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NATIONAL COUNCIL OF THE PAPER INDUSTRY FOR AIR AND STREAM IMPROVEMENT, INC., 260 MADISON AVENUE, NEW YORK, N.Y. 10016

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CARBON MONOXIDE EMISSIONS FROM SELECTED COMBUSTION SOURCES BASED ON SHORT-TERM MONITORING RECORDS

TECHNICAL BULLETIN NO. 416

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Because of a limited information base on which to base carbon monoxide emission estimates to satisfy combustion source permitting needs, some existing carbon monoxide continuous monitoring records of selected combustion sources in the Northwest were examined to determine their utility in satisfying this need. Carbon monoxide continuous source emission monitoring records from kraft recovery furnaces, lime kilns and wood residue fired boilers were examined, or where they did not exist, short-term emission monitoring data was generated by National Council staff in cooperation with member company mills.

The attached technical bulletin is based on work carried out under the direction of Mr. Victor J. Dallons, Research Engineer, assisted by Mr. Dean R. Hoy, Research Technician, both located at the West Coast Regional Center where Andre L. Caron is Regional Manager. The technical bulletin contents describe the measurement principles used in state-of-the-art carbon monoxide monitors and identify potential interferences and gas conditioning requirements if representative sample monitoring data are to be generated. The field study showed that carbon monoxide monitors currently in use generally exhibited three weaknesses; namely, a positive interference from carbon dioxide and moisture, a positive drift from particulate accumulation, and inaccurate transmission of monitor output to the recorder. Because of fluctuations, carbon monoxide emission rates were found to be below the average most of the time and influenced by combustion air use practices which hinder complete combustion either by (a) limited oxygen availability or (b) reduced residence time in the combustion zone. Where flue gas oxygen content fluctuated sufficiently, variation in carbon monoxide emissions from kraft recovery furnaces was related to a range of maximum oxygen content of the flue gas. No firm TRS-carbon monoxide emission relationships were determined for kraft recovery furnaces, although TRS emissions were observed to increase above some base-line carbon monoxide level. The possibility that carbon monoxide might be a surrogate for TRS monitoring at non-DCE furnaces was promising and deserves further study. Carbon monoxide monitoring was indicated, however, to be a beneficial operators' tool in reducing TRS emission excursions. Based on carbon monoxide and oxygen concentrations in the flue gas from kraft recovery furnaces and from wood-fired boilers, some general relationships between carbon monoxide emissions and optimum energy recovery efficiency were developed.

The contents of this technical bulletin should be of particular interest to those (a) estimating carbon monoxide emission rates for permitting new sources, (b) contemplating the purchase of new, or assessing the utility of data generated by existing monitoring systems, or (c) optimizing energy use in selected combustion sources. Particular attention is drawn to the importance of matching carbon monoxide emission rates for permitting purposes with the observed variability in emission levels based on the short-term monitoring records used to prepare this technical bulletin.

Questions and comments on the contents of this technical bulletin, or related investigations which are designed to determine optimum carbon monoxide, nitrogen oxides, and oxygen content in combustion source flue gas, should be directed to me at the telephone number or address above, or to Mr. Victor J. Dallons at the NCASI West Coast Regional Center, P.O. Box 458, Corvallis, Oregon 97339 (telephone 503-754-2015).

Yours very truly,

Russell O. Blosser
Technical Director

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Attach.

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CARBON MONOXIDE EMISSIONS FROM SELECTED COMBUSTION SOURCES BASED ON SHORT-TERM MONITORING RECORDS

I INTRODUCTION

Carbon monoxide is one of the criteria pollutants for which an ambient air quality standard has been adopted under provisions of the Federal Clean Air Act. Therefore, emissions of carbon monoxide (CO) from stationary and mobile sources either are or soon will be regulated. Planning prior to the construction of a new source or a major modification of an existing source may require that the impact of carbon monoxide emissions on air quality be assessed. Little information is available on carbon monoxide emissions from combustion processes associated with the forest products industry, a limited amount being generated during collection of data on volatile organic compound emissions reported in earlier technical bulletins. In an initial attempt to provide the industry an expanded data base, the monitoring records from selected wood-residue fired boilers, kraft recovery furnaces, and lime kilns located in the Pacific Northwest were collected and compiled. Combustion sources included in this study were representative of current design and were operated in a normal manner. Their emissions were therefore considered to be representative of those to be expected from a new or modified source where special measures were not taken to minimize carbon monoxide emissions beyond those described.

Most combustion sources selected for this project had carbon monoxide monitors in place. The monitors used were routinely calibrated by mill personnel. The accuracy of each monitor was checked by NCASI staff using gas chromatographic analysis of stack gas samples. These analyses revealed significant positive interferences to the monitor measurements for which the data had to be corrected. A few sources were sampled using a monitor and sampling system provided by NCASI.

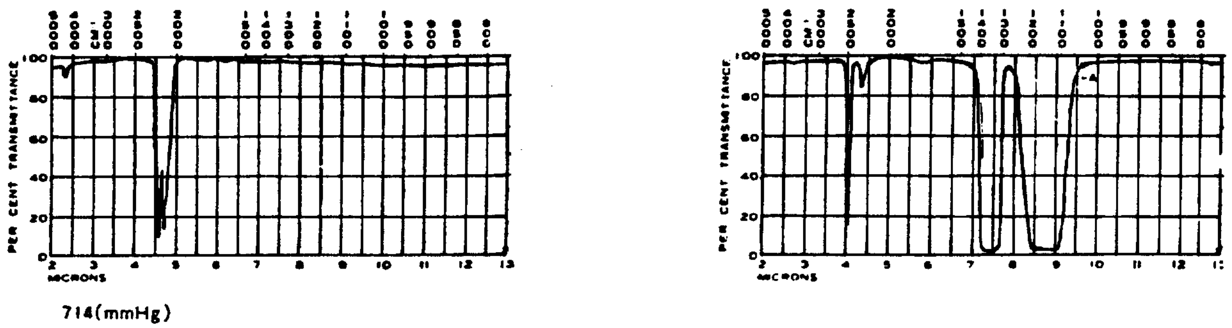
The data presented in this technical bulletin was arranged to show the range of emissions in terms of 1-hour and 8-hour averages expressed in lb per unit production or heat input. The emissions were also correlated with O_2 levels in the exhaust gases to show operating conditions under which the emissions were observed.

II CARBON MONOXIDE MONITORS AND MEASUREMENT PROCEDURES

A. Principle of Operation

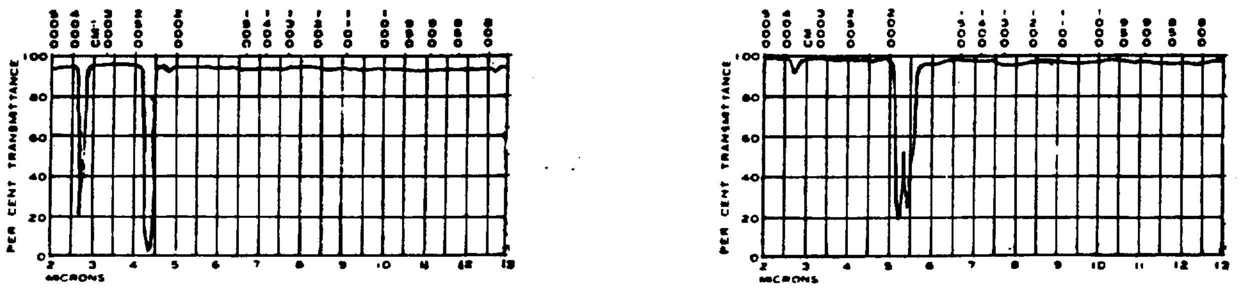
Most continuous carbon monoxide monitoring instruments use the infrared light absorption property of carbon monoxide to measure its concentration in ppm. Carbon monoxide absorbs infrared light from a beam passing through a sample contained in a sample cell or in the stack. The intensity of this beam is compared against a reference beam from the same source. The relative intensity of these light beams are measured by an infrared detector. A variety of filtering techniques are used so that only to those wavelengths of infrared radiation that are absorbed by carbon monoxide are measured.

The absorption spectra of carbon monoxide has a major infrared absorption band centered at 4.6 microns. Infrared spectra for carbon monoxide and other typical combustion source gaseous emission constituents are shown in Figure 1. These spectra indicate potential interferences from carbon dioxide, water, methane, propane, and ethylene. The organic compounds are likely to be present at such low concentrations that they would not constitute major interferences. Although carbon dioxide and water do not have strong absorption bands that overlap those of carbon monoxide, a significant interference occurs because their concentrations in combustion source emissions are at one to two orders of magnitude higher than carbon monoxide. Carbon dioxide and water are therefore major interferences to the determination of carbon monoxide concentrations by infrared absorption when present.



CO (Carbon Monoxide)

SO₂ (Sulphur Dioxide)



CO₂ (Carbon Dioxide)

NO (Nitrogen Oxide)

FIGURE 1

INFRARFD SPECTRA FOR CARBON MONOXIDE,
CARBON DIOXIDE, SULFUR SIOXIDE AND NITROGEN OXIDE

B. Extractive Monitors

Most carbon monoxide monitors currently available are of nondispersive infrared (NDIR) design. The term nondispersive means that the infrared light is not broken into its constituent wavelengths by a prism or defraction grating.

(1) NDIR Microphone Type Detector - Figure 2 illustrates an NDIR with a microphone type detector. The sampled gas is continuously passed through the sample cell in the monitor. A second sealed cell serves as a blank or reference. Infrared light from a common source is directed in parallel through both cells. Carbon monoxide and other sample gas constituents absorb part of the infrared radiation passing through the cell that contains the sample. Infrared radiation passes through the reference cell unaltered. The individual light beams then pass through a two chamber detector. The chambers are separated by a membrane and both contain the same concentration of carbon monoxide so that infrared energy specific to the absorption bands of carbon monoxide is absorbed. Absorption of less infrared energy in the measurement chamber causes the gas to cool and contract in comparison to the reference chamber, flexing the diaphragm to one side. The diaphragm position is detected by a change in electrical capacitance and used to measure the concentration of carbon monoxide.

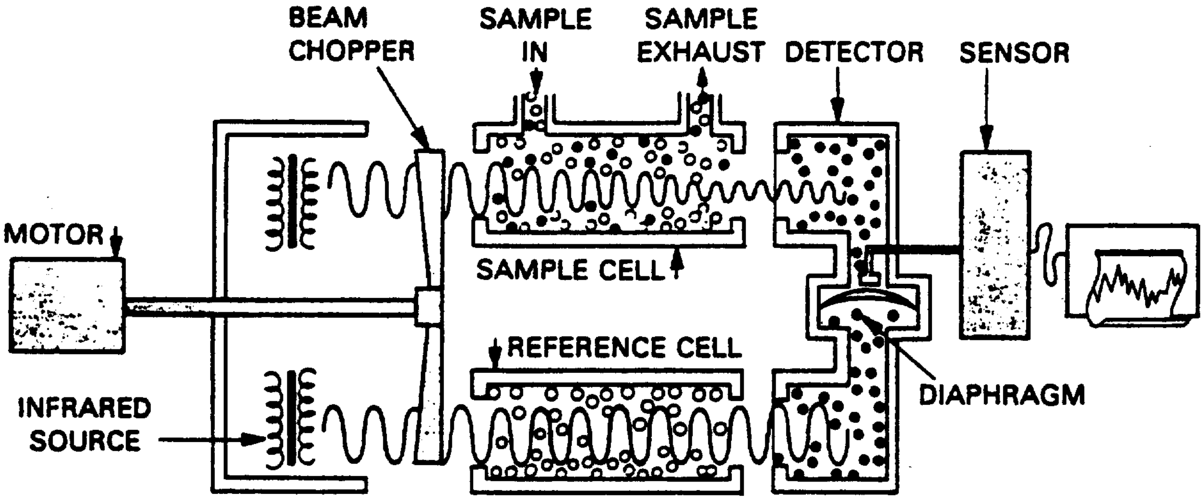


FIGURE 2

NDIR WITH MICROPHONE TYPE DETECTOR

Carbon monoxide monitors of this type are susceptible to interferences. Any overlap in absorption spectra with other constituents in the sample gas will result in an interference. Since water has a major absorption peak at a minor carbon monoxide absorption peak, high water vapor concentrations in the sample gas will result in an interference. Carbon dioxide also has a minor absorption peak at the same wavelength as the major carbon monoxide absorption peak and some overlap of major absorption peaks. Large carbon dioxide concentrations in the sample gas will result in an elevation of the reading. To use this type of carbon monoxide monitor, a dry sample gas free of carbon dioxide must be delivered to the monitor to obtain an accurate measurement.

(2) Negative Filtering Type Monitors - Some carbon monoxide monitors use negative filtering to avoid interferences. This type of instrument uses two chopped light beams alternately passing through the reference cell and the sample cell. The beams then pass through a two chamber detector. The two detector cells are arranged in series as shown in Figure 3. Both chambers contain dissimilar concentrations of carbon monoxide. Both beams of infrared light are partially absorbed as they pass through the detector cell chambers. Wavelengths of the infrared radiation of the major absorption bands of carbon monoxide will be largely absorbed in the first chamber, and some in the second chamber, resulting in a pressure differential between the chambers. Wavelengths of infrared radiation corresponding to the major absorption bands of the interfering gases and minor absorption bands of carbon monoxide will be partially absorbed, but for the most part pass through the first chamber and are absorbed to a similar extent in the second chamber. Because of similar energy absorption in both chambers by the interfering gases there will be no pressure difference caused by the radiation from absorption bands of the potentially interfering gases.

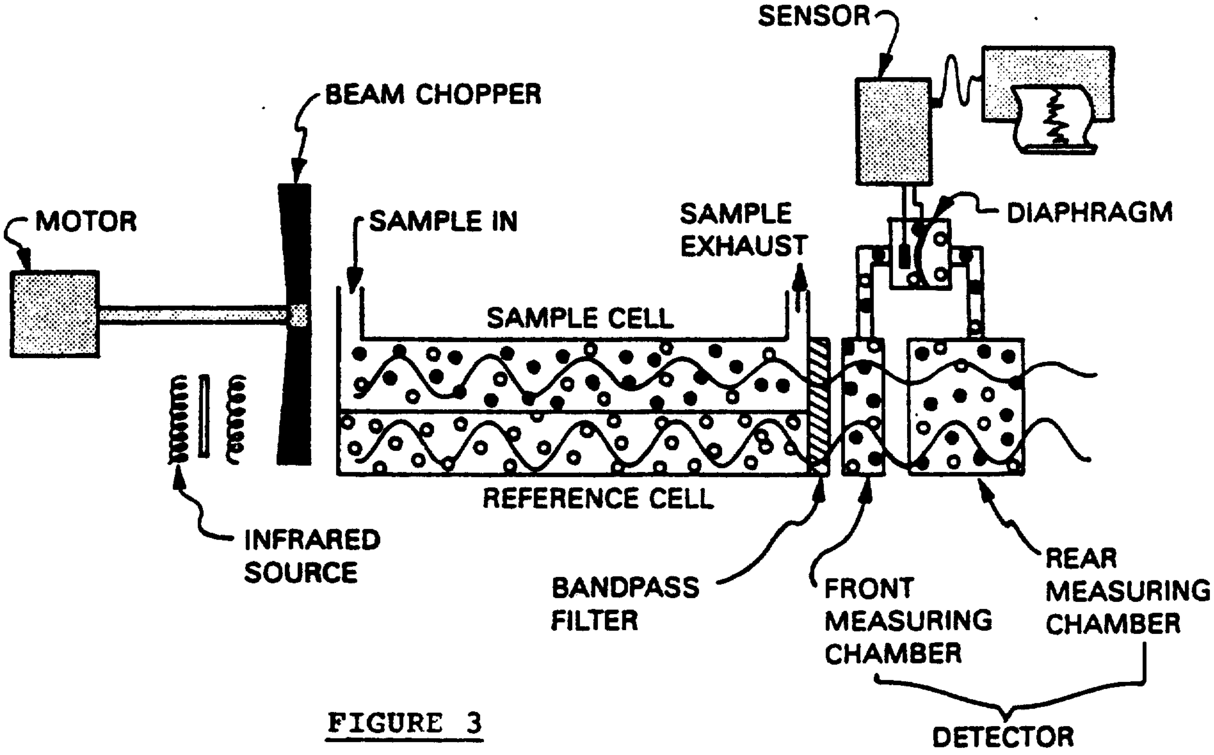


FIGURE 3

NDIR WITH NEGATIVE FILTERING

C. In-Stack Monitors

(1) Gas Filter Correlation Method - Carbon monoxide, along with other gas constituents, can be measured in-stack using the gas filter correlation method. A light beam is passed through the stack to the monitors shown in Figure 4. The beam is then alternately passed through a neutral filter and a cell containing a standard so that absorption of the characteristic wavelengths for the constituent being measured takes place. The difference in intensities of the beams passing through the neutral filter and the cell containing the standard is proportional to the concentration of the constituent of interest in the stack. The neutral filter is used to balance the intensity of both light beams to obtain a zero reading. Particulate matter and gases other than the species being measured that absorb infrared radiation do not interfere with the measurement because they cause a decrease in the light intensity passing through both the neutral filter and the gas cell. Some interference from other constituents in the gas stream may occur but it is small in comparison to the microphone detector method used by extractive monitors. Adjustments must be made to the monitor output to compensate for the molar volume difference between the hot stack gas and gases at standard conditions.

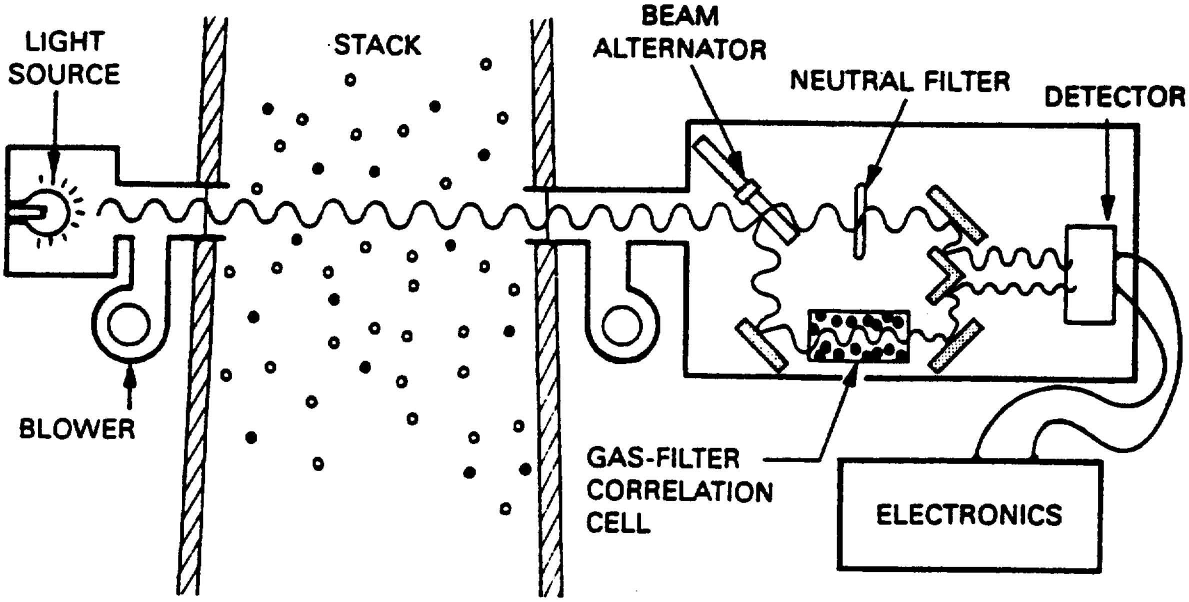


FIGURE 4

IN-STACK NDIR USING THE GAS FILTER CORRELATION METHOD

(2) Spectrum Filter Method - Another type of in-stack carbon monoxide monitor uses filters to sequentially select the wavelength of infrared light at the predominate characteristic absorption wavelengths for carbon monoxide, carbon dioxide, and

water. The beam of light is transmitted to an in-stack chamber and reflected back to the monitor as shown in Figure 5. The in-stack chamber is a porous ceramic filter that allows stack gases to enter the chamber but excludes particulate matter from the entire length of the light beam measured and also protects instrument optics. The intensity of the returned infrared light is compared to the intensity of light alternately directed to the detector and to the in-stack chamber. The differences in intensity are proportional to the gas constituent concentrations and their interferences. Measurement of water, carbon dioxide, and flue gas temperature allows for electronic correction of interferences.

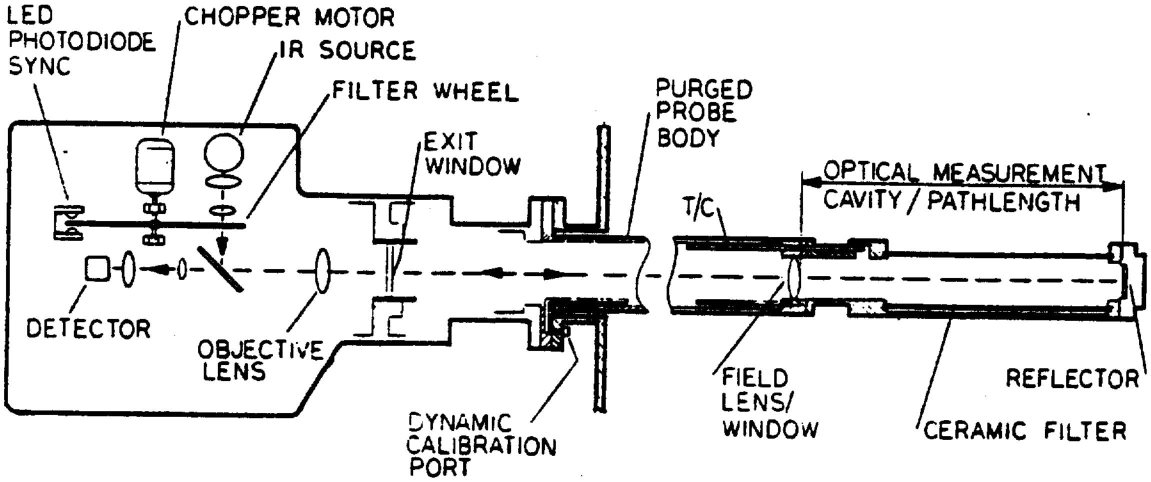


FIGURE 5

IN-STACK NDIR USING THE FILTER SPECTRUM METHOD

D. EPA Reference Method 10

EPA Reference Method 10 recognized two options for measuring carbon monoxide. Carbon monoxide can be measured using either a continuously extracted sample or with an integrated sample. Both methods use the NDIR measurement principle and require that moisture and carbon dioxide be completely removed from the sample gas.

The procedure specifies that the sample gas be drawn through a glass or stainless steel probe fitted with a glass wool filter followed by an air cooled condenser. Condensed moisture is collected in a dropout bottle. From this point the gas is collected in a flexible bag to obtain a time averaged sample, or flows through further gas conditioning and to the carbon monoxide monitor for continuous measurement.

The gas that is collected in a flexible bag is delivered through a flow control valve and a flow meter. The sample is drawn into the flexible bag by placing it in a rigid container and evacuating the container.

Whether analyzing an integrated or continuous sample, the gas is drawn into a system that removes the last traces of water and carbon dioxide. These consist of a silica gel followed by an ascarite tube both placed in an ice bath. A pump delivers the sample to a flow control valve, a flow meter, and the NDIR instrument.

Calculations for determining the carbon monoxide concentration in the stack gas require that the carbon dioxide concentration also be measured to account for the change in gas volume. A complete description of EPA-10 is given in Appendix A. Performance specifications for the NDIR carbon monoxide monitor are presented in Table 1.

TABLE 1 PERFORMANCE SPECIFICATIONS FOR NDIR CARBON MONOXIDE ANALYSES (3)

Range (minimum)	0-1000 ppm
Output (minimum)	0-10 mV
Minimum detectable sensitivity	20 ppm
Rise time, 90 percent (maximum)	30 sec
Fall time, 90 percent (maximum)	30 sec
Zero drift (maximum)	10% in 8 hr
Span drift (maximum)	10% in 8 hr
Precision (minimum)	±2% of full scale
Noise (maximum)	±1% of full scale
Linearity (maximum deviation)	2% of full scale
Interference rejection ratio - CO_2	1000-1
Interference rejection ratio - H_2O	500-1

E. Gas Chromatograph

Carbon monoxide can be analyzed using a gas chromatograph. A sensitive interference free procedure includes separating carbon monoxide from other gas constituents, conversion to methane, and measurement with a flame ionization detector (FID). Numerous column packings and temperatures can be used to accomplish effective separations. A nickel or rhodium catalyst held at 400°C and operated in the presence of hydrogen is necessary to convert carbon monoxide to methane.

III SOURCE DESCRIPTIONS

A. Wood-Residue Fired Boilers

During the course of this study continuous carbon monoxide emission data was collected from three wood-residue fired boilers.

(1) Boiler A - Power boiler A is a spreader-stoker unit rated at 600,000 lb/hr, 850 psig and 750°F steaming capacity, while burning wood-residue fuel derived primarily from Douglas fir with some cedar plus supplemental fuel. Supplemental fuel, either oil or gas, normally accounts for 10 to 35 percent of the boiler's heat input. Wood-residue is spread by four pneumatic stokers onto moving grates. The boiler was manufactured by Combustion Engineering in 1976.

Primary combustion air enters the boiler under the grates. Overfire air enters from several locations below the stokers along the four corners of the boiler in a manner to create a swirling motion in the fire box. Four oil/gas burners (and windboxes) are located above the stokers on the four corners of the boiler.

The combustion chamber has dimensions of 19.9 ft in width, 20.9 ft in depth and 65.75 ft in height, with a volume of about 27,400 cu ft which corresponds to 23.5 cu ft of combustion volume per million Btu fired at rated capacity. Combustion air is preheated and cinders are removed from the flue gas with multiclones and wet scrubbers which follow the ID fan.

The boiler was designed to burn predominantly Douglas fir bark with a dry composition of 6.3 percent hydrogen, 40.5 percent oxygen, 52.3 percent carbon, 0.1 percent nitrogen, and 0.8 percent ash at 50 percent moisture content along with supplemental fuel. The bark has a heating value of 4525 Btu/lb as fired. Supplemental fuel is No. 6 oil with a heat value of about 18,500 Btu/lb or natural gas with a heat value of 1040 Btu/cu ft.

Large swings in steam demand are compensated for by changing the firing rate of wood or supplemental fuel. The boiler steam output remains fairly constant over short periods of time (approximately 1 hr). Small changes in mill steam demand are taken up by other power boilers. This boiler operates under computer control. The computer is programmed to maximize the carbon dioxide concentration in the flue gas by adjusting combustion air feed rate. A secondary control procedure to maintain carbon monoxide emissions below a set point of 300 ppm becomes effective when supplementry fuel is burned.

(2) Boiler B - Boiler B is a spreader-stoker unit rated at 400,000 lb/hr at 1250 psig steam when burning wood-residue fuel with a 55 percent moisture content and at 550,000 lb/hr steam at 1250 psig when burning fuel with a 30 percent moisture content.

Fuel derived predominantly from Douglas fir residues is fed to the boiler with seven pneumatic stokers onto a moving grate. The boiler was manufactured by Foster Wheeler in 1976.

Primary combustion air enters the boiler under the grates and overfire air enters at several locations just above the stokers around the entire perimeter of the boiler. Overfire air can also be added at ports located about 10 ft above the stokers. Opposite and above the stokers are six oil burners in two tiers. Primary air comprises about 60 percent of the total air flow while overfire and windbox air comprise the remainder.

The combustion chamber has dimensions of 33 ft wide, 22 ft deep and 66 ft high, with a volume of about 48,000 cu ft. This corresponds to about 100 cu ft of combustion volume per million Btu fired at rated capacity. Combustion air is preheated and cinders are removed from the flue gas with multiclones. An Electroflux dry scrubber installed for particulate removal follows the ID fan.

The boiler was designed to burn residues with a dry composition of 6.0 percent hydrogen, 40.5 percent oxygen, 52.5 percent carbon, and 1.0 percent ash. The wood-residue has a heat value of 8900 Btu/lb bone dry basis. The boiler has 64 and 75 percent efficiencies when firing wood-residue at 55 and 30 percent moisture contents, respectively.

This boiler is operated on a very steady basis, with mill steam demand swings accommodated by other boilers. Carbon monoxide emission concentrations are reported to the control room but are not used by the operators to adjust boiler operating conditions.

(3) <u>Boiler C</u> - Boiler C is a spreader-stoker rated at a steam production of 300,000 lb/hr at 900 psig and 800°F while burning wood-residue. Wood-residue is spread by five pneumatic stokers onto moving grates. The boiler was manufactured by Peabody Corp. in 1980 and brought on line in early 1981.

Primary combustion air enters the boiler under the grates and overfire air is admitted at the four corners about 5 feet above the stokers and at the windboxes. Air distribution is approximately 49 percent undergrate, 33 percent overfire, and 18 percent windbox when no auxiliary fuel is fired. When auxiliary fuel is fired the proportion of windbox air is increased.

The combustion chamber has dimensions of 23 ft wide, 23 ft long, and 50.6 ft high with a combustion volume of approximately 26,700 cu ft. The boiler was designed to fire 20,900 Btu/hr/ft^3 or 48 ft^3 of combustion chamber volume per million Btu/hr heat input. Combustion air is preheated to 450°F. Particulate emissions are controlled with a variable throat venturi scrubber operated at a 7 to 15 inch water pressure drop. Carbon monoxide emissions are not normally measured at this site.

B. Kraft Recovery Furnaces

Carbon monoxide monitoring records from five kraft recovery furnaces were collected and analyzed. These recovery furnaces represent both DCE and non-DCE units with construction dates ranging from 1964 to 1977. Table 2 lists characteristics of these furnaces.

TABLE 2 RECOVERY FURNACE DESIGN INFORMATION

Furnace	Manufacturer	Installment Date	Type	Rated Black Liquor Firing Rate lb/hr	Average Black Liquor Firing Rate lb/hr	Black Liquor Heat Value Btu/lb Dry Solids
A	CE	1970	NDCE	100,000	80,000	5,717
B	CE	1964	DCE	100,000	103,000	5,955
C	CE	1977	NDCE	190,000	148,000	6,600
D	CE	1975	DCE	137,500	137,000	6,000
E	B & W (short)	1965	DCE	96,000	79,000	--

C. Lime Kilns

Carbon monoxide monitoring data from two recently constructed lime kilns were collected.

(1) Kiln A - Kiln A was a rotary kiln manufactured by Allis Chalmers and began operation in 1968. The kiln has a 9 ft diameter and 250 ft length with provisions for firing on either gas or oil. Noncondensible gases from the pulp mill were not burned in the kiln. The kiln was designed to produce 106 tons lime as CaO per day for the equivalent production of 425 TPD unbleached pulp. Particulate emissions were controlled with a Chemico venturi type scrubber, which used fresh water for makeup.

(2) Kiln B - Kiln B was rotary kiln manufactured by F. L. Smidth and Co., Inc. and began operation in early 1982. The kiln has a diameter of 11.83 ft (less 1.75 ft for the brick lining at the hot end) and a length of 341 ft. The kiln fires No. 6 oil or natural gas and has a lime production capacity of 325 tons per day as CaO. This kiln used lime product coolers to preheat the combustion air. Noncondensible gases from the pulp mill were not burned in this kiln.

IV CARBON MONOXIDE MONITOR DESCRIPTIONS

A. Interference Evaluation and Field Data Verification

The carbon monoxide monitors encountered in the field that were installed as process monitors generally had three weaknesses, namely: (a) a positive interference from carbon dioxide and water vapor, (b) inadequate particulate removal that results in a continual positive drift, and (c) inaccurate transmission of the carbon monoxide monitor output to the control room charts. The above existed to varying degrees depending on the manufacturers of the instrument and mill practices.

The extent of interferences due to the above were evaluated for each monitor using several procedures. Carbon dioxide interferences were evaluated by measuring cylinder gases containing 24 and 211 ppm carbon monoxide in a 13 percent carbon dioxide dilutant gas. These measurements were taken after the instrument had been zeroed and calibration adjustments made.

Samples of stack gas were also taken from the monitor exit in glass flow-through sampling bulbs and returned to the laboratory for gas chromatographic analysis. The sample bulb analyses were used to estimate the extent of interference from water vapor and carbon dioxide. Figure 6 shows the interference to one monitor due to a dry carbon dioxide gas mixture and a moisture content equivalent to saturation at room temperature by observing the differences found between the GC analysis and the monitor reading. The stack gas being measured had been dried by condensing moisture from the sample at ambient temperature. The figure shows an interference from moisture alone equivalent to about 60 ppm carbon monoxide.

The gas chromatographic analysis system used for determining carbon monoxide concentrations was the same system used for EPA Method 25 total nonmethane organic analysis reported in earlier technical bulletins (4,5). The column used was a silicon SF-96 on Chromosorb W (not essential for the separation of carbon monoxide from other gases) followed by 2 ft of Porapack Q (active portion of column for carbon monoxide analysis) operated at -78°C. A 5 mL gas volume was withdrawn from the sample bulb and injected into a nitrogen carrier gas going to the column. Gases eluting from the column passed through MnO_2 oxidation catalyst held at 600°C to oxidize the carbon monoxide to carbon dioxide, mixed with hydrogen in a rhodium catalyst held at 400°C to reduce the carbon dioxide to methane, and the methane concentration measured using a flame ionization detector.

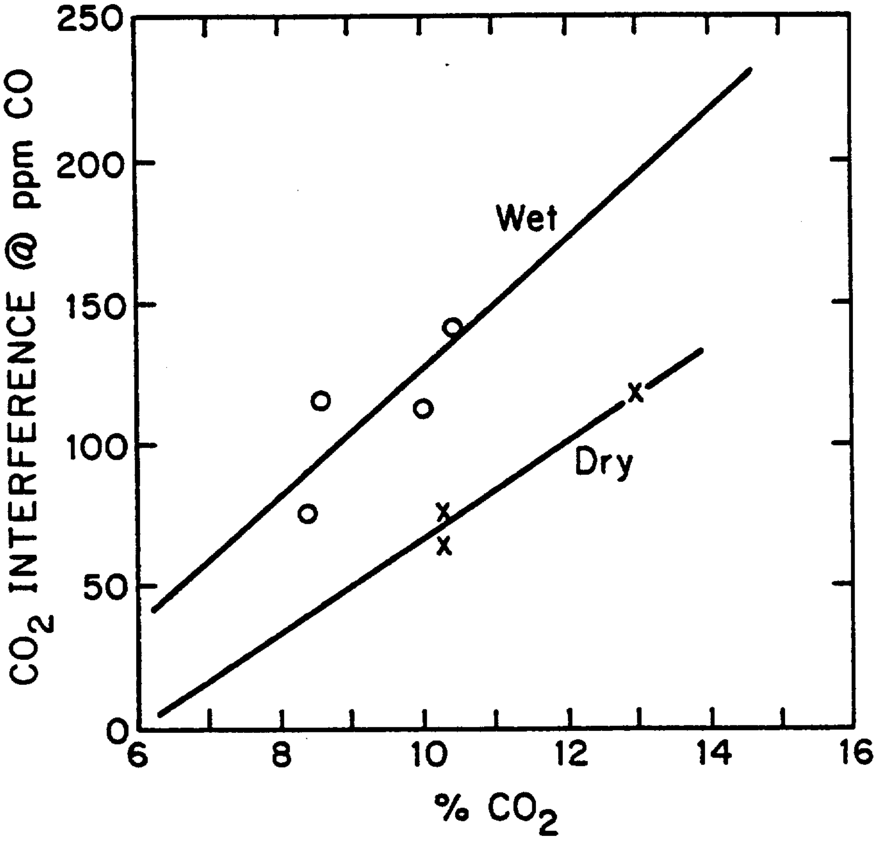


FIGURE 6

INTERFERENCE TO CO MEASUREMENTS RESULTING FROM CARBON DIOXIDE AND WATER IN THE GAS BEING MEASURED

B. Description of Monitoring Systems

A discussion on the precision and accuracy of the carbon monoxide monitors found at the combustion sources studied and the corrections applied to the data gathered follows. Table 3 gives a summary of the monitors used, manufacturers, gas extraction technique, calibration gases used, and calibration frequencies during the data collection period.

(1) Wood-Residue Fired Boiler A - The Measurex carbon monoxide instrument used on this source was an in-stack monitor that measured carbon monoxide, carbon dioxide, and water. Interference to the carbon monoxide measurement by carbon dioxide and water were compensated electronically. The carbon monoxide readings were reported on a wet basis and the data considered accurate. No corrections were made to this data.

TABLE 3 WOOD-RESIDUE FIRED BOILER CARBON MONOXIDE MONITORS

Combustion Source	CO Monitor		Source of Measured Gas	Extraction Technique	Calibration Gas		Span Gas Percent CO_2	Frequency of Calibration
	Manufacturer	Model			CO ppm	Percent CO_2		
WRFB A	Measurex		Following ID fan	In-stack	466	12	0	1/week
WRFB B	Anarad	AR 500 R	Economizer	Water Eductor	1420	0	0	1/day
WRFB C	Horiba	A1A-23 A-S	Following Scrubber	Water Eductor (Recirculated)	1940	0	0	1/day
RF A	Infrared	703	Economizer	Water Eductor (Recirculated)	1740	0	0	1/week
RF B	Infrared	703	Economizer	Water Eductor (Recirculated)	1740	0	0	1/week
RF C	Infrared	703	Economizer	Water Eductor	1603	0	0	5 day/week
RF D	Infrared	703	Economizer	Water Eductor (Recirculated)	1850	--	--	1/day
RF E	Infrared	703	Economizer	Air Eductor after CO monitor	1870	14.2	13.5	1/week
LK A	Bendix	8903	Kiln Cold end	pump	270	0	0	1/day
LK B	Horiba	A1A-23 A-S	Following Scrubber	Water Eductor (Recirculated)	1940	0	0	1/day

(2) Wood-Residue Fired Boiler B - The carbon monoxide monitor on this source exhibited considerable interference from both carbon dioxide and water. The gas chromatographic analysis of samples showed an average difference in reading from the monitor of 375 ppm carbon monoxide and the data was corrected accordingly. The control room charts were properly zeroed and gave a reading that was 14 percent low compared to the monitor output. The gas delivered to the monitor was extracted from the stack by a water eductor that absorbed approximately 80 percent of the carbon dioxide in the flue gas. This resulted in instrument readings that were about 10 percent high due to volume reduction. The oxygen meter used the same sample gas as the carbon monoxide monitor so its readings were also about 10 percent high. In the calculation of emission in terms of lb/10^6 Btu by the emission factor method the error in the carbon monoxide and oxygen readings resulting from the carbon dioxide absorption cancelled out.

(3) Wood-Residue Fired Boiler C - This boiler was monitored with a Horiba A1A-23 [A-S] carbon monoxide instrument supplied by NCASI. Gases were extracted from the stack with a water eductor. Water for the eductor was recirculated to maintain an equilibrium with the stack gas carbon dioxide content so no carbon dioxide absorption took place. The carbon monoxide monitor used the negative correlation method to eliminate the carbon dioxide and moisture interferences. The data collected required no correction.

(4) Recovery Furnace A - The carbon monoxide monitor at this location suffered considerable interference from carbon dioxide and moisture as well as zero drift. The carbon monoxide monitor interferences were a function of the flue gas carbon dioxide concentration and ranged between 120 to 220 ppm. The instrument zero drifted as much as 180 ppm. To compensate for these inadequecies the data was corrected by assuming the monitor zero was equal to the lowest chart reading observed during an 8 hour period.

(5) Recovery Furnace B - Carbon monoxide readings were found to be an average of 195 ppm high due to the carbon dioxide and water positive interferences and the data corrected accordingly. In addition, the charts in the control room were offset by 30 ppm and the values recorded on the chart were 80 percent of the instrument reading. The data was also corrected for these recording errors. During the data collection period the instrument zero drifted 70 ppm. Inspection of minimum carbon monoxide measurements recorded indicated that the zero offset change occurred during a furnace upset. The probable cause of the zero change was dust collecting on the windows of the measurement cell. The data following the upset was adjusted for the zero shift of the monitor. There was no drift in the monitor span reading during the data collection period.

(6) Recovery Furnace C - Carbon monoxide readings were found to be an average of about 90 ppm high due to a positive carbon dioxide and moisture interference in the sample gas. However,

the recorder chart zero read more than 20 ppm low (off the bottom of the chart). In addition the recorded chart values were 5 percent high and pen drag on the chart resulted in peaks that were 20 ppm low and valleys that were 20 ppm high. This monitor exhibited a zero drift of 100 ppm in both the positive and negative directions. Because of the multiplicity of corrections needed, many of which would have a canceling effect, none were made.

(7) <u>Recovery Furnace D</u> - The calibration procedures used on this carbon monoxide monitor were designed to circumvent interferences by carbon dioxide. The instrument zero was set, checked and adjusted using nitrogen gas, then spanned with carbon monoxide in a mixture containing 15 percent carbon dioxide. The instrument gave a response equivalent to 180 ppm when a gas containing 15 percent carbon dioxide and no carbon monoxide was measured. The span reading was reduced by 180 ppm. This resulted in compensation for the carbon dioxide interference when its concentration was 15 percent in the sampled gas, however, it also resulted in a monitor reading reduced by about 10 percent. The control room chart recorded values that were 93 percent of the instrument reading, giving an overall reading that was about 18 percent low. The data was corrected for these errors in the monitor and recording chart. Additional adjustments were made to the carbon monoxide readings to account for changes in carbon dioxide in the flue gas as indicated by the oxygen content and for the moisture interference. No adjustments were made for zero drift. Instrument span and zero settings were checked daily.

(8) <u>Recovery Furnace E</u> - The carbon monoxide monitor at this recovery furnace was zeroed with a gas containing 14 percent carbon dioxide and calibrated with a gas containing 16 percent carbon dioxide. Use of carbon dioxide in the zero and calibration gases resulted in meter readings that were correct when the furnace was operating with carbon dioxide concentrations in the flue gas similar to those in the calibration and zero gases. No corrections were made to the data to account for the carbon dioxide interference.

This instrument was operated under vacuum and calibrated at atmospheric pressure. An adjustment of 17 percent of the monitor reading was made based on calibration gas measurements at the calibration and operating pressures of the instrument to correct for the pressure differences. The data was also adjusted for a 90 ppm offset and a 5 percent span error on the chart recorder.

(9) <u>Lime Kiln A</u> - The carbon monoxide monitor on this lime kiln used a dual cell detector that compensated for interferences. The instrument and chromatographic carbon monoxide measurements compared well. Gas was extracted from the stack through an inertial filter and dried with a Perm-a-Pure dryer. No corrections were made to the results from this monitor.

(10) Lime Kiln B - This lime kiln was monitored with a Horiba A1A-23 [A-S] carbon monoxide monitor supplied by NCASI. Gases were extracted from the stack with a water eductor. Water for the eductor was recirculated to achieve equilibrium with the stack gas carbon dioxide content. The carbon monoxide monitor employed dual detector cells to eliminate interferences. The data collected required no correction.

V RESULTS

A. Data Manipulation

(1) General Data Handling - Carbon monoxide monitors report the data in units of ppm in the stack gas on either a dry or wet gas basis. The ppm values were corrected to 0 percent oxygen on a dry basis to account for differences in excess oxygen or system leaks using the formula:

$$\text{CO corrected} = \text{CO measured} \left(\frac{20.9}{20.9 - \%\ O_2}\right)$$

Corrected carbon monoxide concentrations were then related to boiler energy input for wood-residue fired boilers, black liquor firing rates for kraft recovery furnaces, and energy input and lime production for lime kilns by methods more thoroughly discussed below.

During data analysis a number of points were encountered that were at maximum value or below the minimum detection limit of the instrument. This out-of-range data was incorporated into data summaries using a statistical procedure developed for this project and presented in Appendix B.

Average emission rates for each hour during the study were calculated. Eight hour averages were calculated from eight contiguous hourly averages starting at midnight, 8:00 am, or 4:00 pm. An average of all the data was calculated as well as the median of the 1 and 8 hour averages. Data from each combustion source is presented in diagrams showing the cumulative frequency of occurrence of the 1 and 8 hr averages. A Weibull cumulative frequency distribution is used to linearize the data, if possible, and to indicate the way in which the data is distributed.

(2) Wood-Residue Fired Boilers - Carbon monoxide emission levels expressed in terms of ppm were used to calculate emissions expressed as lb CO/10^6 Btu heat input using the F factor procedures (6). When the emission oxygen concentrations were available the equation used was:

$$E = C \cdot F \frac{20.9}{20.9 - \%O_2}$$

When flue gas carbon dioxide concentrations were available, the equation used was:

$$E = C \cdot Fc \frac{100}{\% CO_2}$$

Where:
E = pollutant emissions, lb/10^6 Btu
C = pollutant concentration, lb/dscf
C = (2.59 x 10^{-9} lb/dscf)(pollutant concentration)(MW) where MW = pollutant molecular weight
F = a factor representing the ratio of the values of dry flue gases generated to the calorific value of the fuel combusted
Fc = a factor representing the ratio of the volume of carbon dioxide generated to the calorific value of the fuel combusted.

The F values used for the oxygen corrections were 9280 dscf/10^6 Btu for wood-residue, 9220 dscf/10^6 Btu for oil, and 8740 dscf/10^6 Btu for gas. Fc values used for the carbon dioxide corrections were 1840 scf CO_2/10^6 Btu for wood-residue, 1430 scf CO_2/10^6 Btu for oil, and 1040 scf CO_2/10^6 Btu for natural gas. When combination fuels were used the F factors were ratioed in accordance with the Btu input of each fuel.

(3) Kraft Recovery Furnaces - Carbon monoxide concentrations were used to calculate emissions in terms of pounds carbon monoxide emitted per pound black liquor solids (bls) fired. Stack gas flow rates were estimated using a correlation developed between black liquor solids firing rate and stack gas flow rate. These correlations were developed at each mill using historical particulate sampling data or measurements by the NCASI staff taken during the conduct of the study. Carbon monoxide emission concentrations and stack flows were corrected to 0 percent oxygen and then to lb CO/lb bls, by the following calculation:

$$\text{lb CO/lb bls} = (\text{CO conc., ppm})(\text{stack flow, dscfm})(7.25 \times 10^{-8} \text{ lb CO/dscf} \cdot \text{ppm})$$

(4) Lime Kiln - Carbon monoxide concentrations were converted to units of lb/ton lime and lb/10^6 Btu fired. Exhaust gas flows at standard conditions and on a dry basis used for the calculations were estimated from oil firing rates and lime production rates at 0 percent oxygen by the formula:

$$\text{Gas Flow, dscfm} = (1390 \text{ dscf/gal oil})(\text{oil firing rate, gpm}) + (14{,}800 \text{ dscf/ton lime})(\text{lime prod. rate/day})\left(\frac{1}{1440}\right)$$

Flows determined by this formula were within the accuracy of measurements made by EPA Reference Methods 1 through 4. Flue gas carbon monoxide concentrations were corrected to 0 percent oxygen with the formula:

$$\text{CO at } 0\% \ O_2 = \text{CO measured } \left(\frac{20.9}{20.9 - \% O_2}\right)$$

Carbon monoxide emissions expressed in terms of lb/10^6 Btu fired and lb/ton lime were calculated with the formulas:

Emission Rate, lb/10^6 Btu = (ppm CO at 0% O_2)(Gas flow, dscfm) (4.8×10^{-7})/(oil fired, GPM)

Emission Rate, lb/ton lime = (ppm CO at 0% O_2)(Gas flow, dscfm) (4.35×10^{-6})/(lime prod., ton/hr)

B. Carbon Monoxide Emissions from Wood-Residue Fired Boilers

Average carbon monoxide emission rates from boilers, A, B, and C, representing more than 150 hourly averages of monitoring data from each unit, are listed in Table 4. These data show average CO emission rates for boilers A, B, and C of between 0.18 and 0.50 lb/10^6 Btu. A previous study showed the average carbon monoxide emissions as based on 6 to 8 one hour samples from four wood-residue fired boilers ranged between 0.20 and 2.5 lb/10^6 Btu (4). Carbon monoxide emission rates tend to be below the average most of the time. Emission levels that are above the average tend to be significantly higher than the average, but occur less frequently. This is illustrated in Figures 7 through 9 which present 1 hr and 8 hr average carbon monoxide emission rates as a function of the cumulative frequency of occurrence plotted on Weibull distribution paper. The carbon monoxide emission rate is less than the value shown on the y axis for the percentage of time shown on the x axis.

TABLE 4 AVERAGE CO EMISSION RATES FROM THREE WOOD-RESIDUE FIRED BOILERS

Boiler	CO (lb/10^6 Btu)	Average O_2 Dry Basis (Percent)
A	0.18	5.6
B	0.50	10.7
C	0.43	8.8

The difference in average CO emissions from these boilers appeared to be associated with oxygen content of the flue gas. The average oxygen content in the flue gas of the boilers sampled is listed in Table 4. High oxygen concentrations in the flue gas appeared to increase carbon monoxide emission rates at boilers A and C as illustrated in plots of carbon dioxide or oxygen vs carbon monoxide for each boiler studied presented in Figures 10 to 12. Figure 12 indicates minimum carbon monoxide emission rates occurred at a flue gas oxygen content of between 6.5 and 8.5 percent on a dry gas basis at the stack. This percent oxygen

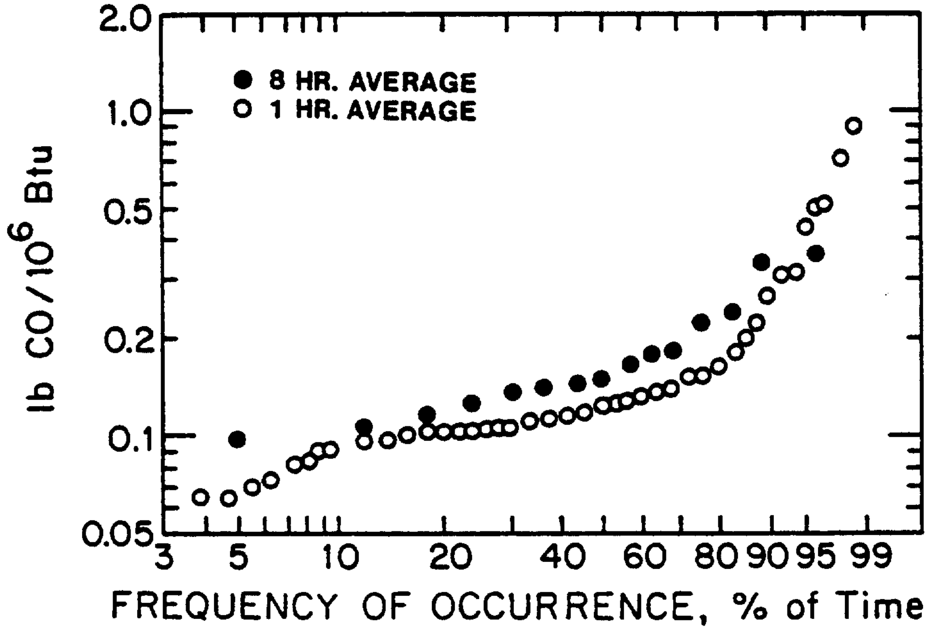


FIGURE 7

FREQUENCY OF OCCURRENCE OF CO EMISSIONS MEASURED AT BOILER A

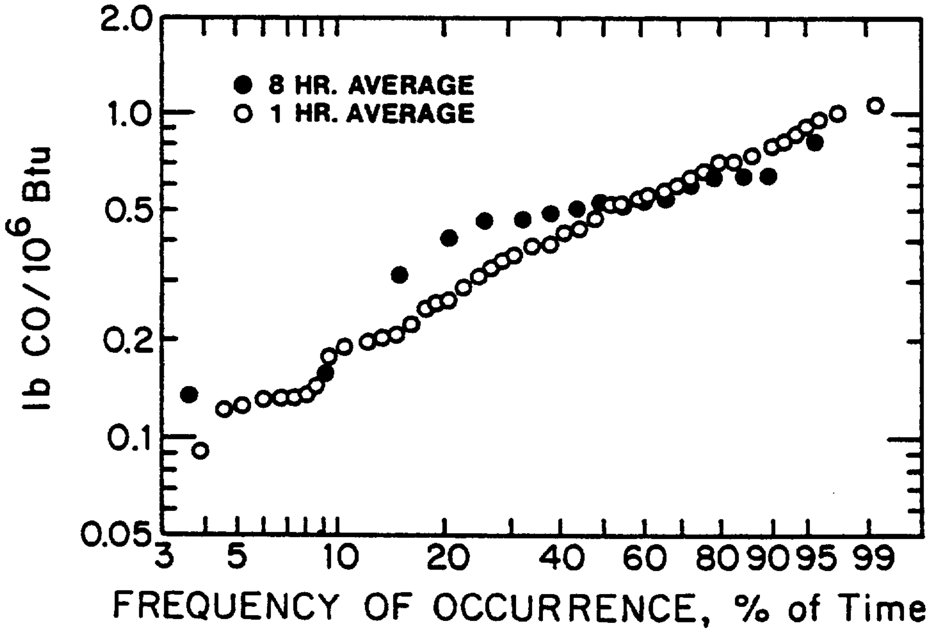


FIGURE 8

FREQUENCY OF OCCURRENCE OF CO EMISSIONS MEASURED AT BOILER B

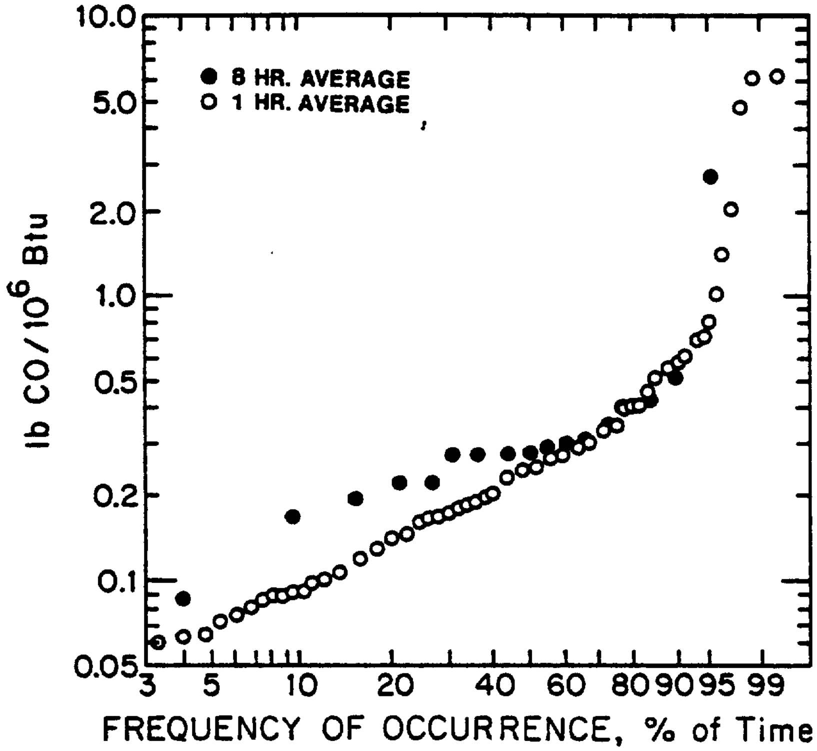


FIGURE 9

FREQUENCY OF OCCURRENCE OF CO EMISSIONS MEASURED AT BOILER C

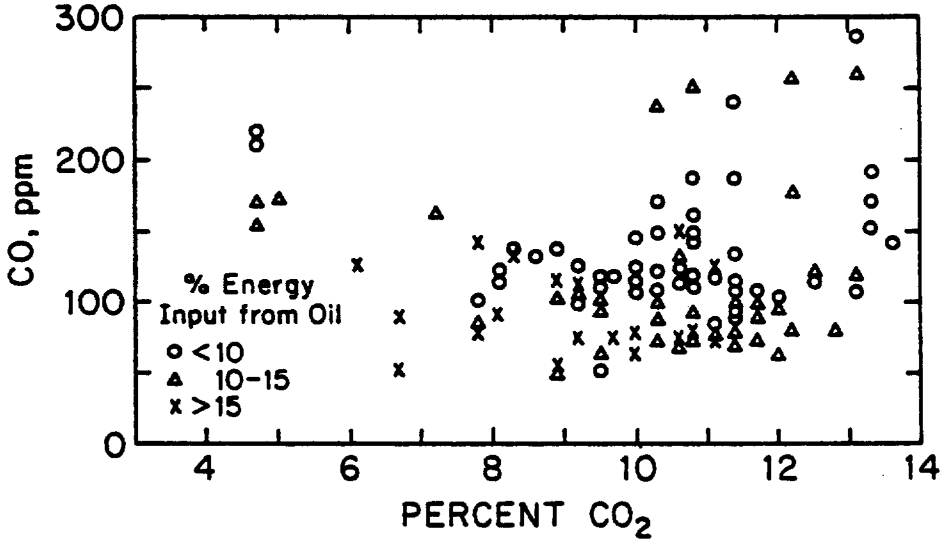


FIGURE 10

CARBON MONOXIDE EMISSIONS FROM BOILER A AS A FUNCTION OF STACK GAS CARBON DIOXIDE CONCENTRATIONS ON A WET BASIS

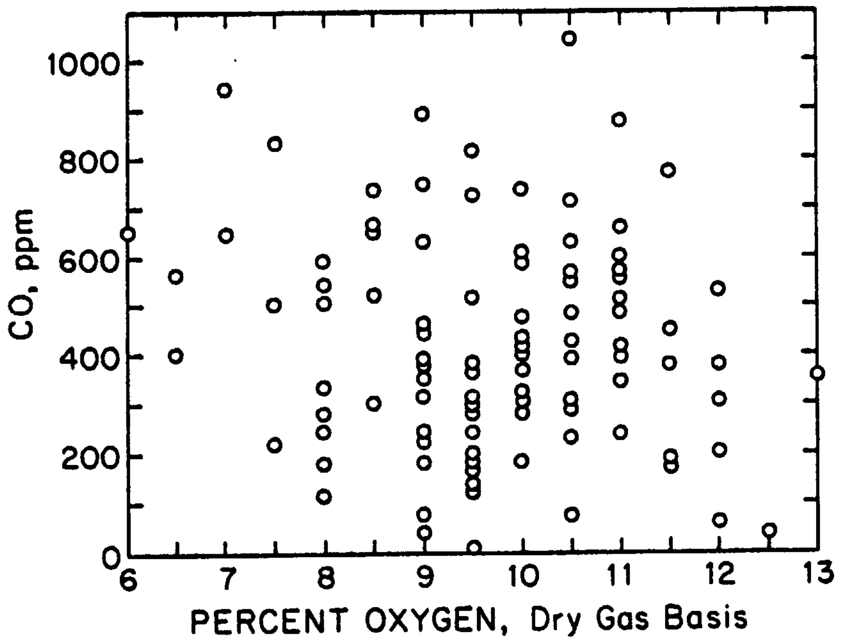


FIGURE 11

CARBON MONOXIDE EMISSIONS FROM
BOILER B AS A FUNCTION OF
STACK GAS OXYGEN CONCENTRATIONS

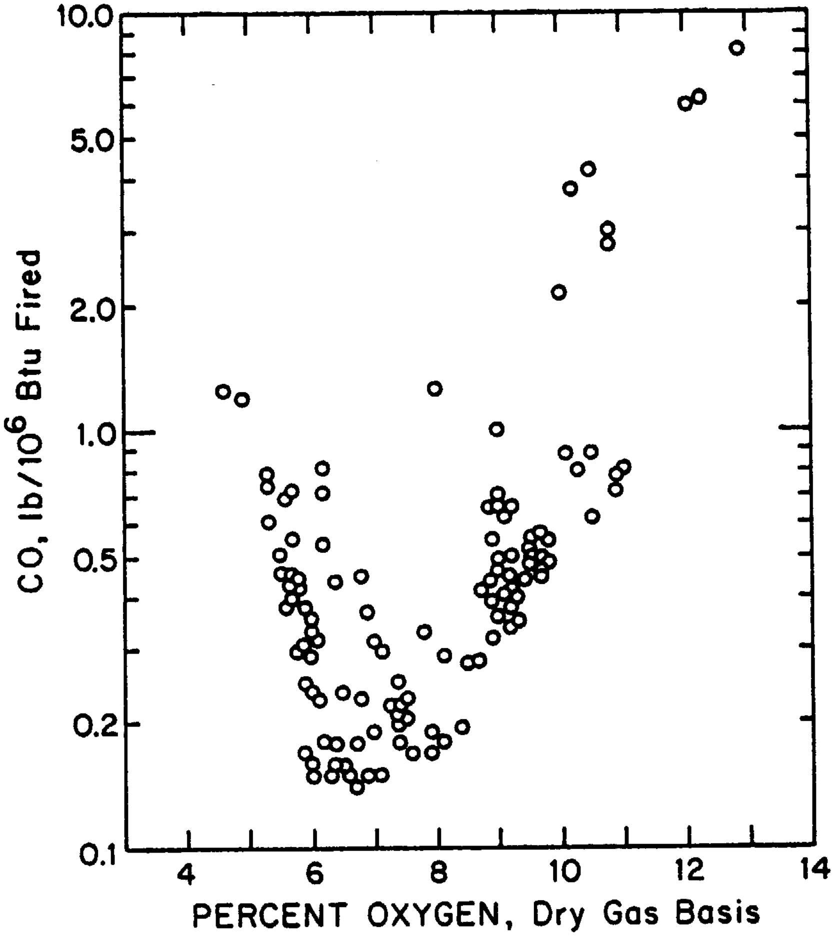


FIGURE 12

CARBON MONOXIDE EMISSIONS FROM
BOILER C AS A FUNCTION OF
STACK GAS OXYGEN CONCENTRATIONS

range corresponded to about 3.0 to 5.0 percent oxygen on a wet gas basis as measured by an in situ oxygen meter. Too little excess air results in carbon monoxide generation because of incomplete combustion, whereas too much excess air reduces combustion zone flame temperature and gas residence time. Either a lack or abundance of oxygen in the flue gas resulted in increased carbon monoxide emission rates.

Figure 10 also shows the effect of auxiliary fuel firing on carbon monoxide emissions. Increased use of auxiliary fuel generally reduced carbon monoxide emission rates. Firing with oil in amounts greater than 50 percent the total energy input resulted in carbon monoxide emissions of less than 0.07 lb/10^6 Btu heat input for this boiler.

C. Carbon Monoxide Emissions from Kraft Recovery Furnaces

Presented in Table 5 are the average carbon monoxide emissions from each recovery furnace over the study period. These values are averages of between 88 and 168 hours of data for each furnace. Also presented in Table 5 are the medians of the 1 hr and 8 hr average emissions for each of the five recovery furnaces studied. Also listed in the table are the average oxygen concentrations measured on a wet basis in the exit gas from each recovery furnace. The average of all carbon monoxide emissions for each furnace ranged from 0.14 to 13.3 lb CO/10^3 lb bls fired, or from 0.43 to about 42 lb carbon monoxide per air dry ton (ADT) unbleached pulp produced. Medians of the 1 hr and 8 hr average data were less than the average data. This was a result of the exponential to logarithmic distribution of the data as illustrated by frequency distribution plots presented in Figures 13 to 17. In these figures the 1 hr and 8 hr average data plotted on Weibull frequency distribution paper show a variability in carbon monoxide emissions of up to two orders of magnitude for each of the recovery furnace studied. For the majority of the time, emissions were in the lower part of the range, but at less frequent intervals relatively high carbon monoxide emission rates were recorded. The level of 8 hr average carbon monoxide emission rates that were exceeded at least 1 percent of the time for furnaces A through E respectively were 0.8, 2.1, 1.3, 11, and 30 lb CO/10^3 lb bls.

A relationship between carbon monoxide emissions and exit gas oxygen concentrations was indicated. Figures 18 to 20 illustrate that at oxygen contents of less than 2 or 3 percent on a wet basis in the furnace exit gas, carbon monoxide emission rates increased rapidly. Similar figures are not shown for furnaces A and C because flue gas oxygen concentrations at these furnaces showed little variation during this study and no relationship to carbon monoxide emissions existed. The recovery furnace with emissions greater than 10 lb CO/10^3 lb bls was generally operating with less than 3 percent oxygen in the furnace exit gas. Recovery furnaces are normally operated at low excess combustion air to aid in reduction of sodium sulfate to sodium sulfide in the smelt.

TABLE 5 CARBON MONOXIDE EMISSION MEASURED AT FIVE KRAFT RECOVERY FURNACES

Furnace	Hours of Data	Total Average lb $CO/10^3$ lb bls	Total Average lb CO/ADT	Median of 1-hr Average CO Emissions	Median of 8-hr Average CO Emissions	Average O_2
A	88	0.14	0.43	0.06	0.08	3.8
B	120	0.60	1.8	0.33	0.48	3.3
C	136	0.64	3.1	0.56	0.60	3.2
D	168	1.87	5.9	0.95	0.96	3.1
E	152	13.3	42	12.2	12.5	2.8

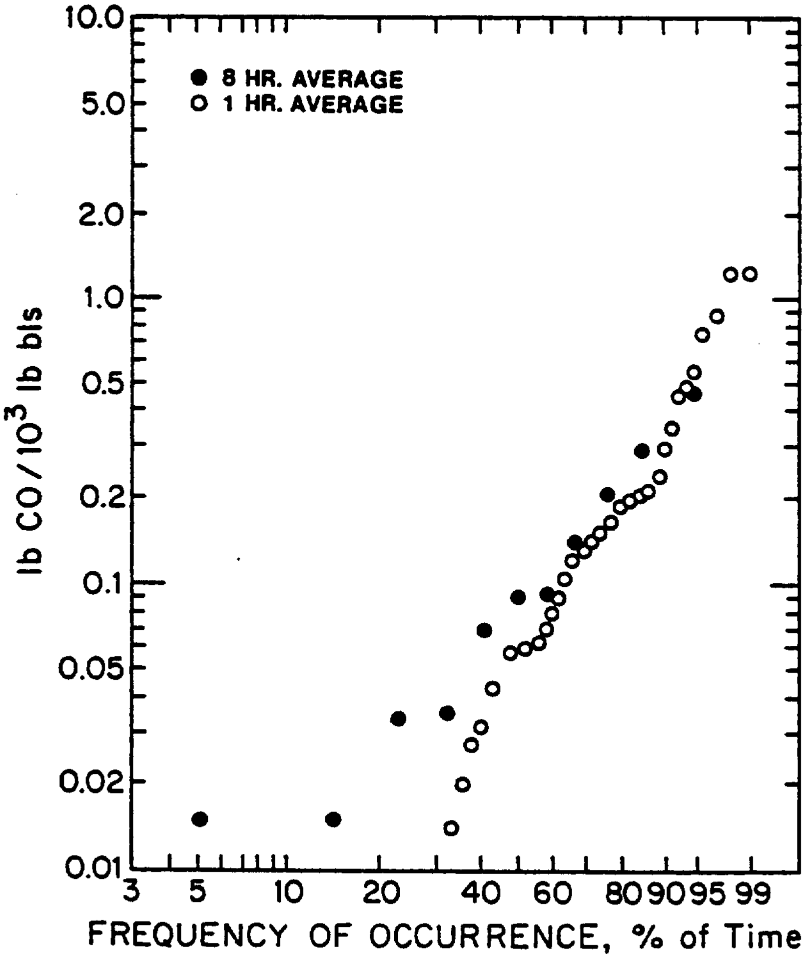


FIGURE 13

FREQUENCY OF CARBON MONOXIDE EMISSIONS FROM KRAFT RECOVERY FURNACE A

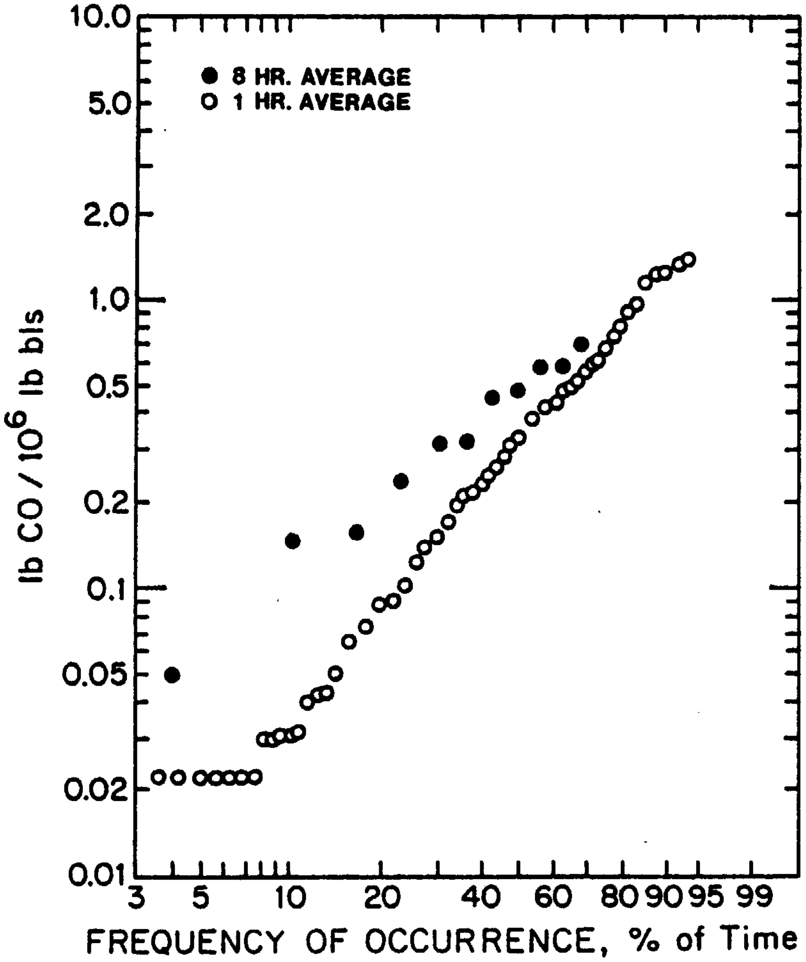


FIGURE 14

FREQUENCY OF CARBON
MONOXIDE EMISSIONS
FROM KRAFT RECOVERY FURNACE B

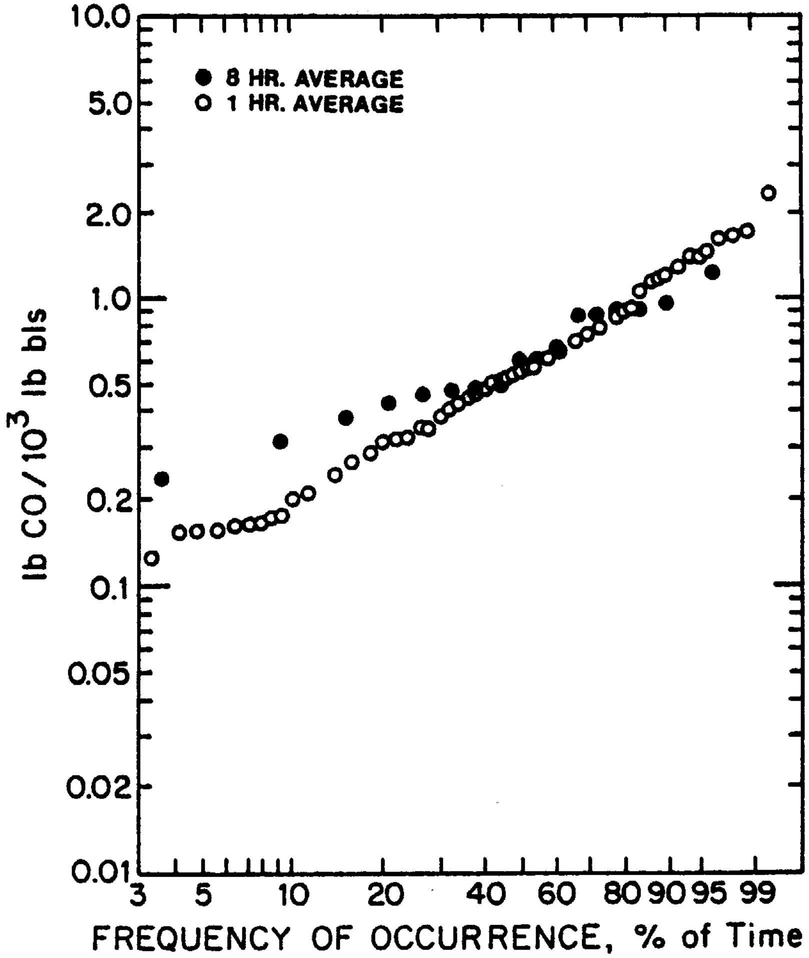


FIGURE 15

FREQUENCY OF CARBON
MONOXIDE EMISSIONS
FROM KRAFT RECOVERY FURNACE C

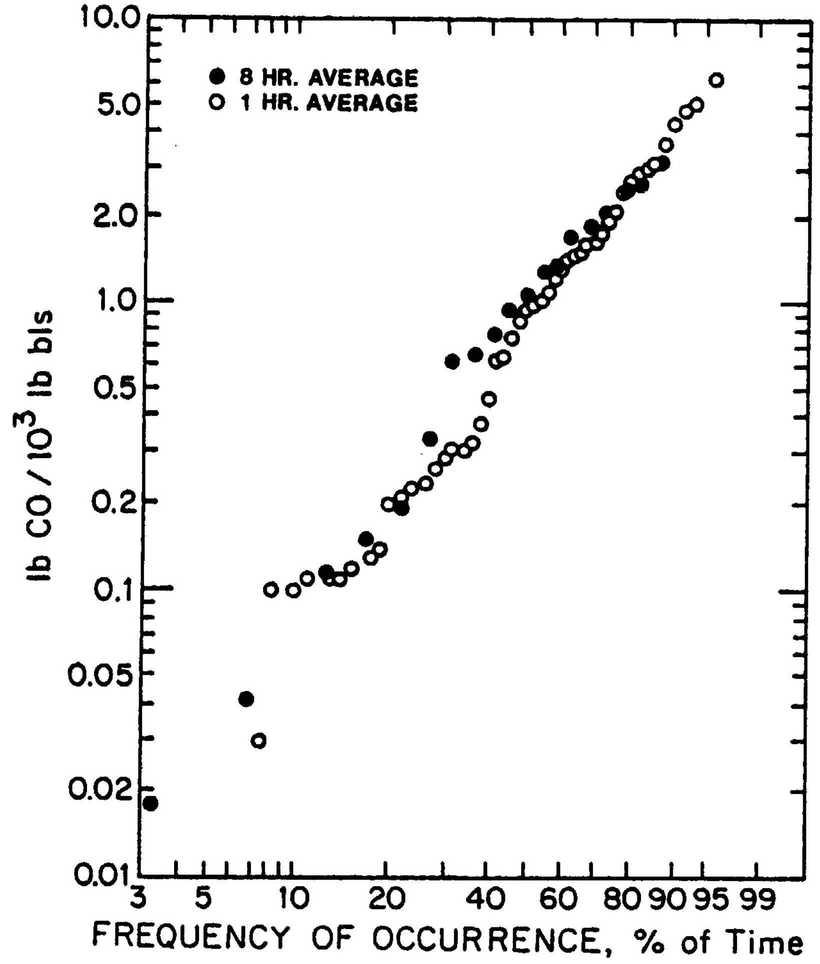


FIGURE 16

FREQUENCY OF CARBON
MONOIXDE EMISSIONS
FROM KRAFT RECOVERY FURNACE D

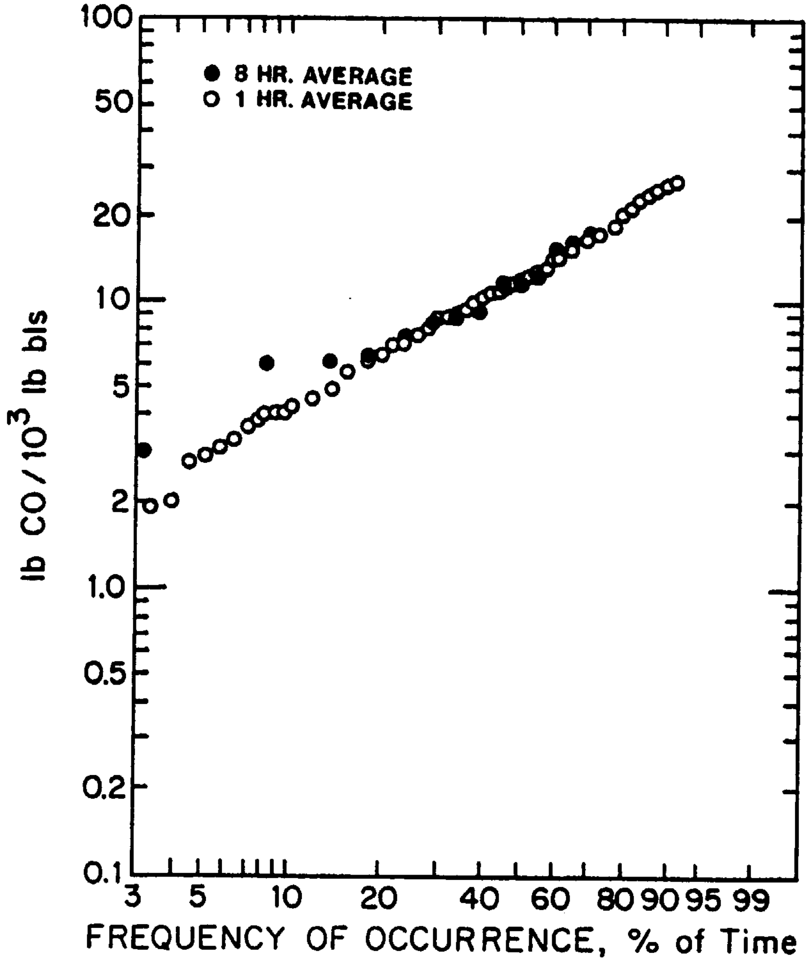


FIGURE 17

FREQUENCY OF CARBON
MONOXIDE EMISSIONS
FROM KRAFT RECOVERY FURNACE E

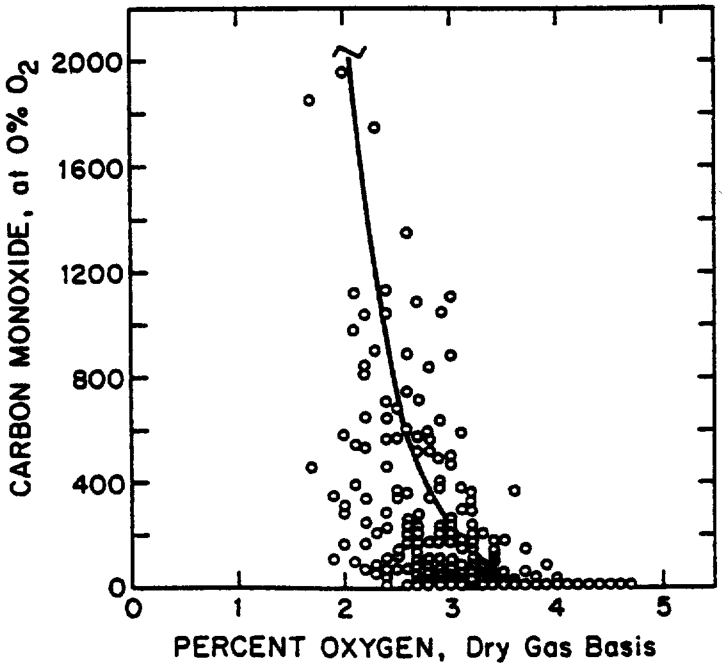


FIGURE 18

CARBON MONOXIDE EMISSIONS FROM KRAFT RECOVERY FURNACE B EXPRESSED AS ppm CORRECTED TO 0 PERCENT O_2 AS A FUNCTION OF STACK GAS OXYGEN CONCENTRATIONS

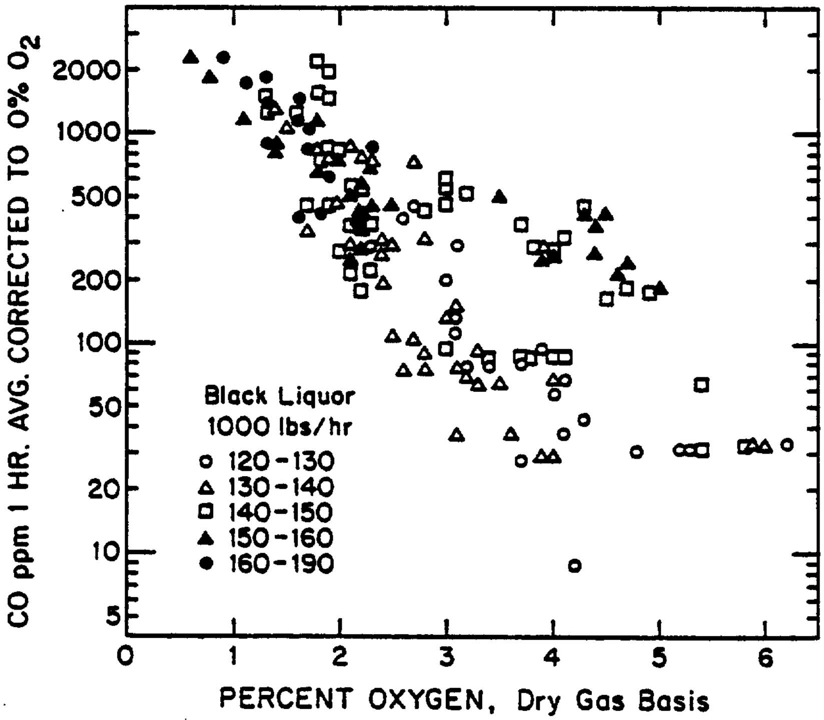
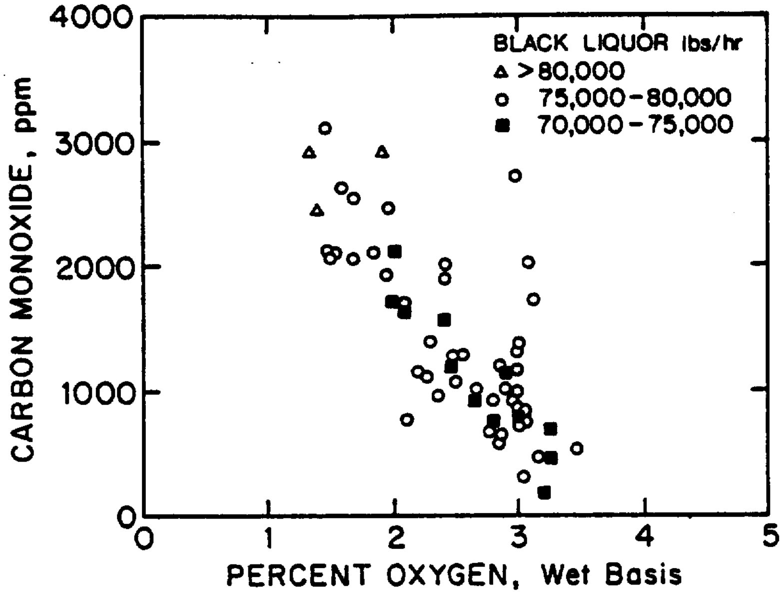


FIGURE 19

CARBON MONOXIDE EMISSIONS FROM KRAFT RECOVERY FURNACE D EXPRESSED AS ppm CORRECTED TO 0 PERCENT O_2 AS A FUNCTION OF STACK GAS OXYGEN CONCENTRATION



<u>FIGURE 20</u>

CARBON MONOXIDE EMISSIONS FROM KRAFT RECOVERY FURNACE E EXPRESSED AS ppm CORRECTED TO 0 PERCENT O_2 AS A FUNCTION OF STACK GAS OXYGEN CONCENTRATION

D. Relationship Between Carbon Monoxide and TRS Emissions from Kraft Recovery Furnaces

Total Reduced Sulfur (TRS) emission data was collected from the recovery furnaces along with the carbon monoxide emission data to look for possible correlation between the two. Both TRS emissions and carbon monoxide emissions for the two DCE equipped recovery furnaces, A and C were low and no relationship could be found. Recognizing the TRS-CO emission relationships on DCE furnaces are tenous because of TRS contributions of the DCE, TRS emissions from this type of kraft recovery furnace tended to increase when carbon monoxide emissions increased above some level. This is illustrated in Figures 21 to 23 where the percent of time the TRS concentration in the exit gas exceeded 5 ppm was plotted as a function of the carbon monoxide concentration for DCE furnaces. These diagrams show that the probability of exceeding a 5 ppm TRS concentration increased with higher carbon monoxide emission levels. If appears unlikely that the increase in TRS emissions, as carbon monoxide increased, would be attributable to the TRS contribution from the contact evaporator. The TRS-carbon monoxide relationship for each DCE recovery furnace was found to be different. In only one case, however, were TRS emissions sufficiently low (Recovery Furnace C) to indicate a critical level of carbon monoxide where TRS emissions started to

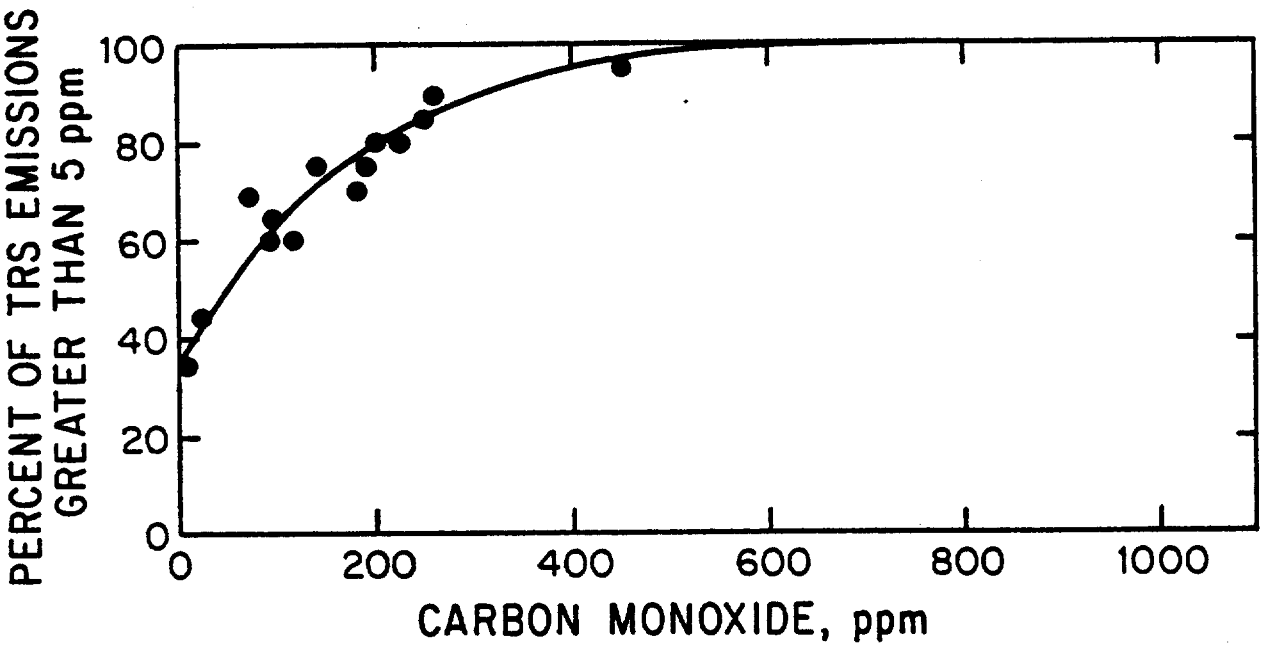


FIGURE 21

PERCENT OF TRS EMISSIONS GREATER THAN 5 ppm
AS A FUNCTION OF CARBON MONOXIDE CONCENTRATIONS
IN THE STACK GASES AT RECOVERY FURNACE A

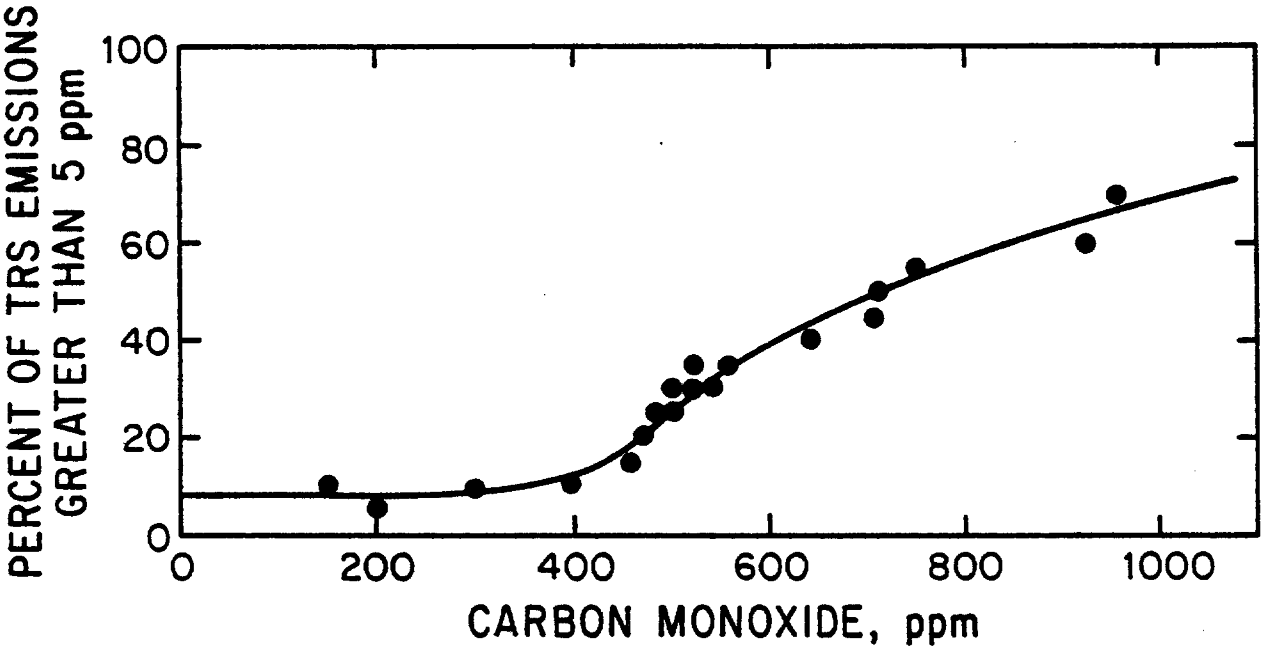


FIGURE 22

PERCENT OF TRS EMISSIONS GREATER THAN 5 ppm
AS A FUNCTION OF CARBON MONOXIDE CONCENTRATIONS
IN THE STACK GASES AT RECOVERY FURNACE B

increase. This was at about 350 ppm carbon monoxide. The kraft recovery furnaces studied that were equipped with non-direct contact evaporators operated with higher furnace exit gas oxygen concentrations than the NDCE-equipped furnaces. These furnaces maintained carbon monoxide below 400 ppm and TRS emissions were below 5 ppm throughout the study period.

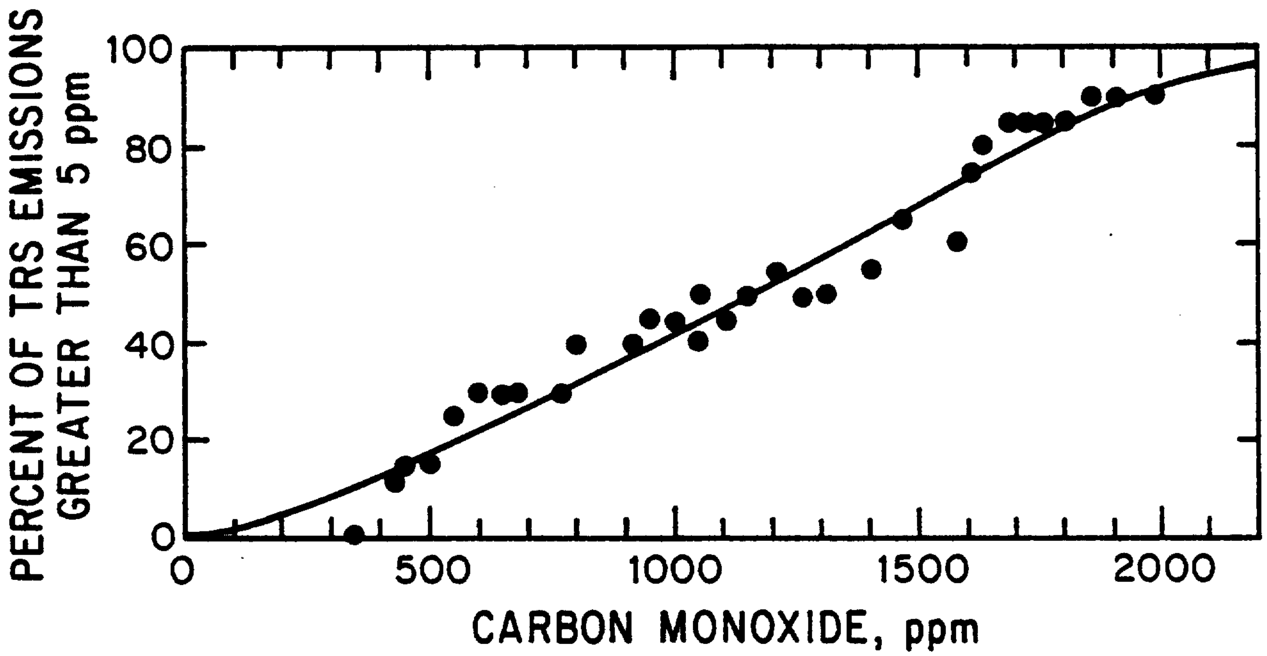


FIGURE 23

PERCENT OF TRS EMISSIONS GREATER THAN 5 ppm AS A FUNCTION OF CARBON MONOXIDE CONCENTRATIONS IN THE STACK GASES AT RECOVERY FURNACE C

Carbon monoxide-TRS emission relationships for these five units were inadequate to determine if carbon monoxide monitoring could serve as a surrogate for TRS monitoring. An additional study is required to determine if this is the case. Carbon monoxide monitoring, however, was indicated to be an effective tool to assist the furnace operator in reducing TRS emissions excursions from the furnace.

E. Lime Kiln Carbon Monoxide Emission

Averages of carbon monoxide emission data collected from two lime kilns during this survey, kilns A and B, representing 200 and 60 hours of data respectively, and two lime kilns during TGNMO emissions survey (5), kilns C and D, are listed in Table 6. Cumulative frequency distributions of 1 hr and 8 hr average carbon monoxide emissions from kilns A and B are shown in Figures 24 and 25. Average 1 hr carbon monoxide emissions from kilns A and B were less than 0.03 lb/10^6 Btu heat input greater than 70 percent of the time. Occasional process upsets, such as too little excess combustion air or unstable flame conditions resulted in occasional short-term, high concentrations of carbon monoxide. Carbon monoxide emissions during these momentary aberrations increased average emissions from baseline levels. Median 1 hr average carbon monoxide emissions were at 0.008 and 0.023 lb/10^6 Btu for kilns A and B respectively. Lime kiln C was an older unit and did not have an operating oxygen monitor when sampled. This may have been in part responsible for the higher carbon monoxide emission rates measured.

TABLE 6 AVERAGE LIME KILN CARBON MONOXIDE EMISSIONS

Kiln	Hours of Data	lb CO/10^6 Btu	lb CO/ton Lime	lb CO/ADT Pulp
A	60	0.038	0.17	0.051
B	200	0.041	0.19	0.058
C	14	0.080	0.41	0.120
D	8	0.020	0.12	0.035

F. Carbon Monoxide Emissions at Optimum Energy Recovery Efficiency

Recovery furnaces and wood-residue fired boilers can be optimized for energy recovery by balancing reduced stack heat losses from low excess combustion air use against energy losses from uncombusted carbon monoxide in the flue gases. Figure 26 shows stack energy losses from three kraft recovery furnaces as a function of the stack gas oxygen concentration and CO concentrations typical of the flue gas oxygen concentration shown for the indicated furnace. Each recovery furnace is indicated to have an optimum operating range. The carbon monoxide emission concentrations in the exit gas at maximum energy recovery were between 300 to 1000 ppm, which corresponded to between 1.1 to 3.8 lb CO/10^3 lb bls. These values will vary somewhat with stack gas temperature. A higher stack gas temperature should result in a narrower range in carbon monoxide emission rates at maximum energy recovery. If recovery furnaces are optimized for energy recovery, it would be expected that carbon monoxide emission rate will be within the range mentioned above. A carbon monoxide concentration of 300 ppm or about 1 lb CO/10^3 lb bls was

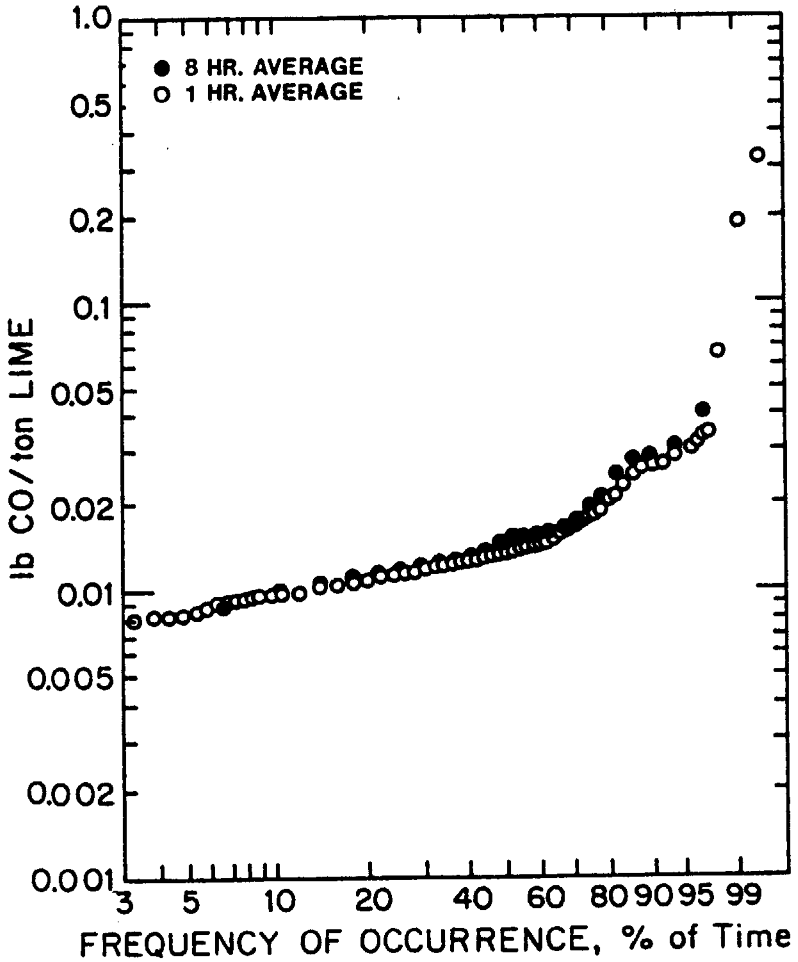


FIGURE 24

FREQUENCY OF OCCURRENCE OF CO
EMISSIONS MEASURED AT LIME KILN A

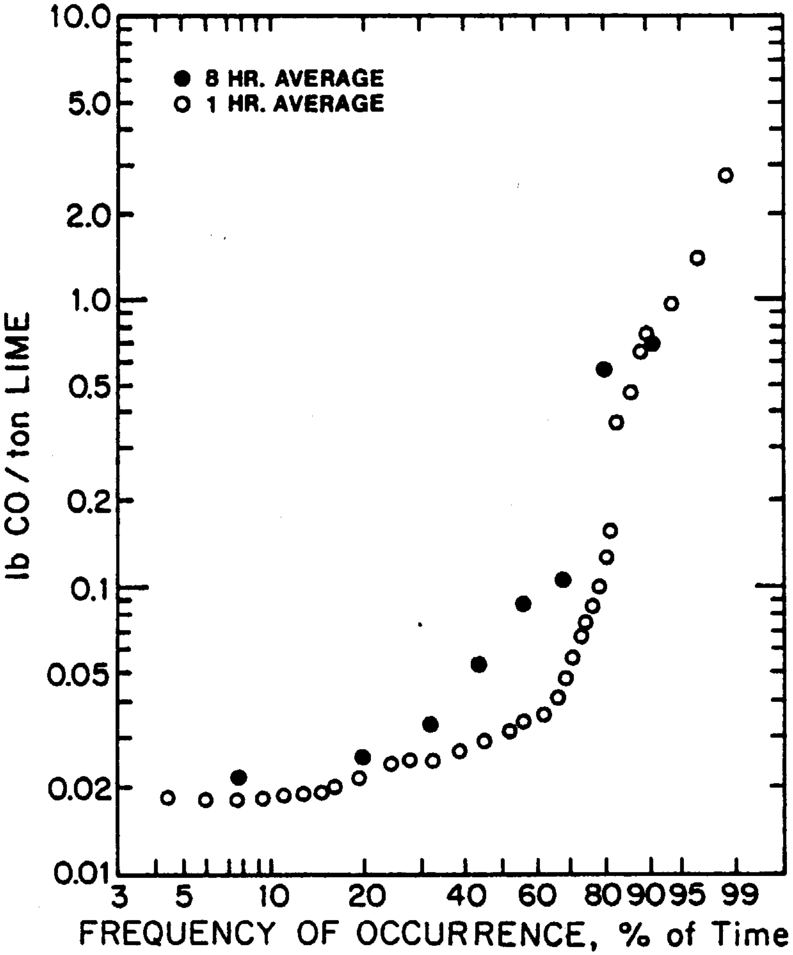


FIGURE 25

FREQUENCY OF OCCURRENCE OF CO
EMISSIONS MEASURED AT LIME KILN B

always within a tenth of a percent of the minimum energy loss. The need to control TRS emissions to less than 5 ppm will result in operation of the boiler such that the carbon monoxide emission concentrations will be at the low end of the range, possibly to the detriment of energy recovery.

Likewise, a minimal energy loss was projected to occur in wood-residue fired boilers at the flue gas oxygen concentration range illustrated in Figure 27. The minimum energy losses would be expected to occur at carbon monoxide emission rates in the range of 0.25 to 1.1 lb/10^6 Btu fired. This corresponds to between 250 and 760 ppm carbon monoxide in the flue gas.

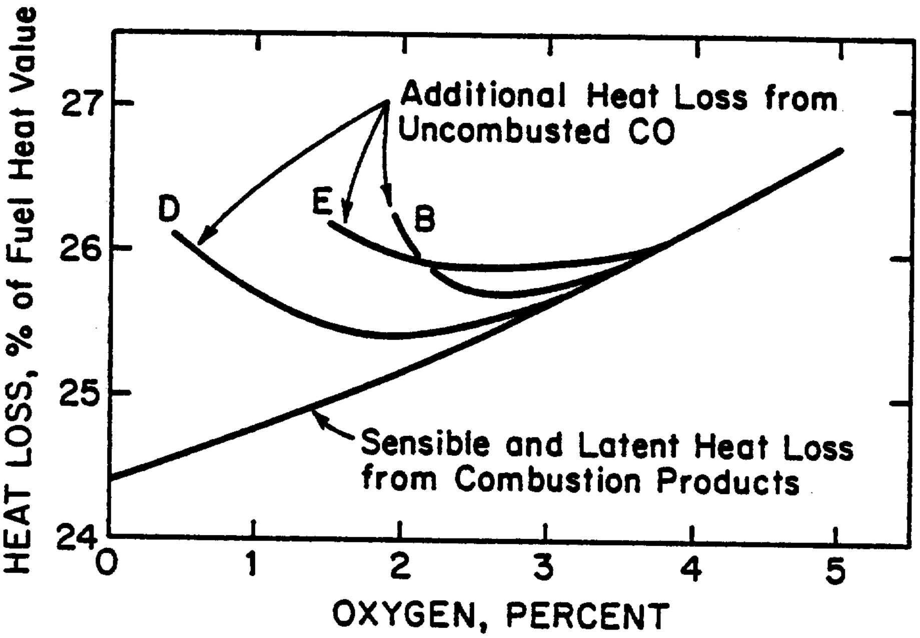


FIGURE 26

CALCULATED HEAT LOSSES IN THE STACK CONTAINED IN THE STACK GAS COMBUSTION PRODUCTS AND EXCESS AIR AND FROM UNCOMBUSTED CARBON MONOXIDE FROM KRAFT RECOVERY FURNACES B, D, AND E

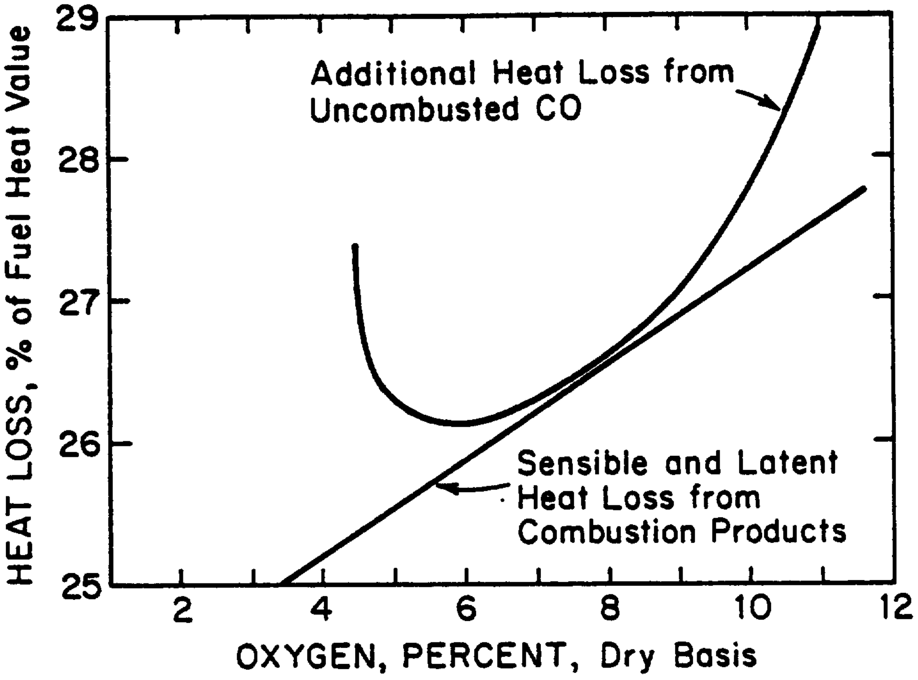


FIGURE 27

CALCULATED HEAT LOSSES UP THE STACK CONTAINED IN THE STACK GAS COMBUSTION PRODUCTS AND EXCESS AIR AND FROM UNCOMBUSTED CARBON MONOXIDE FROM WOOD-RESIDUE FIRED BOILER C

VI SUMMARY

(1) Information on carbon monoxide emission rates from a limited number of forest products industry combustion sources representative of current design and operating practices were collected using in-place process carbon monoxide monitors where available, or supplied where not available.

(2) The monitors in field use generally exhibited three weaknesses namely: (a) a positive interference from carbon dioxide and moisture, (b) a continual positive drift from particulate accumulation, and (c) inaccurate transmission of the monitor output to the recorder.

(3) The average carbon monoxide emission from wood-residue fired boilers over the period of this study ranged between 0.18 and 0.50 lb/10^6 Btu for a 150 hour monitoring period. Both 1 hr and 8 hr average carbon monoxide emissions ranged greater than an order of magnitude. A correlation of carbon monoxide emissions with flue gas oxygen content was observed. High carbon monoxide emissions resulted when either too little or two much excess air was used.

(4) The average carbon monoxide emissions from kraft recovery furnaces over the period of this study ranged between 0.14 and 13.3 lb/10^3 pound of black liquor solids fired. Both 1 hr and 8 hr average carbon monoxide emissions ranged greater than 2 orders of magnitude for four of the furnaces. High carbon monoxide emissions from the source were correlated with low flue gas oxygen concentrations.

(5) Carbon monoxide emissions from two lime kilns that did not burn noncondensibles averaged 0.04 lb/10^6 Btu of fuel fired.

(6) Carbon monoxide-TRS emission relationships for the five recovery furnaces studied were inadequate to determine if carbon monoxide monitoring could serve as a surrogate for TRS monitoring and additional study is required to determine if this is the case. Carbon monoxide monitoring, however, was indicated to be an effective tool to assit the furnace operator in reducing TRS emissions excursions.

(7) An analysis of energy loss in flue gas from kraft recovery furnaces showed that, based on the data in hand, optimization of energy recovery: (a) results in elevated carbon monoxide emission levels, and (b) may not be consistent with meeting a 5 ppm TRS level. A similar analysis of energy loss in flue gas from wood fired power boilers was made.

VII LITERATURE REFERENCES

(1) "Handbook, Continuous Air Pollution Source Monitoring System," USEPA Technology Transfer, EPA 625/6-78, 005 (June 1979).

(2) Manufacturers Brochure

(3) "Method 10 - Determination of Carbon Monoxide Emissions from Stationary Sources," CFR 121:1598.13

(4) "A Study of Wood-Residue Fired Power Boiler Total Gaseous Nonmethane Organic Emissions in the Pacific Northwest," Atmospheric Quality Improvement Technical Bulletin No. 109, NCASI (September 1980).

(5) "A Study of Kraft Process Lime Kiln Total Gaseous Non-Methane Organic Emissions," NCASI Technical Bulletin No. 358 (September 1981).

(6) "Method 19 Determination of Sulfur Dioxide Removal Efficiency and Particulate, Sulfur Dioxide and Nitrogen Oxide Emission Rates from Electric Utility Steam Generators, Part 5.3.1, Oxygen Based F Factor Procedure," 40 CFR 121:1642.

APPENDIX A

EPA METHOD 10 - DETERMINATION OF CARBON MONOXIDE EMISSIONS FROM STATIONARY SOURCES

4.2 Performance Evaluation Tests. The owner of a lidar system shall subject such a lidar system to the performance verification tests described in Section 3, prior to first use of this method. The annual calibration shall be performed for three separate, complete runs and the results of each should be recorded. The requirements of Section 3.3.1 must be fulfilled for each of the three runs.

Once the conditions of the annual calibration are fulfilled the lidar shall be subjected to the routine verification for three separate complete runs. The requirements of Section 3.3.2 must be fulfilled for each of the three runs and the results should be recorded. The Administrator may request that the results of the performance evaluation be submitted for review.

5. References.

5.1 The Use of Lidar for Emissions Source Opacity Determination, U.S. Environmental Protection Agency, National Enforcement Investigations Center, Denver, CO, EPA-330/1-79-003-R, Arthur W. Dybdahl, current edition [NTIS No. PB81-246662].

5.2 Field Evaluation of Mobile Lidar for the Measurement of Smoke Plume Opacity, U.S. Environmental Protection Agency, National Enforcement Investigations Center, Denver, CO, EPA/NEIC-TS-128, February 1976.

5.3 Remote Measurement of Smoke Plume Transmittance Using Lidar, C. S. Cook, G. W. Bethke, W. D. Conner (EPA/RTP). Applied Optics 11, pg 1742, August 1972.

5.4 Lidar Studies of Stack Plumes in Rural and Urban Environments, EPA-650/4-73-002, October 1973.

5.5 American National Standard for the Safe Use of Lasers ANSI Z 136.1-176, 8 March 1976.

5.6 U.S. Army Technical Manual TB MED 279, Control of Hazards to Health from Laser Radiation, February 1969.

5.7 Laser Institute of America Laser Safety Manual, 4th Edition.

5.8 U.S. Department of Health, Education and Welfare, Regulations for the Administration and Enforcement of the Radiation Control for Health and Safety Act of 1968, January 1976.

5.9 Laser Safety Handbook, Alex Mallow, Leon Chabot, Van Nostrand Reinhold Co., 1978.

METHOD 10—DETERMINATION OF CARBON MONOXIDE EMISSIONS FROM STATIONARY SOURCES

1. *Principle and Applicability.*

1.1 *Principle.* An integrated or continuous gas sample is extracted from a sampling point and analyzed for carbon monoxide (CO) content using a Luft-type nondispersive infrared analyzer (NDIR) or equivalent.

1.2 *Applicability.* This method is applicable for the determination of carbon monoxide emissions from stationary sources only when specified by the test procedures for determining compliance with new source performance standards. The test procedure will indicate whether a continuous or an integrated sample is to be used.

2. *Range and sensitivity.*

2.1 *Range.* 0 to 1,000 ppm.

2.2 *Sensitivity.* Minimum detectable concentration is 20 ppm for a 0 to 1,000 ppm span.

3. *Interferences.* Any substance having a strong absorption of infrared energy will interfere to some extent. For example, discrimination ratios for water (H_2O) and carbon dioxide (CO_2) are 3.5 percent H_2O per 7 ppm CO and 10 percent CO_2 per 10 ppm CO, respectively, for devices measuring in the 1,500 to 3,000 ppm range. For devices measuring in the 0 to 100 ppm range, interference ratios can be as high as 3.5 percent H_2O per 25 ppm CO and 10 percent CO_2 per 50 ppm CO. The use of silica gel and ascarite traps will alleviate the major interference problems. The measured gas volume must be corrected if these traps are used.

4. *Precision and accuracy.*

4.1 *Precision.* The precision of most NDIR analyzers is approximately ±2 percent of span.

4.2 *Accuracy.* The accuracy of most NDIR analyzers is approximately ±5 percent of span after calibration.

5. *Apparatus.*

5.1 *Continuous sample* (Figure 10-1).

5.1.1 *Probe.* Stainless steel or sheathed Pyrex[1] glass, equipped with a filter to remove particulate matter.

5.1.2 *Air-cooled condenser or equivalent.* To remove any excess moisture.

5.2 *Integrated sample* (Figure 10-2).

5.2.1 *Probe.* Stainless steel or sheathed Pyrex glass, equipped with a filter to remove particulate matter.

5.2.2 *Air-cooled condenser or equivalent.* To remove any excess moisture.

5.2.3 *Valve.* Needle valve, or equivalent, to adjust flow rate.

5.2.4 *Pump.* Leak-free diaphragm type, or equivalent, to transport gas.

5.2.5 *Rate meter.* Rotameter, or equivalent, to measure a flow range from 0 to 1.0 liter per min. (0.035 cfm).

5.2.6 *Flexible bag.* Tedlar, or equivalent, with a capacity of 60 to 90 liters (2 to 3 ft³). Leak-test the bag in the laboratory before using by evacuating bag with a pump followed by a dry gas meter. When evacuation is complete, there should be no flow through the meter.

5.2.7 *Pitot tube.* Type S, or equivalent, attached to the probe so that the sampling rate can be regulated proportional to the stack gas velocity when velocity is varying with the time or a sample traverse is conducted.

5.3 *Analysis* (Figure 10-3).

5.3.1 *Carbon monoxide analyzer.* Nondispersive infrared spectrometer, or equivalent. This instrument should be demonstrated, preferably by the manufacturer, to meet or exceed manufacturer's specifications and those described in this method.

5.3.2 *Drying tube.* To contain approximately 200 g of silica gel.

5.3.3 *Calibration gas.* Refer to paragraph 6.1.

5.3.4 *Filter.* As recommended by NDIR manufacturer.

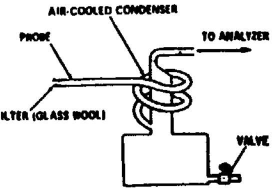


Figure 10-1. Continuous sampling train.

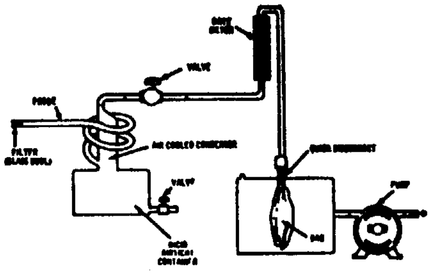


Figure 10-2. Integrated gas-sampling train.

5.3.5 CO_2 removal tube. To contain approximately 500 g of ascarite.

5.3.6 *Ice water bath.* For ascarite and silica gel tubes.

5.3.7 *Valve.* Needle valve, or equivalent, to adjust flow rate

5.3.8 *Rate meter.* Rotameter or equivalent to measure gas flow rate of 0 to 1.0 liter per min. (0.035 cfm) through NDIR.

5.3.9 *Recorder (optional).* To provide permanent record of NDIR readings.

6. *Reagents.*

6.1 *Calibration gases.* Known concentration of CO in nitrogen (N_2) for instrument span, prepurified grade of N_2 for zero, and two additional concentrations corresponding approximately to 60 percent and 30 percent span. The span concentration shall not exceed 1.5 times the applicable source performance standard. The calibration gases shall be certified by the manufacturer to be within ±2 percent of the specified concentration.

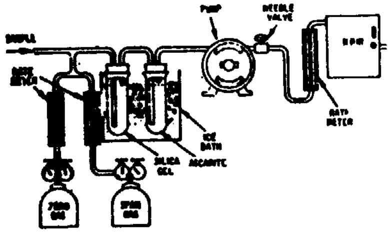


Figure 10-3. Analytical equipment.

6.2 *Silica gel.* Indicating type, 6 to 16 mesh, dried at 175° C (347° F) for 2 hours.

6.3 *Ascarite.* Commercially available.

7. *Procedure.*

7.1 *Sampling.*

7.1.1 *Continuous sampling.* Set up the equipment as shown in Figure 10-1 making sure all connections are leak free. Place the probe in the stack at a sampling point and purge the sampling line. Connect the analyzer and begin drawing sample into the analyzer. Allow 5 minutes for the system to stabilize, then record the analyzer reading as required by the test procedure. (See ¶ 7.2 and 8). CO_2 content of the gas may be determined by using the Method 3 integrated sample procedure (36 FR 24886), or by weighing the ascarite CO_2 removal tube and computing CO_2 concentration from the gas volume sampled and the weight gain of the tube.

7.1.2 *Integrated sampling.* Evacuate the flexible bag. Set up the equipment as shown in Figure 10-2 with the bag disconnected. Place the probe in the stack and purge the sampling line. Connect the bag, making sure that all connections are leak free. Sample at a rate proportional to the stack velocity. CO_2 content of the gas may be determined by using the Method 3 integrated sample procedures (36 FR 24886), or by weighing the ascarite CO_2 removal tube and comput-

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[1] Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

ing CO_2 concentration from the gas volume sampled and the weight gain of the tube.

7.2 *CO Analysis.* Assemble the apparatus as shown in Figure 10-3, calibrate the instrument, and perform other required operations as described in paragraph 8. Purge analyzer with N_2 prior to introduction of each sample. Direct the sample stream through the instrument for the test period, recording the readings. Check the zero and span again after the test to assure that any drift or malfunction is detected. Record the sample data on Table 10-1.

8. *Calibration.* Assemble the apparatus according to Figure 10-3. Generally an instrument requires a warm-up period before stability is obtained. Follow the manufacturer's instructions for specific procedure. Allow a minimum time of 1 hour for warm-up. During this time check the sample conditioning apparatus, i.e., filter, condenser, drying tube, and CO_2 removal tube, to ensure that each component is in good operating condition. Zero and calibrate the instrument according to the manufacturer's procedures using, respectively, nitrogen and the calibration gases.

TABLE 10-1—FIELD DATA

	Comments
Location	
Test	
Date	
Operator	
Clock time	Rotameter setting, liters per minute (cubic feet per minute)

9. *Calculation—Concentration of carbon monoxide.* Calculate the concentration of carbon monoxide in the stack using equation 10-1.

$$C_{CO\ stack}=C_{CO\ NDIR}(1-F_{CO_2})$$

where:

$C_{CO\ stack}$=concentration of CO in stack, ppm by volume (dry basis).

$C_{CO\ NDIR}$=concentration of CO measured by NDIR analyzer, ppm by volume (dry basis).

F_{CO_2}=volume fraction of CO_2 in sample, i.e., percent CO_2 from Orsat analysis divided by 100.

10. *Bibliography.*

10.1 McElroy, Frank, The Intertech NDIR-CO Analyzer, Presented at 11th Methods Conference on Air Pollution, University of California, Berkeley, Calif., April 1, 1970.

10.2 Jacobs, M. B., et al., Continuous Determination of Carbon Monoxide and Hydrocarbons in Air by a Modified Infrared Analyzer, J. Air Pollution Control Association, 9(2): 110-114, August 1959.

10.3 MSA LIRA Infrared Gas and Liquid Analyzer Instruction Book, Mine Safety Appliances Co., Technical Products Division, Pittsburgh, Pa.

10.4 Models 215A, 315A, and 415A Infrared Analyzers, Beckman Instruments, Inc., Beckman Instructions 1635-B, Fullerton, Calif., October 1967.

10.5 Continuous CO Monitoring System, Model A5611, Intertech Corp., Princeton, N.J.

10.6 UNOR Infrared Gas Analyzers, Bendix Corp., Ronceverte, West Virginia.

ADDENDA—A. PERFORMANCE SPECIFICATIONS FOR NDIR CARBON MONOXIDE ANALYZERS.

Range (minimum)	0–1000 ppm.
Output (minimum)	0–10mV.
Minimum detectable sensitivity.	20 ppm.
Rise time, 90 percent (maximum).	30 seconds.
Fall time, 90 percent (maximum).	30 seconds.
Zero drift (maximum)	10% in 8 hours.
Span drift (maximum)	10% in 8 hours.
Precision (minimum)	±2% of full scale.
Noise (maximum)	±1% of full scale.
Linearity (maximum deviation)	2% of full scale.
Interference rejection ratio	CO_2—1000 to 1, H_2O—500 to 1.

B. *Definitions of Performance Specifications.*

Range—The minimum and maximum measurement limits.

Output—Electrical signal which is proportional to the measurement; intended for connection to readout or data processing devices. Usually expressed as millivolts or milliamps full scale at a given impedance.

Full scale—The maximum measuring limit for a given range.

Minimum detectable sensitivity—The smallest amount of input concentration that can be detected as the concentration approaches zero.

Accuracy—The degree of agreement between a measured value and the true value; usually expressed as ± percent of full scale.

Time to 90 percent response—The time interval from a step change in the input concentration at the instrument inlet to a reading of 90 percent of the ultimate recorded concentration.

Rise Time (90 percent)—The interval between initial response time and time to 90 percent response after a step increase in the inlet concentration.

Fall Time (90 percent)—The interval between initial response time and time to 90 percent response after a step decrease in the inlet concentration.

Zero Drift—The change in instrument output over a stated time period, usually 24 hours, of unadjusted continuous operation when the input concentration is zero; usually expressed as percent full scale.

Span Drift—The change in instrument output over a stated time period, usually 24 hours, of unadjusted continuous operation when the input concentration is a stated upscale value; usually expressed as percent full scale.

Precision—The degree of agreement between repeated measurements of the same concentration, expressed as the average deviation of the single results from the mean.

Noise—Spontaneous deviations from a mean output not caused by input concentration changes.

Linearity—The maximum deviation between an actual instrument reading and the reading predicted by a straight line drawn between upper and lower calibration points.

METHOD 11—DETERMINATION OF HYDROGEN SULFIDE CONTENT OF FUEL GAS STREAMS IN PETROLEUM REFINERIES

1. *Principle and applicability.* 1.1 *Principle.* Hydrogen sulfide (H_2S) is collected from a source in a series of midget impingers and absorbed in pH 3.0 cadmium sulfate ($CdSO_4$) solution to form cadmium sulfide (CdS). The latter compound is then measured iodometrically. An impinger containing hydrogen peroxide is included to remove SO_2 as an interfering species. This method is a revision of the H_2S method originally published in the FEDERAL REGISTER, Volume 39, No. 47, dated Friday, March 8, 1974.

1.2 *Applicability.* This method is applicable for the determination of the hydrogen sulfide content of fuel gas streams at petroleum refineries.

2. *Range and sensitivity.* The lower limit of detection is approximately 8 mg/m³ (6 ppm). The maximum of the range is 740 mg/m³ (520 ppm).

3. *Interferences.* Any compound that reduces iodine or oxidizes iodide ion will interfere in this procedure, provided it is collected in the cadmium sulfate impingers. Sulfur dioxide in concentrations of up to 2,600 mg/m³ is eliminated by the hydrogen peroxide solution. Thiols precipitate with hydrogen sulfide. In the absence of H_2S, only co-traces of thiols are collected. When methane- and ethane-thiols at a total level of 300 mg/m³ are present in addition to H_2S, the results vary from 2 percent low at an H_2S concentration of 400 mg/m³ to 14 percent high at an H_2S concentration of 100 mg/m³. Carbon oxysulfide at a concentration of 20 percent does not interfere. Certain carbonyl-containing compounds react with iodine and produce recurring end points. However, acetaldehyde and acetone at concentrations of 1 and 3 percent, respectively, do not interfere.

Entrained hydrogen peroxide produces a negative interference equivalent to 100 percent of that of an equimolar quantity of hydrogen sulfide. Avoid the ejection of hydrogen peroxide into the cadmium sulfate impingers.

4. *Precision and accuracy.* Collaborative testing has shown the within-laboratory coefficient of variation to be 2.2 percent and the overall coefficient of variation to be 5 percent. The method bias was shown to be −4.8 percent when only H_2S was present. In the presence of the interferences cited in section 3, the bias was positive at low H_2S concentration and negative at higher concentrations. At 230 mg H_2S/m³, the level of the compliance standard, the bias was +2.7 percent. Thiols had no effect on the precision.

5. *Apparatus.*

5.1 Sampling apparatus.

5.1.1 Sampling line. Six to 7 mm (¼ in.) Teflon[1] tubing to connect the sampling train to the sampling valve.

5.1.2 Impingers. Five midget impingers, each with 30 ml capacity. The internal diameter of the impinger tip must be 1 mm ±0.05 mm. The impinger tip must be positioned 4 to 6 mm from the bottom of the impinger.

5.1.3 Glass or Teflon connecting tubing for the impingers.

5.1.4 Ice bath container. To maintain absorbing solution at a low temperature.

5.1.5 Drying tube. Tube packed with 6- to 16-mesh indicating-type silica gel, or equivalent, to dry the gas sample and protect the meter and pump. If the silica gel has been used previously, dry at 175° C (350° F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used, subject to approval of the Administrator.

NOTE: Do not use more than 30 g of silica gel. Silica gel absorbs gases such as propane from the fuel gas stream, and use of excessive amounts of silica gel could result in errors in the determination of sample volume.

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[1] Mention of trade names of specific products does not constitute endorsement by the Environmental Protection Agency.

APPENDIX B

A STATISTICAL APPROACH TO INCLUDE OUT-OF-RANGE DATA IN AN AVERAGE

A STATISTICAL APPROACH TO INCLUDE OUT OF RANGE DATA IN AN AVERAGE

Results of sample analysis can often be below the minimum detection level or above the upper detection limit of an analytical procedure. These out of range data points caused difficulties in obtaining true average (geometric mean) of the data. Including out of range data in the average as either zero or the minimum detection level, and the maximum detection level, will result in averages that are above or below the true mean of the events being measured. Likewise, not including the out of range data in the average will also produce an incorrect average.

A statistical procedure to include out of range data in the calculation of an average is described. The procedure uses the concept of mean ranks to determine the median and standard deviation of the data as well as the type of distribution. The median value, with the appropriate transformations, can be used to calculate a mean. Since the median of a population is not affected by the extreme values of a population, it can be found without regard to the accuracy or absolute value of the extreme values of the population. The critical factor in using these methods is assurance that the data has been transformed into a symetrical distribution.

The median of a set of data is the value where 50 percent of the observations are either greater than or less than the value. For normally distributed data the mean is the same as the median. For other types of distributions, transformation of the data into a normal distribution is required so that the mean and the median are the same. For a log-normal distribution the mean is calculated from the median and the standard deviation of the transformed data by the equation:

$$\text{mean} = \theta + \exp\left(u + \tfrac{1}{2}s^2\right)$$

Where θ is the expected minimum value of the data and is often zero.

u is the median of the natural logarithms of the data.

s^2 is the variance calculated using the natural logarithms of the data.

The sample logarithmic mean, u, is the same as the logarithmic median of the data that has been transformed to a normal distribution. Normal and log-normal data distributions are the most commonly encountered in analytical work. Determination of means from other types of distributions will be discussed in a later section.

The median of a set of data can be found by ranking the data and locating the middle point. Data that is out of the range of the analytical procedure is included in the ranking process. The type of distribution of the data can be found by plotting the data on probability paper when sufficiently large sample sizes are available. For smaller sample sizes the distribution type may be assumed from knowledge of similar type samples when sufficient samples are available or from a knowledge of the processes that produced the variation. Probability paper is available for normal, log-normal, or Weibull distributions. When the data plotted on one of these probability papers results in a straight line, the type of distribution is that of probability paper used. Another property of data plotted on probability paper is that the median appears at the intersection of the line formed by the data with the 50 percent probability level and the median plus or minus the standard deviation is located at the intersections with the 84.13 and 15.87 probability levels respectively. These values can be used when calculating the mean of log-normal distributions.

Probability plots are produced by ranking the data from lowest value to highest value. The ranked data are matched with mean ranks. Mean ranks are calculated by the formula: (2)

$$\text{Mean rank} = \frac{j - 3/8}{n + 1/4}$$

Where j is the rank order number and n is the sample size.

A least squares regression analysis of the data plotted on probability paper can be obtained by looking up values for use on the x-axis in a z table using the mean ranks as . Values of z for mean ranks of less than 0.50 are given a negative sign. Values of z for mean ranks greater than 0.50 are found using $(1 - \alpha)$ and giving it a positive sign. For instance, for a mean rank of 0.797, $(\alpha - 1) = 0.206$, and z is 0.82. The y values are the transformed values, if necessary. The intercept of the least squares line is the median and the slope is the standard deviation. This least squares method is mathematically the same as the procedures suggested by Blom (3) and Rowe (4) for normal distributions.

Many data from samples of emissions do not fit a normal or log-normal distribution. The Weibull distribution can be used to fit most data sets. It will not fit bi-model distributions. The normal, log-normal, and exponential distributions are special cases of the Weibull distribution.

The Weibull distribution is described by:

$$y = 1 - \exp - \frac{x - x}{\theta - x_o}^{\,b}$$

where x_o is an off-set, b is the Weibull slope, and θ is a characteristic value. The Weibull cumulative distribution can be linearized with the transformations

$$Y = \ln \ln [1/(1 - y)]$$

$$X = \ln (x - x_o)$$

where the y values are the mean ranks, x is the data point, x_o is an off-set. The linearized variables to the equation; $Y = a_o + aX$ are:

$$a_o = b \ln (\theta - x_o)$$

$$a_1 = b, \text{ the Weibull slope}$$

The value of x_o is found by trial and error to result in a maximum regression coefficient. A clue as to the magnitude of x_o can be found from a plot on Weibull probability paper. The plot will appear curved at the low values. An x_o should be chosen to straighten the line. An x_o is often zero, but may have a value if the measurement device has a constant interference or if there is a constant background in the samples. An estimate of the mean of the Weibull population can be found with the equation:

$$\text{Mean} = (\theta\ [(1/b)!]$$

Special cases of the Weibull distribution occur at slopes where 3.5 approximates a normal distribution with all values greater than x_o, 1.5 is the log-normal distribution, and 1.0 is the exponential distribution.

LITERATURE REFERENCES

(1) Pollard, J.H. A Handbook of Numerical and Statistical Techniques with Examples Mainly from the Life Sciences, Cambridge University Press, Cambridge, Great Britian (1977).

(2) Lipson, C., and Sheth, N.J., Statistical Design and Analysis of Engineering Experiments, McGraw-Hill Book Company, New York, New York (1973).

(3) Blom, G., Statistical Estimates and Transformed Beta - Variables, John Wiley & Sons, Inc., New York, New York (1958).

(4) Rowe, K. E., "Estimation of the Sample Mean and Standard Deviation for Limits," Paper being prepared under EPA contract.

Example 1: Carbon monoxide emissions from a kraft recovery furnace were reported as 8-hour averages of continuously measured concentration values. During portions of the continuous record the CO concentrations were above the measurement capabilities of the monitor. The 8-hour average data listed in Table B-1 that contained above range instantaneous CO readings are listed with a greater than sign (>). Above range data was included in the 8-hour averages as the upper range limit of the measurement instrument. The CO data have been ranked and matched with their mean ranks in Table B-1 and plotted in Figure B-1 on logarithm probability paper and in Figure B-2 on Weibull probability paper.

TABLE B-1 EIGHT HOUR AVERAGE CO EMISSIONS FROM KRAFT RECOVERY FURNACE

Rank	CO ppm	Mean Rank	z
1	16	0.0385	-1.77
2	40	0.1000	-1.28
3	43	0.1615	-0.99
4	65	0.2231	-0.76
5	87	0.2846	-0.57
6	99	0.3462	-0.40
7	126	0.4077	-0.23
8	142	0.4692	-0.08
9	162	0.5308	0.08
10	166	0.5923	0.23
11	196	0.6538	0.40
12	>233	0.7154	0.57
13	>277	0.7769	0.76
14	299	0.8385	0.99
15	>345	0.9000	1.28
16	>384	0.9615	1.77

The data plotted in Figure B-1 shows a nearly straight line, indicating that the data is log-normally distributed. A regression analysis gives an r of 0.986. Approximately 2.7 percent of the variation is not accounted for by the least squares line. The plot on Weibull probability paper (x_o = o) gives a straight line with an r of 0.994. Approximately 1.1 percent of the variation is not accounted for by the regression analysis. This slope indicated the distribution is between a log-normal and an exponential distribution.

The mean of the data found from the log-normal distribution using the formula; mean = $\exp(u + \frac{1}{2}s^2)$. The logarithmetic mean, u, is the intercept of the squares equation, which is found at the 50 percent mean rank (x_{50} = 146). The sample standard deviation is the least squares slope. The difference between the intercept and the slope is the value found at the 15.9 percent rank. The geometric mean calculated to be 277 ppm.

The Weibull distribution mean is found by the equation:

$$\text{mean} = (\Theta)\ [(1/b)!]$$

This is an estimate of the population mean as opposed to an estimate of the sample mean.

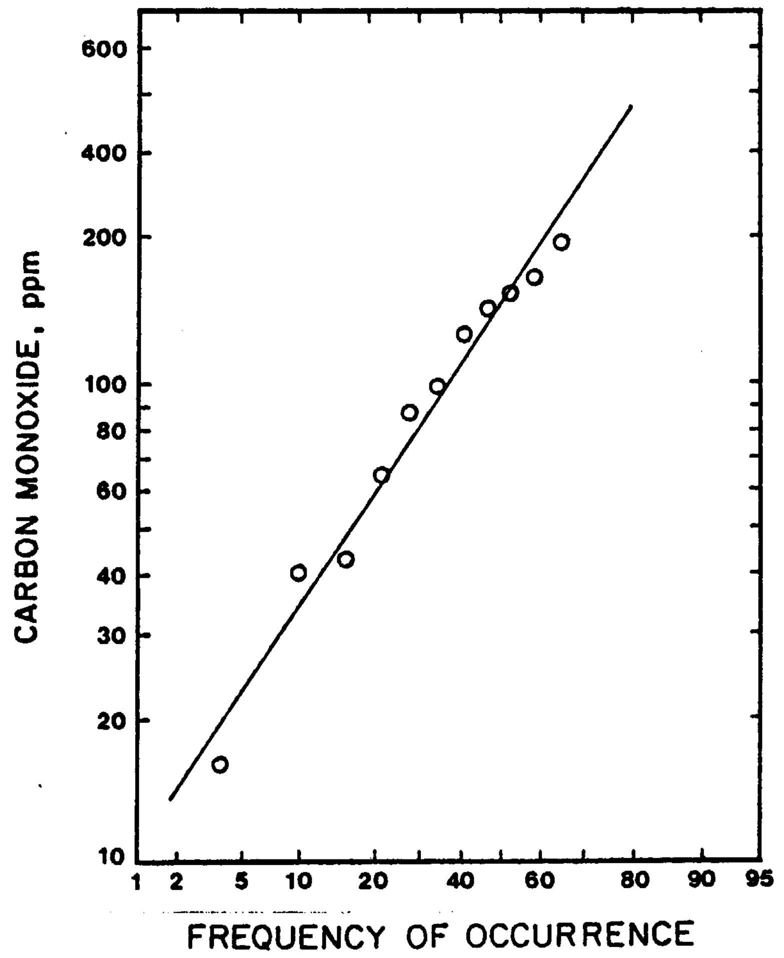

FIGURE B-1

EIGHT HOUR AVERAGE CARBON MONOXIDE
DATA PLOTTED ON LOG NORMAL PROBABILITY PAPER

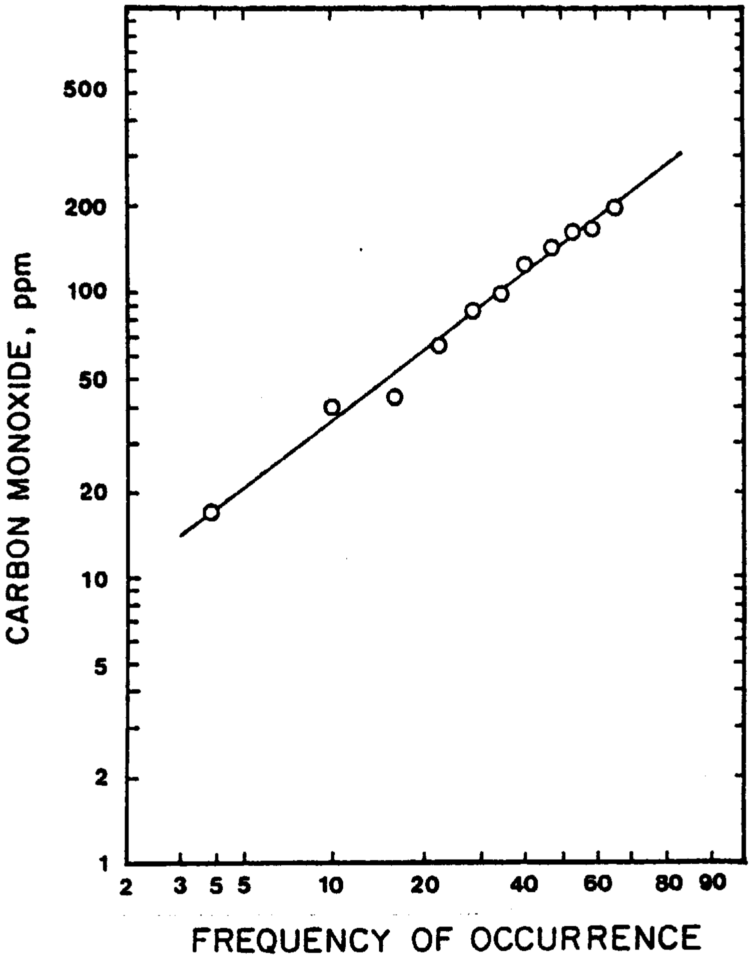

FIGURE B-2

EIGHT HOUR AVERAGE CARBON MONOXIDE
DATA PLOTTED ON WEIBULL PROBABILITY PAPER

The low slope of the Weibull distribution indicates a tendency for the CO emissions to be low with occasional high level excursions.

Ref 2

{Carbon Monoxide Emissions From Selected Combustion Sources Based on Short-Term Monitoring Records

SOURCE CATEGORY: Wood Waste

EXCLUSION CRITERIA CHECKLIST

REFERENCE NCASI Technical Bulletin No. 416, Jan 1984.

CRITERIA	YES	NO
1. Test series averages are reported in units that can be converted to the selected reporting units?	✓	
2. Test series represent compatible test methods?	✓	
3. In tests in which emission control devices were used, the control devices are fully specified?	✓	
4. Is it clear whether or not the emissions were controlled (or not controlled)?	✓	

Form filled out by C. Hal /

Date 6/11/92 / 5-5-92

INDICATE WHETHER ANSWER IS YES OR NO WITH AN "X" IN APPROPRIATE BOX.

IF ALL ANSWERS ARE "YES" PROCEED TO METHODOLOGY/DETAIL CRITERIA CHECKLIST.

SOURCE CATEGORY Wood Waste

METHODOLOGY/DETAIL CRITERIA CHECKLIST

REFERENCE NCASI Technical Bulletin No. 416

CRITERIA	YES	NO	COMMENTS
1. Is the manner in which the source was operated well documented in the report?		✓	Boiler load data not provided
Was the source operating within typical parameters during the test?	✓		Boiler operation described as "normal"
2. Did sampling procedures deviate from standard methods?		✓	
If so, were the deviations well documented?			
Were the deviations appropriate?			
Comment on how any alterations in sampling procedure may have influenced the results.			
3. Were there wide variations in the results?		✓	
If yes, can the variations be adequately explained by information in the report?			NA
If the variations are not well explained, should the data be considered of poor quality?			NA
4. Do the test reports contain the raw data sheets?		✓	
Are the nomenclature and equations used equivalent to those specified by the EPA?	✓		
Comment on the consistency and completeness of the results.			Consistent but not complete, as discussed above.

Form filled out by

Date 5/11/92

INDICATE YES OR NO WITH AN "X" IN THE APPROPRIATE BOX. FILL IN COMMENTS.

IF, BASED ON ABOVE ANSWERS, THE SOURCE REPORT PROVIDES ADEQUATE DETAIL AND DEMONSTRATES SOUND METHODOLOGY, PROCEED TO RATING THE DATA IN THE RATING CRITERIA CHECKLIST.

SOURCE CATEGORY Wood Waste

RATING CRITERIA CHECKLIST

Reference NCAST Technical Bulletin No. 416

	RATING CRITERIA	YES	NO
A	Tests performed by a sound methodology and reported in enough detail for adequate validation?		✓
B	Tests were performed by a generally sound methodology, but not enough detail for adequate validation?	✓	
C	Were tests based on untested or new methodology that lacks significant amount of background data?		
D	Were tests based on generally unacceptable methods, but may provide order-of-magnitude values for the source?		

COMMENTS

From process standpoint, recommend E rating due to lack of adequate detail for validation of representative operating conditions.

Methodology for CO sampling/analysis is best available technology but additional information is limited. Not enough detail for adequate validation. Recommend B rating

Form filled out by

Date 5/11/92 / 5-15-92

BASED ON ANSWERS AND COMMENTS ABOVE, ASSIGN A RANK TO THIS LITERATURE SOURCE:

B	CO

RANK ASSIGNED TO EMISSION SOURCE DATA

11 May 92

NCASI Technical Bulletin No. 416

Carbon Monoxide From Selected Combustion Sources Based on Short-Term Monitoring Records, Jan. 1984.

- Boiler A -
  - Boiler co-fires oil w/ bark. Exclude from AP-42 consideration
- Boiler B
  - Spreader stoker burning wood residue fuel
  - Rated at 400,000 lb/hr steam at 850 psig
  - Installed in 1976. (Foster Wheeler)
  - Both overfire and underfire air.
  - Electroflex dry scrubber installed for PM control.
- Boiler C
  - Spreader stoker boiler rated at 300,000 lb/hr steam at 900 psig and 800 °F.
  - Burns wood residue
  - Both overfire and underfire air
  - PM controlled with variable-throat venturi scrubber.

- Average CO emission rates, representing more than 150 hourly averages of CEM data from each unit:

	CO, (lb/10^6 Btu)	CO, (lb/ton)[a]
Boiler B	0.50	4.5
Boiler C	0.43	3.9

[a] Based on 4,500 Btu/lb wood, as fired

- S&A: CO measured by CEMs.