_2/combustibles ratio, but the careful monitoring of flow rates of H_2 and sample gas required for this could be problematical. This type of analyzer was widely used, but has been largely replaced by paramagnetic analysis.

Paramagnetic oxygen analyzers can be classified into three main groups: thermomagnetic or paramagnetic wind, paramagnetic pressure, and paramagnetic susceptibility. Paramagnetic wind analyzers utilize a cell containing a heated element in a strong magnetic field through which the sample gas flows. The temperature of the element is held constant. The paramagnetic gas is attracted to the magnetic field where it is heated by the element. As the gas is heated its paramagnetic susceptibility decreases, and it is displaced by colder, more susceptible gas. Thus a continuous flow or "magnetic wind" of gas is established which cools the heated element. The flow rate of the gas across the element depends upon the temperature and the strength of the magnetic field, both of which are fixed, and the paramagnetic susceptibility of the gas, which is proportional to the oxygen content. However, other gas properties affect the heat transfer from the element to the sample gas, so that a change in the composition of background gases could cause interference. Thus paramagnetic wind analyzers are limited to measurement of O_2 in binary mixtures or mixtures of constant background properties, situations which do not exist in woodstove flue gases. Paramagnetic pressure analyzers use the increase in pressure produced when a more magnetic substance is attracted to a magnetic field occupied by another substance. This method depends only on the susceptibility of the sample, and is therefore not affected by properties of other gases in the sample. The pressure and temperature of the sample could affect the output of this instrument and should be held constant for all measurements. Paramagnetic susceptibility analyzers measure the susceptibility of a gas directly, and thus the oxygen content of the sample. A typical paramagnetic susceptibility analyzer uses a pair of nitrogen-filled glass spheres mounted at the end of a thin bar, forming a dumbbell. This dumbbell is supported in a horizontal position by a vertical torsion fiber through the center, and is suspended in a strong nonhomogeneous magnetic field. With an oxygen-containing sample in the magnetic field, the nitrogen-filled spheres will be repelled from the strongest part of the magnetic field, displaced by the more magnetic sample gas. The rotation of the dumbbell about its axis will be proportional to the volume susceptibility of the sample, and thus the oxygen concentration.

While both the paramagnetic pressure and paramagnetic susceptibility analyzers would be suitable for continuous analysis of flue gases, the paramagnetic pressure analyzer offers the advantage of fewer moving parts and, therefore, the potential for greater reliability. Paramagnetic oxygen analyzers are susceptible to interference by NO and NO_2, the only other common paramagnetic gases. However, NO and NO_2 are substantially less paramagnetic than O_2, and are typically present only in very small quantities in woodstove exhausts, so that their effect should be negligible. Horiba Instruments has warned of possible interference by other compounds typically found in woodstove exhausts (5). Of these, only CO_2 threatens significant interference since, the presence of CO_2 in the sample causes a slight reduction of the output of this instrument, and much CO_2 is typically present in woodstove exhausts (5-15% is common.). Some organic compounds are shown to be even more susceptible than CO_2, but are usually present only in minute quantities in flue gas samples.

The absorption of infrared radiation by all compounds with covalent bonds (except simple nonpolar diatomics, such as O_2, N_2, H_2, and Cl_2) at combinations of wavelengths characteristic of each compound provides a method for measurement of CO and CO_2. By carefully selecting the wavelength at which this absorption is measured, the concentration of a particular compound can be monitored, even if it is part of a complex mixture. This technique involves the focusing of radiation leaving an infrared light source so that it passes through the sample gas being analyzed, and then onto a detector sensitive to IR radiation. Quantification of the energy absorbed by the sample is most easily accomplished by splitting the light leaving the source into two paths. A gas cell containing a reference gas (N_2 is good, since it does not absorb IR radiation) is placed in one path while a gas cell containing the sample gas is placed in the second path. The light from each of these paths is alternately focussed on the detector. This causes the detector to produce an AC signal which can be amplified. The amplitude of this signal represents the ratio of the energy transmitted through the sample beam to the energy transmitted through the reference beam (the percent transmission of the sample) and can be correlated to the concentration of the compound of interest in the sample.

Infrared gas analyzers can be classified into two basic groups: dispersive and nondispersive. Dispersive analyzers use a monochromator to break the light into its constituent wavelengths prior to reaching the detector. Thus the monochromator can be set for a wavelength characteristic of the compound of interest and only absorption at that wavelength will be measured. Nondispersive analyzers do not disperse the light, instead relying on some means of limiting the sensitivity of the detector to isolate a wavelength (or waveband) characteristic of the compound being measured. This can be done using either a selective detector or a nonselective detector equipped with a bandpass filter to limit its window of sensitivity.

Selective detectors, also known as Luft cell detectors, employ a pair of detector cells, each filled with the gas being measured, which are separated by a flexible membrane. One cell is exposed to light from the reference beam while the other receives light from the sample beam. When the compound being measured is present in the sample cell, the energy of the sample beam is attenuated. This causes the temperature, and thus the pressure, of the gas in the sample beam detector cell to drop below that in the reference beam detector cell. The pressure imbalance causes movement of the membrane, which is a variable capacitor, and produces an output signal. Since the detector cells are filled with the compound of interest, this type of detector is sensitive to absorption only at wavelengths characteristic of that compound. The presence of a compound in the sample gas with absorption bands that overlap those of the component being measured can cause interference. This interference can be avoided, though, by placing a cell containing the interfering gas in the path of the reference beam. Nonselective detectors are solid state devices that produce an electronic signal when exposed to IR radiation. Tuning these detectors to measure absorption due to a specific compound involves the use of a solid bandpass filter to limit the detector's window of sensitivity to coincide with wavelengths characteristic of that compound.

Either type of nondispersive infrared analyzer should be suitable for continuous monitoring of CO and CO_2 in woodstove flue gases. Dispersive infrared analyzers should also be suitable, but are at a disadvantage compared to nondispersive analyzers due to their greater complexity. Interference with measurements of CO and CO_2 by both infrared techniques due to water vapor in the sample has been cited as a drawback to these techniques (4,6,7,8), but can be eliminated by the removal of all water prior to analysis. Some commercial NDIR's also compensate for water content in samples. The differences in the means by which selective and non-selective detectors isolate their respective windows of sensitivity could cause differences in the interference characteristics of these detectors. Selective detectors, being sensitive to absorption at a variety of wavelengths, provide more oportunities for absorption bands of interfering compounds to overlap absorption bands of the compound of interest. Nonselective detectors, however, rely on bandpass filters to isolate a single window of sensitivity. This window could be wider than the absorption band of the component of interest, presenting the opportunity for absorption bands of interferents close to those of the component of interest to fall within the sensitivity window of the detector, causing intereference.

Horiba Instruments supplies a list of interference ratios for its infrared gas analyzers (9). These interference ratios relate the concentrations of interferents present in the sample gas to the elevation in the indicated concentration of the compound of interest. Interference ratios for compounds likely to be present in woodstove flue gases are typically large enough to negate any possibility for significant interferences with infrared analyses of CO and CO_2.

Interferometry has been used for continuous detection of CO_2 and combustibles in gas samples. However, this method measures a bulk property, the refractive index, of the sample and is not specific to CO_2. Combustible compounds in the sample will also interfere with CO_2 measurements, rendering this method useless for woodstove flue gas analysis.

Two electrochemical methods are available for the continuous measurement of oxygen in gas samples. The first of these is known as electrochemical membrane diffusion. The second is typically referred to as the Zirconia diffusion cell method.

Electrochemical membrane diffusion employs a closed cell filled with an aqueous electrolyte. This cell is fitted with a Teflon membrane and a pair of electrodes. The membrane serves to contain the liquid electrolyte while allowing oxygen from the gas sample being analyzed to diffuse into the cell and become dissolved in the electrolyte solution. The cathode is located close to the membrane, while the anode is positioned at some other point within the cell. When the outer surface of the membrane is exposed to an oxygen-containing gas sample, the oxygen diffuses through the membrane where it dissolves in the electrolyte. The oxygen is then reduced at the cathode/electrolyte interface while the anode is simultaneously oxidized, producing a current through the cell which can be measured and used as an indication of the concentration of oxygen in the gas sample. These devices have the advantages of simplicity and low cost. However, since the rate of diffusion of O_2 through the membrane is temperature-dependent, electrochemical membrane diffusion devices are sensitive to ambient temperature variations (temperature coefficients for these cells are typically 2-4% per ^{o}C). The anode is also degenerated during use, so periodic replacement of the cells is necessary. Interference by CO_2 in the gas sample has also been observed, making these devices unsuitable for woodstove flue gas analysis, where large CO_2 concentrations are typical.

The Zirconia diffusion cell method uses a heated zirconium oxide electrolyte in combination with a pair of porous platinum electrodes to produce an output which is proportional to the difference in the partial pressures of O_2 at the electrodes. One electrode is exposed to a reference flow, while the other is exposed to the sample gas being analyzed. These devices are specific to oxygen and have high-speed response, but are unsuitable for woodstove flue gas analysis due to the high temperature to which the electrolyte must be heated. This temperature is typically high enough to oxidize combustibles present in the flue gas stream, causing interference with O_2 measurements.

Mass spectrometers have been used in laboratories for qualitative and quantitative analyses of gas samples. Gas samples analyzed by mass spectrometry are ionized by an electron beam, separated according to mass, and focused on a collector. The flow of ions through the collector produces signals which are proportional to the concentrations of each component in the gas sample. Mass spectrometers have the advantages of precision, speed of response, and capability of measuring all gases, but are very costly and complex compared to other gas analysis techniques.

Gas chromatography can be applied to a wide variety of gas analyses. This technique is used for analysis of discrete samples, and employs the principle of characteristic rates of transit through a packed column for different components of a gas sample. The packing material in the column is chosen specifically for the type of sample being separated. The basic components of a gas chromatographic system are a flowing stream of some carrier gas (Helium is common) with a means of injecting a sample of gas into this stream, chromatographic columns upon which the separation of the sample into its consitituent components may take place, and a detector capable of indicating the quantity of each component as it is eluted from the column. The detector commonly used for analyses of CO_2, CO, and O_2 is the thermal conductivity detector. The output of the detector during a chromatographic analysis is recorded as a function of time on a strip chart. For a given carrier gas flow rate and column temperature, the time required for a particular compound to pass through the column is a characteristic of that compound. This allows identification of the components of a gas sample by their retention times, which are indicated by peaks on the strip chart. The heights of (or areas beneath) these peaks can be correlated to the concentrations of the compounds they represent. GOW-MAC Instruments suggests the use of a Poropak QS column in series with a Molecular Sieve 5A column for analyses of flue gases (10). The Poropak QS will separate CO_2, water, and light hydrocarbons while the Molecular Sieve 5A separates H_2, O_2, N_2, and CO.

The Environmental Protection Agency's standard Method 3 (11) and the American Society of Mechanical Engineers' Performance Test Codes (6) for measurement of CO, CO_2, and O_2 in flue gases call for the use of an orsat apparatus. An orsat analyzer determines the concentrations of these compounds volumetrically, by systematically removing all CO_2, O_2, and CO in the sample and measuring the change in the volume of the sample due to the removal of each compound. Potassium hydroxide is used for absorption of CO_2. Oxygen can be removed using a solution of chromous chloride in hydrochloric acid or an alkaline pyrogallol solution (12). Carbon monoxide can be absorbed using either cuprous chloride or cuprous oxide beta naphthol in sulfuric acid (12) The cuprous oxide beta naphthol solution is preferable, as curpous chloride will desorb carbon monoxide when exposed to a gas containing small quantities of CO (12). The Burrell Corporation claims no interferences with measurements of CO_2 or O_2 using the reagents specified above, but warns that acetylene, ethylene, and propylene could be absorbed by the cuprous oxide beta-naphthol solution (12). However, since emission factors for these compounds are typically much lower than for CO (13), they are unlikely to have a measurable effect on CO readings.

2.2 Sample Conditioning

The presence of particulates, water, and heavy organic compounds in woodstove emissions suggests the need for some form of sample conditioning prior to analysis for concentrations of CO, CO_2, and O_2. Heavy organic matter should be removed to avoid the condensation of these compounds within gas analyzers, which could pose substantial maintenance problems. The Environmental Protection Agnecy's Method 3 (11) suggests the use of a low-temperature trap to remove heavy organic matter and excess water from flue gas samples. This trap should be followed by a filter to remove particulate matter from the sample gas. So that an adequate margin of safety exists between the temperature of the sample within the gas anlayzers and the dew point of the organic material which passes through the trap, the trap should be submerged in an ice bath. Since an orsat analyzer yields a dry-basis analysis (14), the small quantity of water which will pass through an ice-temperature trap is inconsequential to the results obtained from this instrument. However, other analysis techniques such as gas chromatography, infrared absorption, and paramagnetism are affected by small quantities of water vapor in the sample gas. Therefore, all samples should be completely dry before comparable measurements can be made by these various methods. The removal of the water remaining in a sample after passing through an ice-temperature trap can be facilitated by a tube containing some sort of dessicant, such as $CaSO_4$ (Drierite). The gases remaining after this chilling/filtering/drying process will therefore be completely dry and sufficiently volatile to pass through all gas analyzers without difficulty.

2.3 Identification of Interferents by IR Spectroscopy

All organic compounds have characteristic absorption spectra in the infrared region. The locations within the infrared region of the absorption bands produced by each compound are functions of the types of bonds, types of vibrations occurring, and the relationships of the bonds to the overall structure of the molecule. Thus IR absorption spectra can be used to identify constituents of an unknown gas sample. This is typically accomplished by comparing the spectrum of the unknown sample to some of the many standard IR absorption spectra available (15,16).

The units generally used to specify the positions of absorption bands within a spectrum is the wavenumber, $\tilde{\nu}$ (cm^{-1}). The wavenumber is related to the wavelength of the radiation by:

$$\tilde{\nu}\ (cm^{-1}) = \frac{1}{\lambda} \times 10^4$$

where λ is given in units of micrometers (10^{-6}m).

All organic molecules absorb radiation between 3100 and 2750 cm^{-1}. This absorption is caused by the stretching of C-H bonds within the molecules (17). Therefore identification of individual compounds solely by absorption in this region is unlikely. The portion of the spectrum from approximately 1300 to 900 cm^{-1} is generally referred to as the "fingerprint" region. This portion of the spectrum is believed to be unique for every molecular species, proving particularly useful for compound identification (17). Absorption bands observed between 2000 and 1500 cm^{-1} are due to stretching of double bonds within the molecules (17).

Interpretation of spectra of complex molecules requires a thorough knowledge of the frequencies at which the various organic groups characteristically absorb radiation. However, the organic compounds in the fraction of the flue gases of interest here are largely light hydrocarbons (13), which makes possible the identification of flue gas constituents by simple comparison of experimental spectra to standard spectra of these light hydrocarbons.

2.4 Summary

Table 1 gives a brief summary of the measurement techniques available for CO, CO_2, and O_2 measurement. The most suitable methods for measurement of CO, CO_2, and O_2 in woodstove flue gases are likely to be orsat analysis, gas chromatography, and NDIR analysis for CO and CO_2, and orsat, gas chromatography, and paramagnetic analysis for O_2. The continuous methods (NDIR and paramagnetic) may be more desirable for efficiency measurements on woodstoves, since the composition of the flue gases changes continuously, and fluctuations in the composition of the flue gases could be observed more completely by continuous analysis. However, all of these methods should be free from interference, with the exceptions of water interference with NDIR measurements and CO_2 interference with paramagnetic analysis. These problems are readily avoided or corrected for and should be considered insignificant barriers to reliable measurements of woodstove exhausts.

Measurement interferences have been investigated by Jaasma and Borman (18), Matthews, et al. (19, Siewart (20), and Winer, et al. (21). However, the only specific references to interferences with measurements of CO, CO_2, and O_2 are those noted in the discussions of the various measurement techniques in section 2.1 (4-9).

It is generally agreed that woodstove flue gases should be chilled, filtered, and dried prior to analysis for concentrations of CO, CO_2, and O_2.

The identifications of compounds in the flue gases should be relatively simple by direct comparison of infrared absorption spectra of the flue gases to catalogued standard absorption spectra. Verification of the presence or absence of compounds which might interfere with measurements of CO and CO_2 by NDIR is therefore possible.

Table 1. Summary of CO, CO_2, and O_2 Measurement Techniques

Method	Component	Comments
Catalytic filament	CO	Subject to interferences from combustibles.
Catalytic filament	O_2	Requires low O_2/combustibles ratio.
Paramagnetic wind	O_2	Suitable only for binary mixtures containing O_2.
Paramagnetic pressure	O_2	Good stability and selectivity. Subject to slight NO, NO_2, CO_2 interference.
Paramagnetic susceptibility	O_2	Good stability and selectivity. More complex than paramagnetic pressure type.
Infrared absorption	CO,CO_2	Simple. Fast response. Subject to H_2O interference.
Interferometry	CO_2	Subject to combustibles interference.
Electrochemical membrane diffusion	O_2	Simple. Low cost. Temperature sensitive. Subject to CO_2 interference.
Zirconia diffusion cell	O_2	Subject to interference from combustibles.
Mass Spectrometry	CO,CO_2,O_2	Fast response. Precise. Very complex and expensive.
Gas Chromatogrpahy	CO,CO_2,O_2	Good selectivity. Requires batch samples (not continuous).
Orsat Apparatus	CO,CO_2,O_2	Simple. Inexpensive. Requires batch samples.

III. Apparatus and Procedure

3.1 Instrumentation

The methods chosen for CO and CO_2 measurement were gas chromatography, orsat analysis, and nondispersive infrared analysis. Oxygen measurements were made by orsat analysis, gas chromatography, and paramagnetic analysis. These measurement techniques were chosen out of convenience, as the necessary instruments were on hand, and because other laboratories where woodstove efficiency measurements might be made are also likely to have similar gas analyzers available. This section describes in detail the analyzers used to perform each of these analyses.

Two types of nondispersive infrared analyzers were used. The first was a Horiba PIR-2000, which uses a Luft-type detector. Figure 1 shows the arrangement of the PIR-2000 optical bench. Since each PIR-2000 contains only one luft cell detector, two complete PIR-2000 gas analyzers were used: one for CO measurement and the second for CO_2 measurement. Each of these instruments had three ranges of sensitivity, with maximum ranges of 0-5% CO and 0-20% CO_2. The output signals from these instruments were 0-1.0 VDC, and were read with a digital voltmeter. The second type of nondispersive infrared analyzer used was an Infrared Industries model 702 (or IR702). This instrument, shown schematically in Fig. 2, used a solid state detector which, being nonselective, was sensitive to IR radiation over a wide range of wavelengths. This allowed the IR702 to be used for measurement of both CO and CO_2 by using a

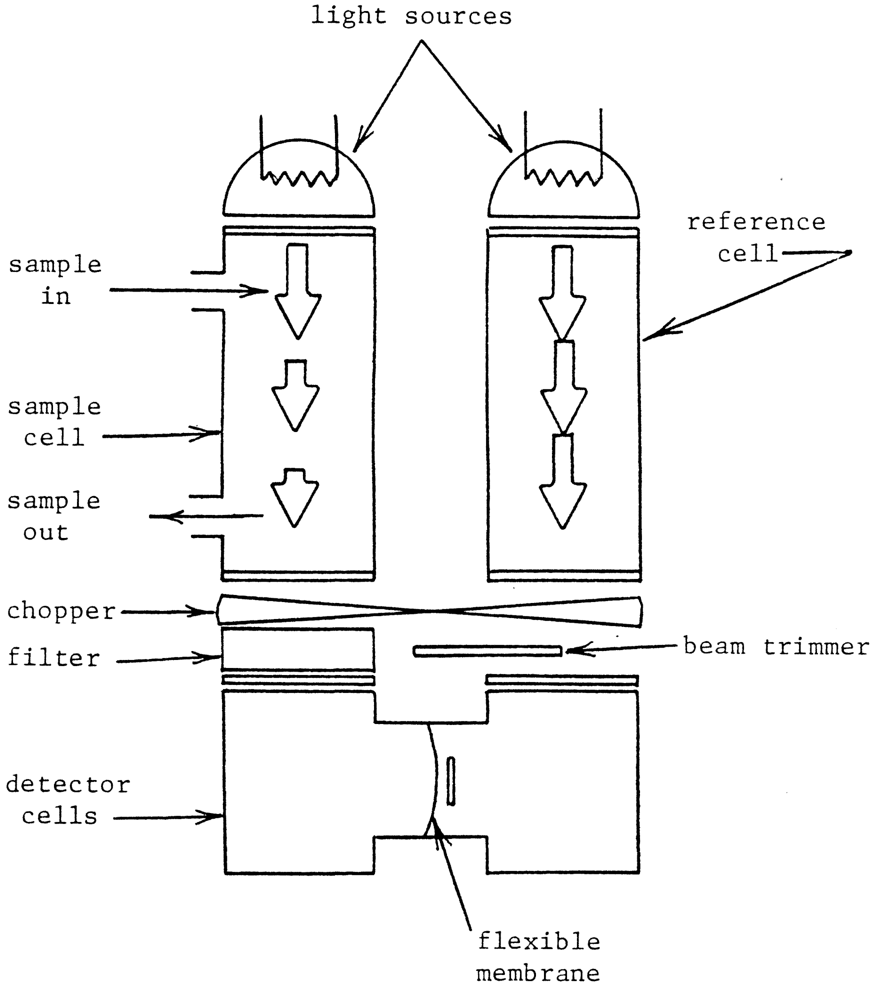

Figure 1. Optical schematic of PIR-2000

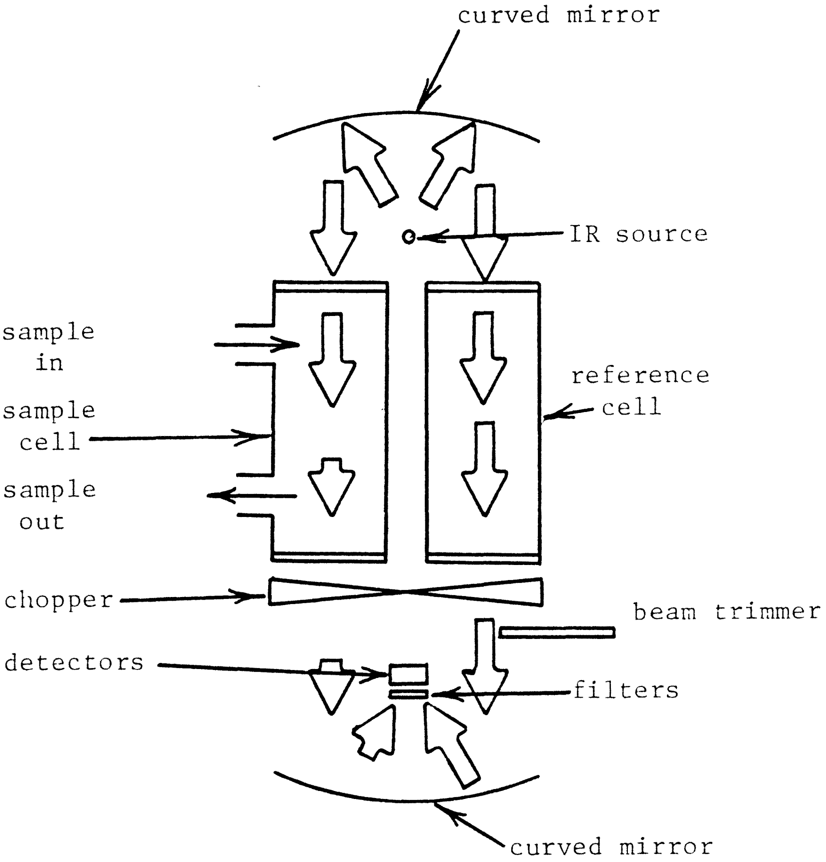

Figure 2. Optical schematic of IR702.

pair of detectors, each equipped with its own bandpass filter, mounted next to each other so that both saw the same beam of light from the sample cell. The band-pass filters limit each of the detector's range of sensitivity to coincide with a waveband at which its component of interest characteristically absorbs radiation. The IR702 had only one range for each compound: 0-3% CO and 0-20% CO_2. The range of output signals from each of the channels of the IR702 was 1-100 mVDC. These outputs were multiplied using a pair of Omega Omni-amps to provide output signals from zero to 1.0 VDC. The outputs of this instrument were measured using a digital voltmeter during all calibration and flue gas tests.

Infrared gas analyzers are sensitive to changes in the pressure of the sample gas being analyzed, so it was important to assure that the pressure within the NDIR analyzer sample cells was held constant during the course of each test. For this reason the sample flow rate through each of these instruments was carefully controlled by a needle valve/rotameter combination upstream of the sample cell with the sample exhausting to atmospheric pressure.

The paramagnetic analyzer used was a Horiba MPA-21 in combination with a Horiba OPE-325 control unit (these two pieces must be used together and will be referred to as the MPA-21). This analyzer, shown schematically in Fig. 3, was a paramagnetic pressure type. The magnetic pole pairs produce an alternating magnetic field, causing O_2 to be drawn into the two sides of the pressure detector cell in an alternating fashion. This fluctuation in the pressures on either side of the mem-

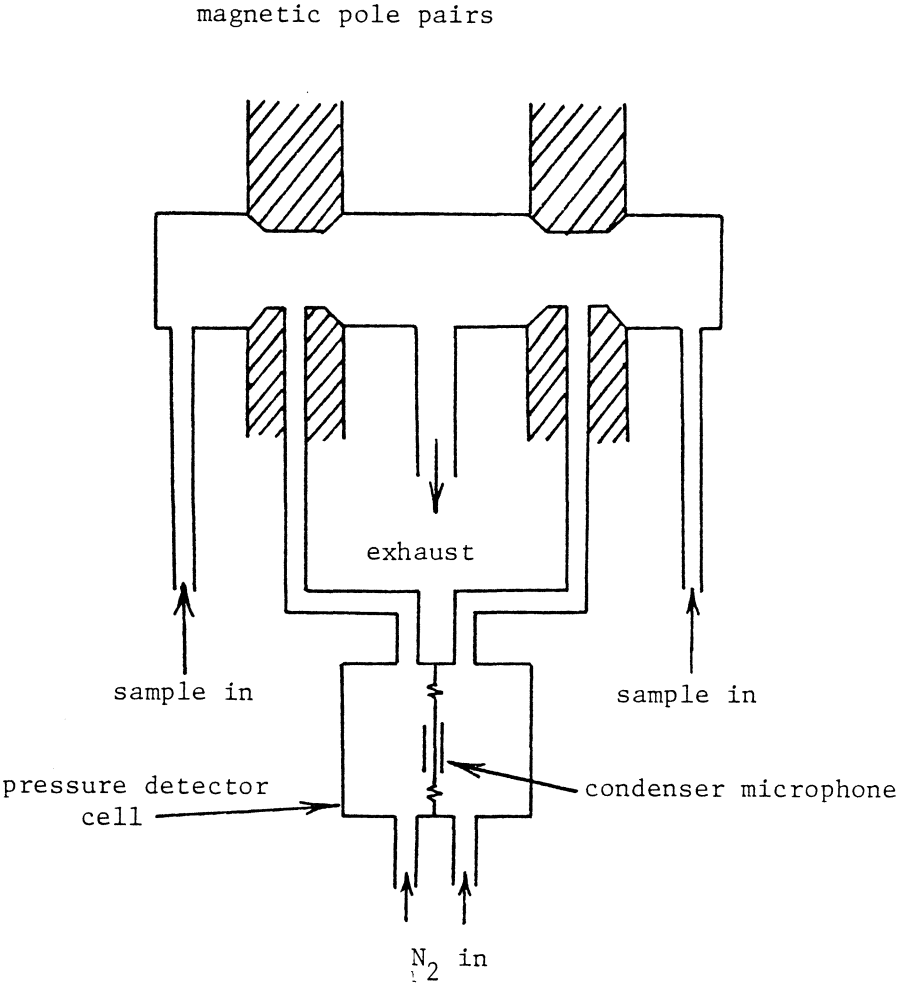

Figure 3. Flow schematic of MPA-21.

brane is detected by a condenser microphone and converted into an electronic signal. A continuous nitrogen purge of the pressure detector cell serves to reduce the response time of the instrument. It had three ranges, the least sensitive of which was 0-25% O_2. The output signal was 0-1.0 VDC and, as with the IR702 and PIR-2000's, was read using a digital voltmeter. The MPA-21 is sensitive to both sample inlet pressure and bypass flow rate, so each of these quantities was carefully regulated.

The chromatographic analysis of the flue gases was carried out on a GOW-MAC model 69-550 isothermal gas chromatograph with thermal conductivity detector. The separation process was facilitated by a Poropak QS column (213.4 cm x 0.3 cm O.D.) in series with a Molecular Sieve 5A column (243.8 cm x 0.3 cm O.D.). Since water and CO_2 can contaminate the molecular sieve column, a series/bypass column switching valve was used to separate the two columns (see Fig. 4). The Poropak QS allowed H_2, O_2, N_2 and CO to pass through quickly while it retarded the flow of CO_2, water, and light hydrocarbons. With a sample injected into the chromatograph with the series/bypass valve in the series mode, all H_2, O_2, N_2 and CO in the sample would pass directly through the Poropak QS onto the Molecular Sieve 5A. The series/bypass valve could then be moved to the bypass mode, trapping the H_2, O_2, N_2, and CO on the Molecular Sieve 5A, and redirecting the flow of CO_2, water, and light hydrocarbons directly to the detector. The series/bypass valve could then be returned to the series position at which time all compounds trapped on the Molecular Sieve column would be separated and eluted to the detec-

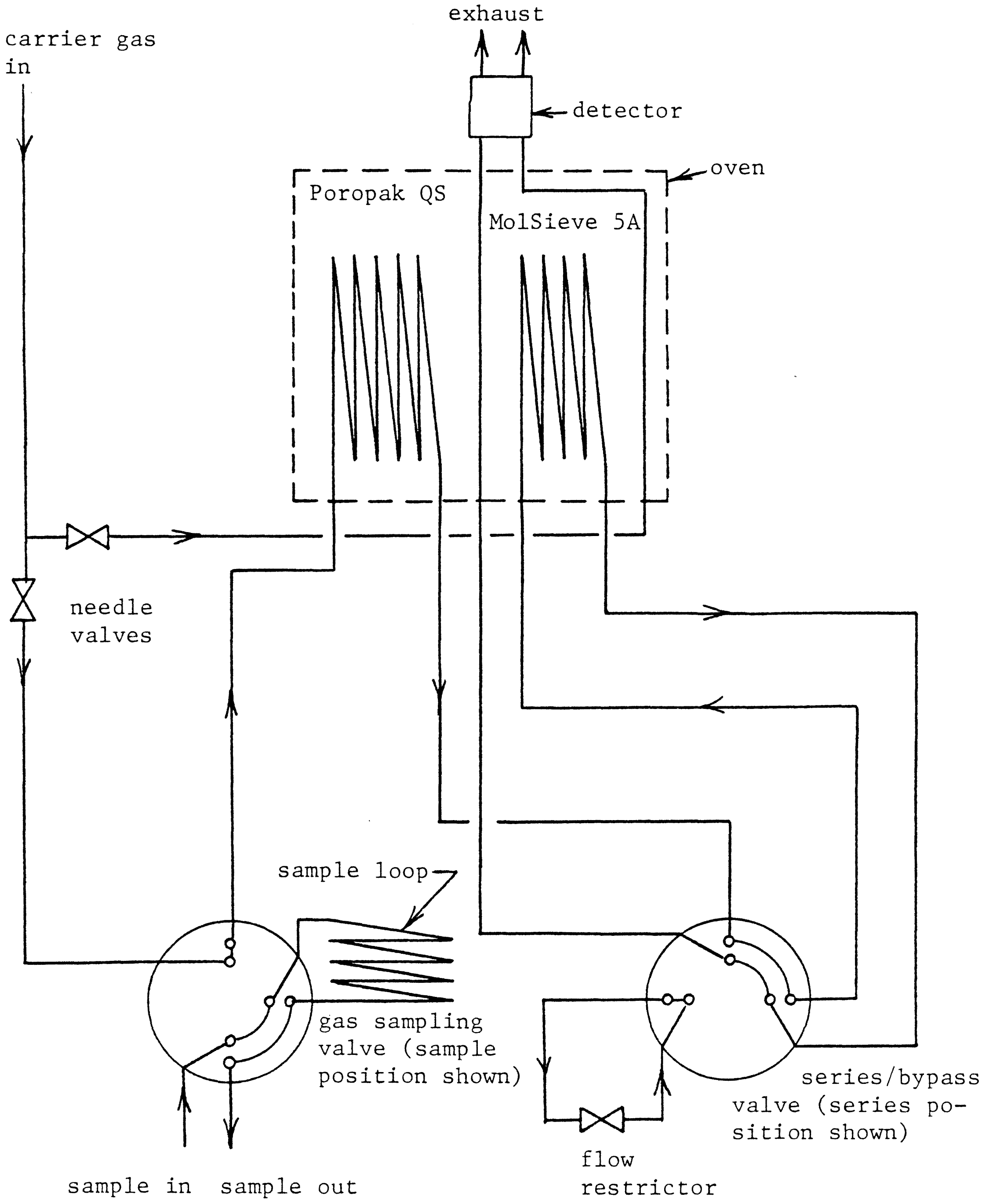

Figure 4. Gas chromatograph flow schematic.

tor. Samples were injected into the chromatographic columns using a gas sampling valve with a 2 cm^3 sample loop. The carrier gas used was Helium at a flow rate of approximately 30 cm^3/min. During all tests the column, detector, and injection port temperatures were held at approximately 55°C, 110°C, and 50°C, respectively. Bridge current for the thermal conductivity detector was recorded on a strip chart recorder with a range of 0-1 mVDC and a chart speed of 1 cm/min. Signals greater than 1 mV leaving the detector were attenuated using an attenuator control on the front panel of the chromatograph.

The orsat analyzer used is shown schematically in Fig. 5. Carbon dioxide was absorbed from the gas sample using potassium hydroxide. A solution of chromous chloride in hydrochloric acid absorbed oxygen. The reagent used for CO absorption was cuprous oxide beta-naphthol in sulfuric acid. Each of the absorption reagents used was manufactured by the Burrell Corporation. The volume of the samples taken was 100 cm^3, and the least count on the graduated burette was 0.2 cm^3. The confining liquid was a solution of 5% Sulfuric Acid by volume and 20% Sodium Sulfate by weight in water as suggested in the Burrell gas analysis manual (12).

The infrared spectrophotometer used for generation of IR absorption spectra of the flue gases was a Perkin-Elmer 283 (see Fig. 6 for optical bench arrangement), which is a double-beam instrument with a grating monochromator. When a sample is placed in the sample beam the absorption spectrum of this sample can be generated and recorded as percent transmission versus wavenumber of the radiation. Gas samples required

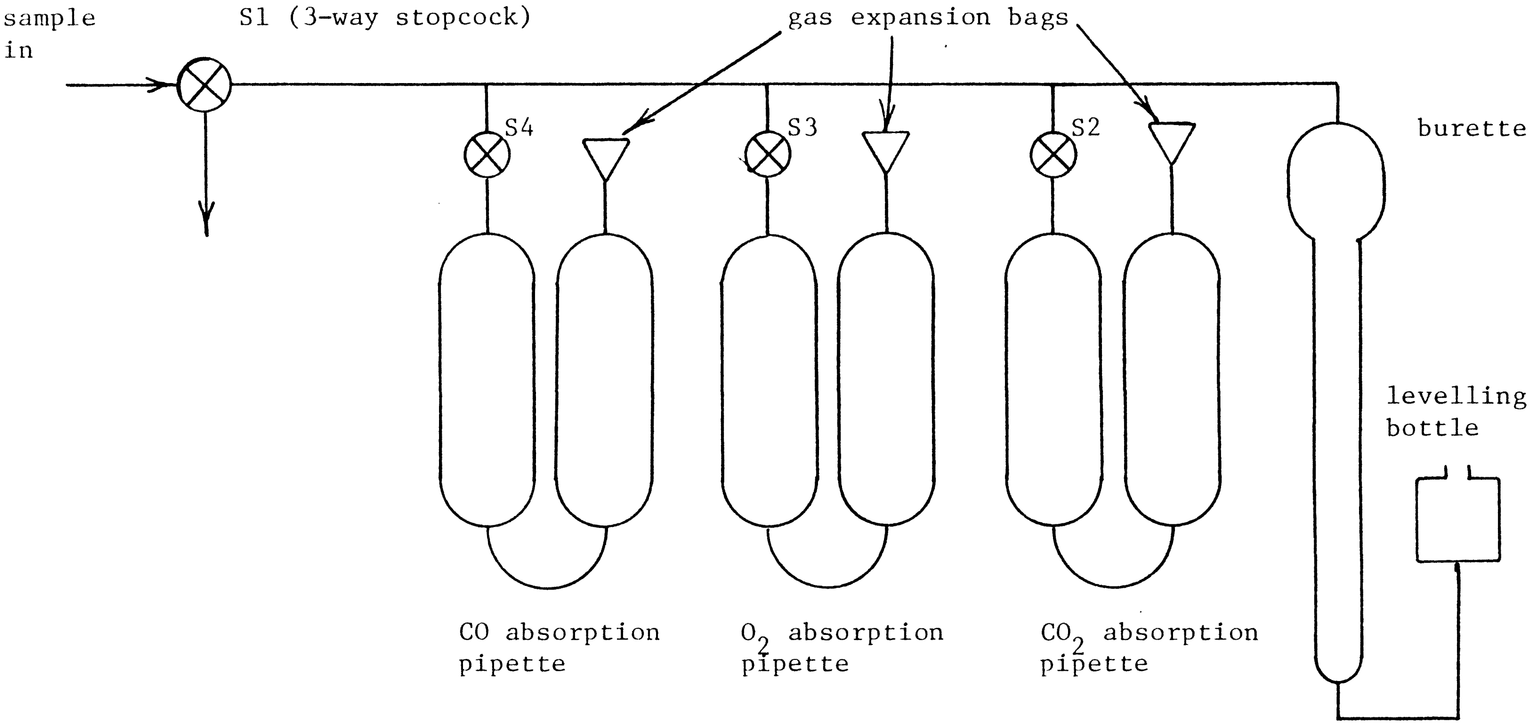

Figure 5. Schematic diagram of orsat apparatus.

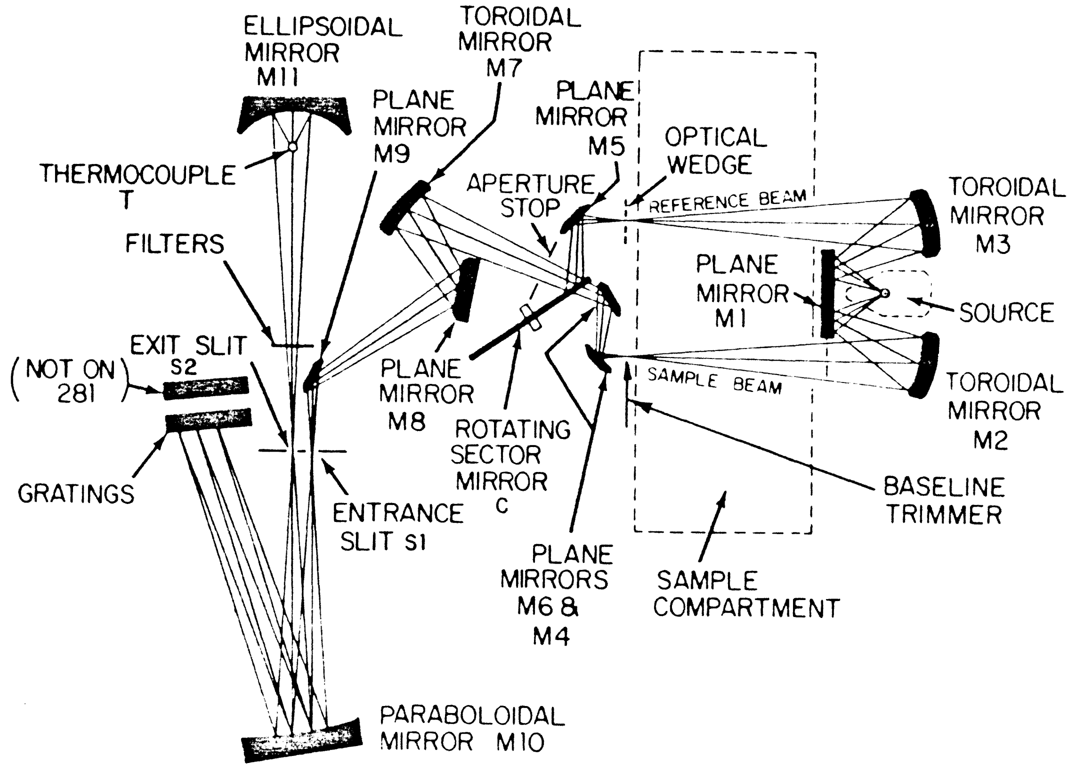

Figure 6. Schematic diagram of PE283.

the use of a pair of gas cells, one each for the reference and sample gases. The reference cell had a length of 7.9 cm and was equipped with Sodium Chloride windows. The sample cell had a length of 9.7 cm and was equipped with Cesium Iodide windows. This pair of cells allowed scanning of the infrared spectrum from 4000 cm^{-1} to approximately 650 cm^{-1}, since the sodium chloride windows of the reference cell were opaque to IR radiation at lower wavenumbers.

3.2 Calibration

The gas chromatograph, MPA-21, IR702, and PIR-2000's were calibrated using samples blended from bottled air and a primary standard calibration gas. The calibration gas contained 19.79% CO_2, 4.90% CO, and 75.31% N_2 by volume, with the concentrations of CO and CO_2 certified to within 0.02% absolute by the manufacturer, Matheson. The concentration of O_2 in the bottle of air was determined by first carefully adjusting the zero and span of the MPA-21 using N_2 and dry room air as the zero and span gases, respectively. The bottled air was then fed into the MPA-21 to measure its O_2 content. This was found to be 21.00%.

A schematic diagram of the apparatus used to blend the calibration samples is shown in Fig. 7. The gas flow rate from each bottle of gas was controlled using a needle valve (V1 and V2 in Fig. 7 for regulation of air and calibration gas, respectively). The delivery pressure from each of the pressure regulators on the gas bottles was set so that the ratio of atmospheric pressure to absolute delivery pressure was substantially lower than 0.528. Thus the flow through the needle valves was

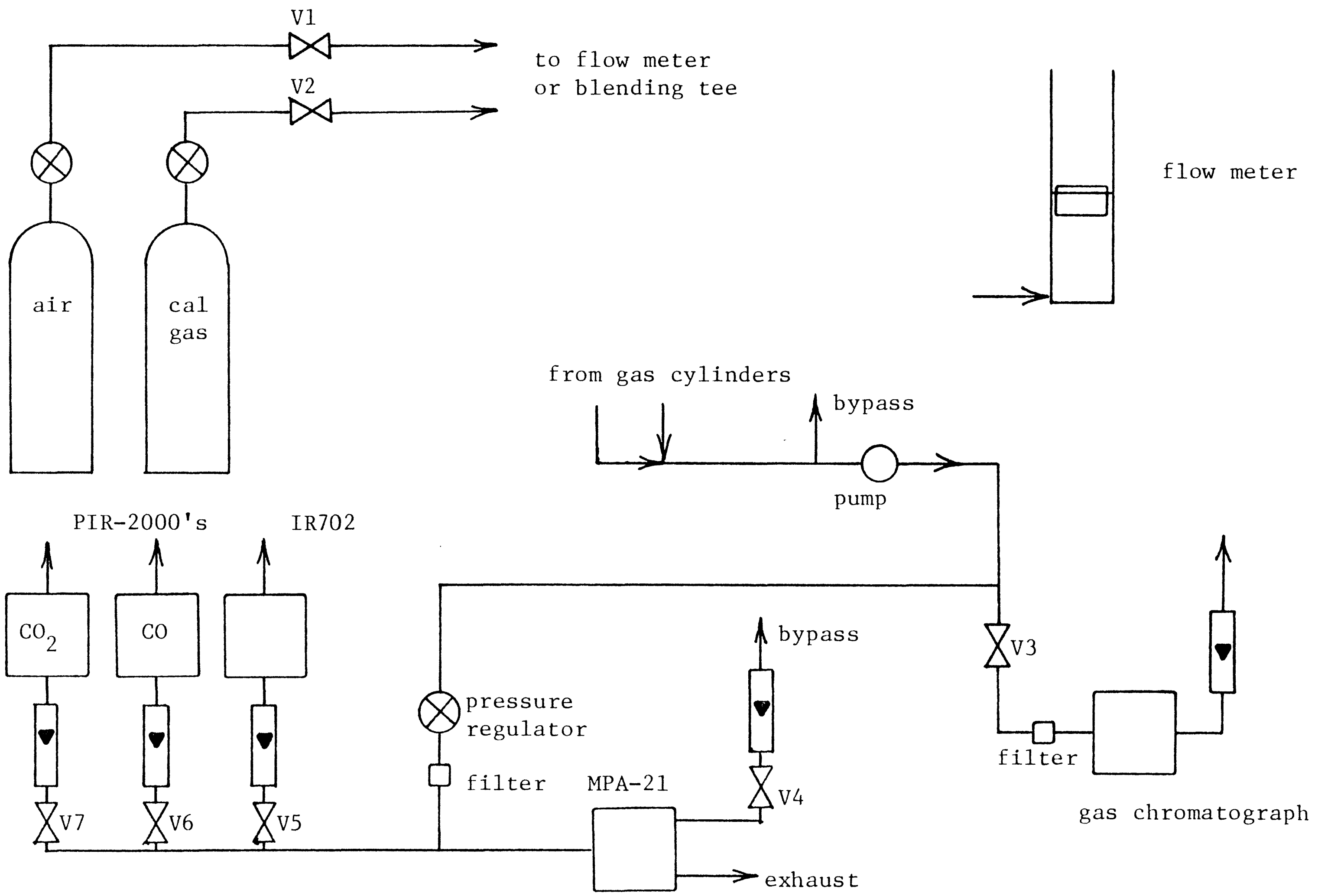

Figure 7. Calibration apparatus.

choked and, for constant regulator delivery pressures, steady and insensitive to small variations in the pressure downstream of the needle valves. Two-stage pressure regulators were used to insure steadiness of delivery pressure.

The flow rates of the air and calibration gas were measured using a Brooks model 1052 Vol-U-Meter. This device consisted of a precision-bore, borosilicate glass cylinder fitted with a piston. The seal between the cylinder and piston was formed by a Mercury O-ring, permitting essentially frictionless movement of the piston. The cylinder was sealed at its base except for a tube fitting through which the sample gas flowed. The flow rate was determined by observing the displacement of the piston and measuring the time required for this displacement. The cylinder was graduated in increments of 500 cm^3, up to 3500 cm^3. The weight of the piston produced an elevation in the pressure of the gas within the cylinder of approximately 4 cm water above atmospheric. This had no effect on the sample compositions calculated using these flow rates, however, as only the relative flows of the two gases are of concern, and both gas sample flow rates were measured at the same back-pressure. For each calibration sample the time required for 3000 cm^3 of gas to enter the cylinder was measured for the air and calibration gas. The respective flow rates were determined by dividing this volume by the average of three trial time measurements.

With the flow rates of the two gas streams known, the air and calibration gas were blended by directing both streams into a tee. The outlet of this tee was then directed to a second tee which split the flow between a sample pump used to supply the instruments with sample, and a flow bypass. The purpose of the flow bypass was to insure that the pressure of the air/calibration gas mixture downstream of the needle valves remained approximately equal to the ambient.

Calibration samples thus blended were simultaneously pumped through the MPA-21, IR702, both PIR-2000's, and the sample loop of the gas chromatograph (with the gas sample valve in the sample position). The flow rates through all instruments were checked and adjusted using metering valves V3, V4, V5, V6, and V7, if necessary. When the readings from the MPA-21, IR702, and PIR-2000's stabilized, these readings were recorded. Then chrmoatographic analysis was begun. A typical calibration chromatographic analysis proceeded as follows:

1. The series bypass valve was moved to the series position.
2. The sample was injected by moving the gas sampling valve from the sample position to the inject position.
3. All O_2, N_2, and CO were permitted to pass through the Poropak QS column and onto the Molecular Sieve column. The time required for this to occur was determined by first injecting a sample of room air in the bypass mode and measuring the time required for the air peak to emerge from the Porpak QS column. This was approximately seventy seconds for the column temperature and carrier flow rate used here.
4. Once these gases had cleared the Poropak QS, the series/bypass valve was moved to the bypass position. The CO_2 peak was eluted within approximately 40 seconds. Any water present in the calibration sample was eluted approximately 3 $1/2$ minutes after the series/bypass

valve was switched. The presence of water in the sample indicated a leak into the system at the inlet to the sample pump, and was cause for disqualification of the sample.

5. The series/bypass valve was returned to the series position, allowing the separation and elution of O_2, N_2 and CO, in that order.
6. The gas sampling valve was moved back to the sample position in preparation for the next sample.

The response of the thermal conductivity detector to the individual components of the calibration samples was quite different, requiring attenuation of the signal from the detector for compounds with relatively large thermal conductivities. These attenuations were noted by their respective peaks on the chromatogram produced by this analysis. After each chromatographic analysis, the heights of the various peaks (CO_2, O_2, N_2, CO) were recorded, as were their respective attenuations.

Analysis of samples using the orsat apparatus was accomplished by first positioning the inlet/exhaust stopcock on the orsat (stopcock S1 in Fig. 5) to allow sample to be pumped into the burette. Then S1 was returned to its original position, allowing sample to flow through the stopcock and be exhausted to the atmosphere, trapping the sample in the burette. The orsat analyzer was zeroed by positioning S1 to permit flow from the burette to the atmosphere, then raising the leveling bottle until the levels of the confining fluid in both the bottle and the burette coincided with the zero mark in the burette, then closing off S1. Thus 100 cm^3 of flue gases at atmospheric pressure were trapped in the burette. Carbon dioxide, oxygen, and carbon monoxide were absorbed from the sample, in that order. The change in the volume of the sample for each successive absorption gave the mole percentage of each of these three compounds directly. Carbon dioxide was removed by opening the stopcock isolating the pipette containing the solution of Potassium Hydroxide (S2 in Fig. 5), then raising the leveling bottle to force the sample into the absorption pipette. Lowering the leveling bottle would draw the sample back from the pipette into the burette, at which time S2 was closed and the new volume of the sample was measured. As before, the leveling bottle was held so that the levels of the confining solution in both the bottle and the burette coincided so that the volume change could be read. The sample was passed into the CO_2 absorption pipette repeatedly until two consecutive passes showed no change in sample volume. Carbon monoxide and O_2 were removed in a similar fashion and the net change in volume due to absorption of each compound was recorded.

This calibration sample handling/measurement process was repeated for a range of concentrations of CO, CO_2, and O_2 until it was decided that the calibration curves for these instruments were sufficiently defined. The CO channel of the IR702 was calibrated for CO concentrations up to 4.90% (the concentration of CO in the primary standard calibration gas), even though its claimed range was only 0-3% CO. The reason for this was twofold: this would allow the use of this calibration gas as a span gas for all of the instruments, negating the need for a separate span gas for the CO channel of the IR702, and because concentrations of CO in the flue gases were expected to exceed 3% on occasion. Unfortunately, the CO channel of the IR702 later ceased to function properly, rendering it useless for stack gas testing.

After the completion of the calibration tests, the author learned that argon is eluted from the Molecular Sieve column concurrently with oxygen. Since dry room air contains approximately 1% argon (14) the exhaust products of wood combustion with room air would have an argon content of approximately 1% when cooled, filtered, and dried. To evaluate the extent of argon interference with O_2 measurements by gas chromatography, the chromatograph was calibrated for peak heights versus percent argon in the immediate vicinity of 1% argon. These calibration samples were blended as previously described using pure argon diluted with pure N_2. The peak height corresponding to 1% argon was determined from this calibration. The chromatograph was then calibrated for peak height versus percent O_2 using blends of pure O_2 and pure N_2 in the range of 0-23% O_2. Finally a sample of dry room air (21% O_2, 1% argon, etc.) was analyzed to determine the peak height corresponding to 21% O_2 plus 1% argon. The peak height for 21% O_2 with no argon was determined using the calibration curve generated using O_2/N_2 blends, and subtracted from the peak height corresponding to 21% O_2 with 1% argon. Now the response of the chromatograph to 1% argon was known with no oxygen in the sample as well as with 21% oxygen in the sample. The latter value was lower than the former by nearly 50%. It was decided to attempt to correct the O_2 peak heights for flue gases by subtracting an estimate of the portion of each O_2 peak which was due to argon content, then use these corrected peak heights in conjunction with the calibration curve generated using O_2/N_2 blends to determine the O_2 content of the samples. The estimate used to make this correction was a linear interpolation between the responses to 1% argon with no O_2 and with 21% O_2 in the samples, and was to be based on the O_2 content of the sample. . The need for this elaborate correction procedure lies in the fact that, for high O_2 concentrations (or O_2 plus argon concentrations), the output of the thermal conductivity detector (as measured by peak height) is not linear with O_2 or O_2 plus argon) content. Thus, beyond the linear range of the detector, successive increases in O_2 concentration cause decreases in the part of the detector's response due to 1% argon in the sample. It should be noted that this type of correction would have been unnecessary had the primary standard calibration gas contained 1% argon, but this was not the case.

As a final check of the concentrations of CO_2, O_2, and CO as indicated by gas chromatography, nitrogen peak heights were calibrated versus N_2 content from 75% N_2 to 86% N_2. The samples were blends of pure O_2 and pure N_2. Then the concentrations of CO_2, O_2, N_2 and CO in several of the calibration samples blended from bottled air and calibration gas as indicated by GC peak heights were summed. One would expect the sum of all of the component concentrations for a sample to equal 100%. However, this was not the case in any of the samples examined, which was cause for suspicion. Samples of dry room air (78% N_2) and a bottle of calibration gas claimed to contain 5.03% O_2, 17.1% CO_2, and 77.87% N_2 were analyzed by gas chromatography. Their N_2 peak heights agreed well with the N_2 calibration curve. However, a sample of the primary standard calibration gas used for previous calibrations produced N_2 peaks considerably larger than predicted by the calibration curve. A local chromatography expert, Dr. Harold McNair of the VPI Chemistry Department, was consulted on this matter, but was unable to aid in its resolution. One additional problem was encountered during preliminary stack gas tests. Concentrations of O_2 in the flue gases were substantially lower (typically one mole percent) as indicated by gas chromatography than as indicated by either the orsat analyzer of MPA-21. This problem also eluded any solution, and it was decided to forego O_2 measurements using gas chromatography.

The MPA-21, IR702, and PIR-2000's were checked for interferences by CO, CO_2, and O_2. This was done by flowing pure samples of each compound through these instruments and noting the various outputs. As one would expect, neither type of NDIR analyzer experienced O_2 interference, nor did the CO and CO_2 channels respond to samples of CO_2 (99.8% pure, supplied by Matheson) and CO (99.5% pure, also supplied by Matheson), respectively. Carbon monoxide produced no reading on the MPA-21, but a sample of CO_2 did produce an output which indicated an oxygen concentration of -0.25% O_2. This corresponds to a decrease in the indicated O_2 concentration of 0.025% for every 10% CO_2 in the sample. This effect was accounted for in the preparation of the calibration curve for the MPA-21.

The PE283 infrared spectrophotometer was calibrated for absorption peak length at 1305 cm^{-1} versus concentration of methane in the sample. Calibration samples were blended from a bottle of 2.83% methane in air and a bottle of pure N_2, and were supplied to the IR sample cell in a manner analogous to that used when calibrating the chromatograph, MPA-21, IR702, and PIR-2000's. Once the sample was blended and passed through the sample cell, the cell was removed from the calibration apparatus and transported to the PE283 for generation of an IR absorption spectrum. Each scan began with a zero and gain check of the PE283. The sample cell was then inserted into the path of the spectrophotometer's sample beam. Then the reference cell, which contained nitrogen, was placed in the path of the reference beam. The baseline control was used to adjust the panel meter on the PE283 to register approximately 80% transmission. The scanning procedure was then initiated, beginning at 4000 cm^{-1} and continuing automatically until manually interrupted at 700 cm^{-1}. The output was presented by the PE283 as a plot of percent transmission versus wave number.

3.3 Stack Gas Testing

The composition of woodstove flue gases changes continuously throughout the burn cycle Therefore, comparison of concentrations of CO, CO_2, and O_2 indicated by the various gas analyzers employed required the collection of a large integrated sample of flue gases. Such a sample would allow the operator to supply the gas analyzers with samples of constant composition for times sufficiently long to permit the various analyses to be carried out. Figure 8 shows a schematic diagram of the apparatus used to collect, condition, and supply the gas analyzers with flue gas samples. The system consists of a sample probe for drawing flue gases from the stack, an ice-temperature cold trap to collect

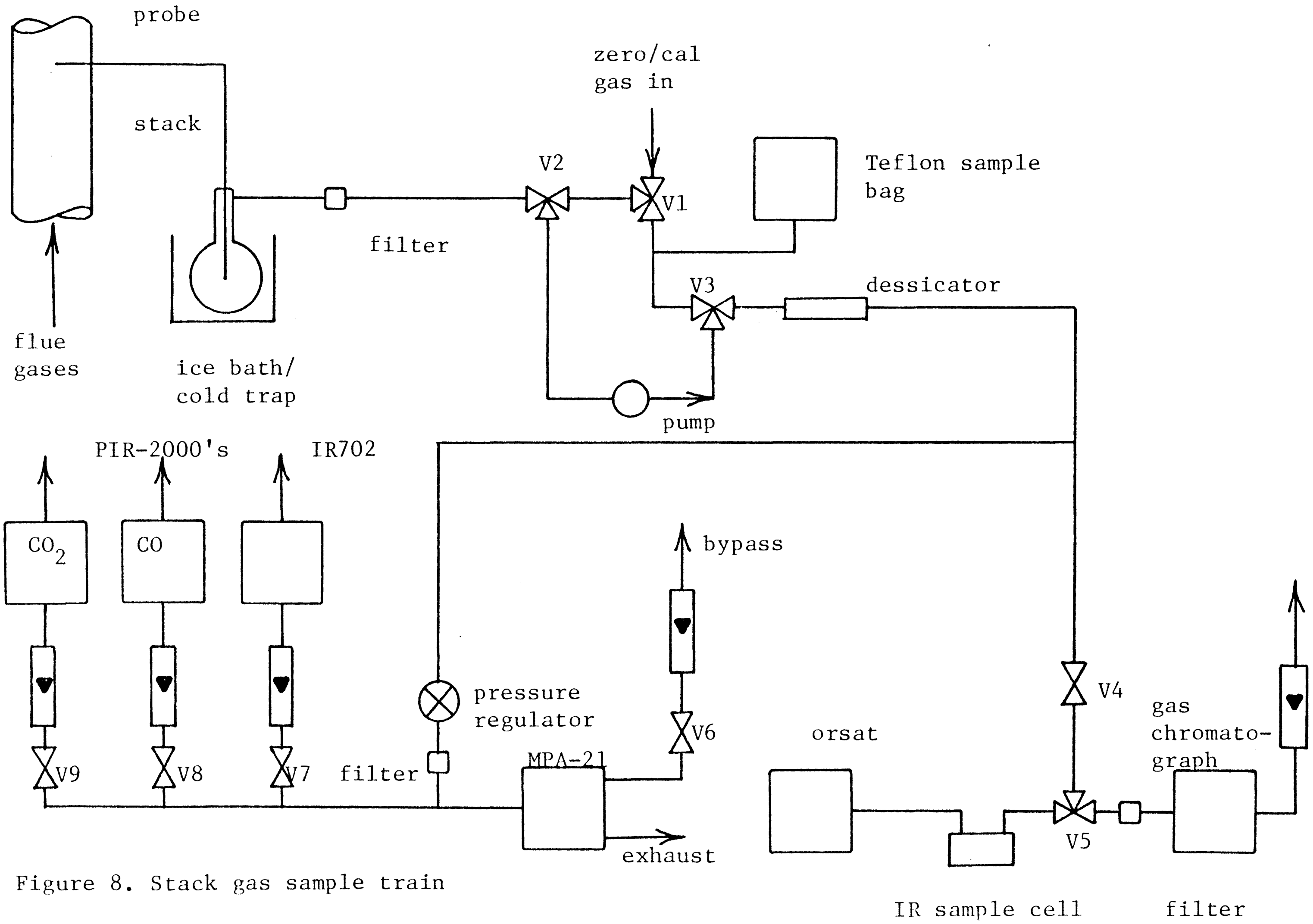

Figure 8. Stack gas sample train

condensible organic material and most of the water in the flue gases, a filter to remove particulate matter, and a large (approximately 50 ℓ capacity) Teflon sample storage bag. A sample pump serves to draw the sample from the stack and feed it to the sample bag, as well as to supply the gas analyzers with sample from the sample bag. A dessicator filled with $CaSO_4$ removes any water from the sample which was not condensed in the cold trap.

Each test began with a careful adjustment of the zero and span controls of the MPA-21, IR702, and PIR-2000's. Zero and calibration gases were supplied to the analyzers though valve V1, with this valve set to allow the pump to draw in the standard gases and supply them to the gas analyzers. Nitrogen was used to zero all of the analyzers. Dry room air was used to span the MPA-21. The primary standard mixture of CO, CO_2, and N_2 was used to span the IR702 and PIR-2000's. At this time a sample of calibration gas was also analyzed by gas chromatography to obtain the standard peak heights for CO and CO_2. These standard peak heights were divided into the peak heights produced by the same sample on the day the chromatograph was calibrated to yield correction factors which would be applied to all peaks for the respective compounds during the current test. A baseline scan was generated for the PE283 using nitrogen in both the reference and sample cells. This was followed by the generation of a calibration standard using a sample from the bottle of 2.83% methane in air discussed in section 3.2. A correction factor was computed for the PE283 in a manner analogous to the gas chromatograph standard correction factor.

The stove was then fired to begin the test. A kindling charge of approximately 2 kg mass was ignited in the stove to produce a bed of coals sufficient to ignite the main charge. The main charge consisted of 15 to 24 kg of oak cord wood with a typical water content of 24 to 25%. Fuel water content was measured prior to each firing by sampling one piece of each main charge, splitting this sample, weighing the sample, then placing the sample in a drying oven to drive off all moisture. The difference between the dry and as-sampled weights was divided by the latter to yield moisture content. It was not necessary to sample each piece of the main charge since all fuel was stored in a humidity-controlled environment, and since the moisture content of the fuel was not used to derive any experimental results. Also, it is unlikely that the results of these tests would be affected by the type of wood or its moisture content, as only the comparison of the various analysis techniques is of importance.

After the main charge was added to the coal bed, the stove door was left open until the operator was satisfied that the fire would sustain itself. The stove door was then closed and the damper set to allow the desired burn rate. Then the gas sample bag was emptied in preparation for the first flue gas sample. This was done by disconnecting the sample line from the inlet of the dessicant tube, allowing the line to discharge to ambient. Then valves V2 and V3 were set to direct flow from the sample bag, through the pump, and through the open tubing. When the sample bag was empty, the position of valve V2 was reversed so that the pump would draw flue gases through the probe, cold trap, and filter, and exhaust them to the atmosphere. This was done to purge the sample train prior to collecting a sample for analysis. While it is true that the volume of the tubing connecting the sample bag to the pump, as well as some dead volume within the sample bag, cannot be purged in this manner, these volumes were certainly negligible compared to the volume of the sample drawn.

While the sample train was being purged with flue gas, the orsat apparatus was prepared for use. This was done by first checking to assure that the level of absorption reagent in each pipette was just below the stopcock separating that pipette from the manifold. Then the burette was purged of any inert residual gases remaining from the previous analysis. This was done by raising the leveling bottle until confining solution completely filled the burette and closing stopcock S1 to prevent any air from entering the orsat.

The sample train having been purged, valve V3 was reversed to direct the discharge of the pump into the sample collection bag. While the sample bag was filling (a process that took approximately 3 minutes), the sample line previously disconnected was reconnected to the inlet of the dessicator tube. When the sample bag was full, valves V2 and V3 were repositioned to allow the pump to draw from the sample bag and discharge through the dessicator to the instruments. The position of valve V5 was set to direct flue gases through the sample loop of the gas chromatograph. At this point flue gas sample was flowing through the sample loop of the chromatograph, as well as the sample cells of the MPA-21, IR702, and PIR-2000's. The flow rates through each of these instruments were checked and adjusted, if necessary, using metering valves V4, V6, V7, V8 and V9.

When the output readings from the MPA-21, IR702, and PIR-2000's had stabilized, their readings were recorded. Then the gas sampling valve on the chromatograph was moved from the sample position to the inject position, allowing carrier gas to flush the sample from the sample loop and into the chromatographic columns. The position of valve V5 was then reversed to direct the flow of flue gases through the IR sample cell and the orsat analyzer. After all O_2, N_2, and CO in the sample had passed through the Poropak QS column and onto the Molecular Sieve column, the series/bypass valve was moved to the bypass mode.

The sample lines downstream of V5 and the IR sample cell were now thoroughly purged with fresh sample. The inlet/exhaust stopcock on the orsat apparatus (stopcock S1 in Fig. 5) was positioned to allow sample to be pumped into the burette. Then S1 was returned to its original position, allowing sample to flow through the stopcock and be exhausted to the atmosphere, trapping the sample in the burette. The sample pump was turned off and the IR sample cell was sealed (using two stopcocks on the cell body) and removed from the system. The flue gas sample was then analyzed using the orsat apparatus as described in section 3.2.

By this time all peaks of interest had emerged from the Poropak QS column of the GC, so the series/bypass valve was returned to the series position, allowing carrier gas to flow through the Molecular Sieve 5A column and separate the O_2, N_2, and CO trapped there. After elution of all of these peaks the analysis of the flue gas sample for CO and CO_2

was complete. The gas sampling valve was returned to the sample position in preparation for a new sample. The gas chromatographic analysis required approximately 15 minutes to perform as carried out during the flue gas tests. This time could be reduced to approximately seven minutes if the series bypass valve were returned to the series position immediately following elution of the CO_2 peak.

The final step of the analysis of the flue gas sample was the generation of an infrared absorption spectrum. This was carried out exactly as described in the calibration section (section 3.2).

This flue gas sampling and analysis process was repeated for each of four samples taken during each of three separate firings. The first sample for each test was drawn shortly after firing the stove. Two more samples were collected during mid-cycle, and one final sample was taken when less than 10% of the main charge remained unburned. Three separate firings were monitored so that the effect of the burn rate on the presence or magnitude of interferences could be observed.

A separate set of three firings was made to examine the effect of the sample train on the concentrations of CO, CO_2, and O_2 in the flue gas samples. Deposits of condensed organic matter which form in the sample lines, cold trap, and filter during sampling of stack gases might absorb CO, CO_2, or O_2 from the sample gases, preventing the sample which reaches the gas analyzers from being representative of the gases within the flue. The tests for these effects consisted of measurements of samples of calibration gas passed through the sample train before and after sampling of flue gases by this sample train. Each of these tests began with a thorough cleaning of the sample lines, cold trap, and filter holder with acetone. The MPA-21, IR702, and PIR-2000's were then carefully zeroed and spanned. Then a sample of primary standard calibration gas consisting of 2.00% CO, 9.99% CO_2 9.98% O_2 and 78.03% N_2 was fed through the sample train to the gas analyzers. The readings from the MPA-21, IR702, and PIR-2000's were recorded. At this point the stove was fired and several flue gas samples were drawn through the sample train. Finally, the primary standard calibration gas was passed through the sample train and analyzed by the MPA-21, IR702, and PIR-2000's.

In order to determine the level of agreement which could reasonably be expected from this parallel arrangement of the various gas analyzers, samples blended from air and calibration gas were supplied to the sample bag and analyzed exactly as the twelve flue gas samples were, the only difference being that the possibility of the presence of interfering compounds was removed. Four such samples were generated and analyzed for concentrations of CO, CO_2, and O_2.

All tests ended with a check of the zero and span readings from the MPA-21, IR702, and PIR-2000's to expose any appreciable instrument drift.

3.4 Data Reduction and Interpretation

The readings obtained from the various gas analyzers for each of the twelve flue gas samples collected were converted into indicated concentrations by linear interpolation between the calibration points of the calibration curves generated as described in section 3.2. These indicated concentrations were divided into three groups, one each for CO, CO_2, and O_2 concentrations. These three groups were further divided into three sub-groups, each containing four sets of data corresponding to the concentrations measured during a particular firing.

Each set of indicated concentrations showed the range of outputs from the various analyzers used to measure the respective compound. The uncertainties in the individual indicated concentrations were determined as described in section 8.1 and tabulated.

Closer examination of these data for evidence of trends in the discrepancies between the indicated concentrations within each set required a graphical representation. First the indicated concentrations which constituted each set were averaged. This average was then subtracted from each indicated concentration within the set to yield the deviations of the individual concentrations from the mean. These deviations were plotted in chronological order and against the average indicated concentration for each set of indicated concentrations. The comparison data generated using air/calibration gas samples was processed in exactly this same manner and plotted against the average indicated concentration for each data set.

If all of the discrepancies between the readings within a set could be explained by uncertainties in those readings, the readings were said to agree. Discrepancies which could not be explained by uncertainties were noted and examined for relationships with the point during the burn cycle at which the sample was drawn (early, middle, or late), the burn rate of the fuel, and the content of organic material in the sample as evidenced by the infrared absorption spectra. Trends in the discrepancies between the outputs of the various gas analyzers were then sought which might either confirm or exclude the possibility of interference with the measurements of CO and CO_2 by NDIR analysis.

The identification of components of the flue gas samples using the infrared absorption spectra generated was accomplished by direct comparison of the experimental spectra to standard spectra obtained from Sadtler (15). Experimental spectra were compared to standard spectra of the C_1 through C_4 hydrocarbons and methanol (CH_3OH). No comparisons were made with standard spectra of heavier hydrocarbons or alcohols. No values pertaining to heavy hydrocarbon compounds ($>C_4$) were included in the tabulated NDIR interference ratios supplied by Horiba (9) for their CO and CO_2 analyzers, so no estimate of the potential for interference by these compounds is possible. However, tabulated interference ratios for the lighter hydrocarbons show that interferent concentrations in the conditioned flue gases would have to exceed 2.5 mole percent to produce measurable interference (a change in the indicated concentration of at least 0.01 mole percent) with CO measurements. Measurable interference with CO_2 measurements would require concentrations of light hydrocarbons in flue gas samples of at least 5.0 mole percent. The only hydrocarbon with C–O bonds for which interference ratios were supplied, ethylene oxide (C_2H_4O), would have to be present in concentrations of 1.5 mole percent to be detected by either CO or CO_2 analyzers. A detailed study of the characteristics of woodstove exhausts has shown concentrations of these types of compounds to be substantially lower than the concentrations required for interference (13).

The concentrations of methane in the stack gas samples was determined by measuring the length of the absorption peak found in experimental spectra at 1305 cm^{-1} and using the calibration curve prepared as described in section 3.2.

IV. Results and Discussion

4.1 Calibration Results

The calibration curves generated as described in section 3.2 are shown in Figs. 9, 10, 11, and 12. The output of the PIR-2000 and gas chromatograph versus CO concentration are shown in Fig. 9. The CO calibration curve for the chromatograph is almost perfectly linear. This is a characteristic of the thermal conductivity detector in the chromatograph for gas concentrations which do not exceed approximately 8 to 10 mole percent. Readings from the IR702, PIR-2000, and gas chromatograph versus CO_2 content are shown in Fig. 10. Note that the calibration curve for CO_2 for the chromatograph is not linear over its entire range, but only at low CO_2 concentrations (<8%). Note also the difference in the shapes of the calibration curves for the IR702 and PIR-2000. The shape of the calibration curve for the PIR-2000 is governed by Beer's Law (4), which predicts an exponential relationship between the concentration of the component of interest and the fraction of the radiation incident upon the sample which is absorbed. The IR702 output was linearized within the electronics of the instrument. Figure 11 shows the output of the MPA-21 versus percent O_2. Here the relationship between O_2 concentration and the increase in the pressure within the magnetic field within the MPA-21 is linear, so no electronic linearization was required. Peak heights from the chromatograph for O_2 measurements were not included here because the chromatograph was not used for O_2 measurements on stack gases. The length of the methane absorp-

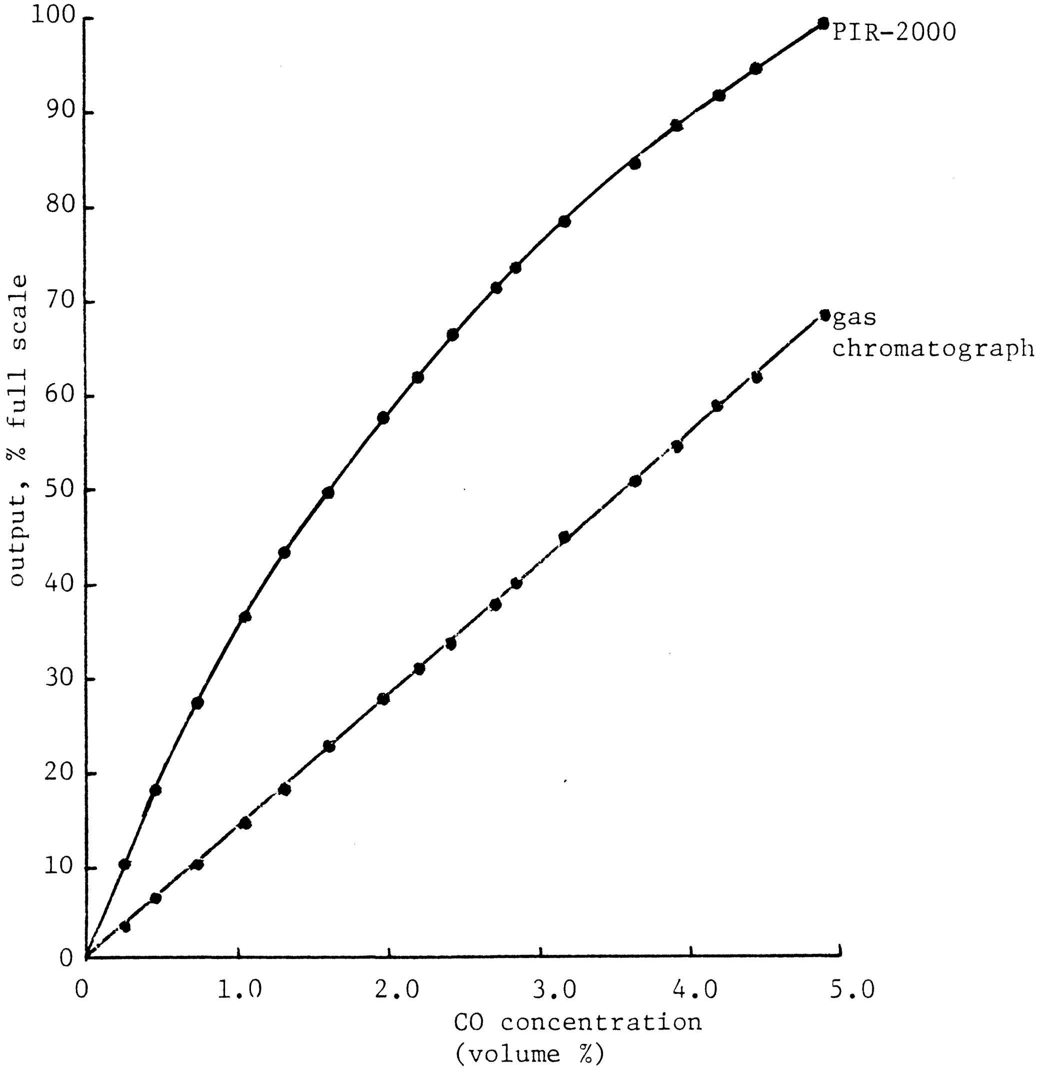

Figure 9. Calibration curves for PIR-2000 and gas chromatograph for output reading vs. CO concentration. Balance gases: CO_2, O_2, N_2.

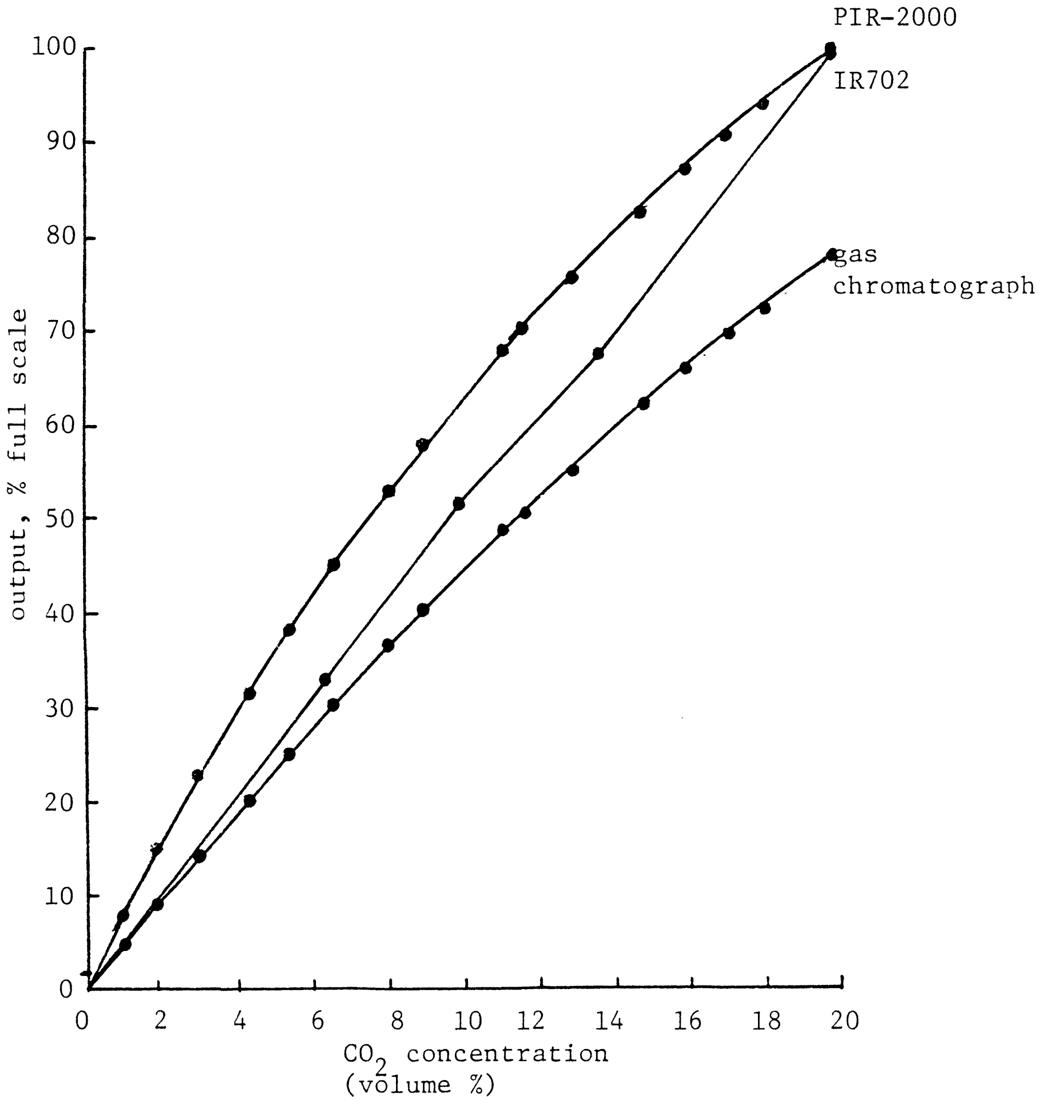

Figure 10. Calibration curves for PIR-2000, IR702, and gas chromatograph for output vs. CO_2 concentration. Balance gases: CO, O_2, N_2.

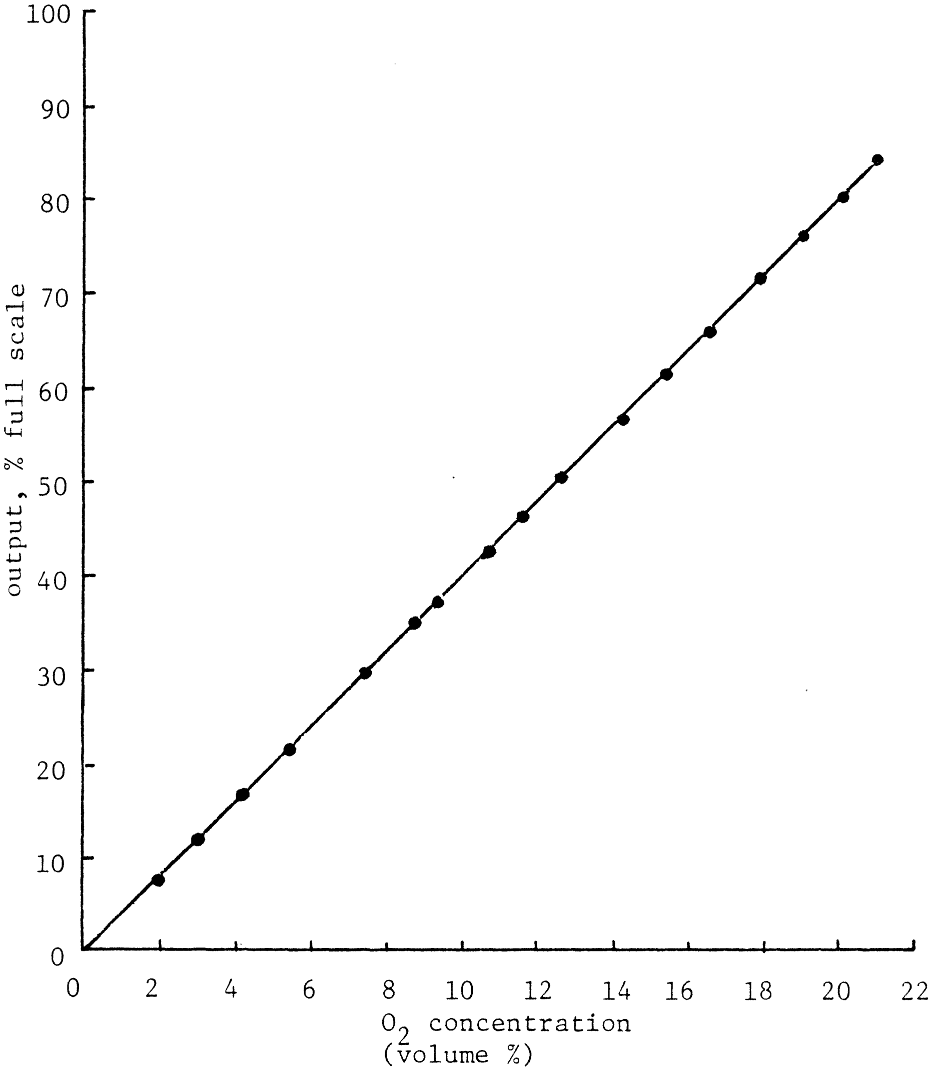

Figure 11. Calibration curve for MPA-21 for output vs. O_2 concentration. Balance gases: CO, CO_2, N_2.

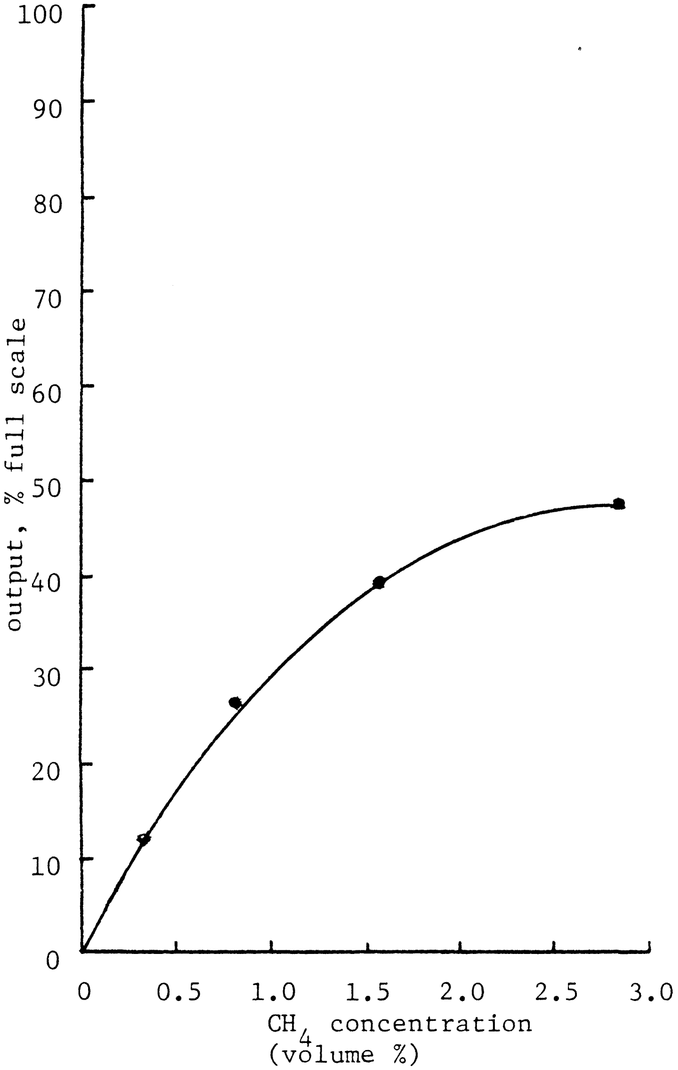

Figure 12. Calibration curve for PE283 for length of absorption peak at 1305 cm^{-1} vs. CH_4 concentration.

tion peak at 1305 cm^{-1} versus CH_4 content for the PE283 is shown in Fig. 12. The shape of this curve is similar to those for both PIR-2000's.

The results of the comparison tests performed using blends of calibration gas (19.81% CO_2, 4.90% CO, 75.31% N_2) and bottled breathing air as samples are tabulated in Table 2 and shown graphically in Figs. 13, 14, and 15. The uncertainty bands shown for each of these points are based on the precisions of each of the gas analyzers at the 95% confidence level. A detailed explanation of the derivations of these uncertainties is presented in section 8.1.

Figure 13 shows relatively good agreement among the PIR-2000, gas chromatograph, and orsat analyzer for measurements of CO, although one sample did show an excessively large discrepancy between the outputs of the PIR-2000 and the chromatograph. As one might expect, the spread in the indicated CO concentrations increases with increasing CO content in the sample. The indicated CO_2 concentrations for the same four samples (Fig. 14) show a considerable amount of disagreement. Two of the four samples show excessive disagreement between the PIR-2000 and the IR702, with the IR702 returning the greater reading in each case. This might suggest a problem with the calibration curve for the IR702, but further examination of Fig. 14 reveals that the IR702 does not return readings greater than those from the PIR-2000 for all of the samples. Also, the differences in the average of the indicated concentrations from these four instruments can be accounted for by uncertainty. The spread in CO_2 readings showed no apparent relationship to the concentration of CO_2 in the sample. Figure 15 shows a comparison of indicated O_2 concentrations from the MPA-21 and orsat. All four sets of readings agree well.

Table 2. Concentrations of CO_2, O_2, and CO indicated by the MPA-21, IR702, PIR-2000's, GC, and orsat for each of four calibration gas samples.

Sample No.	Component	MPA-21 (mole %)	IR702 (mole %)	PIR-2000 (mole %)	GC (mole %)	Orsat (mole %)
1	CO_2	-	14.70	14.55	14.56	14.5
	O_2	5.76	-	-	-	5.8
	CO	-	-	3.63	3.56	3.6
2	CO_2	-	10.58	10.66	10.66	10.5
	O_2	10.08	-	-	-	10.1
	CO	-	-	2.65	2.64	2.6
3	CO_2	-	6.70	6.57	6.51	6.6
	O_2	14.52	-	-	-	14.5
	CO	-	-	1.64	1.61	1.6
4	CO_2	-	4.12	3.94	3.99	3.9
	O_2	17.31	-	-	-	17.3
	CO	-	-	1.00	0.98	1.0

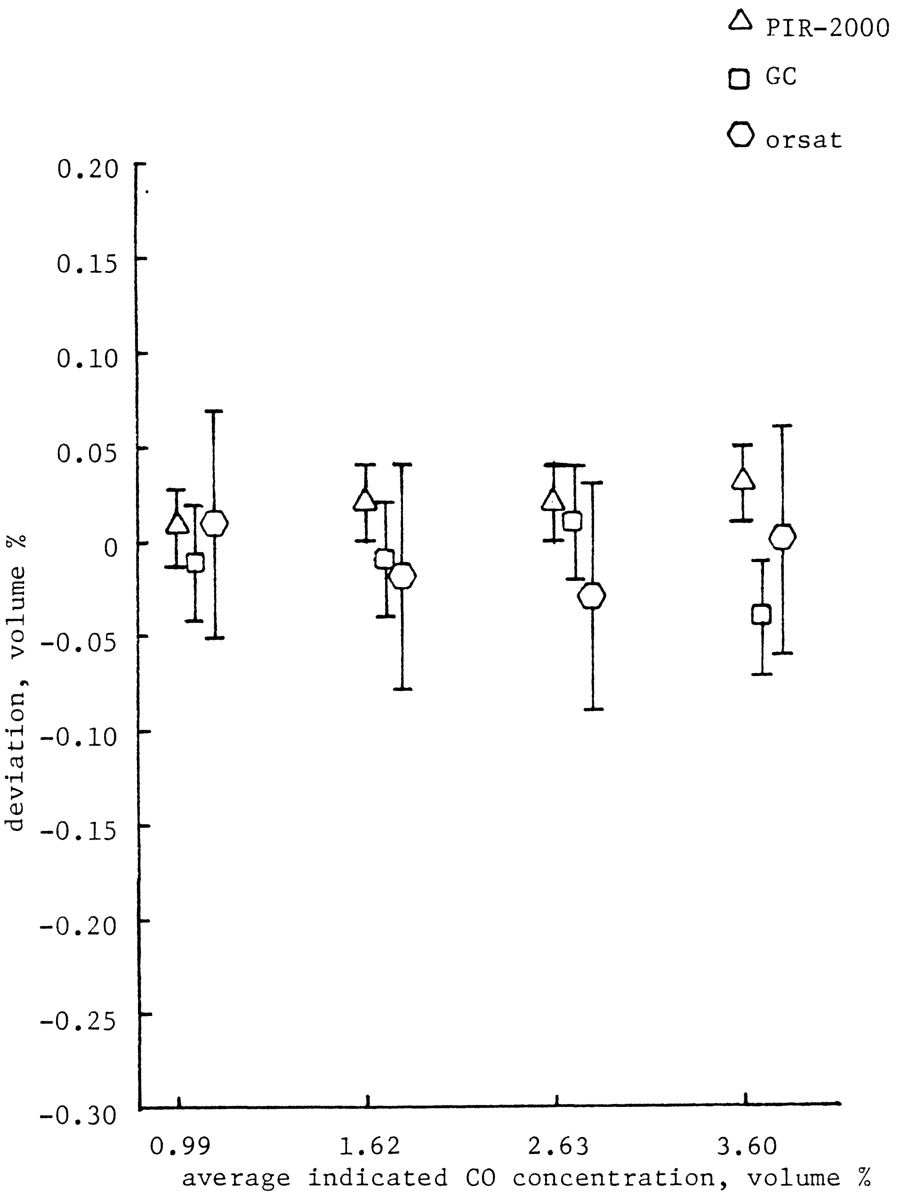

Figure 13. Deviatios of individual indicated CO concentrations from average of indicated CO concentrations for PIR-2000, GC, and orsat. Calibration gas samples.

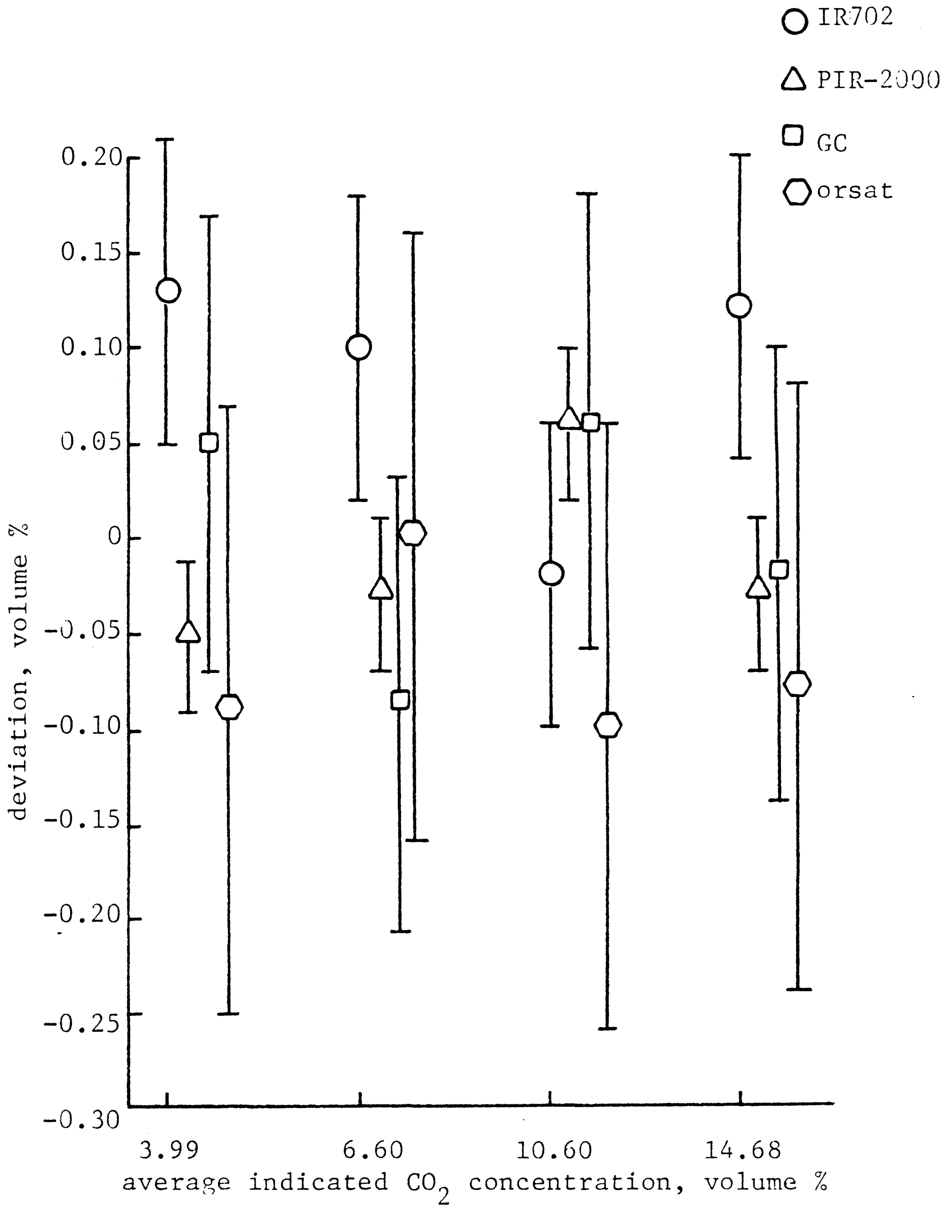

Figure 14. Deviations of individual indicated CO_2 concentrations from average of indicated CO_2 concentrations for IR702, PIR-2000, GC, and orsat. Calibration gas samples.

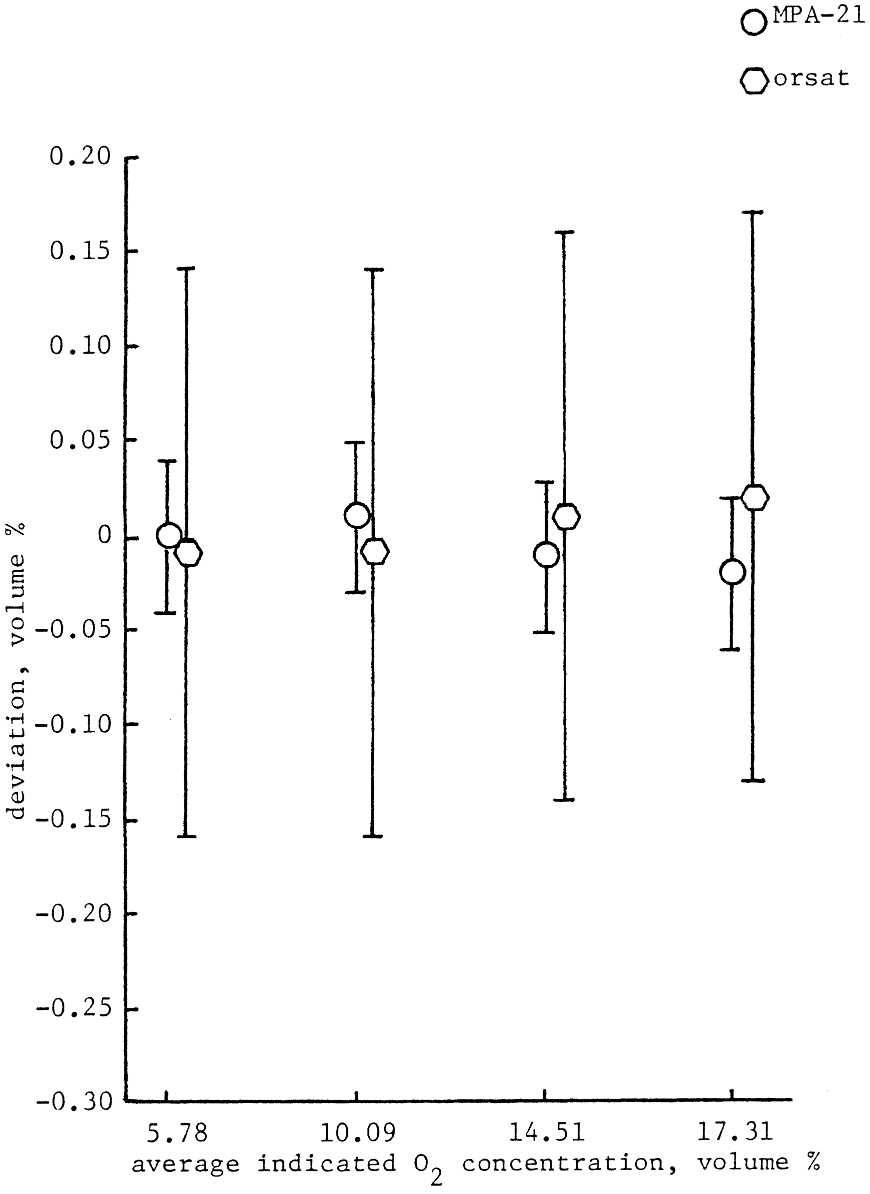

Figure 15. Deviations of individual indicated O_2 concentrations from average of indicated O_2 concentrations for MPA-21 and orsat. Calibration gas samples.

4.2 IR Spectroscopy Results

Prominent absorption bands were observed at several points in the infrared spectra generated for the twelve flue gas samples tested. By comparing these spectra with Sadtler standard infrared absorption spectra, and with spectra generated for calibration gas samples prepared in the VPI combustion laboratory, several of the peaks were quite readily identified. Figure 16 shows the experimental flue gas absorption spectrum generated for the first sample drawn during the first test (low-fire conditions). Spectra for the remaining eleven flue gas samples are shown in Figs. 39-49 in section 8.3. The vertical ties mark intervals of 100 cm^{-1}, beginning at 4000 cm^{-1} on the left-hand side of the spectrum. Peaks at 3705, 3605, 2350, 720, and 667cm^{-1} were produced by CO_2 absorption. The split peak centered at 2140cm^{-1} is a characteristic of CO. The peaks at 1305 and 3020cm^{-1} were produced by methane absorption (see Fig. 17), as were the smaller groups of absorption bands surrounding each of these two larger peaks from about 3140 to 2850 cm^{-1}, and from 1385 to 1250cm^{-1}.

Only two other peaks showed up in the experimental IR spectra: one at approximately 950cm^{-1}, and the second at about 740m^{-1}. Examination of the standard spectra for the C_1 through C_4 hydrocarbons showed that only ethylene absorbs at 950cm^{-1}. Figure 18 shows that ethylene absorbs not only at 950cm^{-1}, but at several other wavelengths as well. (The upper trace extending from 1000 to 800 cm^{-1} shows the ethylene spectrum in this region for a low ethylene concentration.) None of these other peaks appear in the experimental spectra, which might preclude ethylene

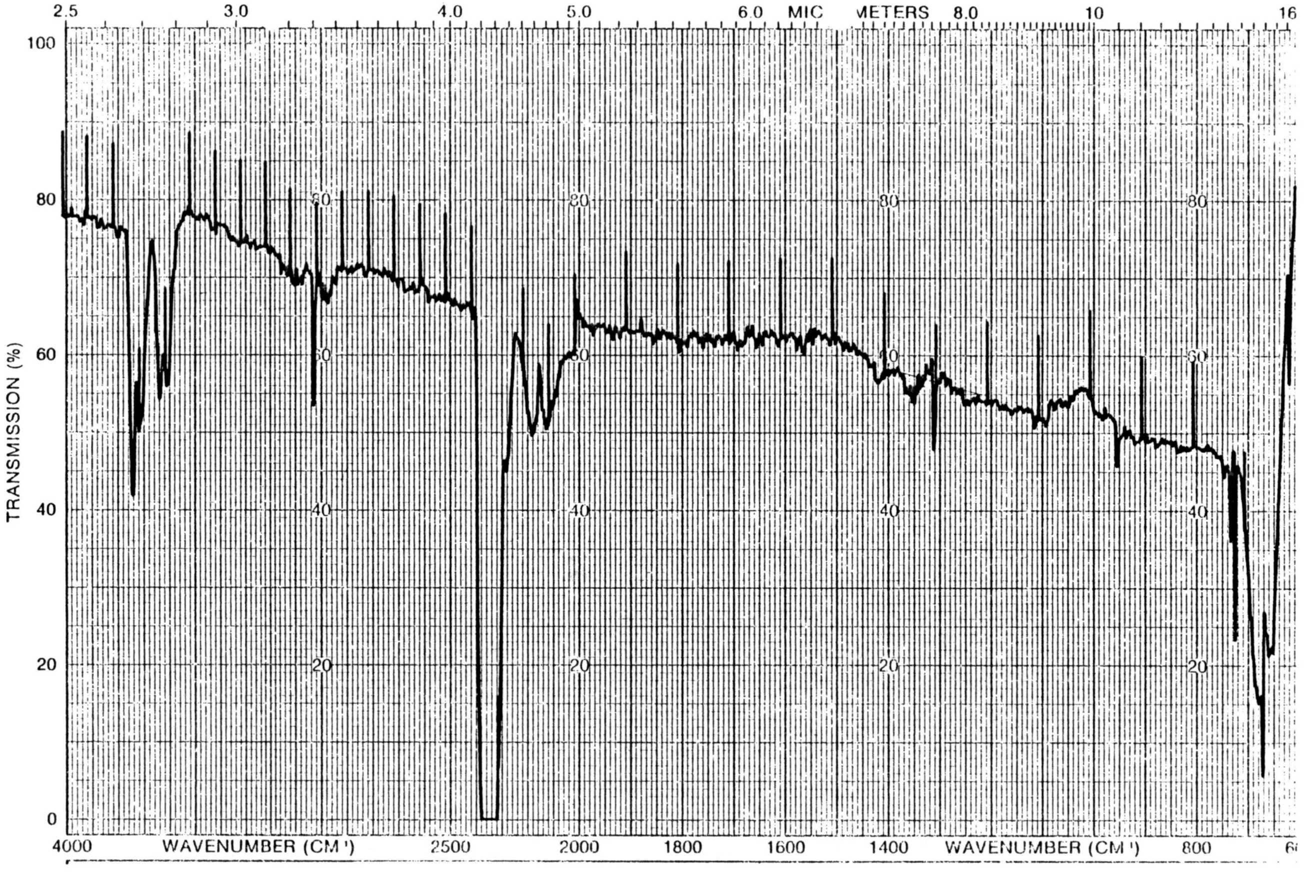

Figure 16. Experimental flue gas spectrum. Test#1, sample#1 (10 minutes into burn cycle).

42923P

METHANE

CH_4 Mol. Wt. 16.04

Source of Sample: MCB Manufacturing Chemists
Norwood, Ohio

CH_4

Gas Cell: 10cm/190mm

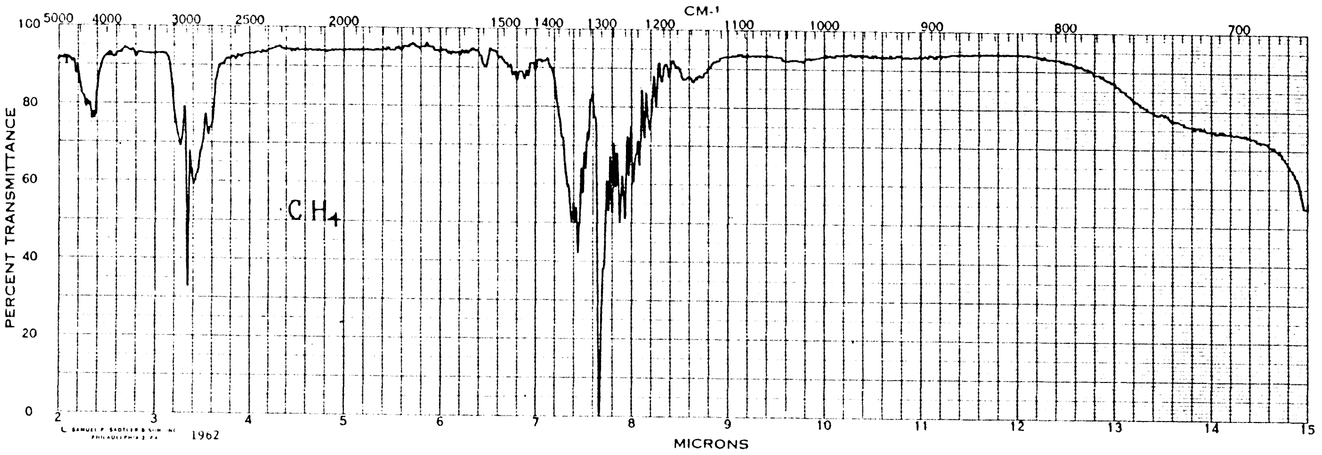

Figure 17. Standard spectrum for methane. © Sadtler Research Laboratories, Division of Bio-Rad Laboratories, Inc., 1975.

41316P

ETHYLENE

C_2H_4 Mol. Wt. 28.05

B.P. -103.9°C

Source of Sample: MCB Manufacturing Chemists
Norwood, Ohio

$CH_2{=}CH_2$

Gas Cell: 5cm

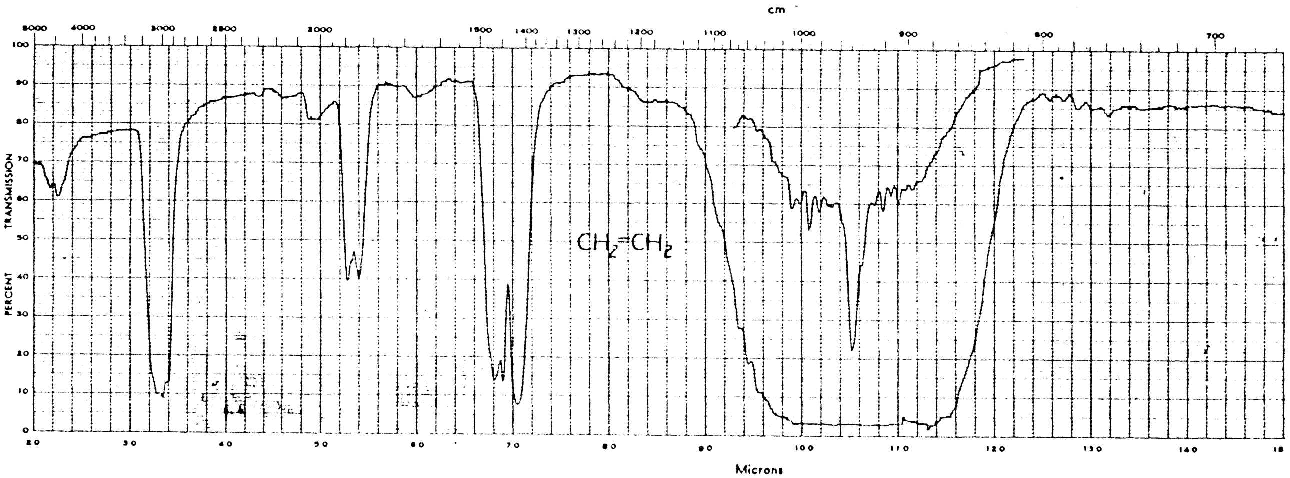

Figure 18. Standard spectrum for ethylene. © Sadtler Research Laboratories, Division of Bio-Rad Laboratories, Inc., 1975.

as a possible component of the flue gases. Consideration of the relative strengths of these peaks, however, shows that the peak at 950cm^{-1} is by far the most intense. This suggests that C_2H_4 is present in the flue gas samples, but in such low concentrations that only the peak at 950cm^{-1} is sufficiently intense to show up on the experimental spectra. The peak at 740cm^{-1} was not certainly identifiable. It is believed that this peak is a so-called "hot band," a peak generated by the transition of a molecule from an excited vibrational mode to a higher vibrational mode.

The significant point to be understood here is that only CO, CO_2, CH_4, and C_2H_4 were present in sufficient quantities to produce measurable absorption in the infrared region. Methane and ethylene do not absorb at wavelengths coincident with CO or CO_2. Therefore it is highly unlikely that any of the compounds present in the flue gases could cause significant interference with measurements of CO and CO_2 by nondispersive infrared analysis. Another interesting point is that measurements of methane in woodstove flue gases by infrared absorption should be possible. Since none of the other compounds present absorb energy at 1305 cm^{-1}, methane measurements using this absorption band should be free from interference.

4.3 Stack Gas Testing Results

The concentrations of CO in each of the twelve flue gas samples as indicated by the PIR-2000, gas chromatograph, and orsat analyzer are given in Table 3. These values, having been reduced to show the differ-

Table 3. Indicated CO concentrations from PIR-2000, GC, and orsat for each of twelve flue gas samples.

Test #	Sample #	PIR-2000 (mole %)	GC (mole %)	Orsat (mole %)	Average (mole %)
1	1	2.11	2.03	2.1	2.08
	2	0.93	0.90	1.0	0.94
	3	1.34	1.30	1.3	1.31
	4	0.79	0.76	0.8	0.78
2	1	1.92	1.81	1.9	1.88
	2	1.22	1.16	1.2	1.19
	3	0.72	0.69	0.8	0.74
	4	0.66	0.63	0.7	0.66
3	1	1.62	1.53	1.7	1.62
	2	1.52	1.43	1.6	1.52
	3	0.84	0.79	0.9	0.84
	4	0.53	0.49	0.6	0.54

ences between the individual outputs of these instruments and the average of the three indicated CO concentrations for each sample, are shown in Figs. 19, 20, and 21. Nine of the twelve samples showed differences between at least two of the indicated concentrations that could not be explained by uncertainties. These figures show a general trend toward increased disagreement among the indicated CO concentrations with increasing burn rate. If these differences were attributable to interference, one would expect them to occur when the presence of possible interferents is most likely. Since the only possible interferents are hydrocarbon compounds, the IR absorption spectra should give positive evidence of the possibility of interference by showing the quantitites of hydrocarbons present in the flue gas samples. Figure 22 shows the concentration of methane in each of the twelve samples as indicated by the absorption peak at 1305 cm^{-1} in the flue gas spectra. The only other compound identified by IR spectroscopy was ethylene, which varied in concentration proportionally with Methane. One can see from Fig. 22 that methane tended to be present in greatest quantities at low burn rates (averaged over an entire test) and toward the beginning of each burn cycle. (The instantaneous burn rate decreased as each test progressed.) But this is not the trend observed in the discrepancies between the CO analyzers. Thus one might conclude that the discrepancies are due to random errors and not interference. As a check on this conclusion, the indicated CO concentrations from each of the analyzers for each of the samples were subjected to a Blocked Factorial Analysis of Variance (ANOVA), which showed a statistical difference between these

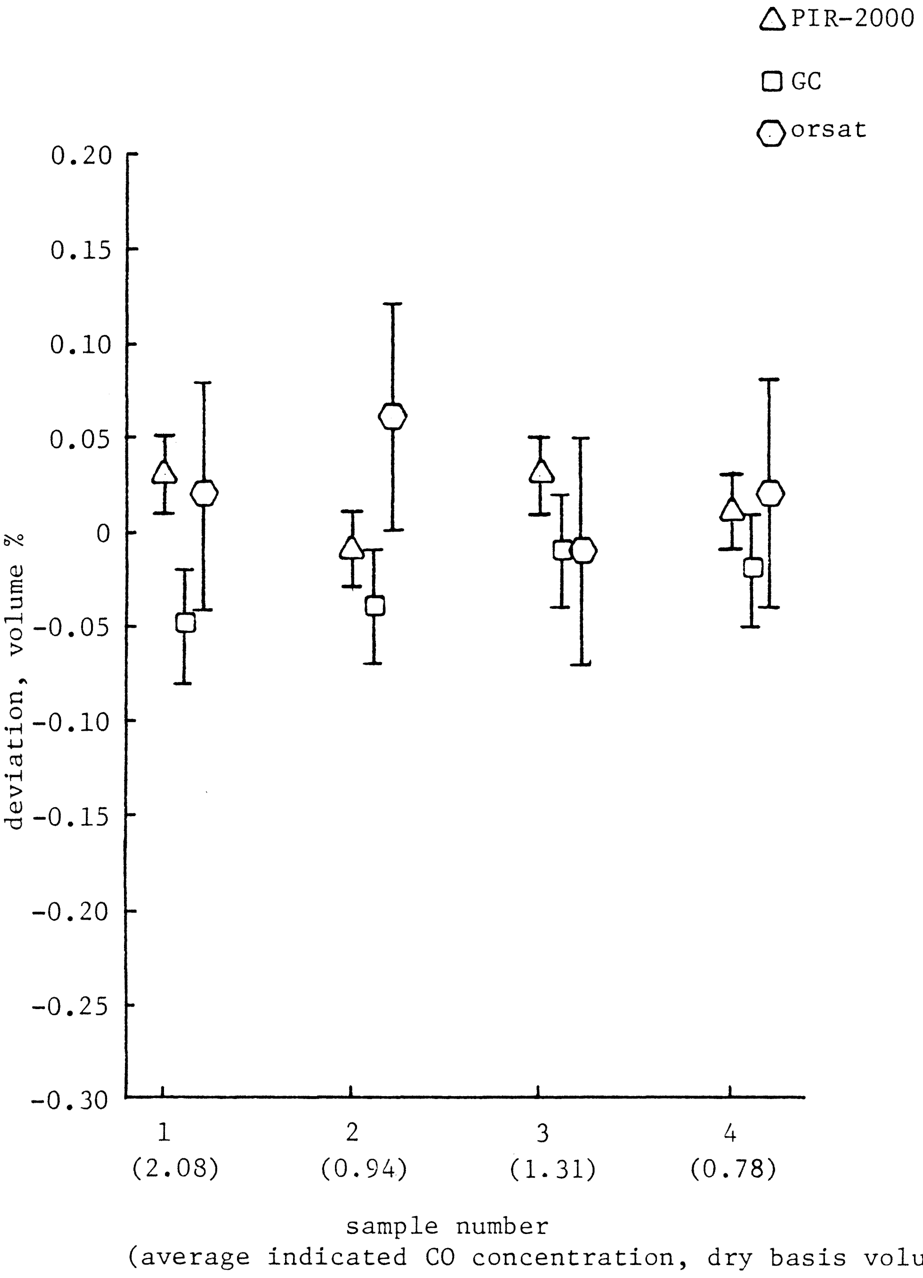

Figure 19. Deviations of individual indicated CO concentrations from average of indicated CO concentrations for PIR-2000, GC, and orsat. Flue gas samples. Test#1 (burn rate=2.1 kg/hr).

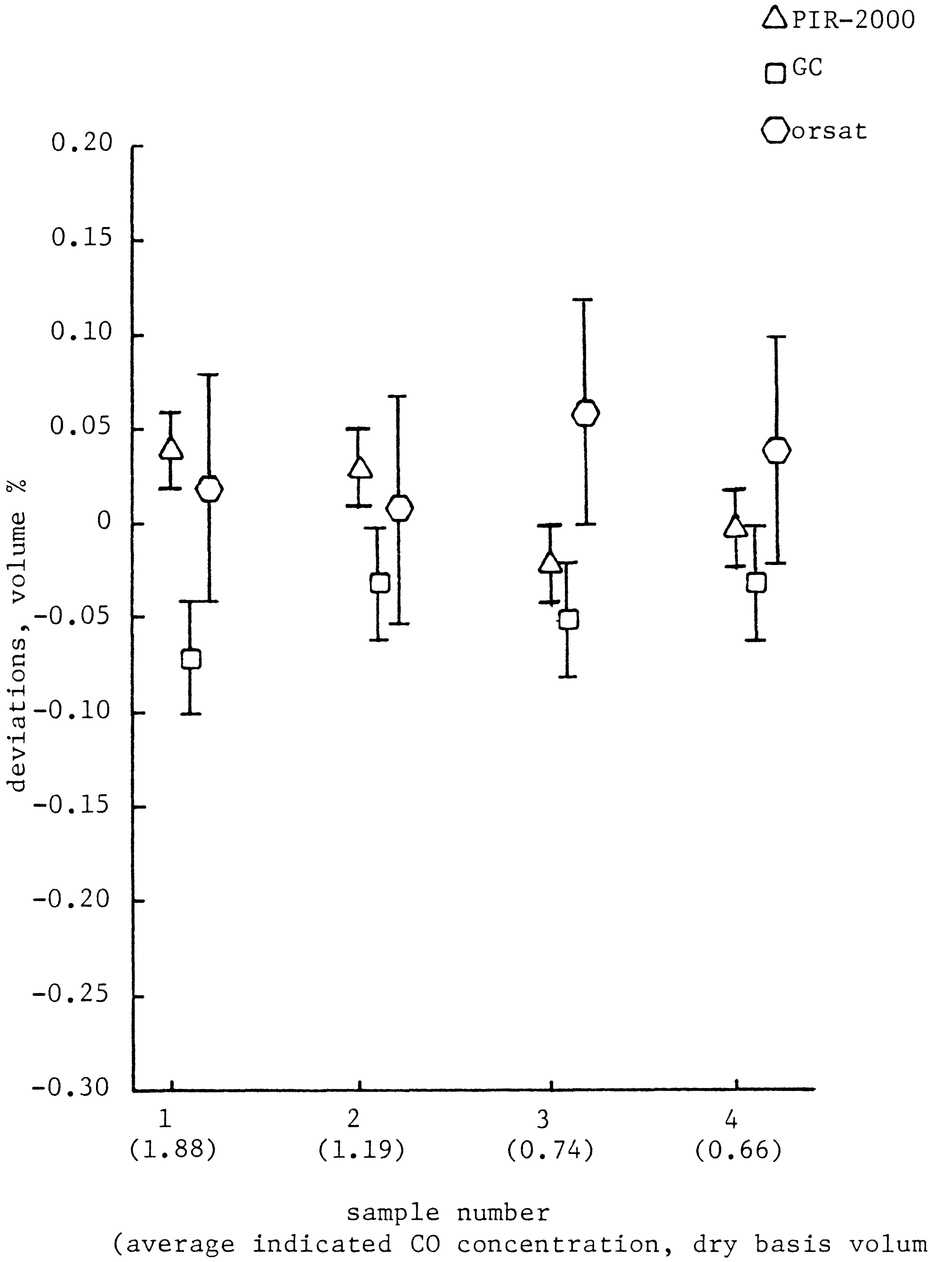

Figure 20. Deviations of individual indicated CO concentrations from average of indicated CO concentrations for PIR-2000, GC, and orsat. Flue gas samples. Test#2 (burn rate=3.6 kg/hr).

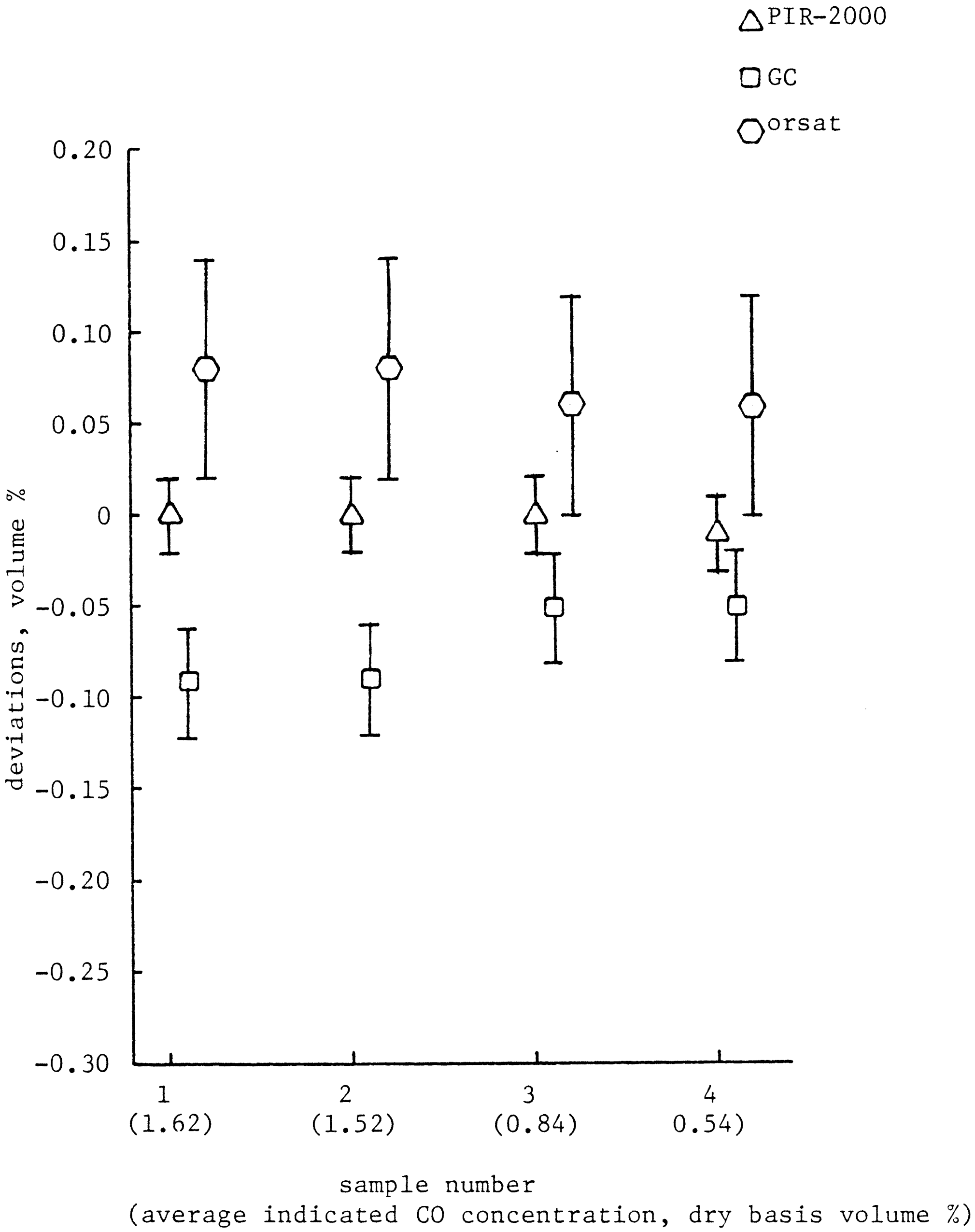

Figure 21. Deviations of individual indicated CO concentrations from average of indicated CO concentrations for PIR-2000, GC, and orsat. Flue gas samples. Test#3 (burn rate=6.3 kg/hr).

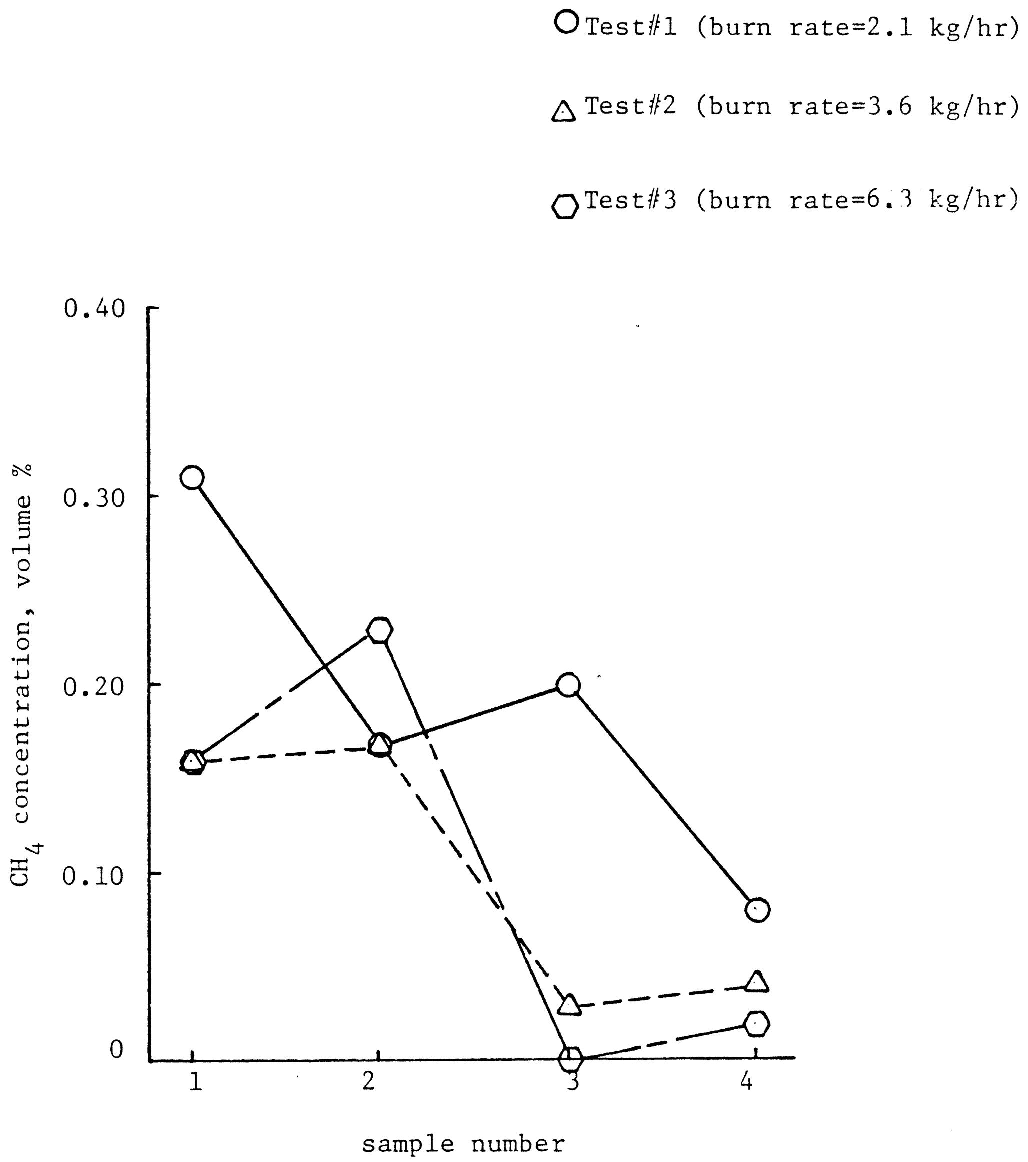

Figure 22. Methane concentrations for four flue gas samples taken during each of three tests.

analyzers at the 95% confidence level. That is, only a 5% chance exists that these discrepancies could be due only to random error. Increasing the confidence level to 99% showed no strong evidence of difference. This conflicting series of facts lends no easy answer to the question of interference with CO measurements in woodstove flue gases. The orsat apparatus is the only one of the three CO analyzers which should be susceptible to any sort of interference (absorption of unsaturated hydrocarbons into the cuprous sulfate beta-naphthol solution), and this apparatus does indeed return higher-than-average CO readings for every sample. In no instance, however, is the orsat reading higher than both the PIR-2000 and gas chromatograph by an amount greater than its uncertainty. Thus no firm conclusion can be drawn from these data, except that interference should not be present.

Table 4 shows the concentrations of CO_2 in each of the twelve flue gas samples as indicated by the IR702, PIR-2000, gas chromatograph, and orsat analyzer. Figures 23, 24, and 25 show the deviations of these individual indicated concentrations from their averages for each of the twelve samples. Six of the twelve samples showed excessive disagreement among the analyzers, with no readily apparent relationship between the incidence of disagreement and burn rate or burn time. The results of a Blocked Factorial ANOVA on these data showed evidence of a statistical difference between the outputs of these four analyzers at both the 95% and the 99% confidence level. The data was not suitable for a statistical determination of which instrument was different from the others. None of the analyzers consistantly returned indicated concentrations

Table 4. Indicated CO_2 concentrations from IR702, PIR-2000, GC, and orsat for each of twelve flue gas samples.

Test #	Sample #	IR702 (mole %)	PIR-2000 (mole %)	GC (mole %)	Orsat (mole %)	Average (mole %)
1	1	11.25	11.25	11.22	11.2	11.23
	2	4.20	4.28	4.22	4.2	4.23
	3	7.89	8.14	7.95	7.8	7.95
	4	6.17	6.29	6.18	6.2	6.21
2	1	12.13	12.10	12.15	11.8	12.05
	2	6.98	7.19	7.17	7.0	7.09
	3	7.75	7.92	7.90	7.8	7.84
	4	5.02	5.00	5.01	4.8	4.96
3	1	10.06	10.14	10.04	9.8	10.01
	2	9.12	9.13	9.01	9.0	9.07
	3	10.66	10.85	10.74	10.6	10.71
	4	6.20	6.18	6.14	6.1	6.16

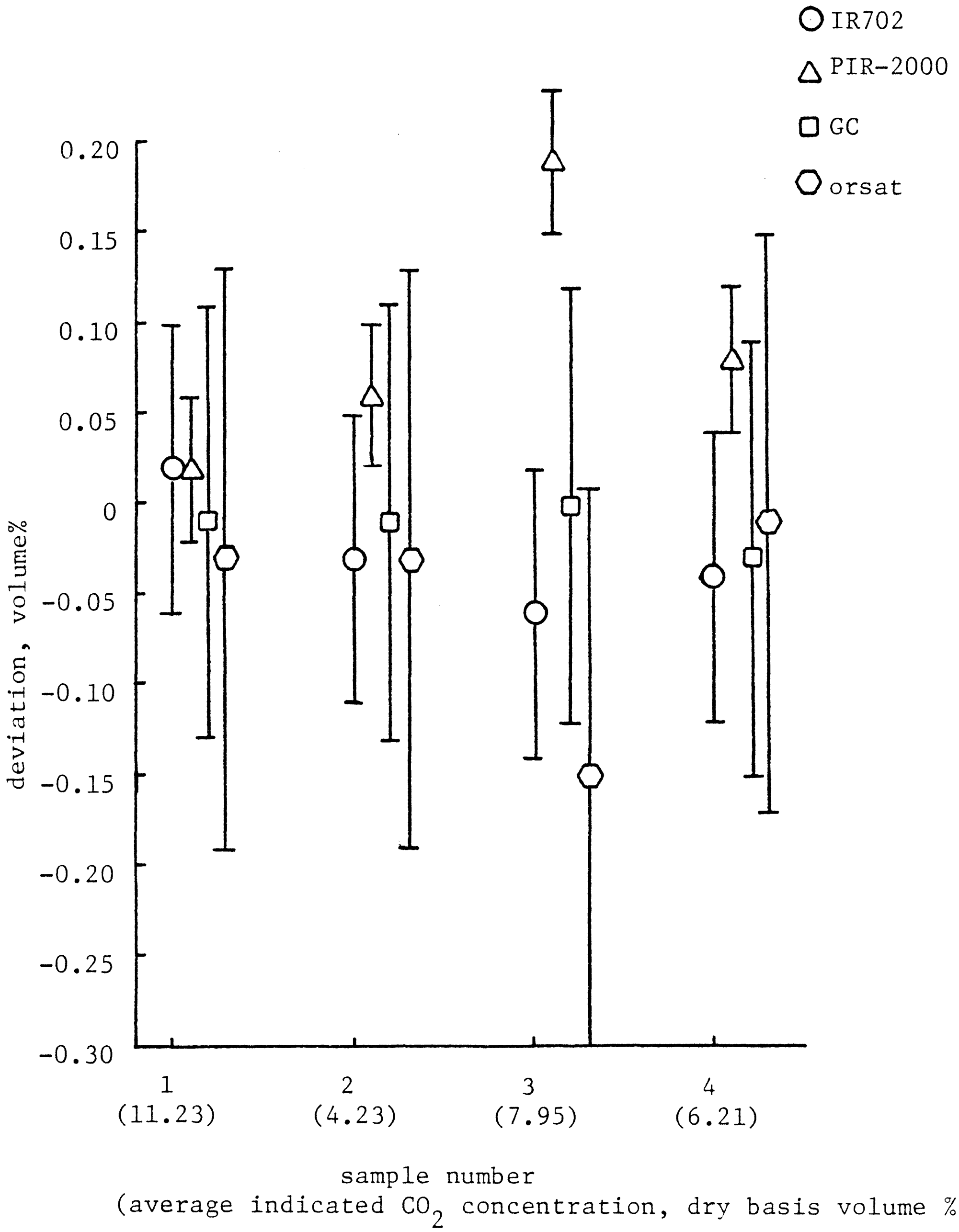

Figure 23. Deviations of individual indicated CO_2 concentrations from average of indicated CO_2 concentrations for IR702, PIR-2000, GC, and orsat. Flue gas samples. Test#1 (burn rate=2.1 kg/hr).

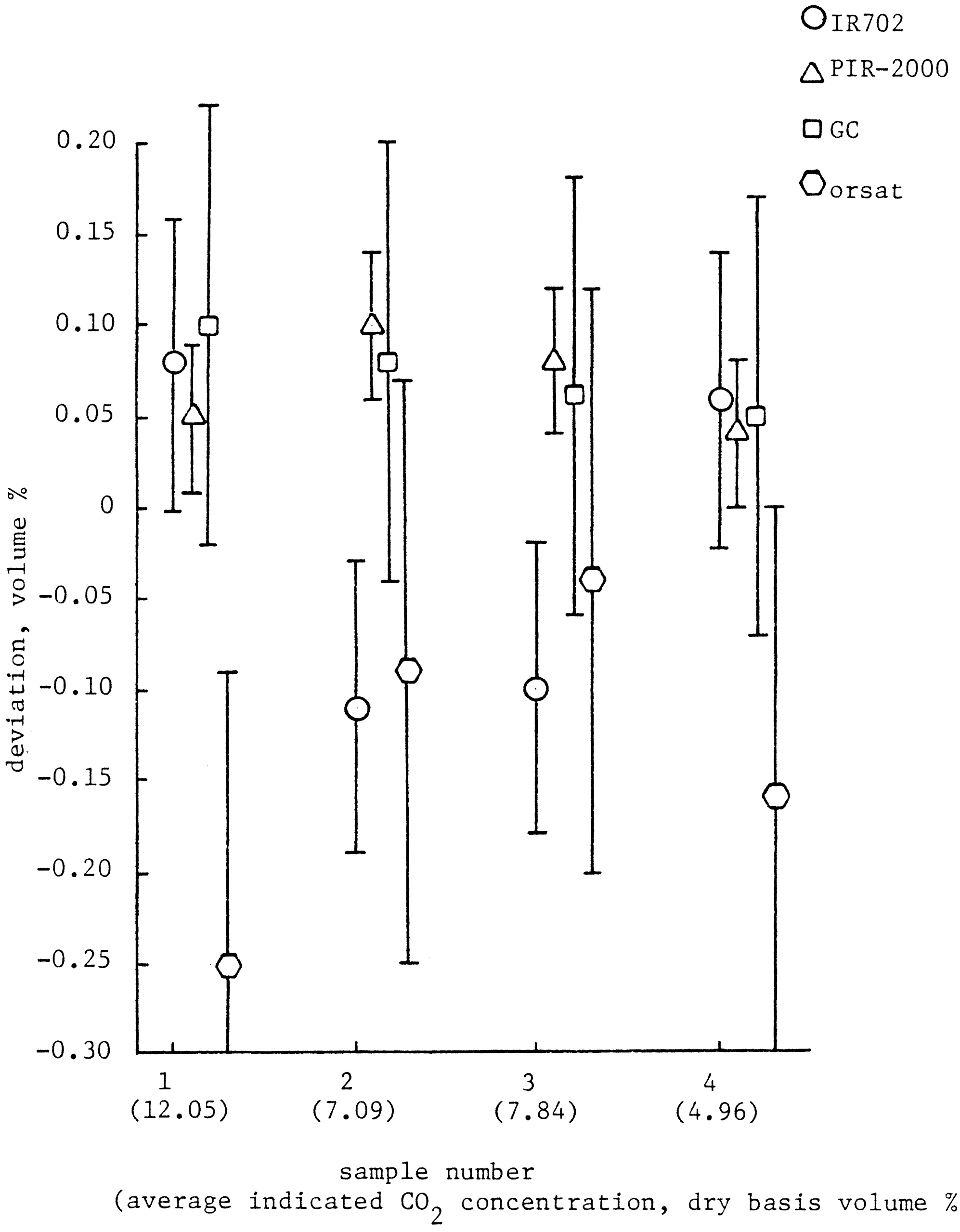

Figure 24. Deviations of individual indicated CO_2 concentrations from average of indicated CO_2 concentrations for IR702, PIR-2000, GC, and orsat. Flue gas samples. Test#2 (burn rate=3.6 kg/hr).

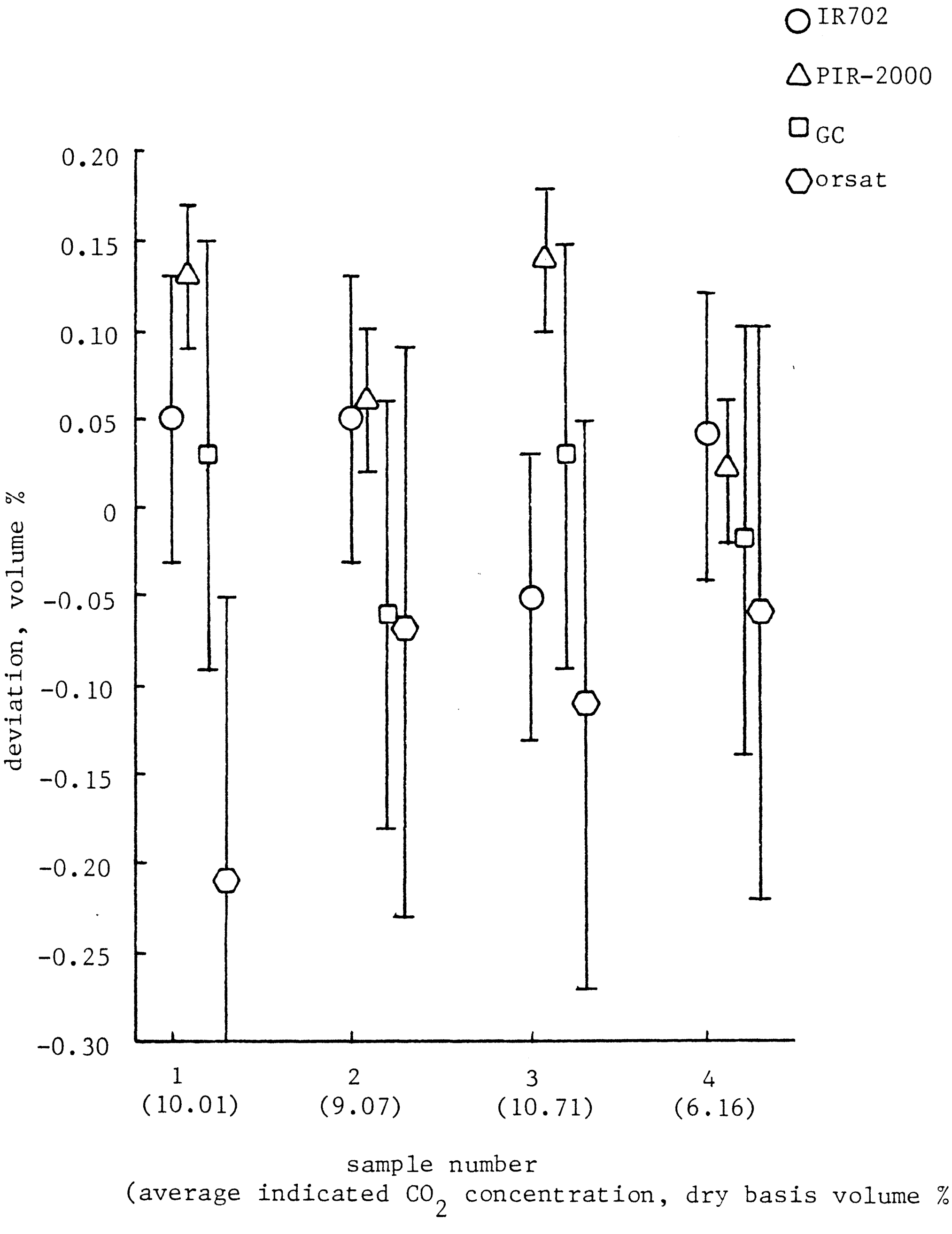

Figure 25. Deviations of individual indicated CO_2 concentrations from average of indicated CO_2 concentrations for IR702, PIR-2000, GC, and orsat. Flue gas samples. Test#3 (burn rate=6.3 kg/hr).

which were higher or lower than the other three instruments, as would be expected when interference is present. It is interesting to note, however, that the orsat results were always lower than the average of the indicated CO_2 concentrations, and that the PIR-2000 results were consistantly higher-than-average. If the orsat sample had become diluted with room air (due to a leak, for example), CO_2 and CO readings by this method would be depressed, while O_2 measurements would likely be elevated. (Oxygen measurements by orsat were not consistently higher than O_2 measurements by paramagnetism, as will be seen in the following discussion of O_2 measurements.) Readings from the IR702 and GC were well scattered with respect to the averages. The IR spectra of the flue gases showed no evidence of the presence of compounds which could interfere with the NDIR analyzers, suggesting that these analyzers ought to agree for flue gas samples. But five of the samples show excessive differences between the PIR-2000 and IR702 readings. In each of these cases the PIR-2000 returned the higher reading. While this might suggest interference with the PIR-2000, this instrument did not always return higher readings than the IR702. Four of the twelve samples show higher indicated CO_2 concentrations from the IR702 than from the PIR-2000 and three other samples showed agreement between the IR702 and PIR-2000 to within 0.03 mole percent. All of this serves to bring the suggestion of interference lent by the ANOVA into serious question.

Table 5 shows the O_2 concentrations indicated by the MPA-21 and orsat apparatus for each of the twelve samples. Figures 26, 27, and 28 show the differences between these readings, which are typically well

Table 5. Indicated O_2 concentrations from MPA-21 and orsat for each of twelve flue gas samples.

Test #	Sample #	MPA-21 (mole %)	Orsat (mole %)	Average (mole %)
1	1	9.00	8.8	8.90
	2	16.58	16.5	16.54
	3	11.88	11.7	11.79
	4	14.12	14.0	14.06
2	1	8.01	8.1	8.06
	2	13.45	13.4	13.43
	3	12.73	12.8	12.77
	4	15.59	15.6	15.60
3	1	10.29	10.5	10.40
	2	11.27	11.2	11.24
	3	9.42	9.5	9.46
	4	14.31	14.3	14.31

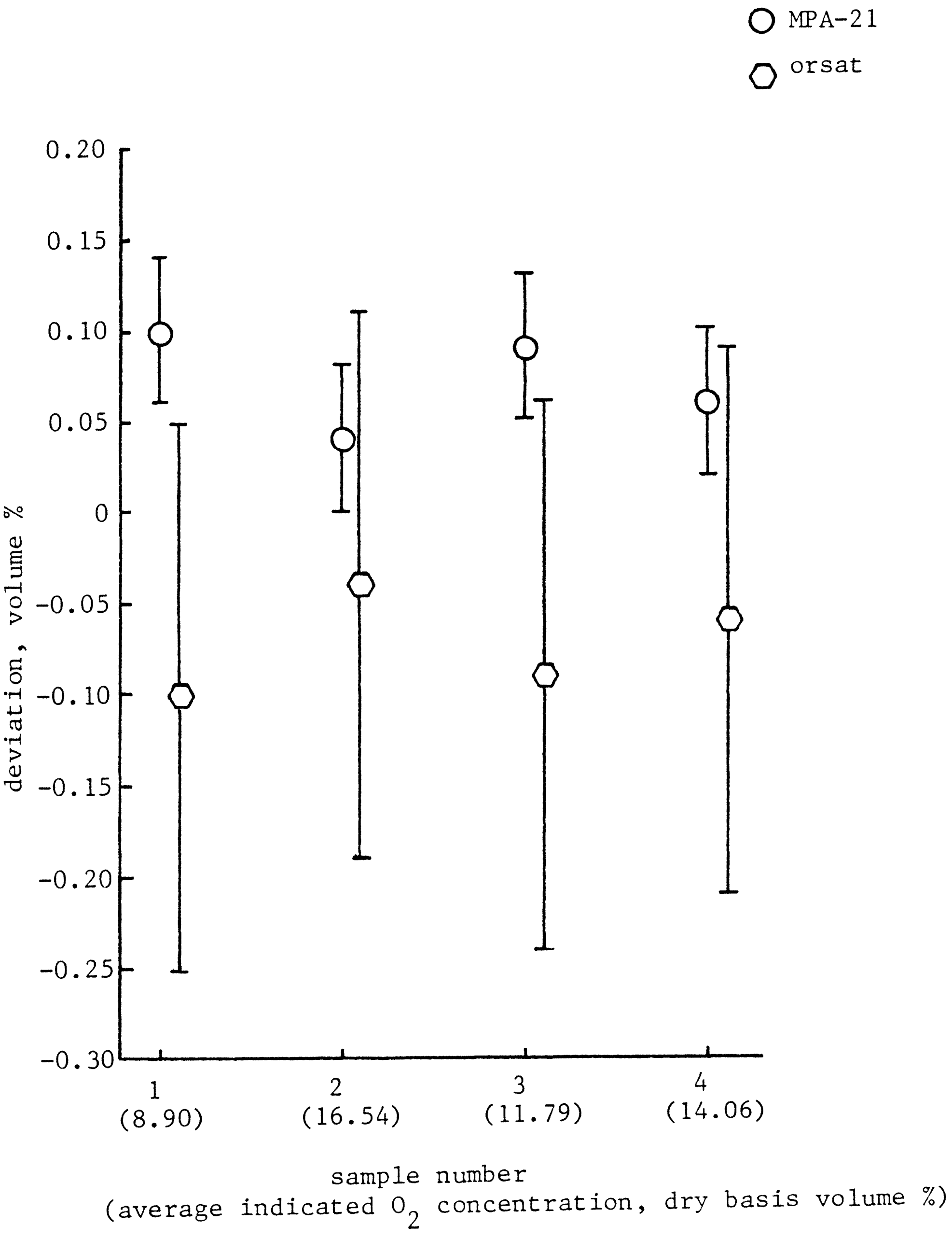

Figure 26. Deviations of individual indicated O_2 concentrations from average of indicated O_2 concentrations for MPA-21 and orsat. Flue gas samples. Test#1 (burn rate=2.1 kg/hr).

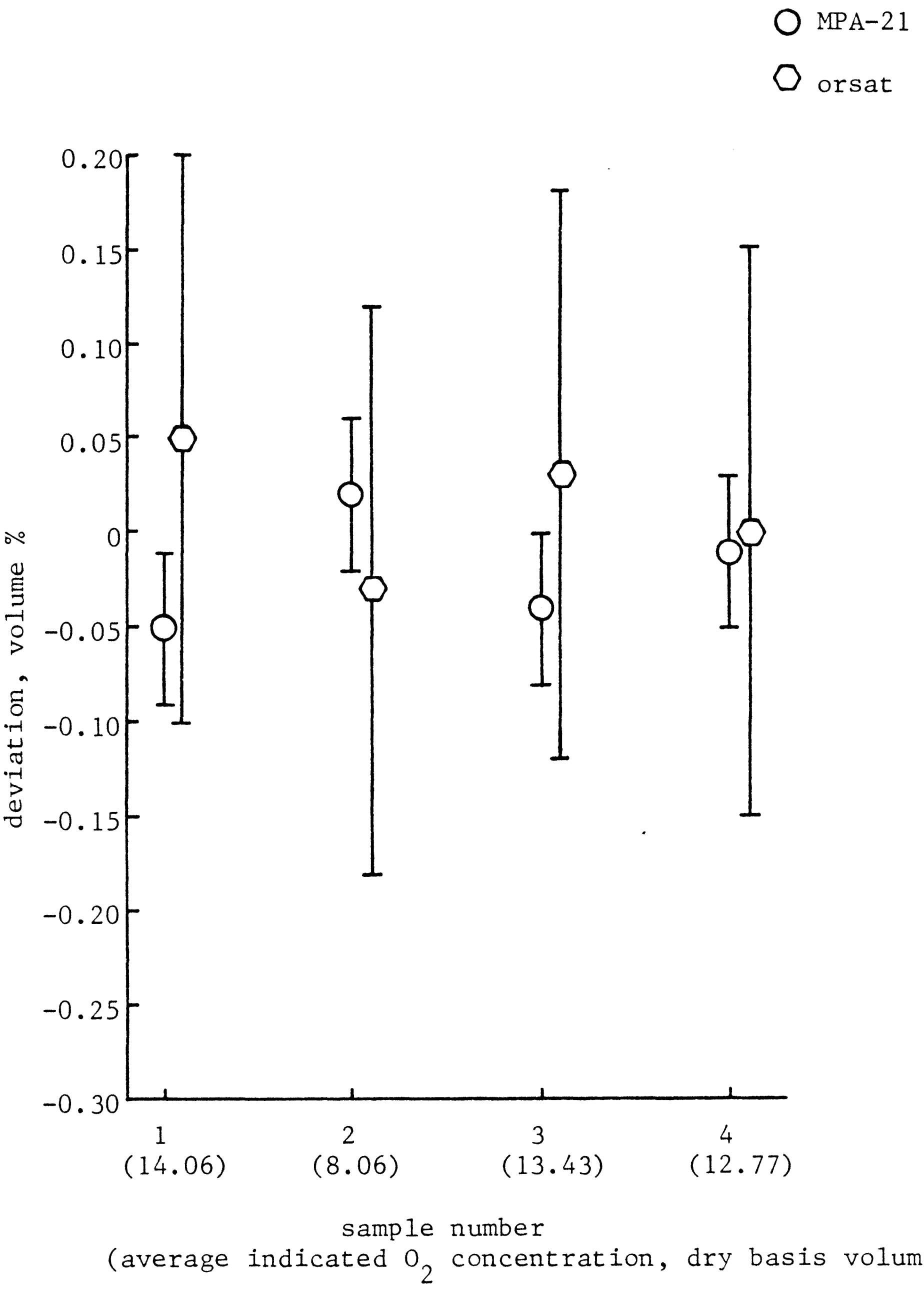

Figure 27. Deviations of individual indicated O_2 concentrations from average of indicated O_2 concentrations for MPA-21 and orsat. Flue gas samples. Test#2 (burn rate=3.6 kg/hr).

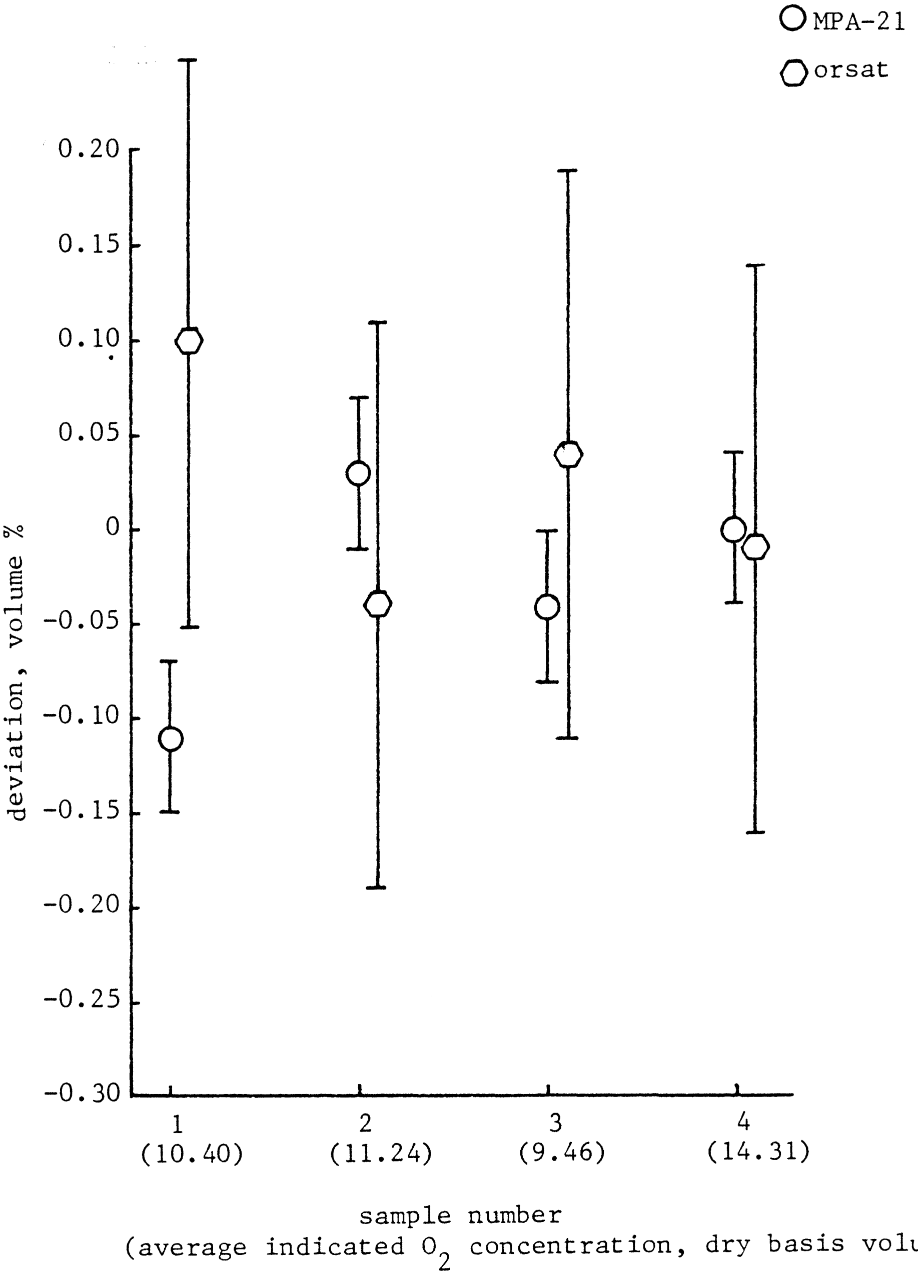

Figure 28. Deviations of individual indicated O_2 concentrations from average of indicated O_2 concentrations for MPA-21 and orsat. Flue gas samples. Test#3 (burn rate=6.3 kg/hr).

within the instruments' uncertainties. Only two of the samples show excessive differences: in one case the MPA-21 is high, and in the second case the orsat is high. Although both of these incidents occurred early in their respective burn cycles, only two of the three burns (low- and high-fire) showed this discrepancy. This suggests that the O_2 measurements made during these tests were not subject to interference, a fact supported by the blocked factorial ANOVA, which showed no evidence of difference between these analyzers.

Excessive discrepancies between CO and CO_2 concentrations indicated by the electronic instruments (IR702, PIR-2000's and gas chromatograph) and those reported by the orsat apparatus could be observed if the actual composition of the primary standard calibration gas used to prepare the calibration curves (Figs. 9,10, and 11) was different from the composition claimed by the manufacturer. For example, if the actual concentration of CO_2 in the calibration gas was lower than the concentration claimed by the manufacturer, each of the points on the calibration curves for the IR702, PIR-2000 (CO_2), and gas chromatograph (CO_2) would have been plotted too far to the right (toward higher concentrations). Thus measurements on flue gases by these instruments would indicate CO_2 concentrations which were erroneously high. Agreement among the IR702, PIR-2000, and chromatograph for CO_2 measurements would not be affected, as all three calibration curves would be shifted by an equal amount. A similar effect on the CO concentrations indicated by the PIR-2000 and gas chromatograph would be observed if the actual CO concentration in the calibration gas were lower than that claimed by the manufacturer of the gas. Measurements on flue gases by orsat analysis would not be affected by bad calibration gases, since this instrument did not require calibration. Calibration of the orsat was not necessary because this instrument gives outputs directly in mole percentages of the compounds being measured. Some error could be incurred if the burette on the orsat apparatus was improperly graduated, but preliminary test of this instrument using a series of sample blended from calibration gas (19.79% CO_2, 4.90% CO, balance N_2) and bottled air showed no irregularities in the burette graduation.

Oxygen measurements made using the MPA-21 would be unaffected by bad calibration gas, as the oxygen in the blended calibration samples was not supplied by the primary stnadard calibration gas bottle. However, since this analyzer was spanned using dry room air (assumed to contain 21.00% O_2 by volume), incorrect oxygen measurements could be obtained if the actual concentration of O_2 in the dry room air used for spanning was different from the assumed value.

Errors in the claimed composition of the primary standard calibration gas used to blend calibration samples for the MPA-21, IR702, PIR-2000's, and chromatograph are not indicated, as the agreement between these instruments and the orsat apparatus is generally good when samples of calibration gases are being analyzed. Agreement among the various instruments during precision testing was particularly good. For example, the range of the average indicated CO_2 concentrations from the IR702, PIR-2000, gas chromatograph, and orsat was only 0.05 mole percent with a nominal CO_2 concentration of 10 mole percent. The average O_2

concentrations reported by the MPA-21 and orsat were 10.25% and 10.22%, respectively, a difference of only 0.03 mole percent. Carbon monoxide readings averaged from 1.98% for the PIR-2000 to 2.02% for the chromatograph. The average CO concentration reported by the orsat differed from the average PIR-2000 reading by only 0.01 mole percent.

The tests conducted to show changes in sample composition due to absorption of CO, CO_2, or O_2 into the organic deposits on the sample line walls showed no evidence of such a problem. The concentrations of CO, CO_2, and O_2 in samples of a calibration gas as indicated by the IR702, PIR-2000's, and gas chromatograph were the same for dirty sample lines as for clean sample lines.

V. CONCLUSIONS

The conclusions of this investigation are:

1. No compounds were present in the flue gas samples which absorbed infrared radiation at wavelengths coincident with CO or CO_2. Therefore, it is unlikely that measurements of CO and CO_2 in woodstove flue gases using infrared gas analysis are subject to interference when the flue gas samples are prepared as described in section 3.3.
2. No firm evidence of interference with measurements of CO or CO_2 concentrations in the flue gas samples analyzed exists. There are, however, several discrepancies between the outputs of the various analysis techniques used for measurements of CO and CO_2 which cannot be explained by uncertainties.
3. Measurements of O_2 in woodstove flue gases by either paramagnetic analysis or orsat analysis (using a solution of cuprous oxide in hydrochloric acid for O_2 absorption) are not subject to interference.
4. Measurements of methane concentrations in woodstove flue gases can be made by monitoring the absorption of infrared radiation by the flue gas sample at 1305 cm^{-1}. No other compound which absorb at this wavenumber were present in the flue gas samples analyzed, suggesting that methane measurements made in this manner may not be subject to interference by other hydrocarbons present in the flue gases.

VI. RECOMMENDATIONS

The following recommendations are presented:

1. Further investigations should be conducted in order to confirm the conclusion that measurements of CO and CO_2 in woodstove flue gases are not subject to interference. This could be accomplished by making repeated measurements of CO and CO_2 concentrations on samples from the same sample bag using the IR702, PIR-2000's, gas chromatograph, and orsat analyzer for each of a number of samples drawn from the stack during a series of stove firings. Comparing the averages of the readings obtained from each of the instruments for each sample will reduce the possibility of mistaking random error for interference. These stove firings should all have low burn rates, since low-fire conditions produce the largest quantities of organic matter, the source of possible interference. The capacity of the sample collection bags will have to be increased to facilitate the increased volume of flue gas sample required for the repeated measurements. The gas analyzers will require a nitrogen purge between measurement repetitions for a given sample, but this can be accommodated without modification to the flue gas sampling system.
2. The MPA-21, IR702, PIR-2000's, gas chromatograph, and orsat analyzer should be calibrated using samples from a series of bottles containing various blends of CO_2, CO, O_2, N_2, and argon. The purpose of these gas blends will be to allow frequent checks of the calibration curve for each instrument using the same series of samples for each check. The bottled gases will also permit precision checks for each

of the instruments over its entire operating range. The concentrations of CO, CO_2, and O_2 in these bottles should cover the ranges from 0-5% CO, 0-20% CO_2, and 0-21% O_2 at regular intervals (for example: 1% CO, 4% CO_2, 4.1% O_2 in one bottle; 2% CO, 8% CO_2, 8.2% O_2 in the second bottle, etc.). The concentration of argon should be the same for all of the bottles, and should be equal to the concentration of argon typically found in a sample of dry room air close to the stove. The presence of the argon in these bottles will facilitate correction of the peak heights obtained from the gas chromatograph to yield oxygen concentrations in woodstove flue gas samples.

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VIII. Appendix

8.1 Uncertainty analysis

The uncertainty bands bracketing the data points shown in Figs. 19-28 are based on the precision of the various instruments. The determination of these precisions was made using repeated analyses of a bottle of primary standard calibration gas claimed to contain 2.00% CO, 9.99% CO_2, and 9.98% O_2. Ten analyses were made by the MPA-21, IR702, PIR-2000's, and orsat. Five analyses were made by gas chromatography. The resulting indicated concentrations of CO, CO_2, and O_2 from these analyses were analyzed to determine the standard deviation of the readings from each instrument. These standard deviations were then multiplied by a factor of 1.96, since the probability distribution curve shows that 95% of all readings from a given instrument for a given sample should fall within plus or minus 1.96 standard deviations of their mean value (22). The concentrations of CO, CO_2, and O_2 indicated by each instrument for each of the samples analyzed are summarized in Table 6. The standard deviations for the various gas analyzers and their respective uncertainties are in Table 7. Figures 29-37 show the precision data for the various analyzers in the form of histograms. Close inspection of Table 6 and Fig. 35 will reveal that the calculated uncertainty in CO_2 measurements made by the orsat analyzer has a total bandwidth that is more than 50% greater than the differnce between the highest and lowest CO_2 readings returned by the orsat apparatus during precision tests. While this is easily explained by the odd shape of the

Table 6. CO_2, O_2, and CO concentrations indicated by the MPA-21, IR702, PIR-2000's, GC, and orsat for calibration gas samples. Claimed composition of sample: 2.00% CO, 9.99% CO_2, 9.98% O_2.

Sample	Component	MPA-21 (mole %)	IR702 (mole%)	PIR-2000 (mole %)	GC (mole %)	Orsat (mole %)
1	CO_2	-	10.03	9.98	10.01	10.0
	O_2	10.25	-	-	-	10.4
	CO	-	-	2.00	2.00	2.0
2	CO_2	-	10.08	9.96	-	9.8
	O_2	10.25	-	-	-	10.3
	CO	-	-	1.96	-	2.0
3	CO_2	-	9.96	9.98	-	9.8
	O_2	10.23	-	-	-	10.2
	CO	-	-	1.99	2.03	2.0
4	CO_2	-	9.96	9.94	-	10.0
	O_2	10.23	-	-	-	10.2
	CO	-	-	1.98	-	2.0
5	CO_2	-	10.01	9.96	9.99	10.0
	O_2	10.28	-	-	-	10.2
	CO	-	-	1.98	2.01	2.0
6	CO_2	-	9.99	9.96	-	9.9
	O_2	10.23	-	-	-10.2	
	CO	-	-	1.97	-	2.0
7	CO_2	-	10.01	9.94	10.08	9.8
	O_2	10.28	-	-	-	10.2
	CO	-	-	1.98	2.01	2.0
8	CO_2	-	9.92	9.96	-	10.0
	O_2	10.25	-	-	-	10.1
	CO	-	-	1.99	-	1.9
9	CO_2	-	9.94	9.94	9.92	10.0
	O_2	10.25	-	-	-	10.2
	CO	-	-	1.97	2.04	2.0
10	CO_2	-	10.01	10.00	-	9.9
	O_2	10.28	-	-	-	10.2
	CO	-	-	1.99	-	2.0

Table 7. Standard deviations of precision data (Table 5) and precisions (for 95% confidence) for MPA-21, IR702, PIR-2000's, GC, and orsat.

Instrument	Compound	Standard Deviation (mole %)	Precision (mole %)
MPA-21	O_2	0.02	0.04
IR702	CO_2	0.04	0.08
PIR-2000	CO	0.01	0.02
	CO_2	0.02	0.04
GC	CO	0.02	0.03
	CO_2	0.06	0.12
Orsat	CO	0.03	0.06
	CO_2	0.08	0.16
	O_2	0.08	0.15

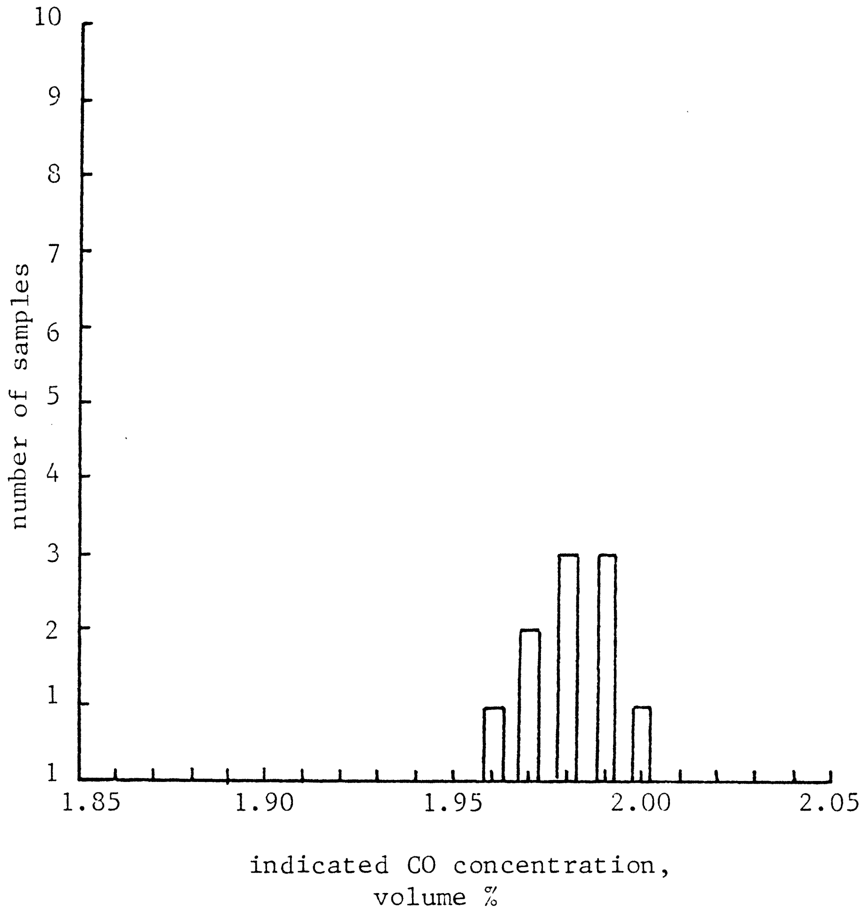

Figure 29. Distribution of precision data for PIR-2000 (indicated CO concentration for 10 calibration gas samples).

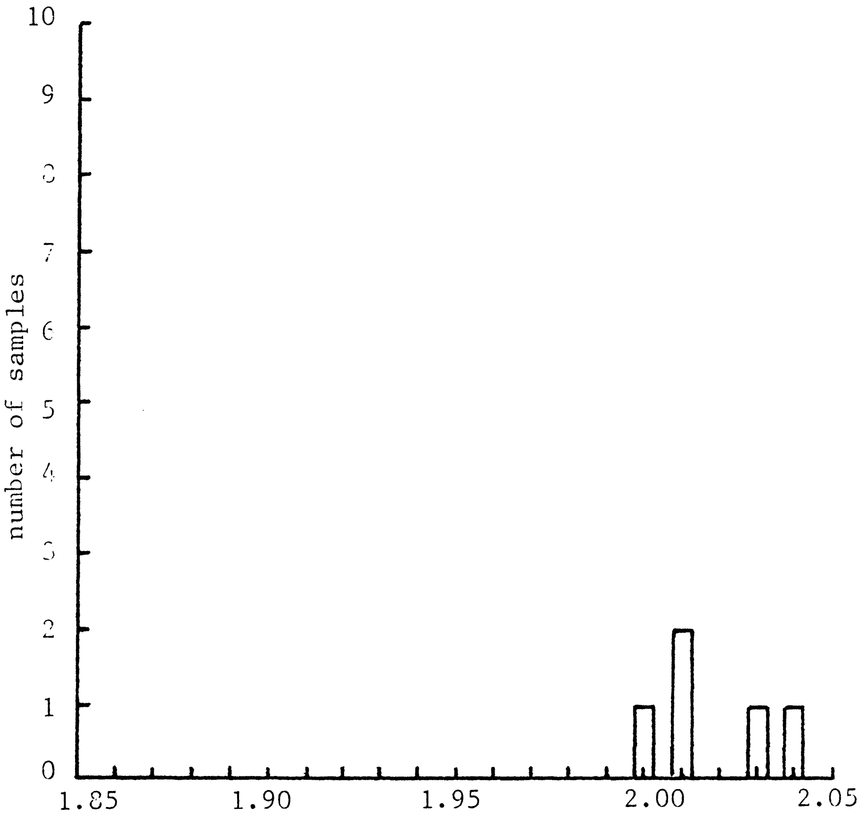

Figure 30. Distribution of precision data for GC (indicated CO concentration for 5 calibration gas samples).

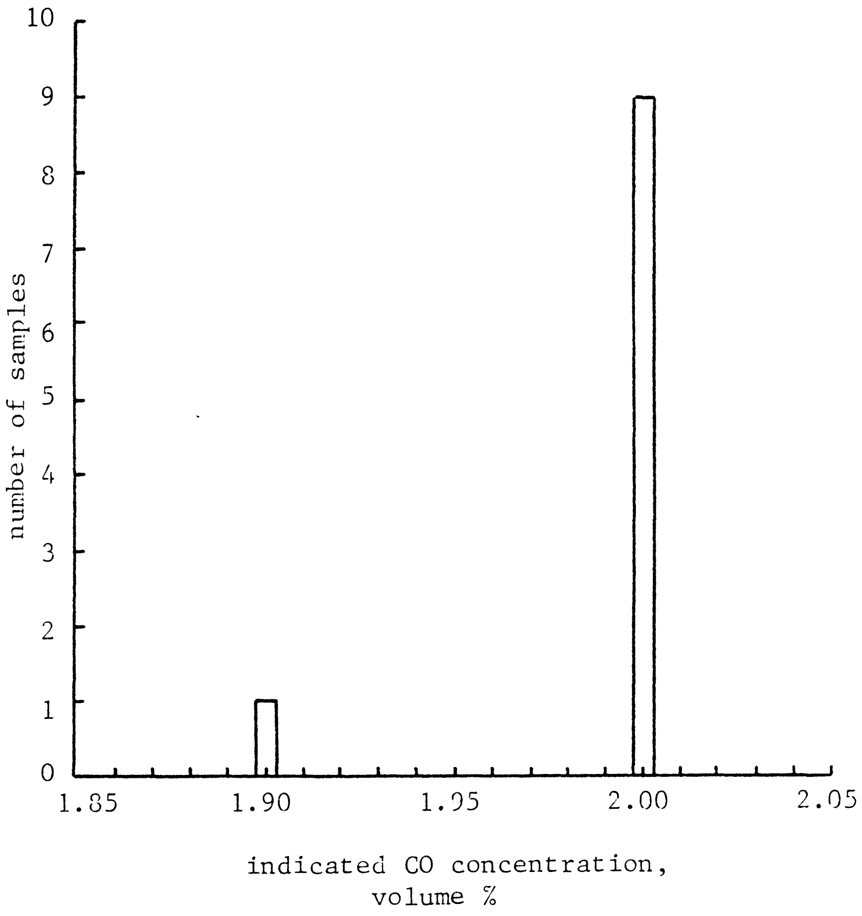

Figure 31. Distribution of precision data for orsat (indicated CO concentrations for 10 calibration gas samples).

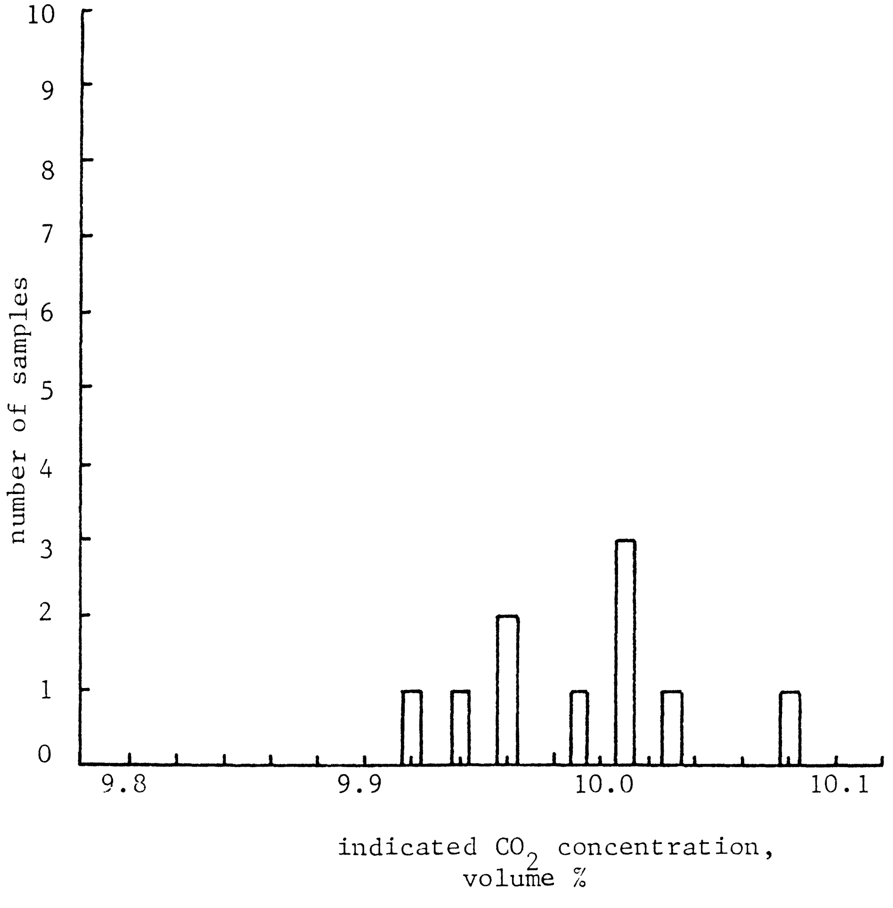

Figure 32. Distribution of precision data for IR702 (indicated CO_2 concentrations for 10 calibration gas samples).

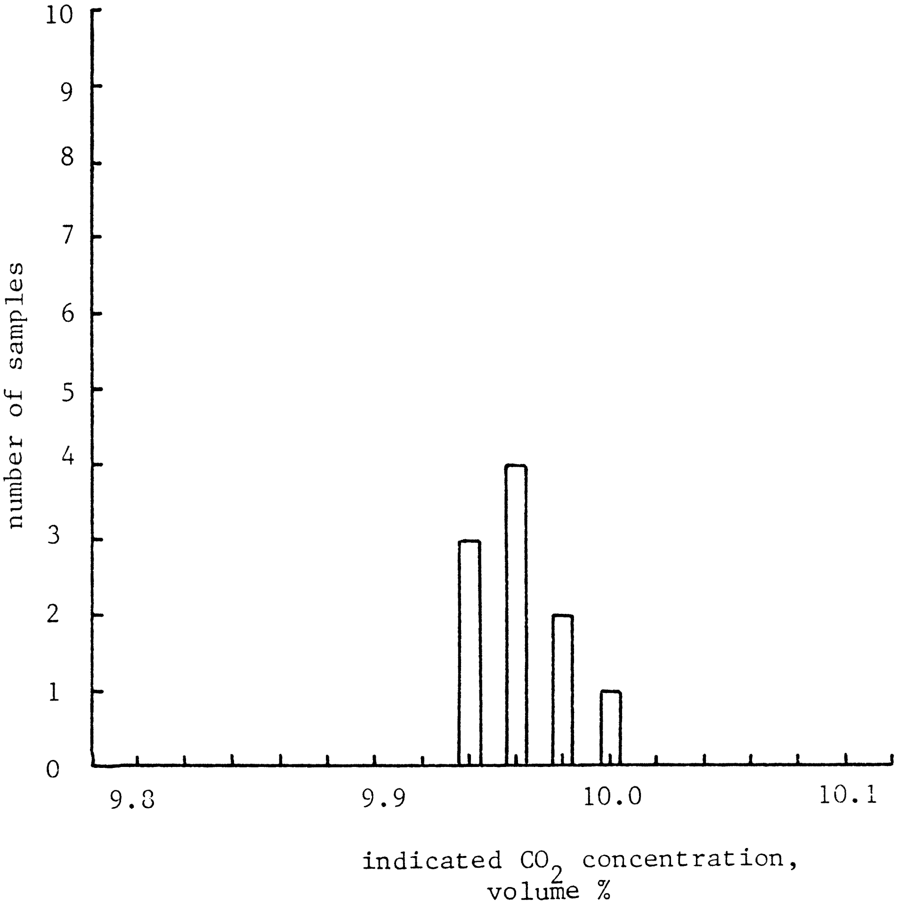

Figure 33. Distribution of precision data for PIR-2000 (indicated CO_2 concentrations for 10 calibration gas samples).

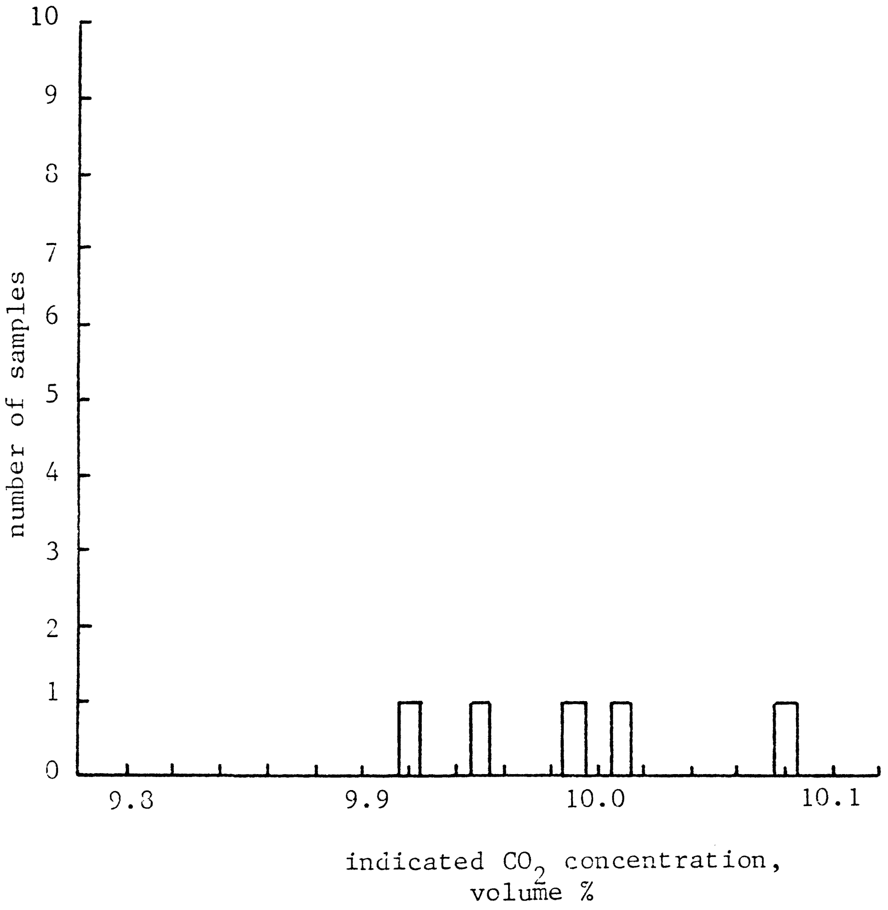

Figure 34. Distribution of precision data for GC (indicated CO_2 concentrations for 5 calibration gas samples).

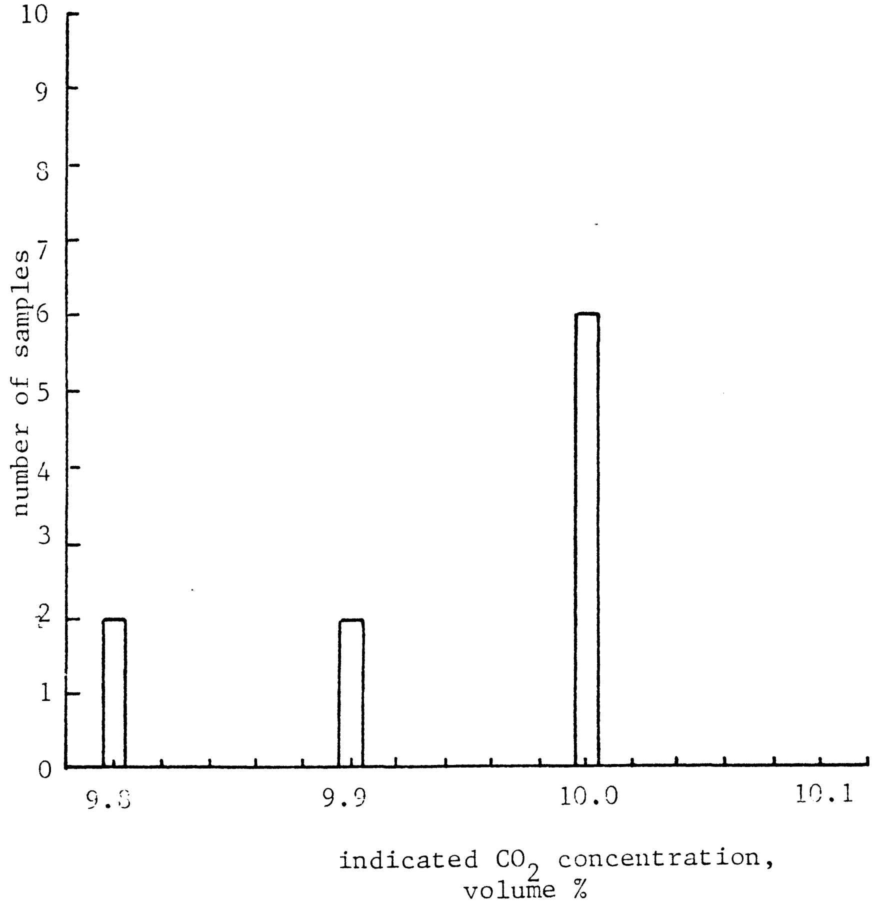

Figure 35. Distribution of precision data for orsat (indicated CO_2 concentrations for 10 calibration gas samples).

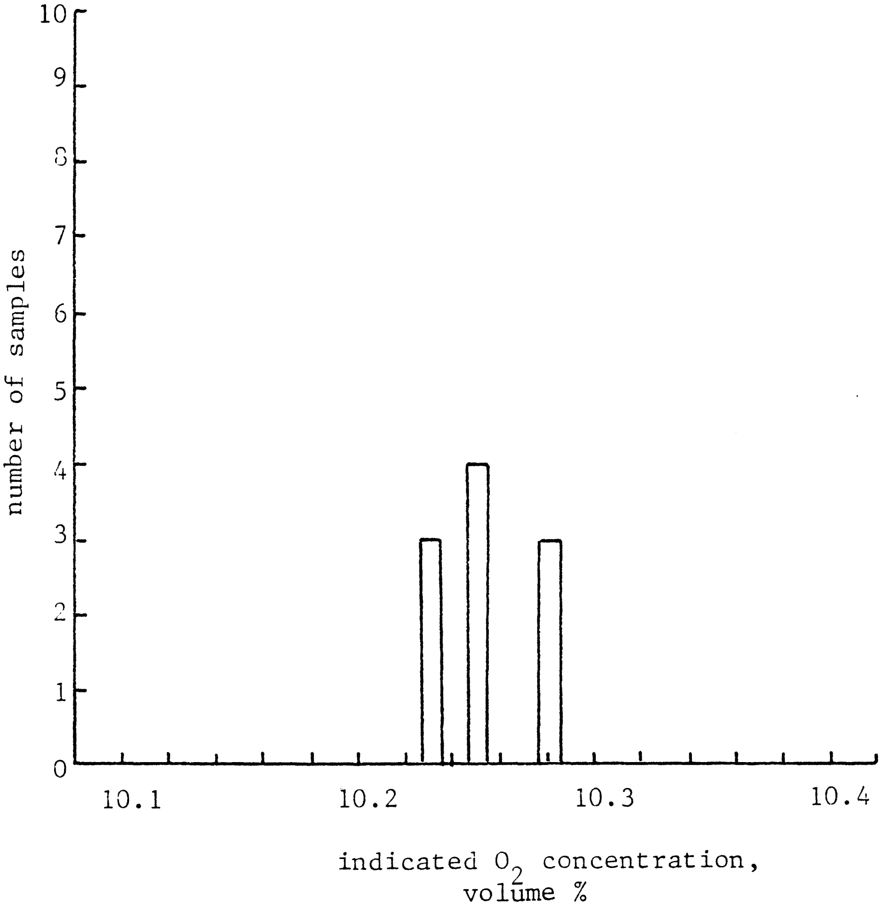

Figure 36. Distribution of precision data for MPA-21 (indicated O_2 concentrations for 10 calibration gas samples).

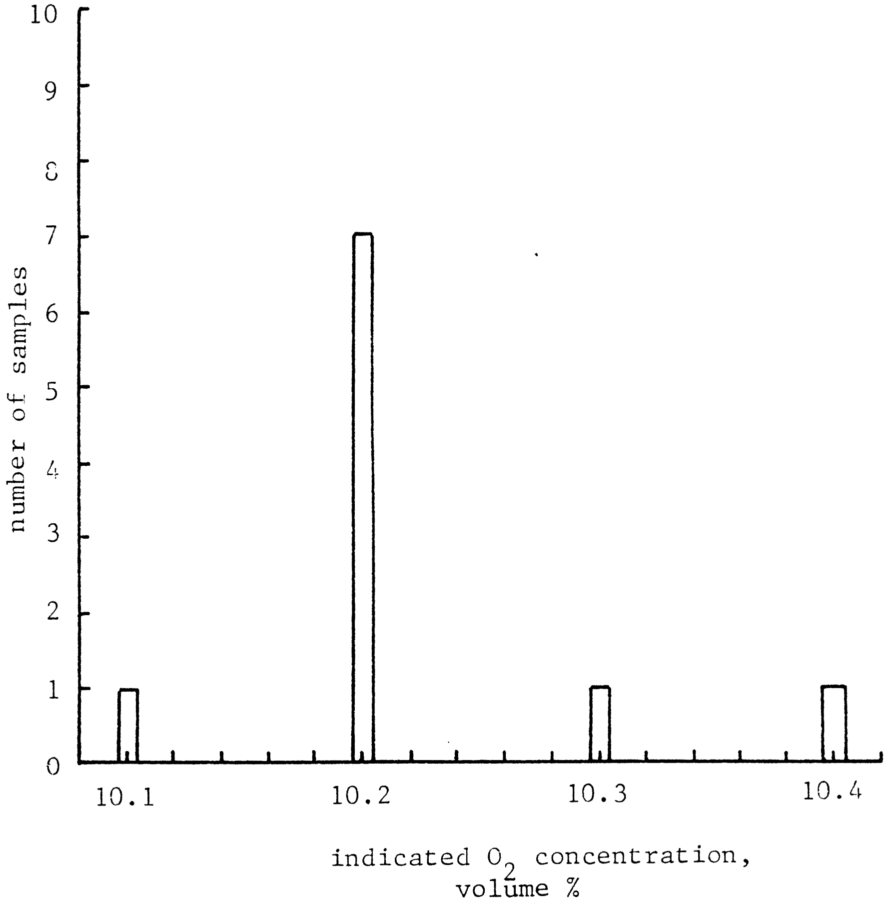

Figure 37. Distribution of precision data for orsat (indicated O_2 concentrations for 10 calibration gas samples).

histogram produced by these readings, the magnitude of the calculated uncertainty in the orsat CO_2 measurements is still larger than that claimed by some seasoned orsat operators. The author believes, however, that the calculated value, shown in Table 6 and in figures comparing CO_2 readings obtained from the various instruments used, is representative of his own ability to reproduce measurements of gas samples by orsat analysis.

8.2 Blocked Factorial Analysis of Variance

The use of a Blocked Factorial Analysis of Variance allows comparison of the outputs of the various instruments used to measure a given compound to determine whether any statistical difference between the instruments exists. The following example will use the CO_2 measurements made by the IR702, PIR-2000, gas chromatograph, and orsat analyzer to illustrate the application of this analysis.

Each of the four analyzers was used to make twelve separate measurements, for a total of 48 readings. Thus the total degrees of freedom associated with these readings is 48 - 1 = 47. These degrees of freedom can be divided to show the relative contributions of the number of burn cycles, the number of analyzers used, the number of samples taken during each burn cycle, and the various interactions between these three basic factors, to the total degrees of freedom. The allocation of degrees of freedom to the various factors is summarized in Table 8.

The three basic factors (burn cycle, sample number, and analyzers) must be classified as to whether they are fixed or random. Anderson and

Table 8. Distribution of degrees of freedom for blocked factorial analysis of variance. CO_2 data shown.

Source	Degrees of Freedom
Burn cycle (random)	3 - 1 = 2
Sample no. (fixed)	4 - 1 = 3
Sample no. x burn cycle interaction restriction error	2 x 3 = 6
Restriction error	0
Analyzer (fixed)	4 - 1 = 3
Analyzer x burn cycle interaction	3 x 2 = 6
Analyzer x sample no. interaction	3 x 3 = 9
Analyzer x burn cycle x sample no. interaction	3 x 2 x 3 = 18
Pure error	0
Total	47

Mclean (23) provide the guidelines for this determination, stating "the notion of fixed factors has been used in factorial experimentation with the understanding that all of the levels of interest of that factor were in the experiment." Since the factors affecting the type of burn cycle observed vary so widely, the burn cycle was chosen to be random. All of the analyzers of interest were in the experiment, so they were taken to be fixed. The series of samples drawn during each burn cycle were determined to represent all of the elements of a burn cycle which were of interest (early, mid, and late during the cycles), so the samples were taken to be fixed. With this determination made, the SAS General Linear Models Procedure was used to calculate the Type 1 sum of squares for the analyzers, and the analyzers-times-sample interaction. Each of these sums of squares was divided by its respective degrees of freedom to yield the Mean Square Error for the analyzers and for the analyzers x sample interaction. The ratio of the former to the latter is the F-factor, which can be compared to tabulated values of F-factors. If the calculated F-factor is greater than the tabulated value, statistical difference between the analyzers is indicated. If the calculated F-factor is less than the tabulated value, no strong evidence of difference exists. The tabulated F-factor used for comparison is chosen based on the degrees of freedom of each of the Mean Square Errors used to calculate the F-factor and the level of confidence desired (typically 95% or 99%). The calculated values of the F-factors for the CO_2, O_2, and CO data, as well as the tabulated values of the F-factors for each set of stack gas data, are tabulated in Table 9. Examination of Table 9

Table 9. Results of blocked factorial analysis of variance.

Source	Degrees of Freedom	Mean square Error	F (calc.)	F (95%)	F (99%)
Co_2:					
Analyzer	3	0.0748	12,83	4.76	9.78
Analyzer x burn cycle interaction	6	0.00583			
O_2:					
Analyzer	1	0.00260	0.11	18.50	98.50
Analyzer x burn cycle interaction	2	0.0234			
CO:					
Analyzer	2	0.0249	11.15	6.94	18.00
Analyzer x burn cycle interaction	4	0.00223			

reveals that the F-factor calculated for the CO_2 readings obtained during stack gas testing is greater than the tabulated F-factors for both the 95% and 99% confidence levels. Thus the blocked factorial ANOVA of these data points shows only a one percent chance that the differences in the outputs of the various analyzers is attributable to random error. The calculated F-factor for the CO readings is bracketed by the tabulated F-factors for the 95% and 99% confidence levels. This shows that the outputs of the PIR-2000, gas chromatograph, and orsat were statistically different at the 95% confidence level, but showed no strong evidence of difference at the 99% confidence level. The fact that the F-factor calculated for the O_2 data is lower than the tabulated values for both confidence levels indicates that no statistical evidence of difference between the orsat and MPA-21 exists.

8.3 Experimental Spectra

Figures 38-49 show IR abosrption spectra genrated by the PE283 during stack gas testing. Figure 38 gives a baseline scan, generated with nitrogen in the reference and sample cells. Figures 39-49 are spectra of flue gas samples drawn during the three stack gas tests.

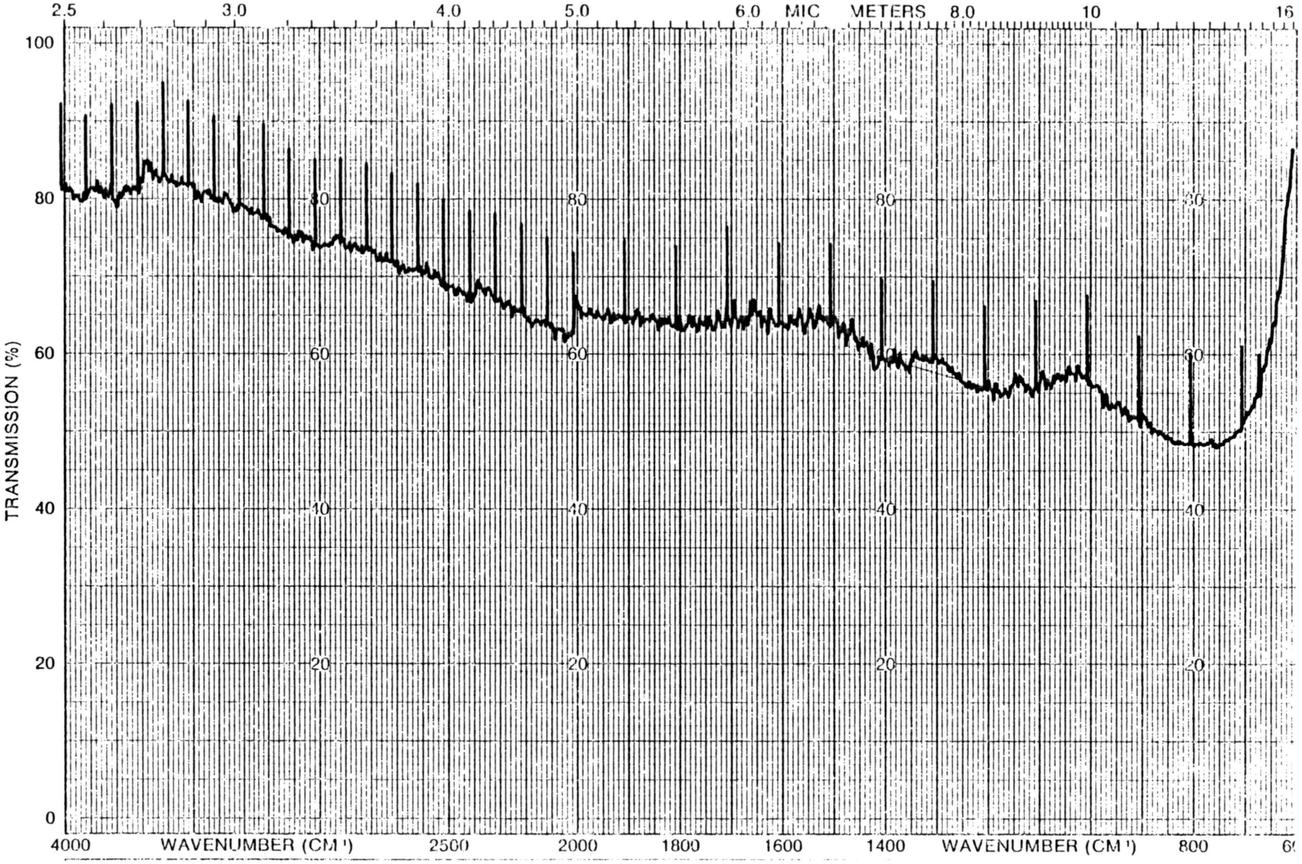

Figure 38. Baseline scan (nitrogen sample).

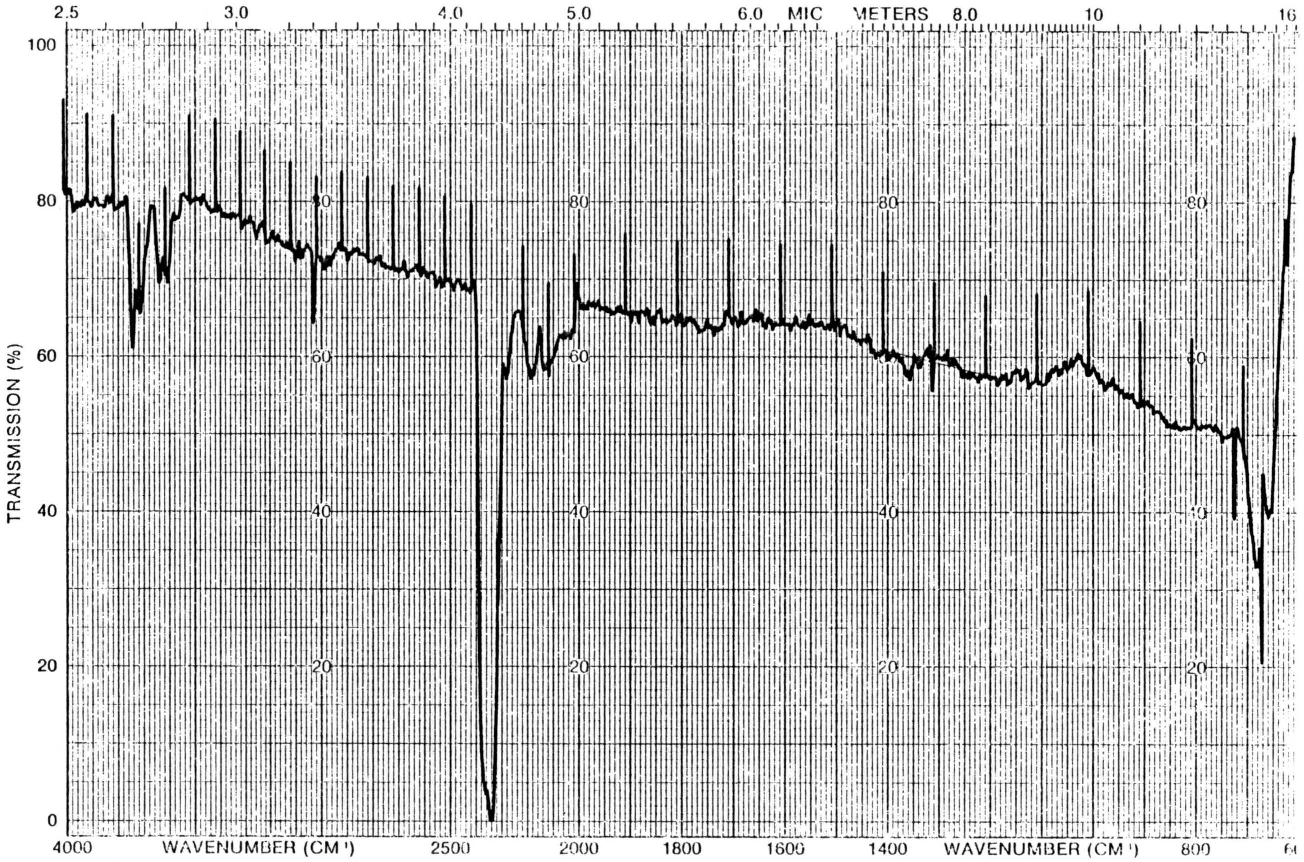

Figure 39. Experimental flue gas spectrum. Test#1, sample#2 (2.0 hours into burn cycle).

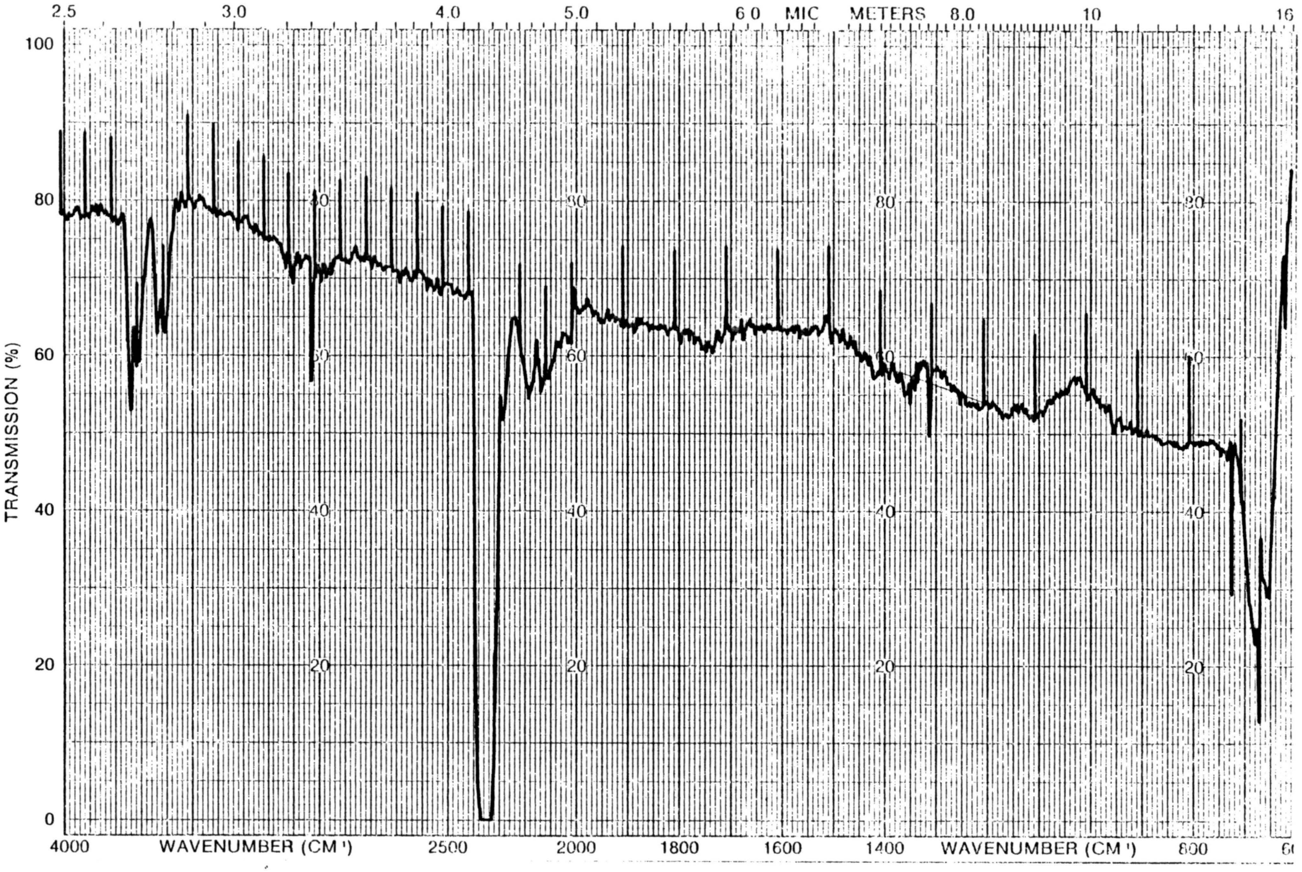

Figure 40. Experimental flue gas spectrum. Test#1, sample#3 (4.3 hours into burn cycle).

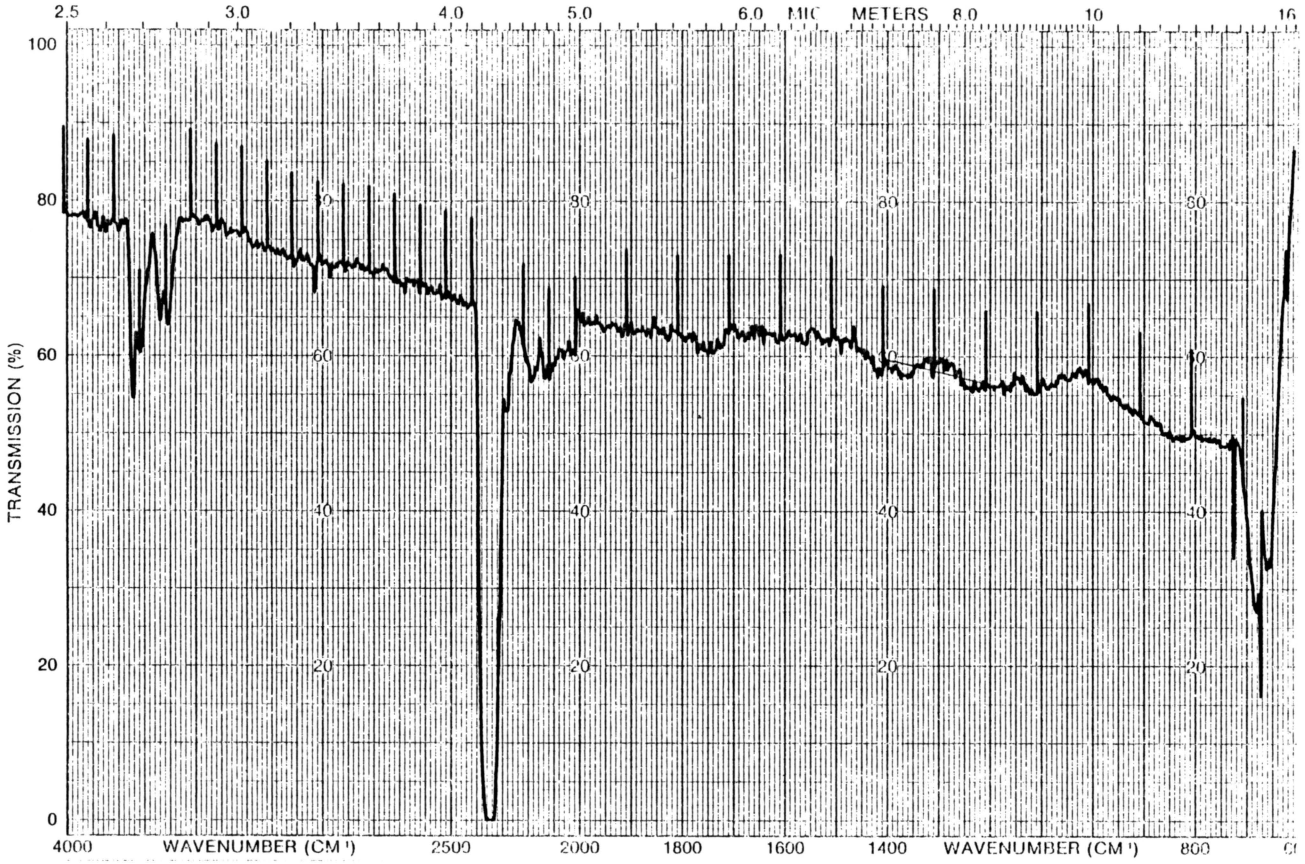

Figure 41. Experimental flue gas spectrum. Test#1, sample#4 (5.4 hours into burn cycle).

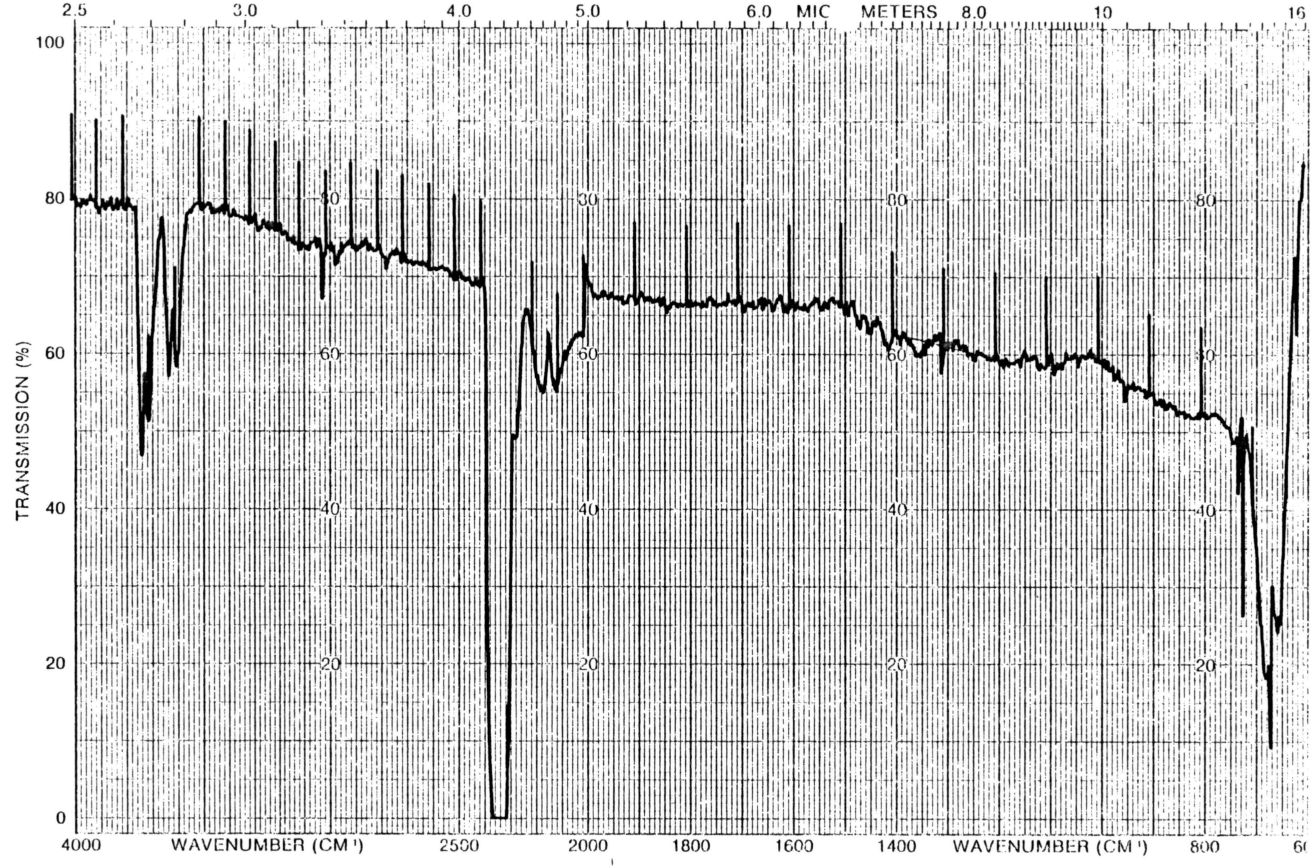

Figure 42. Experimental flue gas spectrum. Test#2, sample#1 (0.2 hours into burn cycle).

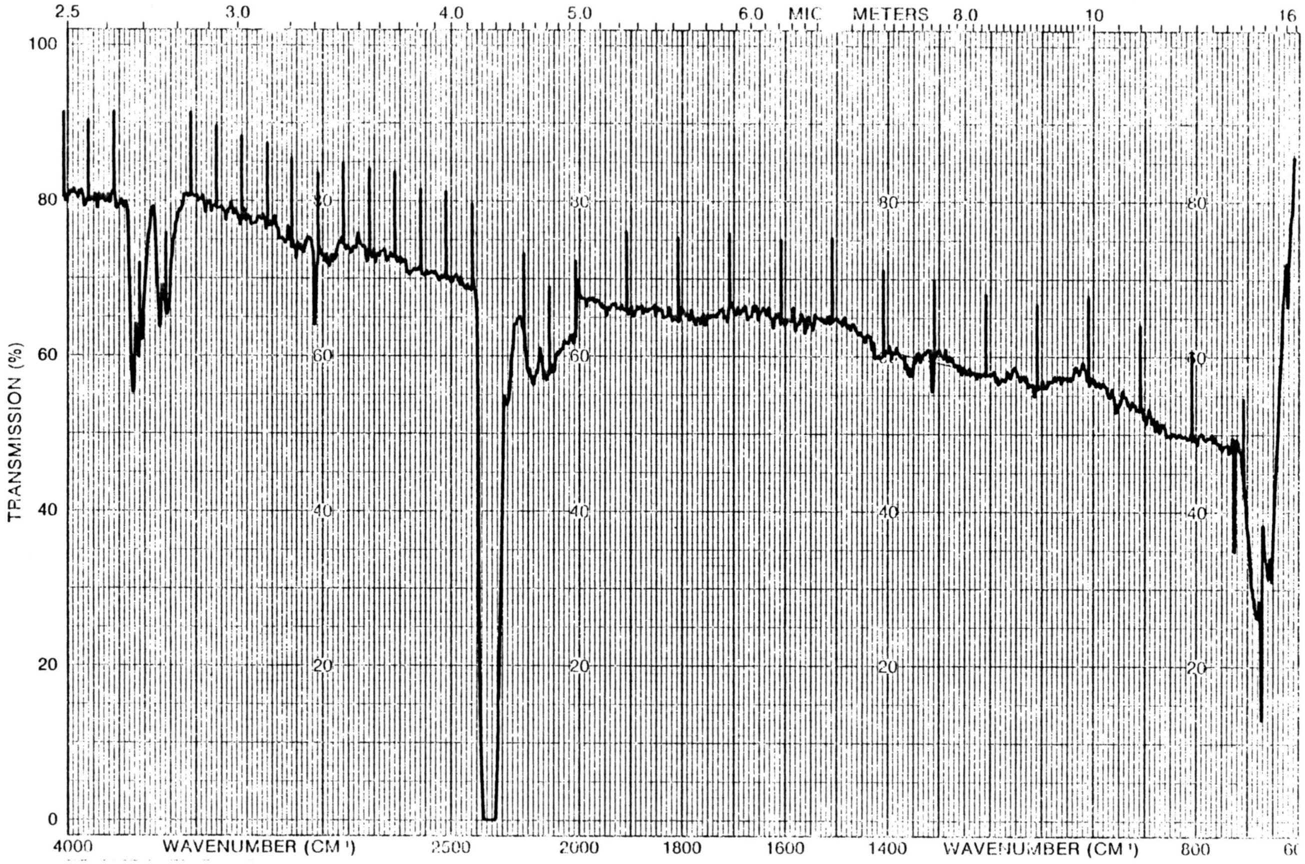

Figure 43. Experimental flue gas spectrum. Test#2, sample#2 (1.0 hours into burn cycle).

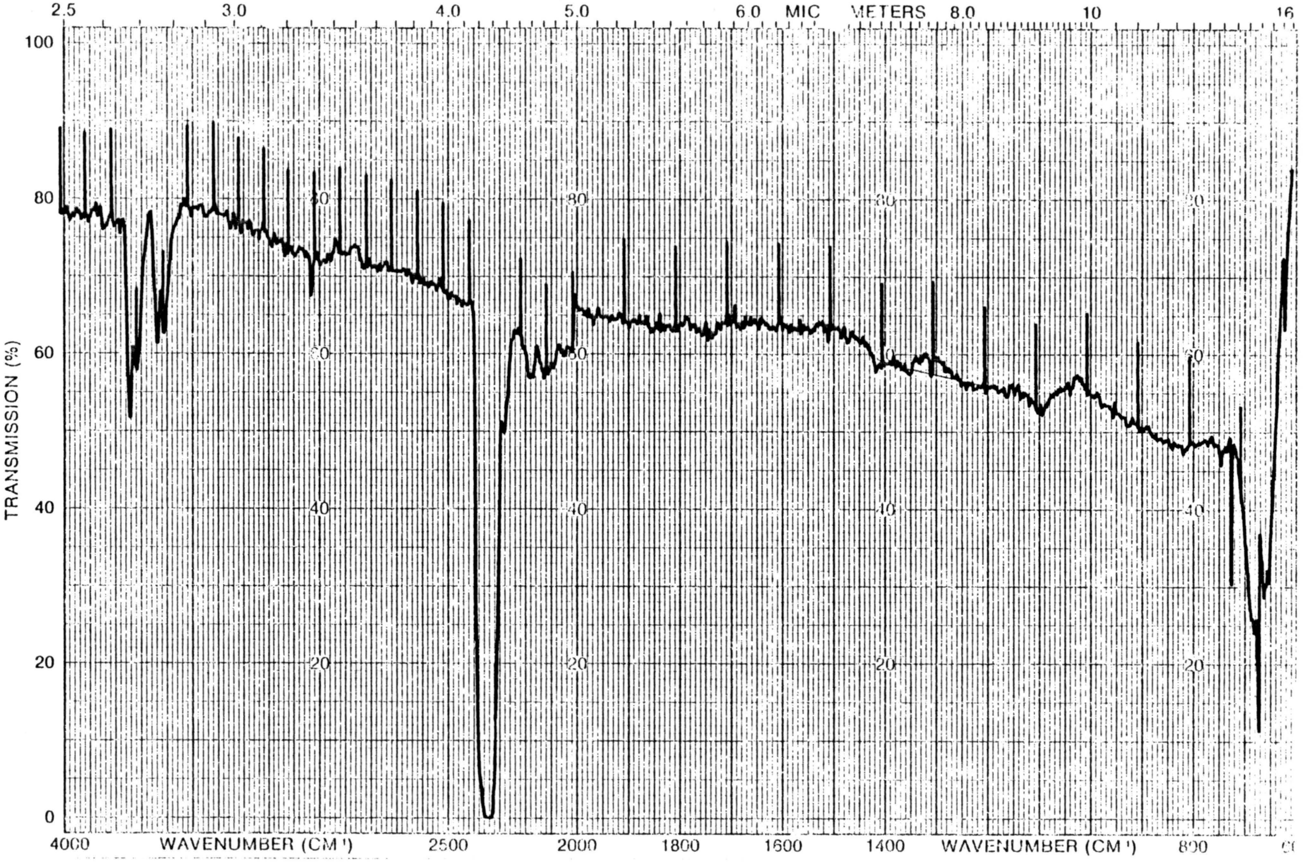

Figure 44. Experimental flue gas spectrum. Test#2, sample#3 (2.4 hours into burn cycle).

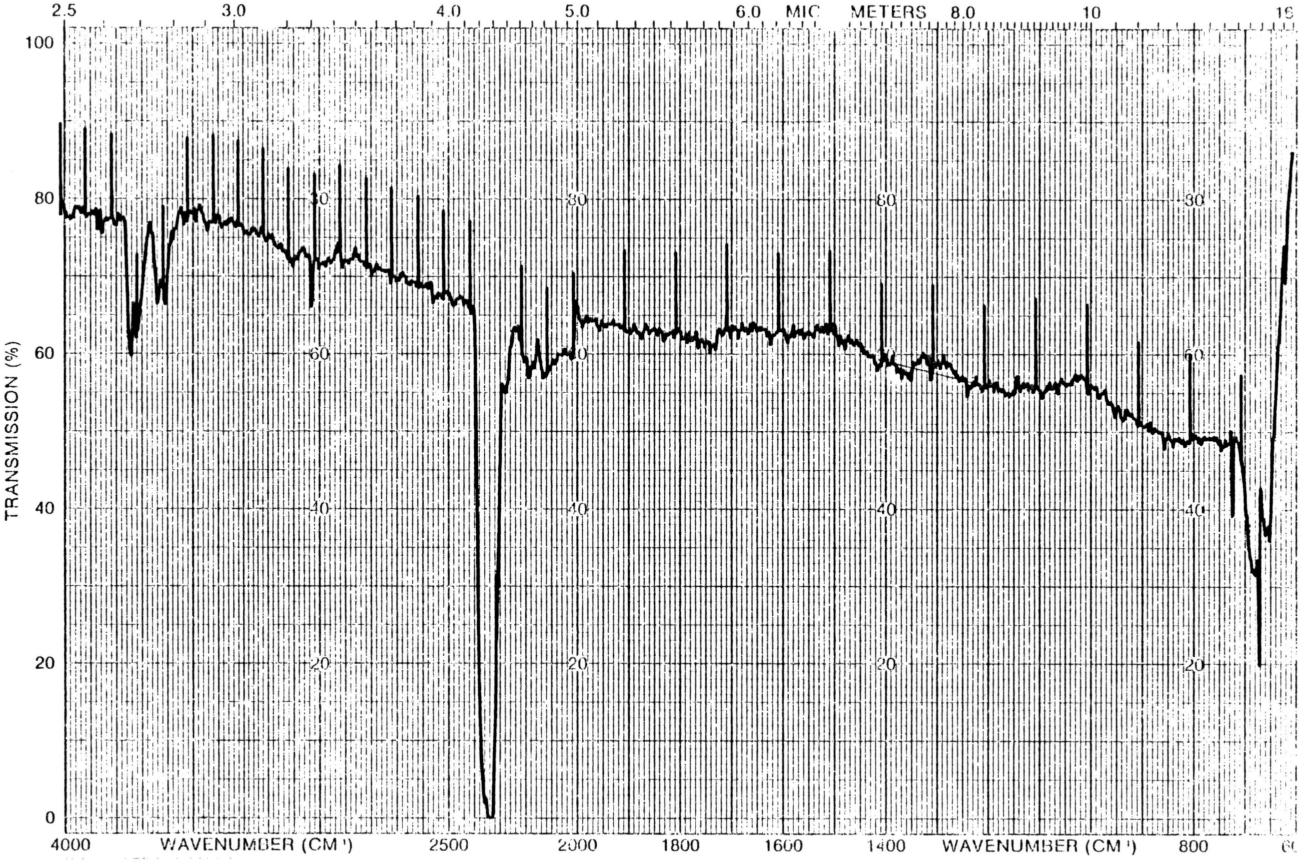

Figure 45. Experimental flue gas spectrum. Test#2, sample#4 (3.6 hours into burn cycle).

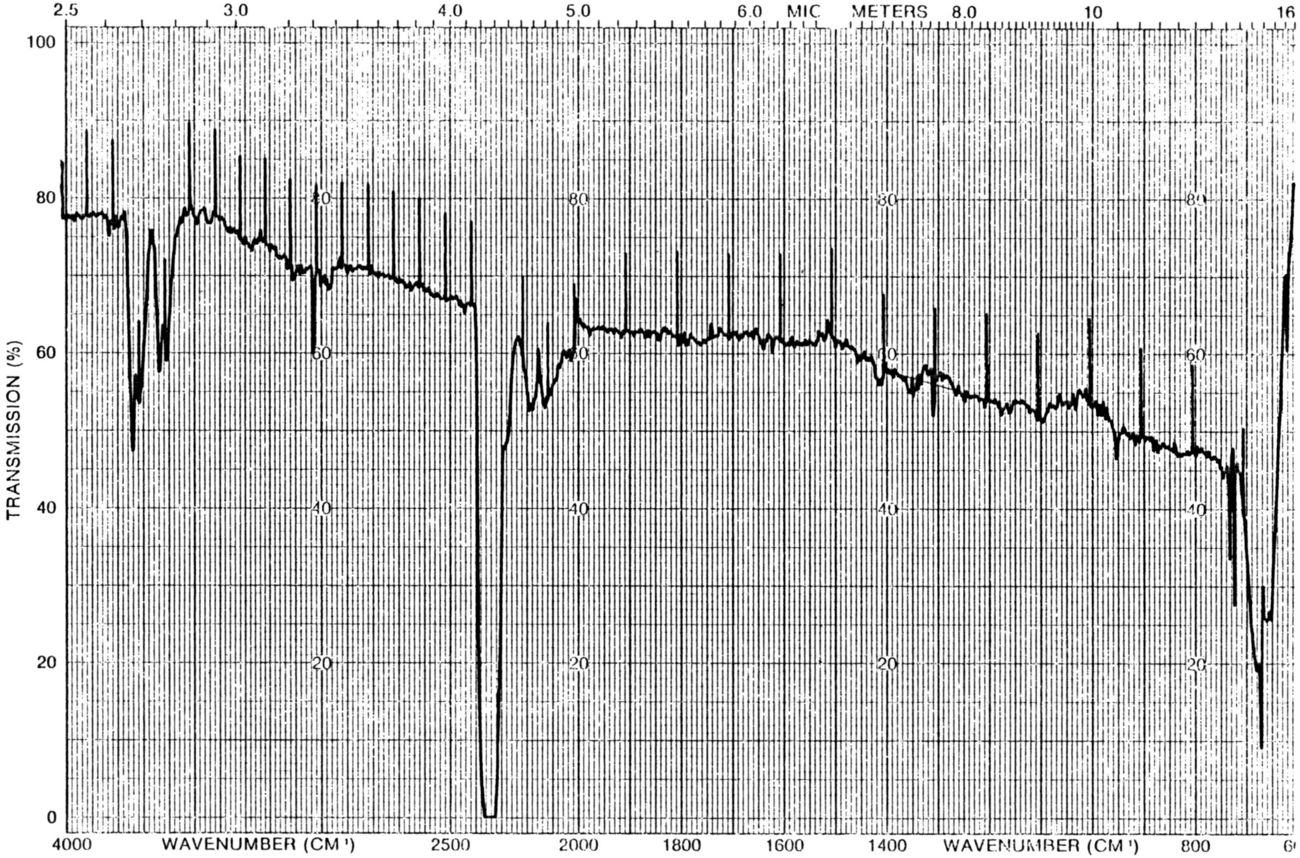

Figure 46. Experimental flue gas spectrum. Test#3, sample#1 (0.2 hours into burn cycle).

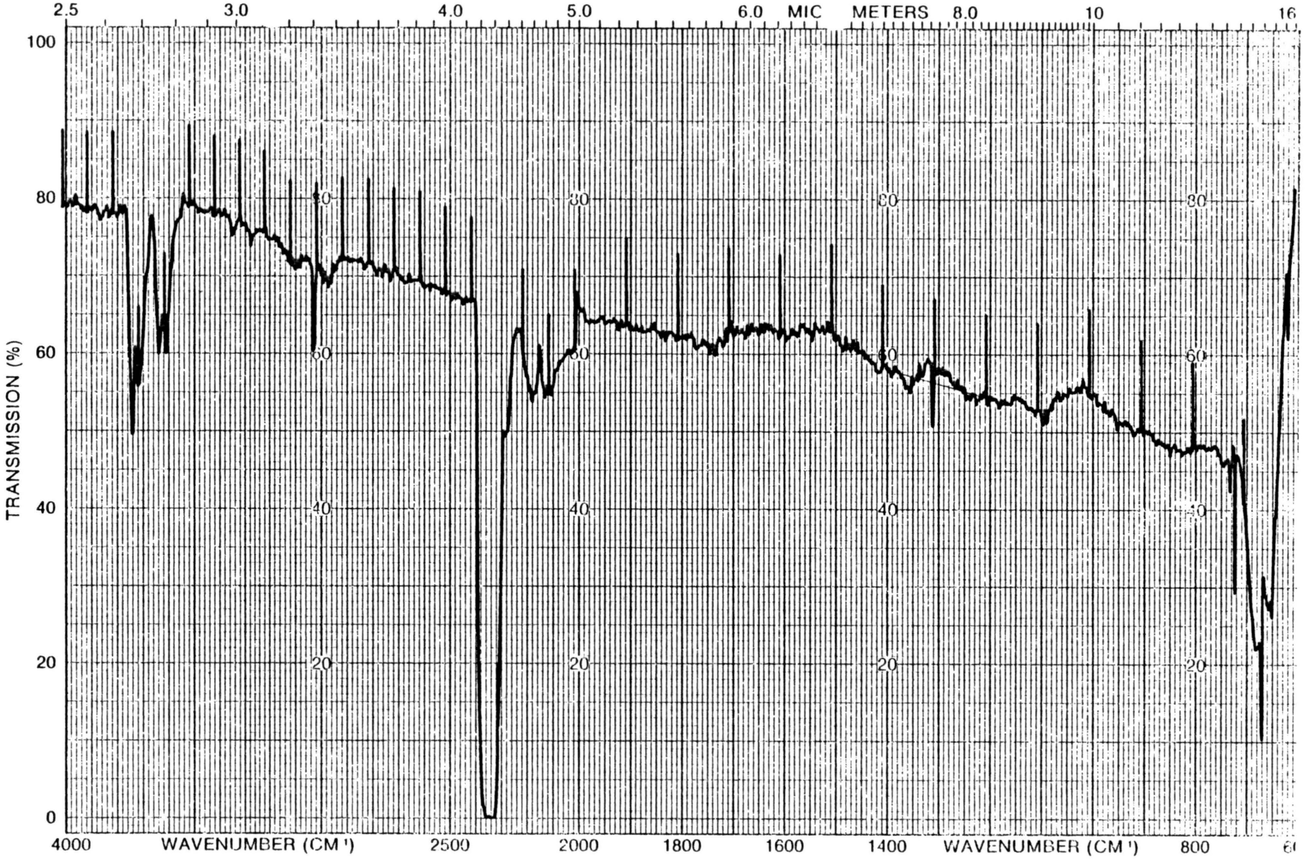

Figure 47. Experimental flue gas spectrum. Test#3, sample#2 (1.0 hours into burn cycle).

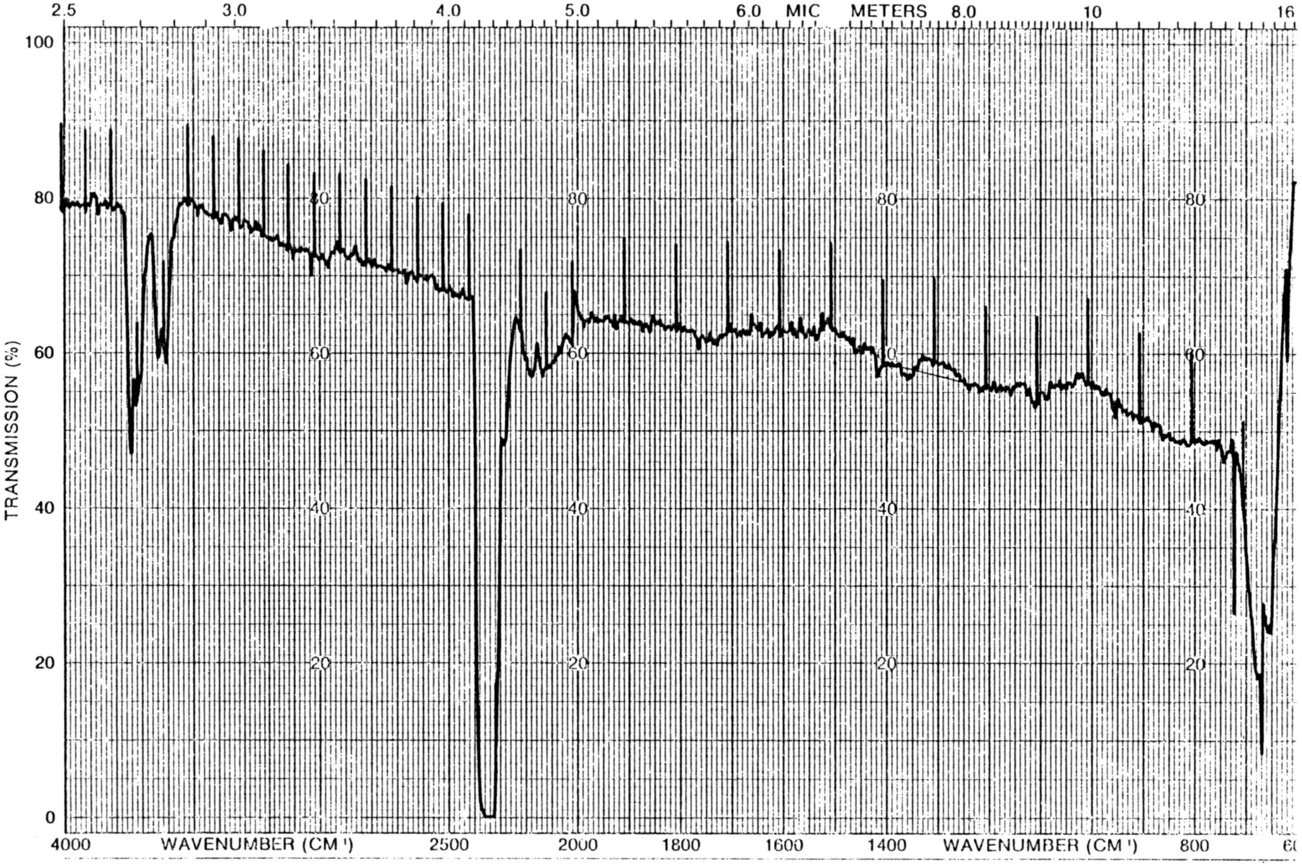

Figure 48. Experimental flue gas spectrum. Test#3, sample#3 (1.8 hours into burn cycle).

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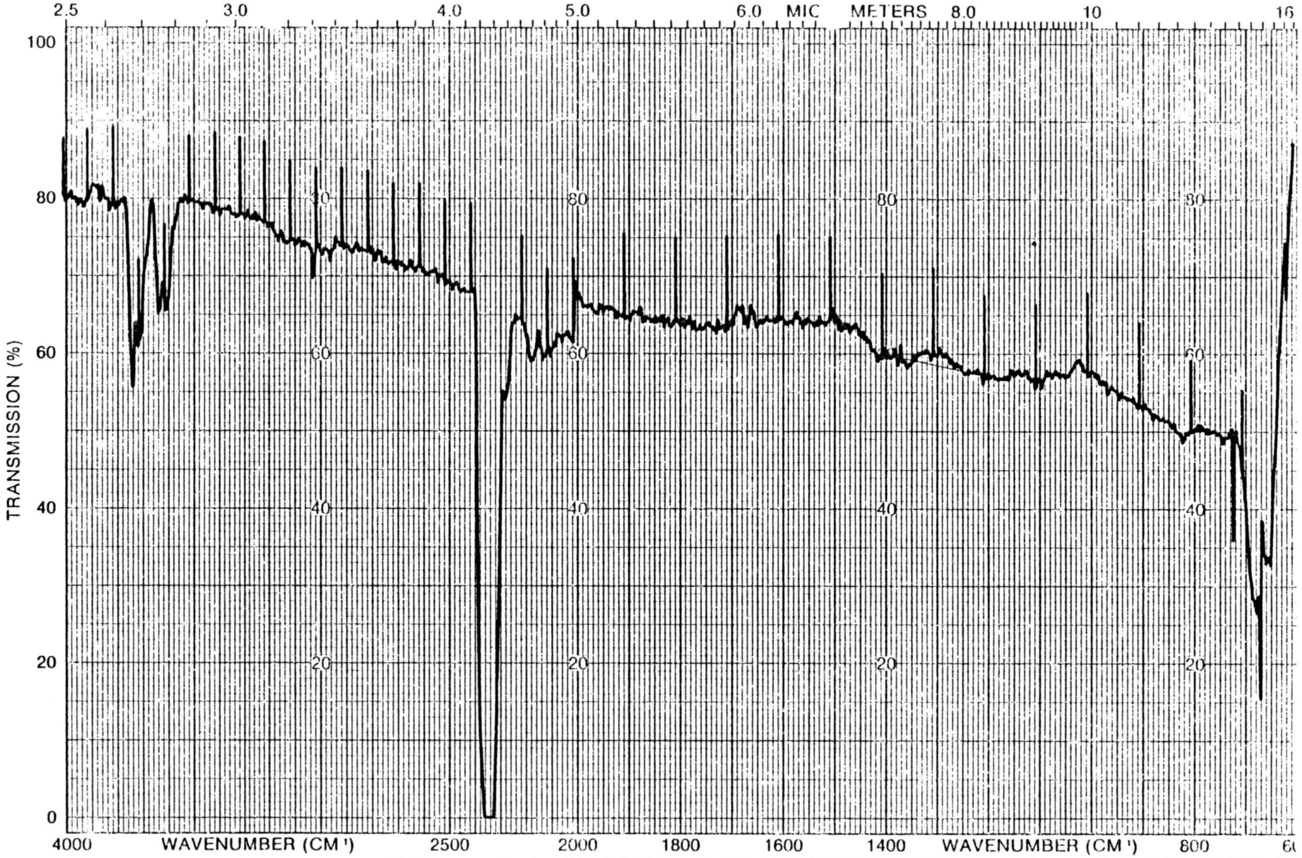

Figure 49. Experimental flue gas spectrum. Test#3, sample#4 (2.9 hours into burn cycle).

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