AC 62-107858

STATE OF FLORIDA
DEPARTMENT OF ENVIRONMENTAL REGULATION

BOB GRAHAM
GOVERNOR
VICTORIA J. TSCHINKEL
SECRETARY
ALEX SENKEVICH
DISTRICT MANAGER

DER
AUG 06 1985
BAQM

APPLICATION TO OPERATE/CONSTRUCT AIR POLLUTION SOURCES

SOURCE TYPE: Lime Kiln [X] New[1] [ ] Existing[1]

APPLICATION TYPE: [X] Construction [ ] Operation [ ] Modification

COMPANY NAME: The Buckeye Cellulose Corporation COUNTY: Taylor

Identify the specific emission point source(s) addressed in this application (i.e. Lime Kiln No. 4 with Venturi Scrubber; Peaking Unit No. 2, Gas Fired) No. 4 Lime Kiln with ESP*

SOURCE LOCATION: Street 5 to 6 miles S.E. of Perry City Perry

UTM: East 256.740 North 3328.700

Latitude 30 ° 03 ' 59 "N Longitude 83 ° 33 ' 12 "W

APPLICANT NAME AND TITLE: Mr. C.E. Wertheimer, Jr., Plant Manager

APPLICANT ADDRESS: Route 3, Box 260, Perry, FL 32347

SECTION I: STATEMENTS BY APPLICANT AND ENGINEER

A. APPLICANT

I am the undersigned owner or authorized representative* of The Buckeye Cellulose Corporation

I certify that the statements made in this application for a Construction permit are true, correct and complete to the best of my knowledge and belief. Further, I agree to maintain and operate the pollution control source and pollution control facilities in such a manner as to comply with the provision of Chapter 403, Florida Statutes, and all the rules and regulations of the department and revisions thereof. I also understand that a permit, if granted by the department, will be non-transferable and I will promptly notify the department upon sale or legal transfer of the permitted establishment.

*Attach letter of authorization

Signed:

C.E. Wertheimer, Jr., Plant Manager
Name and Title (Please Type)

Date: 8-2-85 Telephone No. 904/584-0121

B. PROFESSIONAL ENGINEER REGISTERED IN FLORIDA (where required by Chapter 471, F.S.)

This is to certify that the engineering features of this pollution control project have been designed/examined by me and found to be in conformity with modern engineering principles applicable to the treatment and disposal of pollutants characterized in the permit application. There is reasonable assurance, in my professional judgment, that

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[1] See Florida Administrative Code Rule 17-2.100(57) and (104)

*Minor sources are covered in a companion permit.

the pollution control facilities, when properly maintained and operated, will discharge an effluent that complies with all applicable statutes of the State of Florida and the rules and regulations of the department. It is also agreed that the undersigned will furnish, if authorized by the owner, the applicant a set of instructions for the proper maintenance and operation of the pollution control facilities and, if applicable, pollution sources.

Signed David A. Buff

David A. Buff
Name (Please Type)

Environmental Science and Engineering, Inc.
Company Name (Please Type)

P.O. Box ESE, Gainesville, FL 32602
Mailing Address (Please Type)

Florida Registration No. 19011 Date: 7-31-85 Telephone No. 904/332-3318

SECTION II: GENERAL PROJECT INFORMATION

A. Describe the nature and extent of the project. Refer to pollution control equipment, and expected improvements in source performance as a result of installation. State whether the project will result in full compliance. Attach additional sheet if necessary.

The essence of this project is the replacement of four existing lime combustion units with one large kiln for greater fuel efficiency--appreciably less BTU/ton of lime product. This project results in a dramatic reduction in most criteria pollutants. See Attachment A for details.

B. Schedule of project covered in this application (Construction Permit Application Only)

Start of Construction October 1985 Completion of Construction October 1987

C. Costs of pollution control system(s): (Note: Show breakdown of estimated costs only for individual components/units of the project serving pollution control purposes. Information on actual costs shall be furnished with the application for operation permit.)

Electrostatic Precipitator:	$1,640,000	*Causticizing Lime Bin Baghouse:	$50,000
Continuous Emission Monitors:	$150,000	*Slakers Scrubber:	$75,000
Precoat Filter Size Increase:	$110,000	Total:	$2,040,000
I.D. Fan Increase:	$15,000		

*From companion permit.

D. Indicate any previous DER permits, orders and notices associated with the emission point, including permit issuance and expiration dates.

Not Applicable

E. Requested permitted equipment operating time: hrs/day 24 ; days/wk 7 ; wks/yr 52 ;

if power plant, hrs/yr_____; if seasonal, describe:____________________

F. If this is a new source or major modification, answer the following questions. (Yes or No)

1. Is this source in a non-attainment area for a particular pollutant? No
   a. If yes, has "offset" been applied? --
   b. If yes, has "Lowest Achievable Emission Rate" been applied? --
   c. If yes, list non-attainment pollutants. --
2. Does best available control technology (BACT) apply to this source? If yes, see Section VI. No
3. Does the State "Prevention of Significant Deterioriation" (PSD) requirement apply to this source? If yes, see Sections VI and VII. No
4. Do "Standards of Performance for New Stationary Sources" (NSPS) apply to this source? Yes
5. Do "National Emission Standards for Hazardous Air Pollutants" (NESHAP) apply to this source? No

H. Do "Reasonably Available Control Technology" (RACT) requirements apply to this source? No

   a. If yes, for what pollutants? --
   b. If yes, in addition to the information required in this form, any information requested in Rule 17-2.650 must be submitted.

Attach all supportive information related to any answer of "Yes". Attach any justification for any answer of "No" that might be considered questionable.

See Attachment A for Items F. 3. and F. 4.

SECTION III: AIR POLLUTION SOURCES & CONTROL DEVICES (Other than Incinerators)

A. Raw Materials and Chemicals Used in your Process, if applicable:

Description	Contaminants		Utilization Rate - lbs/hr	Relate to Flow Diagram
	Type	% Wt		
Lime Mud (dry)	Particulate	100%	96,726	Stream 11a
			(Bone dry feed)	

B. Process Rate, if applicable: (See Section V, Item 1)

1. Total Process Input Rate (lbs/hr): 103,872 Bone Dry Feed (Stream 12)
2. Product Weight (lbs/hr): 54,167 lime product, dry basis (Stream 14a and 14b)

C. Airborne Contaminants Emitted: (Information in this table must be submitted for each emission point, use additional sheets as necessary)

Name of Contaminant	Emission[1]		Allowed[2] Emission Rate per Rule 17-2	Allowable[3] Emission lbs/hr	Potential[4] Emission		Relate to Flow Diagram
	Maximum lbs/hr	Actual T/yr			lbs/hr	T/yr	
Particulates	56.20	246.16	*See below.	Gas/Oil 44.7/56.2+	7,146	31,299	13b
Sulfur Dioxide	20.1	85.4	N/A	N/A	20.1	85.4	13b
Nitrogen Oxides	198.0	416.3	N/A	N/A	198.0	416.3	13b
Carbon Monoxide	81.3	355.9	N/A	N/A	81.3	355.9	13b
Vol.Org.Compds	9.5	41.5	N/A	N/A	9.5	41.5	13b

[1] See Section V, Item 2.

[2] Reference applicable emission standards and units (e.g. Rule 17-2.600(5)(b)2. Table II, E. (1) - 0.1 pounds per million BTU heat input)

[3] Calculated from operating rate and applicable standard.

[4] Emission, if source operated without control (See Section V, Item 3).

*NSPS, 40 CFR 60, Subpart BB: Gas firing--0.067 gr/dscf, corrected to 10 percent oxygen.
+This allowable level for oil firing is more restrictive than NSPS.

SECTION III: AIR POLLUTION SOURCES & CONTROL DEVICES (Other than Incinerators)

A. Raw Materials and Chemicals Used in your Process, if applicable:

Description	Contaminants		Utilization Rate - lbs/hr	Relate to Flow Diagram
	Type	% Wt		

B. Process Rate, if applicable: (See Section V, Item 1)

1. Total Process Input Rate (lbs/hr): ____________________

2. Product Weight (lbs/hr): ____________________

C. Airborne Contaminants Emitted: (Information in this table must be submitted for each emission point, use additional sheets as necessary)

Name of Contaminant	Emission[1]		Allowed[2] Emission Rate per Rule 17-2	Allowable[3] Emission lbs/hr	Potential[4] Emission		Relate to Flow Diagram
	Maximum lbs/hr	Actual T/yr			lbs/hr	T/yr	
Tot. Red.Sulfur	3.28	14.37	**See Below	3.28	53.5	227.7	13b

[1] See Section V, Item 2.

[2] Reference applicable emission standards and units (e.g. Rule 17-2.600(5)(b)2. Table II, E. (1) - 0.1 pounds per million BTU heat input)

[3] Calculated from operating rate and applicable standard.

[4] Emission, if source operated without control (See Section V, Item 3).

**NSPS, 40 CFR 60, Subpart BB: 8 ppm by volume, dry basis, corrected to 10 percent oxygen.

D. Control Devices: (See Section V, Item 4)

Name and Type (Model & Serial No.)	Contaminant	Efficiency	Range of Particles Size Collected (in microns) (If applicable)	Basis for Efficiency (Section V Item 5)
Electrostatic Precipitator	Particulate	99.2%	Submicron	See Att. F,
(vendor not yet selected)				pg. F-1, F-2
Process Controls	TRS	93.9%	Not Applicable	See Att. F,
				pg. F-3, F-4

E. Fuels

Type (Be Specific)	Consumption*		Maximum Heat Input (MMBTU/hr)
	avg/hr	max./hr	
Natural Gas	0.170 MMCF	0.170 MMCF	176
No. 6 Fuel Oil	1214 gals.	1214 gals.	176

*Units: Natural Gas--MMCF/hr; Fuel Oils--gallons/hr; Coal, wood, refuse, other--lbs/hr.

Fuel Analysis: No.6 Fuel Oil Natural Gas: 1,040 BTU/scf

Percent Sulfur: 2.5% maximum Percent Ash: 0.1 typical

Density: 8.1 lbs/gal Typical Percent Nitrogen: 0.4 based on 1 test

Heat Capacity: 17,901 BTU/lb 145,000 BTU/gal

Other Fuel Contaminants (which may cause air pollution): None

F. If applicable, indicate the percent of fuel used for space heating.

Annual Average None Maximum

G. Indicate liquid or solid wastes generated and method of disposal.

Particulates collected in precipitator will be recycled dry back into the lime kiln (flow stream 11b). Grits from the two slakers (Streams 5a and 5b) and dregs and CaCO$_3$ from dregs filters (Stream 24) go to onsite solid waste disposal. All liquid wastes go to NPDES treatment system.

H. Emission Stack Geometry and Flow Characteristics (Provide data for each stack):*

Stack Height: 100 to 125 ft. Stack Diameter: 6.5 to 8.5 ft.

Gas Flow Rate: Gas/Oil 108,000/100,000 ACFM Gas/Oil 45,020/41,685 DSCFM Gas Exit Temperature: 290-430 °F.

Water Vapor Content: 30-40 % Velocity: 29 to 54 FPS

*Final stack design will be provided after vendor selection and prior to construction of the stack.

SECTION IV: INCINERATOR INFORMATION

Not Applicable

Type of Waste	Type 0 (Plastics)	Type I (Rubbish)	Type II (Refuse)	Type III (Garbage)	Type IV (Pathological)	Type V (Liq.& Gas By-prod.)	Type VI (Solid By-prod.)
Actual lb/hr Incinerated							
Uncontrolled (lbs/hr)							

Description of Waste ______

Total Weight Incinerated (lbs/hr) ______ Design Capacity (lbs/hr) ______

Approximate Number of Hours of Operation per day ______ day/wk ______ wks/yr. ______

Manufacturer ______

Date Constructed ______ Model No. ______

	Volume $(ft)^3$	Heat Release (BTU/hr)	Fuel		Temperature (°F)
			Type	BTU/hr	
Primary Chamber					
Secondary Chamber					

Stack Height: ______ ft. Stack Diamter: ______ Stack Temp. ______

Gas Flow Rate: ______ ACFM ______ DSCFM* Velocity: ______ FPS

*If 50 or more tons per day design capacity, submit the emissions rate in grains per standard cubic foot dry gas corrected to 50% excess air.

Type of pollution control device: [ ] Cyclone [ ] Wet Scrubber [ ] Afterburner

[ ] Other (specify) ______

Brief description of operating characteristics of control devices: ______

______

______

______

______

Ultimate disposal of any effluent other than that emitted from the stack (scrubber water, ash, etc.):

______

______

______

______

NOTE: Items 2, 3, 4, 6, 7, 8, and 10 in Section V must be included where applicable.

SECTION V: SUPPLEMENTAL REQUIREMENTS

Please provide the following supplements where required for this application.

1. Total process input rate and product weight -- show derivation [Rule 17-2.100(127)]
   See Attachment E.
2. To a construction application, attach basis of emission estimate (e.g., design calculations, design drawings, pertinent manufacturer's test data, etc.) and attach proposed methods (e.g., FR Part 60 Methods 1, 2, 3, 4, 5) to show proof of compliance with applicable standards. To an operation application, attach test results or methods used to show proof of compliance. Information provided when applying for an operation permit from a construction permit shall be indicative of the time at which the test was made.
   See Attachment B for emission estimates and Attachment A for compliance methods.
3. Attach basis of potential discharge (e.g., emission factor, that is, AP42 test).
   See Attachment B.
4. With construction permit application, include design details for all air pollution control systems (e.g., for baghouse include cloth to air ratio; for scrubber include cross-section sketch, design pressure drop, etc.)
   See Attachment F.
5. With construction permit application, attach derivation of control device(s) efficiency. Include test or design data. Items 2, 3 and 5 should be consistent: actual emissions = potential (1-efficiency).
   See Attachment F.
6. An 8 1/2" x 11" flow diagram which will, without revealing trade secrets, identify the individual operations and/or processes. Indicate where raw materials enter, where solid and liquid waste exit, where gaseous emissions and/or airborne particles are evolved and where finished products are obtained.
   See Attachment A.
7. An 8 1/2" x 11" plot plan showing the location of the establishment, and points of airborne emissions, in relation to the surrounding area, residences and other permanent structures and roadways (Example: Copy of relevant portion of USGS topographic map).
   See Attachment A.
8. An 8 1/2" x 11" plot plan of facility showing the location of manufacturing processes and outlets for airborne emissions. Relate all flows to the flow diagram.
   See Attachment A.

9. The appropriate application fee in accordance with Rule 17-4.05. The check should be made payable to the Department of Environmental Regulation. (Check attached)

10. With an application for operation permit, attach a Certificate of Completion of Construction indicating that the source was constructed as shown in the construction permit. Not Applicable

SECTION VI: BEST AVAILABLE CONTROL TECHNOLOGY

Not Applicable

A. Are standards of performance for new stationary sources pursuant to 40 C.F.R. Part 60 applicable to the source?

[ ] Yes [ ] No

Contaminant	Rate or Concentration

B. Has EPA declared the best available control technology for this class of sources (If yes, attach copy)

[ ] Yes [ ] No

Contaminant	Rate or Concentration

C. What emission levels do you propose as best available control technology?

Contaminant	Rate or Concentration

D. Describe the existing control and treatment technology (if any).

1. Control Device/System:
2. Operating Principles:
3. Efficiency:*
4. Capital Costs:

*Explain method of determining

5. Useful Life:

6. Operating Costs:

7. Energy:

8. Maintenance Cost:

9. Emissions:

Contaminant	Rate or Concentration

10. Stack Parameters

a. Height: ft.

b. Diameter: ft.

c. Flow Rate: ACFM

d. Temperature: °F.

e. Velocity: FPS

E. Describe the control and treatment technology available (As many types as applicable, use additional pages if necessary).

1.

a. Control Device:

b. Operating Principles:

c. Efficiency:[1]

d. Capital Cost:

e. Useful Life:

f. Operating Cost:

g. Energy:[2]

h. Maintenance Cost:

i. Availability of construction materials and process chemicals:

j. Applicability to manufacturing processes:

k. Ability to construct with control device, install in available space, and operate within proposed levels:

2.

a. Control Device:

b. Operating Principles:

c. Efficiency:[1]

d. Capital Cost:

e. Useful Life:

f. Operating Cost:

g. Energy:[2]

h. Maintenance Cost:

i. Availability of construction materials and process chemicals:

[1] Explain method of determining efficiency.
[2] Energy to be reported in units of electrical power - KWH design rate.

j. Applicability to manufacturing processes:

k. Ability to construct with control device, install in available space, and operate within proposed levels:

3.

a. Control Device: b. Operating Principles:

c. Efficiency:[1] d. Capital Cost:

e. Useful Life: f. Operating Cost:

g. Energy:[2] h. Maintenance Cost:

i. Availability of construction materials and process chemicals:

j. Applicability to manufacturing processes:

k. Ability to construct with control device, install in available space, and operate within proposed levels:

4.

a. Control Device: b. Operating Principles:

c. Efficiency:[1] d. Capital Costs:

e. Useful Life: f. Operating Cost:

g. Energy:[2] h. Maintenance Cost:

i. Availability of construction materials and process chemicals:

j. Applicability to manufacturing processes:

k. Ability to construct with control device, install in available space, and operate within proposed levels:

F. Describe the control technology selected:

1. Control Device: 2. Efficiency:[1]

3. Capital Cost: 4. Useful Life:

5. Operating Cost: 6. Energy:[2]

7. Maintenance Cost: 8. Manufacturer:

9. Other locations where employed on similar processes:

a. (1) Company:

(2) Mailing Address:

(3) City: (4) State:

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[1] Explain method of determining efficiency.
[2] Energy to be reported in units of electrical power - KWH design rate.

(5) Environmental Manager:

(6) Telephone No.:

(7) Emissions:[1]

Contaminant	Rate or Concentration

(8) Process Rate:[1]

b. (1) Company:

(2) Mailing Address:

(3) City: (4) State:

(5) Environmental Manager:

(6) Telephone No.:

(7) Emissions:[1]

Contaminant	Rate or Concentration

(8) Process Rate:[1]

10. Reason for selection and description of systems:

SECTION VII - PREVENTION OF SIGNIFICANT DETERIORATION Not Applicable

A. Company Monitored Data

1. ____________ no. sites ____________ TSP ____________ ( ) SO^{2}* ____________ Wind spd/dir

Period of Monitoring ____/____/____ to ____/____/____
month day year month day year

Other data recorded ______________________________

Attach all data or statistical summaries to this application.

---

[1] Applicant must provide this information when available. Should this information not be available, applicant must state the reason(s) why.

*Specify bubbler (B) or continuous (C).

2. Instrumentation, Field and Laboratory

a. Was instrumentation EPA referenced or its equivalent? ☐ Yes ☐ No

b. Was instrumentation calibrated in accordance with Department procedures?

☐ Yes ☐ No ☐ Unknown

B. Meteorological Data Used for Air Quality Modeling

1. _____ Year(s) of data from ____/____/____ to ____/____/____
month day year month day year

2. Surface data obtained from (location)________________________________

3. Upper air (mixing height) data obtained from (location)________________________

4. Stability wind rose (STAR) data obtained from (location)________________________

C. Computer Models Used

1. ________________________________ Modified? If yes, attach description.

2. ________________________________ Modified? If yes, attach description.

3. ________________________________ Modified? If yes, attach description.

4. ________________________________ Modified? If yes, attach description.

Attach copies of all final model runs showing input data, receptor locations, and principle output tables.

D. Applicants Maximum Allowable Emission Data

Pollutant	Emission Rate
TSP	________________________ grams/sec
SO^2	________________________ grams/sec

E. Emission Data Used in Modeling

Attach list of emission sources. Emission data required is source name, description of point source (on NEDS point number), UTM coordinates, stack data, allowable emissions, and normal operating time.

F. Attach all other information supportive to the PSD review.

G. Discuss the social and economic impact of the selected technology versus other applicable technologies (i.e., jobs, payroll, production, taxes, energy, etc.). Include assessment of the environmental impact of the sources.

H. Attach scientific, engineering, and technical material, reports, publications, journals, and other competent relevant information describing the theory and application of the requested best available control technology.

First in cellulose The Buckeye Cellulose Corporation

Mailing Address: Route 3 Box 260 Perry, Florida 32347 Phone: (904) 584-0121

July 12, 1982

Mr. Doug Dutton
Florida Department of Environmental Regulation
3426 Bills Road
Jacksonville, FL 32207

Dear Mr. Dutton:

The purpose of this letter is to provide the required delegation of authority for the Foley Plant Manager to communicate orally and in writing with the Florida Department of Environmental Regulation with respect to environmental matters involving the Foley Plant.

Effective July 1, 1982, Mr. C. E. Wertheimer, Jr. has succeeded Mr. G. B. Ellis as the Plant Manager at Foley. Attached are copies of the appropriate announcement and delegation of authority to Mr. Wertheimer.

I believe this meets the requirements for delegation of authority.

Very truly yours,

THE BUCKEYE CELLULOSE CORPORATION

John Millican

J. H. Millican
Environmental Control Manager

JHM/eph

Attachments

bcc: T. H. Donnelly
C. E. Wertheimer
S. J. Kruger - Memphis
D. E. Ross - Legal DX-6/Cinti.

BEST AVAILABLE COPY

The Buckeye Cellulose Corporation
Mailing Address P. O. Box 6407, Memphis, Tennessee 38108
Offices 949 Tillman Street, Phone (901) 324-8881
a subsidiary of The Procter & Gamble Company

DELEGATION OF AUTHORITY TO EXECUTE CONTRACTS

By Law 15 of the Board of Directors of The Buckeye Cellulose Corporation provides as follows:

The President or any Vice President may, by designation in writing, delegate to employees of this Company, The Procter & Gamble Company, or of any of either of their subsidiaries the right to execute:

A. Contracts for the purchase or sale of raw materials;
B. Contracts for the purchase or sale of finished products;
C. Contracts for the purchase of supplies, equipment and insurance;
D. Contracts for the purchase of services (including research performed by universities, foundations, commercial laboratories, and consultants);
E. Contracts for the rental of warehouse space or other storage facilities and services;
F. Agreements involving the receipt of confidential disclosures of technical information;
G. Such instruments as may be necessary in connection with the operation and fulfillment of the above-named contracts and agreements;
H. Tax returns and such instruments as may be necessary in connection with the settlement of any tax claims;
I. Notices, statements and certifications required by health and safety regulatory agencies of Federal and State Governments;
J. Documents pertaining to the furnishing of surety bonds.

Accordingly, I hereby delegate to the:

Foley Plant Manager
Manager, Flint River Operations
Flint River Production Plant Manager
Memphis Plant Manager
Huntsville Plant Manager
Southeastern Lands and Timber Manager

the authority to communicate orally and in writing with the appropriate Federal and State Environmental Regulation Departments with respect to environmental matters involving his/her area of operations.

These delegations are limited to matters for which these Managers have apparent authority resulting from their positions as the employees directly responsible for the overall operations of their respective facilities, such as permit and variance applications, permit and variance renewals, routine and special report forms and answering inquiries. These Managers are not authorized to bind the Corporation to financial or legal obligations such as Consent Agreements, Consent Stipulations (either covered by bond or otherwise), or other similar instruments. This supersedes any previous authority.

April 15, 1981
Date

R E Cannon
R. E. Cannon, President

ANNOUNCEMENT

This is to announce the following organization changes in the Cellulose & Specialties Division:

Mr. C. E. Wertheimer, Jr., currently Memphis Plant Manager, will be appointed Foley Plant Manager effective July 1, 1982, succeeding Mr. G. B. Ellis whose new assignment will be announced at a later date. In preparation for this assignment, Mr. Wertheimer will be transferred to Special Assignment effective April 1, 1982.

Mr. B. G. Mullins, currently Group Manager, Huntsville Plant, will be appointed Memphis Plant Manager, effective April 1, 1982, succeeding Mr. Wertheimer.

cw
2/9/82

ATTACHMENT A

PROJECT DESCRIPTION AND SOURCE APPLICABILITY DETERMINATION

1.0 PROJECT DESCRIPTION

The Buckeye Cellulose plant, located near Perry, Florida, produces kraft dissolving cellulose. The proposed project consists of the construction of a new causticizing system, a lime kiln of 650-TPD lime product capacity and associated lime storage facilities. The new equipment will replace existing equipment. The new system will be capable of supporting current and anticipated production rates.

Basically, this modernization project consists of replacing four existing obsolete lime burning units with one new large, state-of-the-art lime kiln. This new kiln will yield a significant fuel savings in terms of BTU per ton of lime product--roughly 70% of the old kilns fuel usage. This large fuel savings also will result in a benefit to the environment--much less pollutants are produced from the combustion of fuel. Furthermore, this new kiln, the largest in the kraft pulp industry in North America, is designed for maximum combustion efficiency and, hence, those pollutants which evolve from incomplete combustion (CO and VOC) are drastically reduced.

This new single kiln, compared to the four existing units, will discharge flue gases which contain 89% less TRS (odor), 86% less CO, 64% less VOC, 10% less particulates, and virtually the same amount of NO_x. The SO_2 is increased very slightly by the new project but the increase is below the de minimus level which triggers a PSD study.

It is noteworthy that the decreases are for a lime kiln production rate of 650 TPD compared to the present rate (1983/1984) of 511 TPD. TRS (odor), the only non-criteria or health-related pollutant, will be reduced by about 88%, and this reduction will be accomplished much sooner than the schedule outlined in the recently adopted TRS regulation.

The process flow diagram (Figure A-1) details the flow of materials and air emission points. A flow diagram (Figure A-2) is also provided for the existing systems.

The new causticizing system will consist of the following:

1. The existing Nos. 2, 3, and 4 smelt tanks will feed an existing tank, newly converted to be a surge tank. The surge tank will feed two existing tanks, newly converted to be green liquor clarifiers. One existing and a new dregs filter will support the green liquor clarifiers. Dregs filters are fugitive total reduced sulfur (TRS) emission sources.
2. Two new lime slakers, equipped with a condensing scrubber, will replace the existing pre-slakers and slakers. The new slakers and existing pre-slakers are sources of particulate (PM) emissions (Stream 2; refer to Figure A-1).
3. A new causticizing line will replace two existing causticizing lines.
4. The existing white liquor clarifiers, lime mud washers, mud precoat filter, and centrifuges and belt filters will be replaced by a white liquor pressure filter, a lime mud pressure filter, and two lime mud precoat filters. A third new pressure filter will be installed as a standby for the two new pressure filters. The new mud precoat filters will be fed from the lime mud surge tank after the lime mud pressure filter (Stream 25). Lime mud from water treatment will also feed the surge tank. The new white liquor and lime mud pressure filters are vented to the atmosphere and are TRS emission points (Streams 7 and 9). The new lime mud precoat filters are fugitive TRS emission sources.
5. The three existing lime kilns and the existing calciner, all with venturi scrubbers (total permitted lime product capacity of 784 TPD), will be replaced by a single 650-TPD lime product kiln with an electrostatic precipitator. This new lime kiln (No. 4

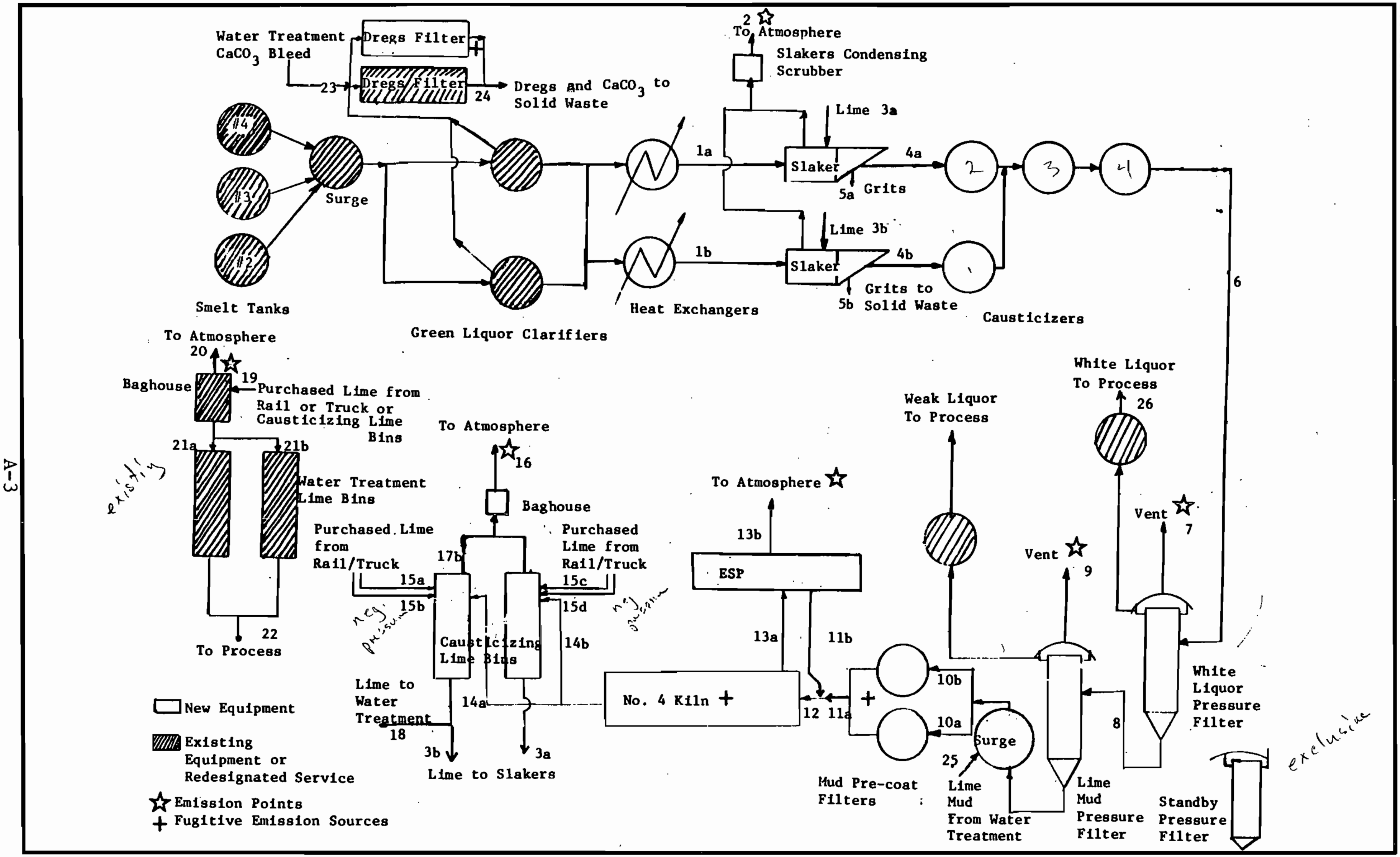

Figure A-1
CONCEPTUAL FLOW DIAGRAM — PROPOSED CAUSTICIZING SYSTEM

SOURCE: ESE, 1985.

Buckeye Cellulose Corporation

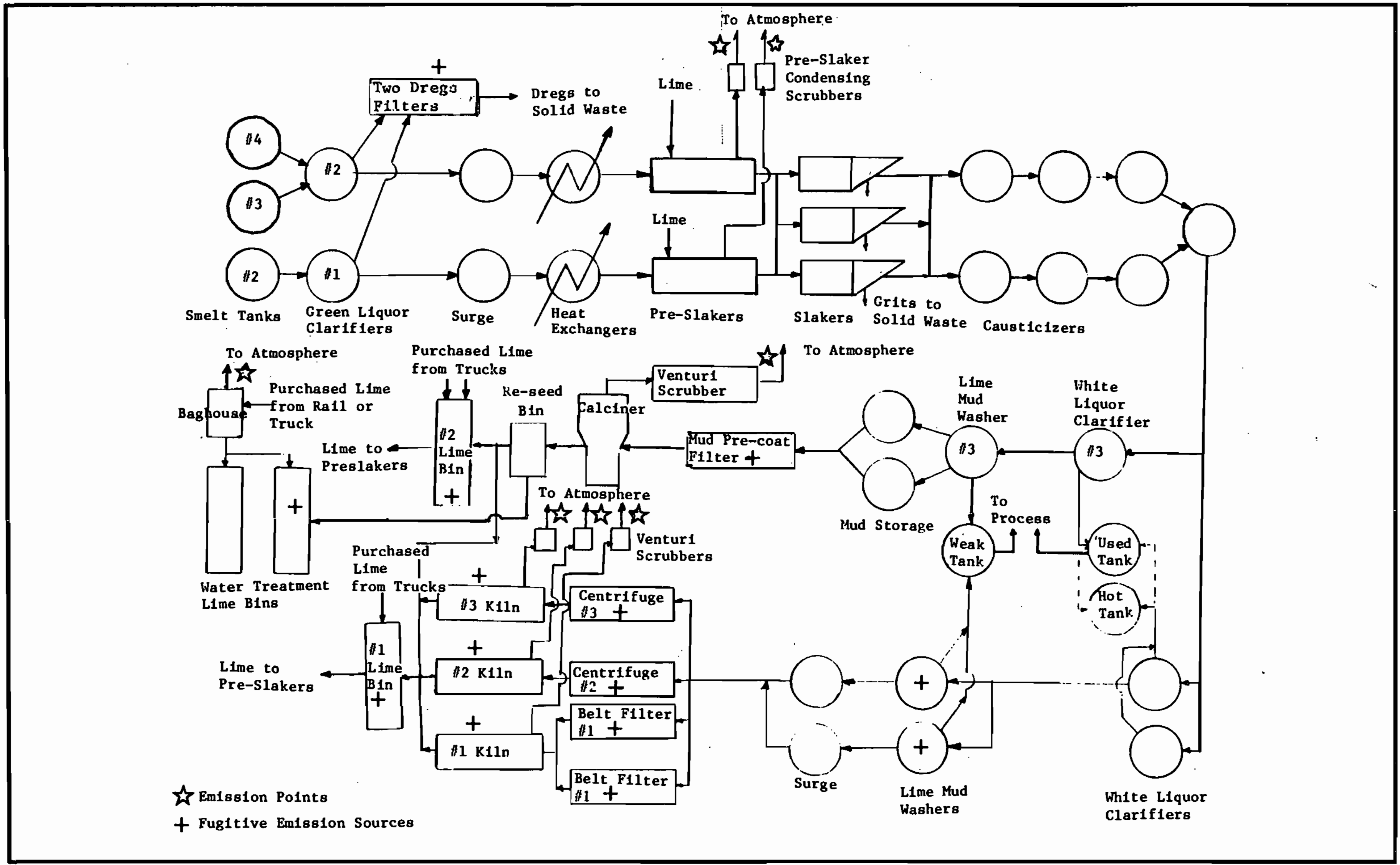

Figure A-2
CONCEPTUAL FLOW DIAGRAM — EXISTING CAUSTICIZING SYSTEM

SOURCE: ESE, 1985.

Buckeye Cellulose Corporation

Lime Kiln) will be a source of PM, TRS, sulfur dioxide (SO_2), nitrogen oxides (NO_x), carbon monoxide (CO), and volatile organic compounds (VOC) (Stream 13b).

6. The two existing causticizing lime bins, currently uncontrolled, will be replaced by two new causticizing lime bins, dust controlled by a single baghouse. The new causticizing lime bins will be sources of PM (Stream 16). The lime bins will receive lime from the kiln by bucket elevator (Streams 14a and b) and purchased lime by rail or truck through pneumatic conveyors (Streams 15a, b, c, and d). Lime will be transferred to the lime slakers (Streams 3a and b) by gravity feed or to the water treatment lime bins by pneumatic conveyoring (Stream 18).
7. The two existing water treatment lime bins will continue to be used for lime storage for water treatment. Currently, the existing baghouse controls dust emissions while lime is loaded into only one bin. The conveying system will be modified such that in the future the baghouse will control emissions (Stream 20) when loading lime into both bins (Stream 19). The water treatment lime bins will be capable of receiving purchased lime from rail or truck and lime from the causticizing lime bins, all through pneumatic conveyors (Stream 19).

A site location map of the Buckeye Cellulose plant is presented in Figure A-3. A plot plan of the facility is shown in Figure A-4. Figures A-4 and A-5 detail the locations of the proposed emission points.

Construction of the new system is scheduled to begin as early as October 1985 and should be completed within 2 years.

This air construction permit application addresses the new No. 4 Lime Kiln. In addition, a Prevention of Significant Deterioration (PSD) source applicability analysis is presented, which quantifies emissions of regulated pollutants from the new sources and from the existing sources which will be shut down or modified. A companion air construction permit application addresses minor source emissions and fugitive emissions from the proposed project.

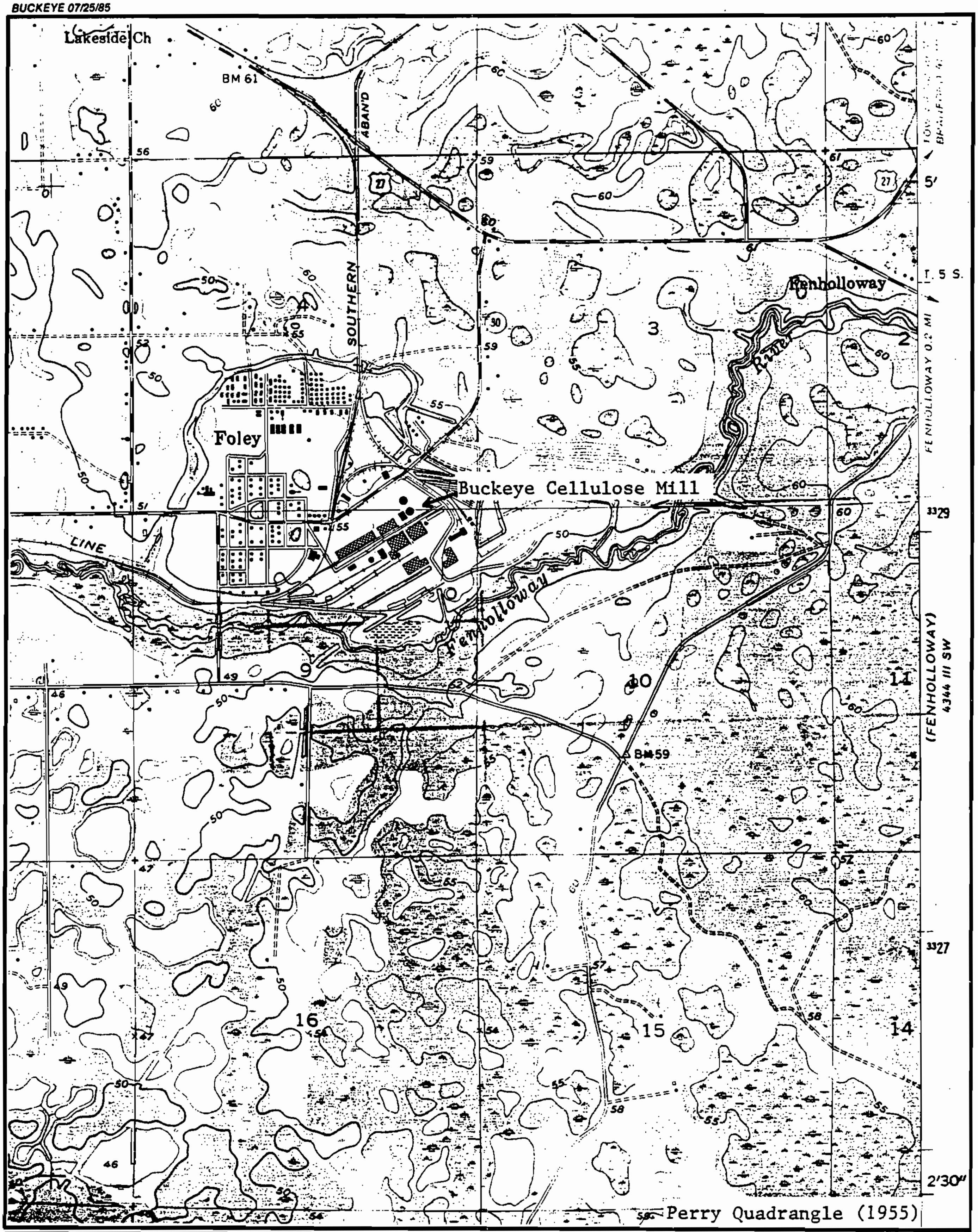

Figure A-3
LOCATION MAP

SOURCE: USGS, 1955.

Buckeye Cellulose Corporation

BUCKEYE 07/25/85 rev.

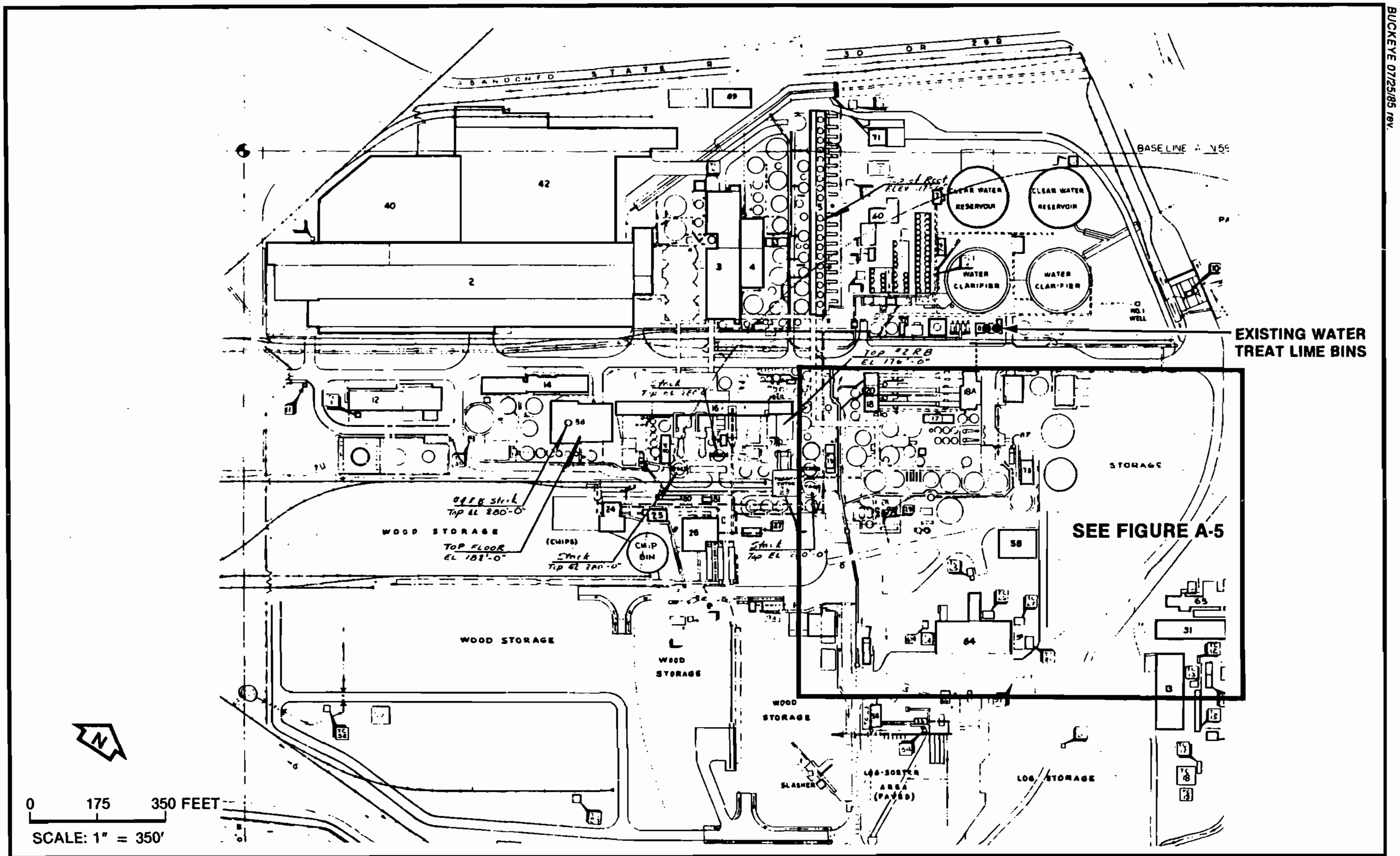

Figure A-4
PLOT PLAN — BUCKEYE CELLULOSE PLANT

SOURCE: BUCKEYE, 1985.

Buckeye Cellulose Corporation

BUCKEYE 07/25/85 rev.

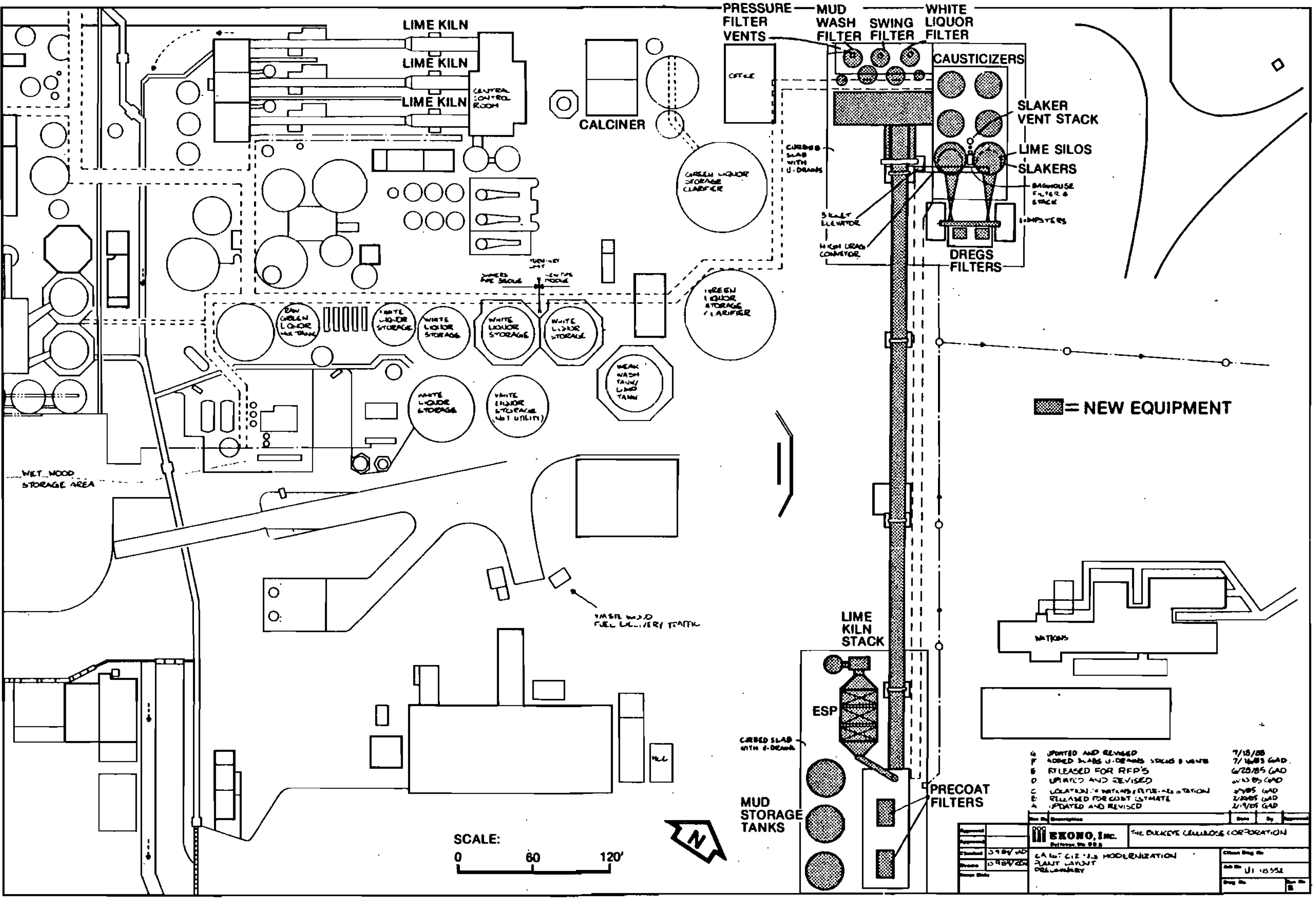

Figure A-5
PLOT PLAN OF CAUSTICIZING MODERNIZATION PROJECT

SOURCE: BUCKEYE, 1985.

Buckeye Cellulose Corporation

2.0 PSD SOURCE APPLICABILITY DETERMINATION

The Buckeye Cellulose plant is an existing major stationary source under PSD regulations since it currently emits regulated pollutants in quantities greater than 100 tons per year (TPY). Table A-1 details the history of air permits issued for the plant.

As described in Section 1.0, the proposed causticizing modernization will involve construction of new facilities, modification of certain existing equipment, and shutdown of other existing equipment. Estimated emissions from the proposed No. 4 Lime Kiln are presented in Attachment B. Attachment A of the companion air construction permit application provides estimated emissions for other equipment associated with the causticizing modernization project (i.e., causticizing lime bins, water treatment lime bins, slakers, etc.). The emission offsets provided by the existing sources to be either shut down or modified are detailed in Attachment C of this application. Emission estimates for those sources to be shutdown or modified are based upon actual operation during calendar years 1983 and 1984. Emission estimates for new sources are based upon maximum anticipated operating rates. See Table A-2, page A-13, for a complete emissions summary.

Under PSD regulations, all contemporaneous emission changes which have occurred at the source during the 5 years prior to permit application may be accounted for when determining source applicability. Based upon a complete application submittal date of August 1985, the contemporaneous period would begin in August 1980. There have been small contemporaneous increases and decreases at the mill during this period. These changes are described and detailed in Attachment D of this application.

Documents supporting all calculations, emission factors, and assumptions in arriving at the emissions estimates are presented in the Appendix to this application.

Table A-1. Summary of Air Permits Issued for Buckeye Cellulose Plant

Source	Permit No.	Issuance	Expiration	Comments
No. 1 Power Boiler	A062-2121	09/19/73	09/20/78	Operating permit
	A062-10945	10/10/78	09/20/83	Operating permit renewal
	A062-70263	08/18/83	08/18/88	Operating permit renewal
No. 2 Power Boiler	A062-2122	09/19/73	09/20/78	Operating permit
	A062-10946	10/10/78	09/20/83	Operating permit renewal
	A062-70265	08/18/83	08/18/88	Operating permit renewal
No. 2 Recovery Boiler with Smelt Tank	A062-2004	08/29/73	08/29/78	Operating permit
	AC62-2199	04/02/74	12/15/75	Smelt tank scrubber construction
	A062-2577	07/14/76	07/14/81	Operating permit
	A062-41724	06/11/81	06/11/86	Operating permit renewal
No. 3 Recovery Boiler with Smelt Tanks	A062-2092	05/18/73	07/01/75	Operating permit
	AC62-2221	05/15/74	07/01/75	Precipitator construction
	AC62-2222	05/15/74	07/01/75	Smelt tank scrubber construction
	A062-2578	07/14/76	02/28/81	Operating permit
	A062-37217	02/10/81	01/31/86	Operating permit renewal
No. 4 Recovery Boiler with Smelt Tanks	A062-2002	08/14/73	07/01/75	Construction permit
	A062-4776	01/16/78	07/08/82	Operating permit
	A062-54432	06/15/82	06/15/87	Operating permit renewal
	A062-54432	08/22/83	06/15/87	Increase BLS burning rate
No. 1 Bark Boiler	A062-2093	05/18/73	07/01/75	Operating permit
	A062-2245	07/29/74	07/01/75	Mechanical collector construction
	A062-2663	08/01/77	02/28/82	Operating permit
	AC62-30463	07/21/80	08/31/82	Increase steam rate and install wet scrubber
	A062-48928	01/05/82	01/04/87	Operating permit
	A062-48928	08/17/83	01/04/87	Revision to increase maximum wood waste firing rate
No. 2 Bark Boiler	A062-2434	08/06/75	07/31/80	Operating permit as No. 3 power boiler
	AC62-2571	05/25/76	08/31/78	Conversion to No. 2 bark boiler and wet scrubber installation
	A062-2707	08/26/77	08/26/82	Operating permit
	AC62-30466	07/21/80	08/31/82	Increase steam rate, install bark dryer and wet scrubber
	A062-48929	01/05/82	01/04/87	Operating permit
	A062-48929	09/12/83	01/04/87	Revision to increase maximum wood waste firing rate

Table A-1. Summary of Air Permits Issued for Buckeye Cellulose Plant (Continued, Page 2 of 2)

Source	Permit No.	Issuance	Expiration	Comments
No. 1 Lime Kiln	AC 341	01/20/71	12/20/71	Construction permit
	A062-878	10/27/72	10/06/74	Operating permit
	A062-2264	09/20/74	09/20/79	Operating permit
	A062-2651	12/28/76	11/30/81	Operating permit
	A062-46527	11/04/81	11/04/86	Operating permit
No. 2 Lime Kiln	AC 340	01/20/71	08/20/72	Construction permit
	A062-2265	09/20/74	09/20/79	Operating permit
	A062-2576	07/14/76	04/30/81	Operating permit
	A062-38423	02/18/81	02/18/86	Operating permit
No. 3 Lime Kiln	AC 339	01/20/71	06/20/72	Construction permit
	A062-880	10/27/72	10/06/74	Operating permit
	A062-2266	09/20/74	09/20/79	Operating permit
	A062-2652	12/28/76	11/30/81	Operating permit
	A062-46530	11/04/81	11/04/86	Operating permit
Calciner	AC62-14796	12/20/78	09/28/81	Construction permit
	PSD-FL-020	06/17/79	—	PSD permit granted
	PSD-FL-020	05/22/80	—	Revision to PSD permit to allow simultaneous operation of three existing kilns and the new calciner
	A062-39144	02/19/81	02/19/86	Operating permit

Source: ESE, 1985.

Table A-2. Summary of Net Emission Increases, Buckeye Cellulose Causticizing Modernization

Source	Net Emissions Change (TPY)					
	PM	SO_2	TRS	CO	NO_x	VOC
<u>Previous Contemporaneous Changes</u>						
No. 2 Bark Boiler—Wood Dryer Mod. (1/5/82)	0	0	0	0	0	0
Woodyard Improvements (82/83)	--- Unquantified PM Reduction Not Claimed ----					
No. 1 Bark Boiler—Woodwaste Rate Change (8/17/83)	0	0	0	35.0	0	14.2
No. 4 Recovery Boiler/SDT-BLS Change (8/22/83)	0	1.2	1.0	23.9	23.7	9.5
No. 2 Bark Boiler—Woodwaste Firing Rate (9/12/83)	0	3.5	0	26.3	0	11.5
Fines Burning Test (Shutdown 1/85)	----- Temporary Emissions Shutdown ------					
SUBTOTAL	0	4.7	1.0	85.2	23.7	35.2
<u>Proposed New or Modified Sources</u>						
New Lime Kiln NSPS 8760 hrs/yr 0.067 / 0.130 gr/dscf vs. 0.091	246.16	85.4	14.37	355.9	416.3	41.5
New Miscellaneous Sources:						
Slakers 2.08 lb/hr - based on vendor's spec. x 10 →	9.13	—	—	—	—	—
Causticizing Lime Bins 90% E on scrubber 0.543 lb/hr - 0.02 gr/dscf - vendor	1.50	—	—	—	—	—
Water Treat Lime Bins* 99.9% E - baghouse 0.103 lb/hr 0.02 gr/dscf - vendor	0.45	—	—	—	—	—
Lime Mud Pressure Filter 99.9% E - baghouse	—	—	0.07	—	—	—
White Liquor Pressure Filter	—	—	0.08	—	—	—
Miscellaneous Fugitive Sources:						
Kiln Leaks 1.205 lb/hr - attach. C-13 Emission Factor assumption of 50% than old	5.28	—	—	—	—	—
Lime Mud Precoat Filters	—	—	1.96	—	—	—
Dregs Filters	—	—	1.44	—	—	—
SUBTOTAL	262.52	85.4	17.92	355.9	416.3	41.5
<u>Proposed Contemporaneous Decreases (Shutdowns/Modifications)</u>						
Lime Kilns 1, 2, 3, and Calciner	-204.2	-52.0	-156.6†	-2,618.5	-417.8	-114.4
Slakers	-11.66	—	—	—	—	—
Causticizing Lime Bins	-6.91	—	—	—	—	—
Water Treat Lime Bins**	-0.16	—	—	—	—	—
Kiln Leaks	-16.60	—	—	—	—	—
Lime Mud Centrifuges, Belt and Precoat Filters	—	—	-1.75	—	—	—
Dregs Filter	—	—	-1.33	—	—	—
SUBTOTAL	-239.53	-52.0	-159.68†	-2,618.5	-417.8	-114.4
NET EMISSIONS CHANGE	22.99	38.1	-140.76†	-2,177.4	22.2	-37.7
PSD SIGNIFICANCE LEVEL	25	40	10	100	40	40

*Emissions after modification.

†Based upon estimated actual TRS emissions. If creditable TRS emissions are based on the new TRS existing source rule (20 ppm), then the calculated emission offset is 23.4 TPY, and the net emissions change is -4.48 TPY.

**Emissions before modification.

Table A-2 is a summary of the contemporaneous emission increases at the plant during the contemporaneous period and the emission estimates for the new, modified, and shutdown sources associated with the causticizing modernization project. As shown, the previous contemporaneous increases did not trigger PSD applicability since the totals of previous increases were below the PSD significance level. When these previous increases are considered along with the net emissions change from the proposed project, the new net emissions increase is below the PSD significance level for all pollutants. As a result, PSD does not apply to the proposed construction/modification project.

3.0 NSPS APPLICABILITY

The new lime kiln is subject to and will comply with NSPS under 40 CFR 60, Subpart BB. The kiln is subject to the following emissions limitations under NSPS:

Particulate matter	0.067 gr/dscf, corrected to 10 percent oxygen, when gaseous fossil fuel is burned and 0.13 gr/dscf, corrected to 10 percent oxygen, when liquid fossil fuel is burned.
Total reduced sulfur	8 ppm by volume on a dry basis, corrected to 10 percent oxygen.

Buckeye Cellulose will comply with the NSPS requirements to:

1. Install, calibrate, maintain, and operate a TRS continuous emissions monitor and an oxygen monitor for the lime kiln exhaust gases. The monitors will be located downstream of the control device for the lime kiln [40 CFR 60.284(a)(2)].
2. Perform daily TRS emission rate calculations and report any excess emissions based upon 40 CFR 60.284.
3. Utilize current particulate matter and TRS test methods as specified in FAC Chapter 17-2.
4. Install stack sampling access and ports for the No. 4 Lime Kiln in conformance with FAC Chapter 17-2.700(4). A drawing detailing the sampling access and sampling ports will be submitted to DER prior to construction of the stack.

The sources included in the companion permit will have controls as described in the application which will meet applicable standards and will be tested with appropriate methods if required by the Department. Total TRS and particulate emissions from these sources are insignificant (total less than 25 TPY). Based on this factor, it is expected that routine testing will not be required.

4.0 CONSTRUCTION/SHUTDOWN SCHEDULE

Construction is scheduled to begin immediately upon receipt of the construction permit. The construction schedule is based upon receipt of the permit on or before October 1, 1985. Construction will be expedited and startup will occur as soon as possible, but startup is not expected to be sooner than December 1986 and could be significantly later.

A phased startup of the causticizing modernization project lasting 4 to 6 months is anticipated. The existing equipment will be shutdown and new equipment brought on-line during this period. The new No. 4 Lime Kiln will be phased in over the startup period and will be the last major piece of new process equipment brought on-line. As the new kiln's production rate is increased, the old lime reburning equipment will be phased out, consistent with meeting plant production requirements. During the new kiln's startup period, the average lime production for the entire plant will not exceed 650 TPD.

ATTACHMENT B

EMISSION CALCULATIONS

PROPOSED NEW LIME KILN

A. PARTICULATE MATTER

1. MAXIMUM AND ALLOWABLE

NSPS for lime kilns, 40 CFR 60, Subpart BB

Gas Firing: 0.067 gr/dscf corrected to 10% O_2

Oil Firing: 0.130 gr/dscf corrected to 10% O_2

Maximum emissions for oil firing based on more restrictive level of 0.091 gr/dscf, corrected to 10% O_2 (70% of NSPS).

Flue gas flow rates:

Gas: 108,000 acfm @ 430°F, 30% - 40% H_2O, 2% - 4% O_2

Oil: 100,000 acfm @ 430°F, 30% - 40% H_2O, 2% - 4% O_2

Correct to dscfm: To estimate maximum dscfm, and therefore maximum emissions, the minimum % H_2O was used.

Gas: 108,000 (1-0.30)(530/430 + 460) = 45,020 dscfm

Oil: 100,000 (1-0.30)(530/430 + 460) = 41,685 dscfm

Correct gr/dscf for oxygen:

$C_{corr} = C_{act}\ (21 - X)/(21 - Y)$

X = Corrected O_2 = 10%

Y = Actual O_2 = 2% (minimum O_2 results in maximum concentration)

$C_{corr} = C_{act}\ (21-10)/(21-2) = 0.579\ C_{act}$

$C_{act} = C_{corr}/0.579$

Gas--0.067 gr/dscf/0.579 = 0.1157 gr/dscf @ 2% O_2

Oil--0.091 gr/dscf/0.579 = 0.1572 gr/dscf @ 2% O_2

Emissions:

Gas--45,020 dscfm x 0.1157 gr/dscf / 7,000 gr/lb x 60 min/hr = 44.7 lb/hr PM

Oil--41,685 x 0.1572 / 7,000 x 60 = 56.2 lb/hr PM

56.17

Annual emissions based upon worst case emissions (oil firing):
56.2 lb/hr x 8760 hr/yr / 2,000 lb/ton = 246.16 TPY PM

2. POTENTIAL EMISSIONS

From page E-1, maximum dust loss from kiln = 7,146 lb/hr
= 31,299 TPY PM

B. TOTAL REDUCED SULFUR

1. MAXIMUM AND ALLOWABLE

NSPS for lime kilns, 40 CFR 60, Subpart BB

8 ppm by volume, dry basis, corrected to 10% O_2

Correct for oxygen:

$C_{corr} = C_{act}\ (21 - X)/(21 - Y)$

X = Corrected O_2 = 10%

Y = Actual O_2 = 2% (minimum O_2 results in maximum concentration)

$C_{corr} = (21 - 10)/(21 - 2) = 0.579\ C_{act}$

$C_{act} = C_{corr}/0.579$

C_{act} = 8 ppm/0.579 = 13.82 ppm

Maximum flow rate is for gas firing: 108,000 acfm @ 30% - 40% H_2O

100,000

Minimum moisture results in a maximum dry flow and, therefore, maximum emissions:

Dry flow--108,000 x (1-0.30) = 75,600 cfm, dry basis

70,000

$PV = mRT \quad m = PV/RT$

$R = 1{,}545\ ft\text{-}lb_f/lb_{mole}\text{-}°R$

Molecular weight TRS (as H_2S) = 34 lb_m/lb_{mole}

$R = 45.44\ ft\text{-}lb_f/lb_m\text{-}°R$

$$m = \frac{(14.7 \times 144)\ lb_f}{ft^2} \times \frac{75{,}600\ ft^3}{min} \times \frac{lb_m\text{-}°R}{45.44\ ft\text{-}lb_f} \times \frac{1}{(430+460)°R} \times \frac{60\ min}{hr}$$

$$\times \frac{13.82}{10^6} = 3.28\ lb/hr\ TRS\ as\ H_2S$$

3.28 lb/hr x 8,760 hr/yr / 2,000 lb/ton = 14.37 TPY TRS as H_2S (gas)
3.04 13.31 TPY (liquid fossil fuel)

2. POTENTIAL EMISSIONS

53.5 lb/hr TRS as H_2S

227.7 TPY (see Attachment G, Item 1.0) TRS as H_2S

C. SULFUR DIOXIDE

1. MAXIMUM AND POTENTIAL EMISSIONS

20.1 lb/hr SO_2

85.4 TPY (see Attachment G, Item 2.0) SO_2

D. NITROGEN OXIDES

1. HOURLY MAXIMUM AND POTENTIAL EMISSIONS

Reference NCASI Technical Bulletin No. 107, "A Study of Nitrogen Oxides Emissions from Lime Kilns." This document indicates NO_x emissions are highly variable from lime kilns fired with oil and/or gas. Because of this variability, the highest measured emission factor was used: 1.125 lb/10^6 BTU.

Lime kiln heat input = 650 TPD x 6.5 x 10^6 BTU/ton / 24 hr/day
= 176 x 10^6 BTU/hr

176 x 10^6 BTU/hr x 1.125 lb/10^6 BTU = 198.0 lb/hr NO_x

2. ANNUAL ACTUAL AND POTENTIAL EMISSIONS

From NCASI No. 107, Table 3, average NO_x emissions from gas firing were 0.54 lb/10^6 BTU. Review of data shown in Figure 3 of this document indicates no significant difference in oil firing. This average factor was used for estimation of annual emissions for both gas and oil firing.

Average hourly = 176 x 10^6 BTU/hr x 0.54 lb/10^6 BTU
= 95.0 lb/hr NO_x

95.0 lb/hr x 8,760 hr/yr / 2,000 lb/ton = 416.3 TPY NO_x

E. CARBON MONOXIDE

1. MAXIMUM AND POTENTIAL EMISSIONS

Reference NCASI Technical Bulletin No. 416, "Carbon Monoxide Emissions from Selected Combustion Sources Based Upon Short-Term Monitoring Records." This document indicates CO emission from lime kilns to be variable. Of the four kilns evaluated in this study, Kiln B is the only kiln representative of modern, energy efficient kilns and, therefore, was used as the basis of the emission factor. From Table 6 and Figure 25 of this document, 99% of all 1-hour measurements are less than 3 lb/ton lime. This factor was used to be conservative.

650 TPD x 3.0 lb/ton / 24 hr/day = 81.3 lb/hr CO = 355.9 TPY CO

F. VOLATILE ORGANIC COMPOUNDS

1. MAXIMUM AND POTENTIAL EMISSIONS

Reference NCASI Technical Bulletin No. 358, "A Study of Kraft Process Lime Kiln Total Gaseous Non-Methane Organic Emissions." Three kilns were tested: Kiln C was considered most representative of the proposed new lime kiln (this is the same as Kiln B in NCASI No. 416). The highest emission rate from Kiln C (Table 6 in NCASI No. 358) was selected: 0.35 lb/ton lime product.

650 TPD x 0.35 lb/ton / 24 hr/day = 9.5 lb/hr VOC
= 41.5 TPY VOC.

G. OTHER REGULATED POLLUTANTS

No data or emission factors exist which indicate emissions of other regulated pollutants from lime kilns.

ATTACHMENT C

EMISSION CALCULATIONS

EXISTING SOURCES TO BE SHUTDOWN

I. EXISTING LIME KILNS AND CALCINER

A. PARTICULATE MATTER

From Annual Emissions Reports submitted to the Florida Department of Environmental Regulation (DER):

	1983	1984
No. 1 Lime Kiln	35.8	46.5
No. 2 Lime Kiln	48.8	56.9
No. 3 Lime Kiln	51.4	60.0
Calciner	54.5	54.4
Total	190.5	217.8

Average = 204.2 tons per year (TPY) PM

Note: Actual emissions are below the allowable levels for each unit.

B. TOTAL REDUCED SULFUR

1. LIME KILNS

a. Actual Emissions

Based upon the lb/hr reported in the TRS Inventory form submitted to DER for 1983, annual TRS emissions for the lime kilns were calculated as follows:

	TRS (lb/hr)	Operating Hours 1983	Operating Hours 1984	TRS (TPY) 1983	TRS (TPY) 1984
No. 1 Lime Kiln	11.0	5,956	6,774	32.8	37.3
No. 2 Lime Kiln	16.0	6,816	7,195	54.5	57.6
No. 3 Lime Kiln	17.0	7,289	7,425	62.0	63.1
				149.3	158.0

Average = 153.7 TPY TRS as H_2S

b. Emissions Required Under New TRS Rule in 1988 if Kilns are not Replaced

Calculation is based upon TRS Rule for line kilns: 20 ppm on a dry basis, corrected to standard conditions at 10% O_2.

Use the last two years of representative stack test data to calculate exhaust gas flow per ton of lime mud feed.

Lime Kiln	Year	Lime Mud (dry TPH)	dscfm	Average dscfm/TPH Lime Mud
No. 1	1983	15.84	13,693	
	1984	15.40	14,471	
	Avg.	15.62	14,082	901.5
No. 2	1984	13.80	15,708	
	1985	15.80	17,489	
	Avg.	14.80	16,599	1,121.6
No. 3	1983	18.61	14,412	
	1984	16.08	14,311	
	Avg.	17.35	14,362	827.8

Calculate average dscfm for each kiln based upon average dscfm/ton/hr calculated above and 1983/1984 average kiln lime mud feed (from Annual Emissions Reports).

	Total Lime Mud (TPY)		Operating Hours Hr/Yr		Average Lime Mud (TPH)			Average
Lime Kiln	1983	1984	1983	1984	1983	1984	Average	dscfm
No. 1	66,413	76,491	5,956	6,774	11.15	11.29	11.29	10,115
No. 2	101,080	102,213	6,816	7,195	14.83	14.21	14.52	16,286
No. 3	105,312	109,137	7,289	7,425	14.45	14.70	14.58	12,069

Correct 20 ppm at 10% O_2 to stack O_2:

From 1983 TRS Inventory Form submitted to DER, O_2 in lime kiln stacks is estimated at 5%.

$C_{corr} = C_{act}\ (21 - 10)/(21 - 5) = C_{act} \times 0.688.$

$C_{act} = C_{corr}/0.688$

$C_{corr} = 20$ ppm

$C_{act} = 20/0.688 = 29.1$ ppm

TRS Emissions:

$PV = mRT \quad m = PV/RT$

$R = (1{,}545/34)\ \text{ft-lb}_f/\text{lb}_m\text{-°R} = 45.44\ \text{ft-lb}_f/\text{lb}_m\text{-°R}$

$T = 530\text{°R}$

$P = 14.7 \times 144 = 2{,}116.8\ \text{lb}_f/\text{ft}^2$

No. 1 Lime Kiln:

$$m = 2{,}116.8\ \frac{\text{lb}_f}{\text{ft}^2}\ \frac{10{,}115\ \text{ft}^3}{\text{min}}\ \frac{29.1}{10^6}\ \frac{\text{lb}_m\text{-°R}}{45.44\ \text{ft-lb}_f}\ \frac{1}{530\ \text{°R}}\ \frac{60\ \text{min}}{\text{hr}}$$

= 1.55 lb/hr

No. 2 Lime Kiln: m = 2.50 lb/hr

No. 3 Lime Kiln: m = 1.85 lb/hr

Annual emissions based upon 1983/1984 average actual hours of operation from Annual Emissions Reports:

No. 1 Lime Kiln: 6,365 hr/yr x 1.55 lb/hr / 2,000 lb/ton
= 4.93 TPY TRS as H_2S

No. 2 Lime Kiln: 7,005.5 x 2.50/2,000 = 8.76 TPY TRS as H_2S

No. 3 Lime Kiln: 7,357 x 1.85/2,000 = 6.81 TPY TRS as H_2S

Total TRS from all lime kilns = 20.5 TPY TRS as H_2S

2. CALCINER

From Annual Emissions Reports

1983: 3.0 TPY TRS as H_2S

1984: 2.7 TPY TRS as H_2S

Average: 2.9 TPY TRS as H_2S

Note: The calciner emissions are below the allowable level for this unit.

3. TOTAL TRS, KILNS AND CALCINER

153.7 + 2.9 = 156.6 TPY TRS as H_2S

4. TOTAL TRS, KILNS AND CALCINER UNDER NEW 20 PPM RULE

20.5 + 2.9 = 23.4 TPY TRS as H_2S

C. SULFUR DIOXIDE

1. LIME KILNS AND CALCINER

52.0 TPY (see Attachment G, Item 3.0) SO_2

D. NITROGEN OXIDES

1. LIME KILNS

From 1983/1984 Annual Emissions Reports, lime kiln emissions were based upon natural gas usage and 0.54 lb/10^6 BTU. NCASI Technical Bulletin No. 107 was the reference. The inventory did not include NO_x emissions due to oil firing. However, data in NCASI No. 107 indicate NO_x emissions when burning gas or oil can be equally as high. Therefore, the 0.54 lb/10^6 BTU factor is considered appropriate for gas and oil burning in the lime kilns. This is the same factor used for gas and oil burning in the new kiln (see page B-3), as no significant differences are expected.

Fuel specifications: Natural gas--1,040 BTU/scf
No. 6 Oil--145,000 BTU/gal

	1983		1984	
	Gas (10^6 scf)	No. 6 Oil (10^3 gal)	Gas (10^6 scf)	No. 6 Oil (10^3 gal)
No. 1 Lime Kiln	289.5	168.8	355.3	56.6
No. 2 Lime Kiln	378.4	220.5	354.8	195.2
No. 3 Lime Kiln	412.5	25.8	391.4	187.8
Totals	1,080.4	415.1	1101.5	439.6
BTU x 10^9	1,123.6	60.2	1145.6	63.7
NO_x Emissions	303.4	16.3	309.3	17.2

Total NO_x, Lime Kilns 1, 2, and 3: 1983--319.7 TPY NO_x
1984--326.5 TPY NO_x

2. CALCINER

Because of the calciner's lower combustion zone temperature (about 1,650°F) compared to lime kilns (2,000 to 2,100 °F), the calciner is expected to have lower NO_x emissions. Based upon NCASI Technical Bulletin No. 107, "A Study of Nitrogen Oxide Emissions from Lime Kilns," Figure 4, page 16, a leveling off of NO_x is experienced below temperatures of about 1,800°F. This level is about 0.37 lb/10^6 BTU. This factor was used to estimate calciner NO_x emissions.

Fuel specifications: Natural gas--1,040 BTU/scf
No. 6 Oil--145,000 BTU/gal
No. 2 Oil--140,000 BTU/gal

	1983			1984		
	Gas (10^6 scf)	No. 6 Oil (10^3 gal)	No. 2 Oil (10^3 gal)	Gas (10^6 scf)	No. 6 Oil (10^3 gal)	No.2 Oil (10^3 gal)
Fuel Usage	487.6	3.3	12.6	484.5	48.5	23.6
BTU x 10^9	507.1	0.5	1.8	503.9	7.0	3.3
NO_x (TPY)	93.8	0.1	0.3	93.2	1.3	0.6

Total Calciner NO_x: 1983--94.2 TPY NO_x
1984--95.1 TPY NO_x

3. TOTAL NO_x, KILNS AND CALCINER

1983--319.7 + 94.2 = 413.9 TPY NO_x

1984--326.5 + 95.1 = 421.6 TPY NO_x

Average = 417.8 TPY NO_x

E. CARBON MONOXIDE

1. LIME KILNS

2,602.1 TPY (see Attachment G, Item 4.0) CO

2. CALCINER

Emissions based upon attached letter which stated 25 ppm CO in exhaust gases.

Calciner exhaust gas flow rate is relatively constant regardless of production rate. Exhaust gas flow rate for calculating emissions based upon last two years of stack tests:

Month/Year	ACFM	Temperature (°F)
Nov. 1984	50,695	156
Feb. 1985	49,398	159
May 1985	55,752	165
May 1985	53,146	159
Average	52,248	160

$PVT = mRT$

$$m = \frac{PV}{RT} = \frac{(14.7 \text{ x } 144) \text{ lb}_f}{2} \text{ x } \frac{52,248 \text{ ft}^3}{\text{min}} \text{ x } \frac{60 \text{ min}}{\text{hr}} \text{ x } \frac{28 \text{ lbm-°R}}{1,545 \text{ ft-lb}_f}$$

$$\text{x } \frac{1}{(160+460)\text{°R}} \text{ x } \frac{25}{10^6} = 4.85 \text{ lb/hr CO}$$

Calciner average 1983/1984 operating hours from Annual Emissions Reports: (7,069 + 6,418) / 2 = 6,743.5 hr/yr

4.85 x 6,743.5 hr/yr / 2,000 lb/ton = 16.4 TPY CO

3. TOTAL CO, KILNS AND CALCINER

2,602.1 + 16.4 = 2,618.5 TPY CO

F. VOLATILE ORGANIC COMPOUNDS

1. LIME KILNS

VOC emissions from the three lime kilns have not been quantified in the Annual Emissions Reports. No AP-42 factor exists. The emission factor selected was based upon NCASI Technical Bulletin No. 358, "A Study of Kraft Process Lime Kiln Total Gaseous Non-Methane Organic Emissions," 1981. Of the three kilns surveyed, Kiln B is most like the existing kilns. The average emission factor of 1.6 lb/ton lime product for this kiln was selected.

Based on production from the Annual Emissions Reports:

	Lime product (tons)	
	1983	1984
No. 1 Lime Kiln	34,064	39,233
No. 2 Lime Kiln	44,780	45,282
No. 3 Lime Kiln	48,259	50,012
Totals	127,103	134,527
VOC (TPY)	101.7	107.6

2. CALCINER

VOC emissions from the calciner have not been quantified in the Annual Emissions Reports. Because of the more efficient combustion in the calciner than the existing kilns, it is expected that VOC emissions are similar to those expected from the new lime kiln (see new lime kiln calculation). This factor is 0.35 lb/ton lime product.

Based on production:

1983: 59,730 tons lime product/yr x 0.35 lb/ton lime product / 2,000 lb/ton = 10.5 TPY VOC

1984: 51,665 tons lime product/yr x 0.35 lb/ton lime product / 2,000 lb/ton = 9.0 TPY VOC

3. TOTAL VOC FROM KILNS AND CALCINER

1983: 101.7 + 10.5 = 112.2 TPY VOC

1984: 107.6 + 9.0 = 116.6 TPY VOC

Average = 114.4 TPY VOC

II. EXISTING LIME SLAKERS

PARTICULATE MATTER

Each slaker is controlled by a water spray and emissions are discharged through separate vents. From AP-42, Table 8.15-1 (4/77), emission factor is 0.1 lb/ton of hydrated lime produced or 0.125 lb/ton of lime feed to hydrator. All lime produced by kilns and calciner is hydrated in the existing slakers:

Total = 186,514 TPY from page C-8.

186,514 x 0.125 / 2,000 = 11.66 TPY PM

III. EXISTING LIME BINS (FROM KILN, RAIL, AND TRUCK)

PARTICULATE MATTER

Currently: two bins for causticizing--uncontrolled
two bins for water treatment, one has baghouse

From "Technical Guidance for Control of Industrial Process Fugitive Particulate Emissions," EPA 450/3-77-010, 1977, Section 2.9, Lime Manufacturing:
Source No. 11--Truck, rail loading of quicklime and hydrated lime, plus lime product silo vents: uncontrolled emission factor = 0.236 lb/ton.

Based upon "Workbook for Estimation of Emissions and Dispersion Modeling for Fugitive Particulate Sources," Table 3.2.17-2, control efficiency for weathertight enclosure is given as 70%. This factor was considered appropriate for the existing causticizing and water treatment lime bins which are not controlled by a baghouse.

Controlled emission factor = 0.236 lb/ton x (1 - 0.70)
= 0.0708 lb/ton

1. Purchased lime unloading to causticizing area (trucks only are unloaded):

1983	6,358 tons
1984	11,412 tons
Average	8,885 TPY

8,885 TPY x 0.0708 lb/ton / 2,000 lb/ton = 0.31 TPY PM

2. Purchased lime unloading to water treatment (rail and truck)--all conveyed to baghouse @ 22 TPH

1983	17,901 tons
1984	18,333 tons
Average	18,117 TPY

Baghouse manufacturer's data: Baghouse rated at 0.02 gr/scf @ 600 scfm.

18,117 TPY / 22 TPH = 824 hr/yr operation.

0.02 gr/scf x 600 scfm x 60 min/hr / 7,000 gr/lb = 0.103 lb/hr.

0.103 x 824 / 2,000 = 0.04 TPY PM

3. Transfer of lime from causticizing lime bins to water treatment lime bins; not controlled by baghouse

1983	3,916 tons
1984	2,642 tons
Average	3,279 TPY

3,279 TPY x 0.0708 lb/ton / 2,000 lb/ton = 0.116 TPY PM

4. Transfer of lime from kilns to causticizing lime bins. All lime is transferred to causticizing bins.

Based upon Annual Emissions Reports:

	Lime Production (Tons)		
	1983	1984	Average
Kiln 1	34,064	39,233	36,649
Kiln 2	44,780	45,282	45,031
Kiln 3	48,259	50,012	49,136
Calciner	59,730	51,665	55,698
Totals	186,833	186,192	186,514

186,514 TPY x 0.0708 lb/ton / 2,000 lb/ton = 6.603 TPY PM

5. Totals

Causticizing Lime Bins: 0.31 + 6.603 = 6.913 TPY PM

Water Treatment Lime Bins: 0.04 + 0.116 = 0.156 TPY PM

IV. EXISTING KILN LEAKS

FUGITIVE PARTICULATE MATTER EMISSIONS

Kiln leaks occur at feed and discharge ends.

From "Technical Guidance for Control of Industrial Process Fugitive Particulate Emission," EPA 450/3-77-010, 1977, Section 2.9, Lime Manufacturing.

From Table 2-53, Source No. 3 is the uncontrolled emission factor for transfer points and associated conveying (0.8 lb/ton CaO). Review of Figure 2-19 shows that a total of nine fugitive dust generating activities comprise this total emission factor. The average emission factor per source (activity) = 0.8 / 9 = 0.089 lb/ton. This factor was applied to the kiln leaks.

Feed end: 186,514 TPY x 0.089 lb/ton / 2,000 lb/ton = 8.30 TPY PM
Discharge end: 186,514 TPY x 0.089 lb/ton / 2,000 lb/ton
= 8.30 TPY PM
Totals: 8.30 + 8.30 = 16.6 TPY PM

V. EXISTING LIME MUD CENTRIFUGES AND PRECOAT AND BELT FILTERS

FUGITIVE TRS EMISSIONS

1. NORMAL OPERATIONS

Based on field tests, Eurocan Pulp and Paper in Kitimat B.C., Canada, has developed fugitive TRS emission estimates for precoat filters. For a 900 gpm white liquor production at 31 percent sulfidity, estimated TRS emissions are 9 lb/day. It is reasonable to assume emissions are directly related to sulfidity and throughput. The existing system operates at an average of 1,150 gpm and 27% sulfidity.

a. $\frac{(27)}{31} = \frac{x}{9}$ x = 7.8 lb/day at 27% sulfidity

then:

$\frac{1,150}{900} = \frac{x}{7.8}$ x = 10.0 lb/day at 1,150 gpm average and 27% sulfidity

b. 10.0 lb/day / 24 hr day = 0.417 lb/hr TRS as H_2S

c. 10.0 lb/day x 350 day/yr / 2,000 lb/ton
= 1.744 TPY TRS as H_2S

2. ACID WASHING

Centrifuges and belt filters are not acid washed. The calciner lime mud precoat filter is acid washed twice per week. Because the existing precoat filter is smaller in size, it is expected that the total volume of residual white liquor per wash will be about 20 percent of the volume used for estimating TRS fugitive emissions from acid washing. (See Attachment A, pages A-10 and A-11, of the companion permit) $0.2 \times 0.5\ ft^3 = 0.1\ ft^3$.

$$\frac{0.1\ ft^3}{} \times \frac{2.27\ lb/wash}{2\ ft^3} \times \frac{2\ washes}{week} \times \frac{52\ weeks}{yr} \ / \ \frac{2{,}000\ lb}{ton} = 0.006\ TPY$$

3. TOTAL

   1.744 + 0.006 = 1.75 TPY TRS as H_2S

VI. EXISTING DREGS FILTER

FUGITIVE TRS EMISSIONS

1. NORMAL OPERATION

The information from Eurocan Pulp and Paper includes an estimate for dreg filter fugitive TRS emissions at 75 percent of the lime mud Precoat filter emissions. Calculated emissions are:

0.75 x 10.0 lb/day = 7.5 lb/day

7.5 lb/day / 24 hr/day = 0.312 lb/hr

7.5 lb/day x 350 days/yr / 2,000 lb/ton = 1.312 TPY

2. ACID WASHING

The existing dregs filters are acid washed about once per month. Emissions are calculated based on 75 percent of the emissions from the new white liquor pressure filter. This is the same basis used for calculating emissions for the new dregs filter (see Attachment A, page A-12, of the companion permit). Calculated emissions are:

$$0.75 \times \frac{2.27\ \text{lb}}{\text{wash}} = 1.70\ \text{lb/wash}$$

$$1.70\ \text{lb/wash} \times 2\ \text{filters} \times \frac{1\ \text{wash}}{\text{month}} \times \frac{12\ \text{months}}{\text{yr}} \ / \ \frac{2{,}000\ \text{lb}}{\text{ton}}$$

$$= 0.020\ \text{TPY TRS as}\ H_2S$$

3. TOTAL

1.312 + 0.020 = 1.33 TPY TRS as H_2S

ATTACHMENT D

BASIS FOR CONTEMPORANEOUS EMISSIONS INCREASES SINCE JULY 1980

1. CALCINER

The DER construction permit for the calciner was granted in 1978. A federal PSD permit for the calciner was issued in 1979 and revised in May 1980. Startup of the calciner was in May 1980, and the DER operating permit was granted in February 1981. Operation began before the 5-year contemporaneous period. In addition, the PSD permit "wiped the slate clean" in regards to determining net emissions increases for subsequent actions at the Buckeye Cellulose mill.

2. NO. 2 BARK BOILER--WOOD DRYER MODIFICATION

Construction Permit AC62-30466 Issued 7/21/80
Operating Permit A062-48929 Issued 1/5/82
This modification only involved addition of bark dryer and improved wet scrubber. No emissions were to increase as a result of this modification.

3. WOOD YARD IMPROVEMENTS

This project simplified materials handling in the woodyard resulting in an unquantified reduction in particulate emissions for which no credit was claimed. This project was reviewed with DER and because of a reduction in emissions it was agreed that no construction permit was required. These changes occurred in 1982 and 1983.

4. NO. 1 BARK BOILER--WASTE WOOD FEED RATE CHANGE

Operating Permit A062-48928 Issued 8/17/83.
This modification increased the permitted waste wood firing rate from 250 x 10^6 BTU/hr to 300 x 10^6 BTU/hr to allow full steam production on 100 percent waste wood firing. The permitted fuel oil firing rate remained at 250 x 10^6 BTU/hr. The maximum permitted or estimated emissions before and after the modification for each pollutant are as follows:

	Before Modification		After Modification	
Pollutant	Maximum lb/hr	Basis	Maximum lb/hr	Basis
PM	47.25	Bubble with No. 2 Bark Boiler	47.25	Emissions well below allowable even at higher wood-firing rate
NO_x	102.7	Oil firing at 250 x 10^6 BTU/hr and AP-42 factor of 60 lb/1,000 gal	102.7	Oil firing, 250 x 10^6 BTU/hr (waste wood firing at 300 x 10^6 BTU/hr, 6,250 BTU/lb wet and using AP-42 factor of 2.8 lb/ton (wet) = 67.2 lb/hr)
SO_2	672.0	2.5% S Oil Firing at 250 x 10^6 BTU/hr and AP-42 factor of 157 S lb/1,000 gal	672.0	Same basis as before [wood firing at 300 x 10^6 BTU/hr and using factor of 0.0214 lb/10^6 BTU (NCASI No. 96) results in 6.4 lb/hr]
CO	40.0	Wood firing at 250 x 10^6 BTU/hr, 6,250 BTU/lb wet, and 2 lb CO/ton (wet) (former AP-42 factor)	48.0	Same basis except waste wood firing rate of 300 x 10^6 BTU/hr
VOC	16.25	Wood firing rate of 250 x 10^6 BTU/hr, 0.065 lb/10^6 BTU (average emissions from four boilers, NCASI No. 109)	19.50	Same basis, except waste wood firing rate of 300 x 10^6 BTU/hr

The emission factors for waste wood firing used above are those which were used in the permit to revise the No. 2 Bark Boiler waste wood burning rate (see pages D-4 thru D-6). As indicated, oil-firing produces much greater emissions for NO_x and SO_2. The annual emissions of these pollutants would vary from year to year, depending upon fuel mix. But the increased waste wood-firing rate did not increase maximum permitted emissions from the boiler. For CO and VOC, waste wood firing causes the maximum emissions. Based upon full capacity operation, the increases due to the increased waste wood firing rate would be:

CO: 48 - 40 = 8 lb/hr = 35.0 TPY

VOC: 19.50 - 16.25 = 3.25 lb/hr = 14.2 TPY

5. NO. 4 RECOVERY BOILER AND SMELT DISSOLVING TANK--BLACK LIQUOR SOLIDS CHANGE

Operating Permit A062-54432 Issued 8/22/83

This modification increased the Black Liquor Solids (BLS) burning rate from 180,000 lb/hr at 63 percent solids to 195,000 lb/hr at 63.5 percent solids. The increase in emissions are documented in the operating permit application (see pages D-7 through D-13). The increases were as follows:

PM	0 TPY
SO_2	1.2 TPY
TRS	1.0 TPY
CO	23.9 TPY
NO_x	23.7 TPY
VOC	9.5 TPY

6. NO. 2 BARK BOILER--WASTE WOOD FIRING RATE

Operating Permit A062-48929 Issued 9/12/83

This modification increased the maximum waste wood firing from 45 tons/hr to 48 tons/hr at 30 percent H_2O and from 563.5×10^6 BTU/hr to 601×10^6 BTU/hr. The emissions increases due to this change were documented in the permit application (see pages D-4 to D-6). The increases were as follows:

PM	0 TPY
SO_2	3.5 TPY
NO_x	0 TPY
CO	26.3 TPY
VOC	11.5 TPY

7. FINES BURNING TEST

A temporary permit was issued for the fines burning project. This project was terminated in accordance with the permit on January 25, 1985, and the increased emissions ceased.

First in cellulose The Buckeye Cellulose Corporation

Mailing Address: Route 3 Box 260 Perry, Florida 32347 Phone: (904) 584-0121

September 2, 1983

Mr. Doug Dutton
Florida Department of Environmental Regulation
3426 Bills Road
Jacksonville, FL 32207

Re: A062-48929
No. 2 Bark Boiler
Operating Permit

Dear Mr. Dutton:

The purpose of this letter is to request a minor modification in the current permit for no. 2 bark boiler. The modification is a 6.7% increase in the steam flow rate. The specific revisions requested are as follows:

Page 3 - Item A: Change waste wood prodgcts utilization from "45 tons/hour at 30% H_2O" to "48 tons/hour at 30% H_2O".

Page 3 - Item B-2: Change "waste wood products and/or F.F. 375 M lbs/hour expressed as steam" to "waste wood products and/or F.F. 400 M lbs/hour expressed as steam".

Page 4 - Item E: Change "waste wood products 45 tons/hour - 30% H_2O - 563.5 MMBTU/hour" to "waste wood products 48 tons/hour - 30% H_2O - 601 MMBTU/hour". Also change "waste wood and/or F.F. 563.5 MMBTU/hour" to "waste wood and/or F.F. 601 MMBTU/hour".

No change in allowable emissions is requested. An emissions test showing compliance with particulate emissions at the higher rate is attached. A PSD review (Attachment 1) shows that no PSD increment would be exceeded by the increase. Also, this boiler has never been a part of any Federal PSD construction permit.

Your advice for processing these permit requests has simplified and reduced the work required. I appreciate this very much.

Very truly yours,

THE BUCKEYE CELLULOSE CORPORATION

John Millican

J. H. Millican
Environmental Control Manager

JHM/eph

Enclosures

bcc: T. H. Donnelly
R. W. Meissner
S. J. Kruger - Memphis
J. E. Farmer

PSD REVIEW

No. 2 Bark Boiler Rate Increase
Summary of Projected Air Emission Increases
(tons/year)

Source	Particulate	SO_2	NO_x	CO	VOC
No. 2 Bark Boiler	0	3.5	0	26.3	11.5

Cummulative increase since last PSD review to include no. 4 recovery boiler rate increase.

Source	Particulate	SO_2	NO_x	CO	VOC
No. 4 Recovery Boiler	0	1.2	23.7	23.9	9.5
Total Emission Increase	0	4.7	23.7	50.2	21.0
PSD Significant Net Increase	25	40.0	40.0	100.0	40.0

No PSD review required.

FOLEY

No. 2 Bark Boiler Rate Increase
Projected Air Emission Increases

Basis

Increase no. 2 bark boiler steaming rate from 375,000 to 400,000 lbs/hr. No increase in fossil fuel firing.

TPH bark = 45 x 400/375 = 48 TPH

$$\text{Heat Input Increase} = 563.5 \times \frac{400 - 375}{375} = 37.6 \text{ MMBTU/hr}$$

Particulate Emissions

No increase in allowable particulate emissions is requested. Stack tests at the 400,000 lbs/hr firing rate show compliance with the currently permitted rate of 375,000 lbs/hr.

SO_2 Emissions

NCASI Technical Bulletin No. 96 has an average SO_2 emission factor for waste wood firing of 0.0214 lbs/MMBTU.

$$SO_2 \text{ Increase} = (601 - 563.5)(0.0214) \times \frac{24 \times 365}{2{,}000} = 3.5 \text{ TPY}$$

NO_x Emissions

Testing of the boiler by Harmon Engineering shows a reduction in NO_x emissions from 177 lbs/hr at 375,000 lbs/hr steaming rate to 125 lbs/hr at the 400,000 lbs/hr steaming rate. Attachment 2 is a copy of the Harmon report.

CO Emissions

The AP-42 emission factor for CO when firing bark is 2 lbs/Ton of bark fired.

$$\text{CO Increase} = (48 - 45) \times 2 \times \frac{24 \times 365}{2{,}000} = 26.3 \text{ TPY}$$

VOC Emissions

NCASI Technical Bulletin No. 109 has a VOC emission factor for waste wood firing of 0.07 lbs/MMBTU.

$$\text{VOC Increase} = (601 - 563.5)(0.07) \times \frac{24 \times 365}{2{,}000} = 11.5 \text{ TPY}$$

First in cellulose The Buckeye Cellulose Corporation
Mailing Address: Route 3 Box 260 Perry, Florida 32347 Phone: (904) 584-0121

August 22, 1983

Mr. Doug Dutton
Florida Department of Environmental Regulation
3426 Bills Road
Jacksonville, FL 32207

Re: A062-54432
No. 4 Recovery Boiler
Operating Permit

Dear Mr. Dutton:

In accordance with our discussion on August 19, 1983, I am writing this letter to request a minor modification in the current permit for no. 4 recovery boiler. The modification is a 9.2% increase in black liquor burning rate. The specific revisions requested are as follows:

Page 3 - Item A: Change black liquor flow to read "195,000 pounds/hour at 63.5% solids". Change smelt to SDT to read "52,254 pounds/hour". Change weak wash solids to read "12,399 pounds/hour".

Page 3 - Item B: Change total process input rate to read "123,825 pounds/hour BLS + 12,399 pounds/hour weak wash solids". Change product weight to read "450,000 pounds/hour as steam / 52,254 pounds/hour as smelt".

No change in allowable emissions is requested. An emissions test showing compliance with TRS and particulate emissions at the higher rate was previously submitted on May 23, 1983. A PSD review (Attachments I and IA) shows that no PSD increment would be exceeded by the increase. Also, this boiler has never been a part of any Federal PSD construction permit.

I believe all of the information we discussed has been included, however, if you have any questions, please call me at (904) 584-0347.

The unfailing courtesy and cooperation I receive from you and every member of your staff makes my job a real pleasure. I do indeed appreciate it.

Very truly yours,

THE BUCKEYE CELLULOSE CORPORATION

John Millican

J. H. Millican
Environmental Control Manager

Enclosures

bcc: T. H. Donnelly
S. J. Kruger - Memphis
R. W. Meissner
J. E. Farmer

PSD REVIEW

No. 4 Recovery Boiler Rate Increase

Summary of Projected Air Emission Increases
(Tons/Year)

Source	Particulate	SO_2	TRS	CO	NO_x	VOC
No. 4 Recovery Boiler	0	0	1.0	23.9	23.7	9.5
No. 4 Smelt Dissolving Tank	0	1.2	0	0	0	0
Total Emission Increase	0	1.2	1.0	23.9	23.7	9.5
PSD Significant Net Increase	25.0	40.0	10.0	100.0	40.0	40.0

No. 4 RECOVERY BOILER RATE INCREASE

Projected Air Emission Increases

Basis

Increase no. 4 recovery boiler burning capacity from 180,000 pounds/hour at 63.0% black liquor solids to 195,000 pounds/hour at 63.5% solids. Black liquor solids heat content is 5200 BTU/pound.

Increase in heat input:

$$[195{,}000\ (.635) - 180{,}000\ (.63)]\ 5200 = 54.2\ \text{MMBTU/hr}$$

The Foley plant averaged 3870 pounds of black liquor solids per ton of unbleached pulp produced in 1982.

Particulate Emissions

No increase in allowable particulate emissions is requested for no. 4 recovery boiler ESP or SDT. Stack tests at the 195,000 pounds/hour firing rate show compliance with the currently permitted rate of 180,000 pounds/hour.

SO_2 Emissions

The bases for determining the increase in SO_2 emissions resulting from the rate increase from 180,000 pounds/hour of black liquor to 195,000 pounds/hour are as follows:

1. A comparison of SO_2 emissions at the respective rate using a Barton coulemetric titrator to monitor SO_2 emission during the period June 12, 1982 through September 10, 1982.
2. No effort was made to control operation of the boiler for SO_2 emission during the test. Periods of operation at the respective rates were extracted from the continuous chart and converted to hourly averages in parts per million for statistical analyses (Attachment I-A). This analysis shows that at the 5% level of significance there is no difference between the new SO_2 emissions at the respective rates; i.e., no SO_2 emission increase.
3. AP-42 factor is 0.1 pounds of SO_2 per ton of unbleached pulp from the SDT.

   Equivalent unbleached pulp rate:

$$\frac{(195{,}000 \times .635 - 180{,}000 \times .63)}{3820} = \frac{123{,}825 - 113{,}400}{3820} = 2.73\ \text{tons/hour}$$

   SO_2 emission increase:

$$2.73\ \text{tons/hour} \times 0.1 \times \frac{24 \times 365}{2000} = 1.2\ \text{TPY}$$

TRS Emissions

1. No. 4 recovery boiler TRS emissions were estimated at 10.7 tons per year in the 1982 annual operating report.

   Assume the increase in TRS emissions is proportional to the firing rate:

   $$\text{Emission increase} = \frac{10.7 \times 195{,}000\ (.635)}{180{,}000\ (.63)} - 10.7 = 1.0\ \text{TPY}$$

2. No significant increase in TRS emissions from no. 4 SDT is expected.

CO Emissions

1. AP-42 gives a range of CO emission factors for recovery boilers of 2-60 lb/ton unbleached pulp. Since a CO monitor has recently been installed on No. 4 recovery boiler and will be used to control air flows to the boiler, use the 2 lb/ton unbleached pulp emission factor:

   $$\text{CO increase} = 2.73 \times 2 \times \frac{24 \times 365}{2{,}000} = 23.9\ \text{TPY}$$

   With the new CO monitor and controller, it is expected that the CO emissions at the 195,000 lbs/hour firing rate will be less than the unmonitored and uncontrolled CO emissions at the 180,000 lbs/hour firing rate.

2. No. 4 SDT is not a combustion source and no CO emissions are anticipated. AP-42 gives a 0.00 emission factor for this source.

NO_x Emissions

1. NCASI Technical Bulletin No. 105 has an average NO_x emission factor of 0.10 lbs. NO_x per MMBTU of heat input for non-contact (low odor) recovery furnaces.

   $$NO_x\ \text{increase} = 0.10 \times 54.2\ \text{BTU/hr} \times \frac{24 \times 365}{2{,}000} = 23.7\ \text{TPY}$$

2. No. 4 SDT is not a combustion source. Therefore no NO_x emissions are anticipated.

VOC Emissions

1. NCASI Technical Bulletin No. 112 has an average VOC emission factor of 0.04 lbs per MMBTU of heat input for non-contact (low odor) recovery furnaces.

   $$\text{VOC increase} = 0.04 \times 54.2\ \text{BTU/hr} \times \frac{24 \times 365}{2{,}000} = 9.5\ \text{TPY}$$

2. Smelt dissolving tanks have not been identified as a VOC emission source. AP-42 has no emission factor.

No. 4 RECOVERY BOILER

SO_2 Emission Analysis

This attachment summarizes the results of the SO_2 emission test. The objective of the test was to determine if there is a significant difference in the SO_2 emission production between the 195 M#/hour and 180 M#/hour black liquor burning rates on recovery boiler no. 4.

Conclusion

Evidence to-date shows that there is no statistical difference between the mean SO_2 emission production at 180 M#/hour and 195 M#/hour black liquor burning rates at the 95% confidence level.

Discussion

SO_2 emission data was collected under two black liquor burning rates. One operated at 180 M#/hour, the other operated at 195 M#/hour. A random sample of 212 and 480 SO_2 emissions was gathered for the 180 M#/hour and 195 M#/hour, respectively. The SO_2 emission in ppm for the 180 M#/hour was measured to be 48.783 ppm on the average with a standard deviation, S = 37.662. The average SO_2 emission for the 195 M#/hour was 46.979 ppm with a standard deviation, S = 35.605. Table I calculated the upper and lower limits of the SO_2 emission for the 180 M#/hour and 195 M#/hour at the 95% confidence level. This predicts that the variation about the average SO_2 emission will be held within two standard deviation 95% of the time.

Pages 2 and 3 provide an explanation of the method of calculation for testing of a statistical significance concerning mean SO_2 emission between two black liquor burning rates.

TABLE I: 95% CONFIDENCE LIMIT CALCULATION

Black Liquor Burning Rate (lbs/hour) / SO_2 Emission (ppm)	μ	95% Confidence Limit		δ	No. of Samples
		Lower	Upper		
180,000	48.783	43.71	53.85	37.662	212
195,000	46.979	44.08	49.876	35.605	580

CHK/eph
6/6/83

Let μ_1 and μ_2 denote the true mean SO_2 emission for black liquor burning rate at 180,000 lbs/hr and 195,000 lbs/hr, respectively. Then if we wish to test the hypothesis that the means are equal, we will test μ_0: $(\mu_1 - \mu_2) = 0$; against H_a: $(\mu_1 - \mu_2) \neq 0$.

$\overline{X}_1 = 48.783$ $\qquad$ $S_1^2 = 1418.464$

$\overline{X}_2 = 46.979$ $\qquad$ $S_2^2 = 1267.754$

At the 5% significance level, equally divided between the two tails of the Z distribution, we will reject H_o for $Z > Z_{\alpha/2} = Z_{.025} = 1.96$

Since our sample size is quite large, the sample variance provides good estimates of their corresponding population variances. We can calculate the Z statistics by using the formula:

$$Z = \frac{\overline{X}_1 - \overline{X}_2}{\sqrt{\frac{\delta_1^2}{N_1} + \frac{\delta_2^2}{N_2}}} = \frac{48.783 - 46.979}{\sqrt{\frac{1418.644}{212} + \frac{1267.754}{580}}}$$

$$= .6055$$

This value $Z = .6055$ lies in the interval (-1.96, 1.96), we accept H_o and conclude that the difference observed is not significant.

CHK/eph
6/6/83

ATTACHMENT E

DERIVATION OF PROCESS RATE

DERIVATION OF PROCESS RATE

Basis: Product rate = 650 TPD lime product (dry)
= 27.0833 TPH = 54,167 lb/hr

To be conservative, assume the product is 100 percent CaO (Stream 14), dust loss based upon highest expected grain loading when firing oil in the kiln (Stream 13a), and all dust lost is recycled back into the kiln (Stream 11b).

Calculate lb lime mud feed/ton product:
2,000 lb lime/ton product x (100 lb $CaCO_3$/56 lb CaO)
= 3,571.4 lb lime mud feed/ton product

Therefore, Stream 11a = 27.0833 TPH product x 3,571.4 lb feed/ton product
= 96,726 lb/hr lime mud feed (dry)

Maximum dust loss for oil firing (Stream 13a):
From page B-1, maximum gas flow for oil firing = 41,685 dscfm
From page F-1, maximum inlet loading to ESP = 20 gr/dscf at actual stack O_2
41,685 dscf x 20 gr/dscf / 7,000 gr/lb x 60 min/hr = 7,146 lb/hr

Assuming all dust is recycled back into kiln; therefore, Stream 11b = Stream 13a = 7,146 lb/hr

Stream 12 = Stream 11a + Stream 11b = 96,726 + 7,146 = 103,872 lb/hr

ATTACHMENT F

CONTROL EQUIPMENT INFORMATION

1.0 PARTICULATE CONTROL

The control device selected is an electrostatic precipitator (ESP) because it can provide a greater control efficiency with much lower energy consumption. The kiln fossil fuel consumption is reduced because of dry recycle of particulate. In addition, the power required for an ESP is much lower than that for a conventional venturi scrubber. The lower power consumption results in reductions in pollutants generated to produce purchased power. There also will be a reduction in operating costs.

The vendor for the ESP has not been chosen. Specific design information will be submitted to DER, Bureau of Air Quality Management, prior to beginning installation of the ESP. The following design specifications formed the basis for the vendor bids.

Design capacity = 650 TPD lime product output
Fuels: Natural gas or No. 6 fuel oil
Flue gas conditions before ESP:

Parameter	Natural Gas	No. 6 Oil
Flue Gas Flow (ACFM)	108,000	100,000
Flue Gas Temperature (°F)	430	430
% O_2	2-3	2-3
% H_2O	30-40	30-40
Inlet Dust Loading (gr/dscf)	10-20	10-20

Construction: One chamber, three fields minimum, dry bottom, trough hopper, rigid frame, insulated to prevent condensation and corrosion.

Efficiency Calculation:

The efficiency calculation is based on not exceeding maximum outlet dust loading under maximum inlet dust loading conditions. The maximum outlet dust loading is based on not exceeding the PSD significance level for particulate.

From Attachment B, page B-1, maximum outlet dust loading (oil firing) = 0.157 gr/dscf at stack O_2.
Maximum inlet dust loading = 20 gr/dscf.
Efficiency = (Inlet - Outlet)/Inlet x 100
= (20 - 0.157)/20 x 100 = 99.2 percent

Vendor information indicates efficiency should be 99.7 percent or greater at typical inlet dust loadings.

Guarantees:

Particulate performance guarantees shall be based upon not exceeding maximum particulate emissions as shown in the air construction permit application, while burning either gas or oil. Test methods will be the current methods as specified in FAC Chapter 17-2.

2.0 TRS CONTROL

Process design and control is the foundation of good TRS control. Best Demonstrated Technology (BDT) has long recognized the importance of such factors as good mud washing and good kiln combustion control to achieve good TRS control. The system design will provide TRS control equal to or better than BDT. We understand that it will be necessary to meet this level of control or retrofitting or replacement will be expected.

2.1 PRECOAT FILTER

The precoat filter size will be equal to or greater than BDT to assure good oxidation of the sulfides. Hot clean water will be used for washing. Fines from the ESP will be recycled in dry form directly to the kiln feed, bypassing the precoat filter. This removes some mud load from the filter and reduces plugging caused by fine particles, thereby improving filter effectiveness.

2.2 MUD WASHING

White liquor clarification and mud washing will be accomplished through the use of pressure filters. Pressure filters produce a higher solids mud than can be produced by conventional clarifiers. The higher solids mud allows greater dilution hence better washing thereby reducing residual chemicals in the lime mud feed to the kiln. This new technology also provides tighter process control and reliability than conventional clarifiers.

2.3 INERTS

Green liquor equipment included in this project will provide surge capacity and double the effective clarifier capacity. The improved green liquor quality will result in lower inerts in the lime mud, and thereby improve lime mud filterability. The lime mud from the water treatment softeners characteristically is high in inerts. There will be a controlled bleed of this source (Stream 23) to reduce the inerts in the lime mud feed to the kiln. This lower level of inerts in the lime mud feed means lower TRS emissions from the lime kiln.

2.4 KILN COMBUSTION

The design will include O_2 measurement in the stack and kiln plus cold end temperature measurement. Improved seals will reduce air in leakage thereby providing better kiln combustion control. The new kiln will be of modern, energy-efficient design.

2.5 ESTIMATED CONTROL EFFICIENCY

From Attachment B, maximum TRS emissions = 3.28 lb/hr TRS as H_2S

Potential TRS emissions = 53.5 lb/hr TRS as H_2S

Efficiency = (53.5 - 3.28)/53.5 x 100 = 93.9%

REFERENCES

Buckeye Cellulose Corporation. 1984. Excerpts from TRS Inventory Forms Submitted to the Florida Department of Environmental Regulation on March 28, 1985.

Goklany, I.M., Curreri, J., Heinold, D., and Lewis, R. 1981. Workbook on Estimation of Emissions and Dispersion Modeling for Fugitive Particulate Sources. Washington, D.C. P-A857.

National Council of the Paper Industry for Air and Stream Improvement, Inc. 1978. Information on the Sulfur Content of Bark and Its Contribution to SO_2 Emissions When Burned as a Fuel. New York, New York. TB No. 96.

National Council of the Paper Industry for Air and Stream Improvement, Inc. 1980a. A Study of Nitrogen Oxides Emissions from Lime Kilns. New York, New York. TB No. 107.

National Council of the Paper Industry for Air and Stream Improvement, Inc. 1980b. A Study of Wood-Residue Fired Power Boiler Total Gaseous Non-Methane Organic Emissions in the Pacific Northwest. New York, New York. TB No. 109.

National Council of the Paper Industry for Air and Stream Improvement, Inc. 1981. A Study of Kraft Process Lime Kiln Total Gaseous Non-Methane Organic Emissions. New York, New York. TB No. 358.

National Council of the Paper Industry for Air and Stream Improvement, Inc. 1984. Carbon Monoxide Emissions from Selected Combustion Sources Based on Short-Term Monitoring Records. New York, New York. TB No. 416.

PEDCo Environmental, Inc. 1977. Technical Guidance for Control of Industrial Process Fugitive Particulate Emissions. Cincinnati, Ohio. EPA-450/3-77-010.

U.S. Environmental Protection Agency. 1984. Supplement No. 15 for Compilation of Air Pollutant Emission Factors. Third Edition (Including Supplements 1-7), Research Triangle Park, North Carolina. AP-42.

Reference 1

Excerpts from TRS Inventory forms
submitted to DER on March 28, 1984

Table 5-1. TRS EMISSIONS FROM AN UNCONTROLLED 907 MEGAGRAMS PER DAY (1000 TONS PER DAY) KRAFT PULP MILL(1)

Source	Typical Exhaust Gas Flow Rate m^3/s(acfm)	TRS Emission Range		Average(2) TRS Emission Rate		
		ppm	g/kg ADP (lb/T ADP)	ppm	g/s(lb/hr)	g/kg ADP(lb/T ADP)
Recovery Furnace	212(450,000)	18-1303	0.75-31(1.5-62)	550	79(625)	7.5(15.0)
Digester System	3(6,200)	1525-30,000	0.24-5.3(0.47-10.5)	9,500	8(63)	0.75(1.5)
Multiple-Effect Evaporator System	1(2,200)	92-44,000	0.015-3.2(0.03-6.3)	6,700	5(42)	0.5(1.0)
Lime Kiln	37(79,200)	3-613	0.01-2.1(0.02-4.2)	170	4(33)	0.4(0.8)
Brown Stock Washer System	71(150,000)	-	0.005-0.5(0.01-0.9)	30	2(13)	0.15(0.3)
Black Liquor Oxidation System	14(30,000)	3-335	0.005-0.37(0.01-0.73)	35	0.5(4)	0.05(0.1)
Smelt Dissolving Tank	27(58,100)	5-811	0.007-1.9(0.013-3.70)	60	1(8)	0.1(0.2)
Condensate Stripper System	2(4,000)	-	-	5000	10(83)	1.0(2.0)

(1) Uncontrolled emission data for condensate strippers were obtained from Reference 13. Data for all other sources were obtained from Reference 5.

(2) Average values listed are calculated from data listed in Reference 5. Insufficient information was available in Reference 5 to evaluate the operation of the units for which data were reported.

STATE OF FLORIDA
DEPARTMENT OF ENVIRONMENTAL REGULATION
TRS INVENTORY FORM

1. Firm: The Buckeye Cellulose Corporation
2. Facility: Foley
3. Facility Address: Rt. 3, Box 260
4. City: Perry
5. County: Taylor
6. Zip: 32347
7. Contact Person: J. H. Millican
8. Contact Address: Rt. 3, Box 260
9. City: Perry
10. Zip: 32347
11. Phone: (904) 584-0347
12. UTM Coordinates a. Zone: 17 b. East: 256,740 c. North: 3,328,700
13. Source: #1 Lime Kiln
14. DER Permit: No. A062-46527 Exp. Date: 11/4/86
15. Initial Construction: Mo. Yr. 1953
16. Major Modification to Permitted Source: Mo. Yr.
17. Maximum Capacity Of The Facility (ADT): 1983 Average 1329 T/D

18. If The Source Is A Recovery Boiler
a. Mfg.:
b. Non-DCE: ☐ Yes ☐ No
c. ☐ Straight Kraft ☐ Cross Recovery
d. 2-Stage Black Liquor Ox. (If DCE Furnace): ☐ Yes ☐ No

Other TRS Controls:

e. Membrane Or Welded Wall Construction: ☐ Yes ☐ No
f. Emission Control Designed Air System: ☐ Yes ☐ No
g. Wet Bottom ESP: ☐ Yes ☐ No

19. If The Source Is A Lime Kiln a. Length: 175' b. Diameter: 11' x 10'
c. Type Of Mud Filter: Belt Filter

20. If The Source Is A Digester System, No. of Digesters:
21. Maximum Operating Times a. Hr/Day: 24 b. Day/Wk: 7 c. Wk/Yr: 52
22. Maximum % Operation By Season N/A a. DJF b. MAM c. JJA d. SON

23. Raw Material And/Or Fuel For 13 Above.	24. Input RATE MAX		25. Units (Lb.) (ADT)	26. Fuel HHV (Btu/Lb.) or if Raw Material (Lb./ADT)
	Hr	Day		
Lime Mud (BDF)	29,170		lb	22

27. Green Liquor Sulfidity %:
28. Lb. Black Liquor Solids/ADT Pulp: 4400

29. Sources With Common Stack: N/A

30. Stack or Vent No.:	31. Stack or Vent I.D. No. on Diagram: Vent 08-3

32. Bldg. Ht. (Ft.): 151	33. Stack Ht. (Ft.): 96	34. Exit Diameter (Ft.) 4
35. Exit Temp. (°F): 160	36. Water Vapor (% v/v): 24	37. Actual Flow (CFM): 23,000
38. Exit Velocity (FPS): 25	39. Standard Flow Rate (DSCFM): 12,500	40. Oxygen (% v/v): 5 CO_2 (% v/v): 18

41. Allowable TRS Emissions N/A		42. ~~Max~~ 24-Hr Avg. TRS Emissions Estimate		43. Basis For Emissions In 42:
a. ppm	b. Lb./Hr.	a. ppm	b. Lb./Hr.	☒ Estimate
		58	11	☐ Sampling
44. Allowable SO_2 Emissions N/A		45. ~~Max~~ 24-Hr Avg. SO_2 Emissions Estimate		46. Basis For Emissions In 45:
a. Lb./10^6Btu	b. Lb./Hr.	a. Lb./10^6Btu	b. Lb./Hr.	☒ Estimate
		0.055	2.8	☐ Sampling

47. Source Of TRS Emissions Estimate: See attachment to cover letter

48. Source Of SO_2 Emissions Estimate: AP-42/0.3 lbs/ADT

49. Is This Source Equipped With A TRS Continuous Monitor?

☒ No ☐ DuPont

☐ Barton ☐ Other ____________

50. Has This Source Been Sampled For TRS?

☒ No ☐ Barton

☐ Method 16 ☐ DuPont

☐ Method 16A ☐ Other ____________

51. Is This Source Connected To A TRS Collection Or Control System?

☒ No ☐ Yes, Describe Fully:

52. Date: 84 Yr. 3 Mo. 27 Day

STATE OF FLORIDA
DEPARTMENT OF ENVIRONMENTAL REGULATION
TRS INVENTORY FORM

1. Firm: The Buckeye Cellulose Corporation
2. Facility: Foley
3. Facility Address: Rt. 3, Box 260
4. City: Perry
5. County: Taylor
6. Zip: 32347
7. Contact Person: J. H. Millican
8. Contact Address: Rt. 3, Box 260
9. City: Perry
10. Zip: 32347
11. Phone: (904) 584-0347
12. UTM Coordinates a. Zone: 17 b. East: 256,740 c. North: 3,329,700
13. Source: #2 Lime Kiln
14. DER Permit: No. A062-38423 Exp. Date: 2/18/86
15. Initial Construction: Mo. Yr. 1957
16. Major Modification to Permitted Source: Mo. Yr.
17. Maximum Capacity Of The Facility (ADT): 1983 Average 1329 T/D

18. If The Source Is A Recovery Boiler
a. Mfg.:
b. Non-DCE: ☐ Yes ☐ No
c. ☐ Straight Kraft ☐ Cross Recovery
d. 2-Stage Black Liquor Ox. (If DCE Furnace): ☐ Yes ☐ No

Other TRS Controls:

e. Membrane Or Welded Wall Construction: ☐ Yes ☐ No
f. Emission Control Designed Air System: ☐ Yes ☐ No
g. Wet Bottom ESP: ☐ Yes ☐ No

19. If The Source Is A Lime Kiln a. Length: 175' b. Diameter: 11' x 10'
c. Type Of Mud Filter: Centrifuge

20. If The Source Is A Digester System, No. of Digesters:
21. Maximum Operating Times a. Hr/Day: 24 b. Day/Wk: 7 c. Wk/Yr: 52
22. Maximum % Operation By Season N/A a. DJF b. MAM c. JJA d. SON

23. Raw Material And/Or Fuel For 13 Above.	24. Input RATE MAX Hr	24. Input RATE MAX Day	25. Units (Lb.) (ADT)	26. Fuel HHV (Btu/Lb.) or if Raw Material (Lb./ADT)
Lime Mud (BDF)	32,660		lb	2.5

27. Green Liquor Sulfidity %:
28. Lb. Black Liquor Solids/ADT Pulp: 4400

29. Sources With Common Stack: N/A

30. Stack or Vent No.:	31. Stack or Vent I.D. No. on Diagram: Vent 08-2

32. Bldg. Ht. (Ft.): 151	33. Stack Ht. (Ft.): 96	34. Exit Diameter (Ft.) 4
35. Exit Temp. (°F): 175	36. Water Vapor (% v/v): 40	37. Actual Flow (CFM): 26,000
38. Exit Velocity (FPS): 38	39. Standard Flow Rate (DSCFM): 12,500	40. Oxygen (% v/v): 5 CO_2 (% v/v): 18

41. Allowable TRS Emissions N/A		42. ~~Maxx~~ 24-Hr Avg. TRS Emissions Estimate		43. Basis For Emissions In 42:
a. ppm	b. Lb./Hr.	a. ppm	b. Lb./Hr.	☒ Estimate
		81	16	☐ Sampling
44. Allowable SO_2 Emissions N/A		45. ~~Maxx~~ 24-Hr Avg. SO_2 Emissions Estimate		46. Basis For Emissions In 45:
a. Lb./10^6Btu	b. Lb./Hr.	a. Lb./10^6Btu	b. Lb./Hr.	☒ Estimate
		0.073	4.2	☐ Sampling

47. Source Of TRS Emissions Estimate: See attachment to cover letter

48. Source Of SO_2 Emissions Estimate: AP-42

49. Is This Source Equipped With A TRS Continuous Monitor?

☒ No
☐ DuPont
☐ Barton
☐ Other ____________

50. Has This Source Been Sampled For TRS?

☒ No
☐ Method 16
☐ Method 16A
☐ Barton
☐ DuPont
☐ Other ____________

51. Is This Source Connected To A TRS Collection Or Control System?

☒ No
☐ Yes, Describe Fully:

52. Date: 84 Yr. 3 Mo. 27 Day

/

STATE OF FLORIDA
DEPARTMENT OF ENVIRONMENTAL REGULATION
TRS INVENTORY FORM

1. Firm: The Buckeye Cellulose Corporation | 2. Facility: Foley

3. Facility Address: Rt. 3, Box 260

4. City: Perry | 5. County: Taylor | 6. Zip: 32347

7. Contact Person: J. H. Millican | 8. Contact Address: Rt. 3, Box 260

9. City: Perry | 10. Zip: 32347 | 11. Phone: (904) 584-0347

12. UTM Coordinates | a. Zone: 17 | b. East: 256,740 | c. North: 3,328,700

13. Source: #3 Lime Kiln | 14. DER Permit: No. A062-46530 Exp. Date: 11/4/86

15. Initial Construction: Mo. Yr. 1964 | 16. Major Modification to Permitted Source: Mo. Yr.

17. ~~Maximum~~ Capacity Of The Facility (ADT): 1983 Average 1329 T/D

18. If The Source Is A Recovery Boiler

a. Mfg.: | b. Non-DCE: ☐ Yes ☐ No

c. ☐ Straight Kraft ☐ Cross Recovery

d. 2-Stage Black Liquor Ox. (If DCE Furnace): ☐ Yes ☐ No

Other TRS Controls:

e. Membrane Or Welded Wall Construction: ☐ Yes ☐ No

f. Emission Control Designed Air System: ☐ Yes ☐ No

g. Wet Bottom ESP: ☐ Yes ☐ No

19. If The Source Is A Lime Kiln | a. Length: 181' | b. Diameter: 11' x 10'

c. Type Of Mud Filter: Centrifuge

20. If The Source Is A Digester System, No. of Digesters:

21. Maximum Operating Times | a. Hr/Day: 24 | b. Day/Wk: 7 | c. Wk/Yr: 52

22. Maximum % Operation By Season N/A | a. DJF | b. MAM | c. JJA | d. SON

23. Raw Material And/Or Fuel For 13 Above.	24. Input RATE MAX		25. Units (Lb.) (ADT)	26. Fuel HHV (Btu/Lb.) or if Raw Material (Lb./ADT)
	Hr	Day		
Lime Mud (BDF)	35,000		lb	26

27. Green Liquor Sulfidity %: | 28. Lb. Black Liquor Solids/ADT Pulp: 4400

29. Sources With Common Stack: N/A

30. Stack or Vent No.:	31. Stack or Vent I.D. No. on Diagram: Vent 08-1

32. Bldg. Ht. (Ft.): 151	33. Stack Ht. (Ft.): 96	34. Exit Diameter (Ft.): 4
35. Exit Temp. (°F): 165	36. Water Vapor (% v/v): 35 -	37. Actual Flow (CFM): 27,000
38. Exit Velocity (FPS): 34	39. Standard Flow Rate (DSCFM): 14,000	40. Oxygen (% v/v): 5 CO_2 (% v/v): 18

41. Allowable TRS Emissions N/A		42. ~~Max~~ 24-Hr Avg. TRS Emissions Estimate		43. Basis For Emissions In 42:
a. ppm	b. Lb./Hr.	a. ppm	b. Lb./Hr.	☒ Estimate
		87	17	☐ Sampling
44. Allowable SO_2 Emissions N/A		45. ~~Max~~ 24-Hr Avg. SO_2 Emissions Estimate		46. Basis For Emissions In 45:
a. Lb./10^6Btu	b. Lb./Hr.	a. Lb./10^6Btu	b. Lb./Hr.	☒ Estimate
		0.076	4.5	☐ Sampling

47. Source Of TRS Emissions Estimate: See attachment to cover letter

48. Source Of SO_2 Emissions Estimate: AP-42

49. Is This Source Equipped With A TRS Continuous Monitor?

☒ No ☐ DuPont

☐ Barton ☐ Other ____________

50. Has This Source Been Sampled For TRS?

☒ No ☐ Barton

☐ Method 16 ☐ DuPont

☐ Method 16A ☐ Other ____________

51. Is This Source Connected To A TRS Collection Or Control System?

☒ No ☐ Yes, Describe Fully:

52. Date: 84 Yr. 3 Mo. 27 Day

Reference 2

WORKBOOK ON ESTIMATION OF EMISSIONS AND DISPERSION MODELING FOR FUGITIVE PARTICULATE SOURCES

Document P-A857

September 1981

Prepared for

UTILITY AIR REGULATORY GROUP
1919 Pennsylvania Avenue N.W.
Washington, D.C. 20036

By

Indur M. Goklany
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David Heinold
Roberta Lewis

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TABLE 3.2.17-2

TRANSFER POINTS:

EFFICIENCIES OF CONTROL TECHNIQUES AND METHODS

Technique	Control Efficiency	Comments	Reference
Enclosure	90% 70-99%*		Szabo 1978 EPA 1978a
Enclosure with control device	99(+)%	See Appendix A for calculating controlled emissions.	EPA 1978a
Spraying	70-95%		EPA 1978a
Telescopic chutes	75%		EPA 1978a

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*Lower value uses "weathertight" system; higher value utilizes dust collection system.

Reference 3

ncasi technical bulletin

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

INFORMATION ON THE SULFUR CONTENT OF BARK AND ITS CONTRIBUTION TO SO_2 EMISSIONS WHEN BURNED AS A FUEL

ATMOSPHERIC QUALITY IMPROVEMENT

TECHNICAL BULLETIN NO. 96

AUGUST, 1978

ncasi

NATIONAL COUNCIL OF THE PAPER INDUSTRY FOR AIR AND STREAM IMPROVEMENT, INC.
260 MADISON AVE. NEW YORK, N.Y. 10016 (212) 532-9000

Russell O. Blosser
Technical Director
(212) 532-9001

ATMOSPHERIC QUALITY IMPROVEMENT
TECHNICAL BULLETIN NO. 96

August 18, 1978

INFORMATION ON THE SULFUR CONTENT OF BARK AND ITS CONTRIBUTION TO SO_2 EMISSIONS WHEN BURNED AS A FUEL

There has been conjecture about the SO_2 emissions resulting from the burning of wood residues since current New Source Performance Standards for large power boilers permit the use of the Btu in wood residues in calculating allowable SO_2 emission rates. The concern that has arisen is based on available knowledge of the sulfur content of bark and wood residues which, if stoichiometrically converted to SO_2, would account for SO_2 levels of about 130 ppm or greater in the flue gas, depending on the initial sulfur content of the wood residue. Unfortunately, this line of reasoning is apparently the background for selection of an emission factor of 0.375 lbs SO_2 per million Btu of wood residue fired that is included in EPA resource documents which are used extensively for estimating and decision-making in the regulatory process.

The attached technical bulletin describes a field study carried out to determine the amount of SO_2 generated when burning representative bark. The work was carried out by H. Scott Oglesby, Investigative Programs Manager, Southern Regional Center, assisted by William E. Green and David B. Newport, at that Center.

The study involved a sulfur fuel balance around the combustion device by determining sulfur content of the bark fed, and sulfur leaving the boiler in solid and gaseous forms, namely ash, fly ash, and SO_2. The study showed that just over 5% of the sulfur contained in the bark was emitted as SO_2 which amounted to 0.0001 to 0.002 lbs SO_2 per million Btu in the bark fed. The remainder of the sulfur was accounted for in the ash combustion products. The findings support the conclusion that the sulfur content of wood is not stoichiometrically converted to SO_2, probably because it is present mainly in sulfate form.

Your questions and comments on the contents of this technical bulletin are solicited.

Yours very truly,

Russell O. Blosser
Technical Director

ROB
mfs
Attachment

TABLE OF CONTENTS

INFORMATION ON THE SULFUR CONTENT OF BARK AND ITS CONTRIBUTION TO SO_2 EMISSIONS WHEN BURNED AS A FUEL

I INTRODUCTION

In order for the pulp and paper industry to meet their commitment to (a) incrementally decrease purchased energy consumption over the next several years or (b) become energy sufficient, increasing emphasis will be placed on the utilization of bark and wood residues as a primary fuel. Although it is logical to expect that appropriate concessions might be offered relative to allowable emission levels in order to encourage the use of these energy resources, current indications are that increasingly more attention will focus on these sources insofar as regulatory action is concerned. This bulletin addresses one of the issues which has already been raised regarding the emissions from burning wood residues, namely their SO_2 contribution as a result of their sulfur content.

A. Background

Recently there has been conjecture in EPA about the SO_2 derived from the sulfur content contained in typical tree barks. This question arose due to the recent amendments to Subpart D, Standards of Performance for New Stationary Sources (40 CFR 60). Essentially this regulation as amended by the EPA November 22, 1976, (41 FR 51397), permits the use of the Btu content of wood in calculating allowable SO_2 emissions from combination fuel-fired boilers. The issue has been raised as to the levels of sulfur contained in barks, and the subsequent emission levels of SO_2 which would be associated with the combustion of these fuels. Subsequently, a project was included in the NCASI 1978 technical studies program to address these issues.

B. Published Information

In contrast to the extensive literature available on the chemistry of wood, relatively little is published on the chemistry of bark. Nevertheless, limited information was located from seven sources, suggesting that the sulfur content of bark may vary from 0 to 0.2 percent on a dry weight basis. However, these references were for the most part not specific as to the specie of bark involved. The EPA's emission factors for wood waste-fired boilers are based on the same range of 0 to 0.2 percent sulfur content, where an arbitrary average of 0.1 percent is selected, resulting in an emission factor of 0.375 pounds SO_2 per million Btu (86 percent stoichiometric conversion). These values suggest gaseous concentrations of SO_2 on the order of 130 ppm while the limited data available indicated measured concentrations approaching one tenth of these levels.

The investigative efforts described in this bulletin involved emission measurements, laboratory analysis, and data compilation associated during the operation of four different bark boilers.

II OBJECTIVES

Consistent with the issues which have been raised; i.e., the SO_2 emission levels associated with the combustion of bark and wood residues in dedicated boilers or combination fuel-fired boilers, a straightforward investigation was undertaken. Accordingly, the objectives of this investigation were to, (a) determine what was known about the sulfur content of bark (and wood residues) based on published information and (b) perform field testing at selected sites to determine the fate of sulfur contained in bark and wood residue type fuels when fired in boilers burning bark or sulfurless fossil fuel. During these investigations, an attempt was made to account for all of the sulfur, to the extent possible, by developing a sulfur balance around the boiler system.

III INVESTIGATIVE PROGRAM AND PROCEDURES

A. Scope of Work

In order to properly address the pertinent issues, the following elements were considered a minimum to support this investigative effort:

(1) Compile a summary of the available information on the sulfur content of bark and wood.

(2) Perform field testing at selected sites to determine the fate of sulfur contained in bark and wood residue type fuels when fired in dedicated boilers. During these investigations, an attempt was made to account for all of the sulfur, to the extent possible, by obtaining material samples and measurements as follows:

   (a) The SO_2 emission levels in boiler stack gases were continuously monitored for sufficient duration, during a stable operating period.

   (b) Samples of particulates being emitted during these test periods were collected and analyzed for sulfate content. Also, samples were collected from the particulate control device for the same purpose.

(c) Samples from the boiler ash hopper were also collected and analyzed for sulfates.

(d) A composite sample of the bark being fired was collected and analyzed for total sulfur content.

(e) The pertinent boiler operating information was recorded during the test periods at each site.

(3) The results of these analyses were used to develop a sulfur distribution profile for the specific fuel being burned at each test site.

(4) It was also anticipated that in projecting the fate of the available sulfur, additional insight would be gained relative to any SO_2 - particulate interactions.

B. Summary of Published Information Relative to Sulfur Content of Bark and Wood Waste

(1) Sulfur Content of Bark - In contrast to the extensive technical literature available on the chemistry of wood, relatively little exists on the chemistry of bark. Nevertheless, limited information was located from several sources (1, 2, 3, 4, 5, 6, 7), suggesting that the sulfur content of bark may vary from 0 to 0.2 percent on a dry weight basis. However, these references were for the most part not specific as to the specie of wood involved.

Based on studies by the Institute of Food and Agricultural Sciences, University of Florida (1), to determine the components of forest fire smoke, sulfur oxides have not yet been detected in forest fire smoke, and only organic soils contain more than a negligible amount. The EPA's Compilation of Air Pollutant Emission Factors (2) states that bark contains less carbon and nitrogen than wood, but more sulfur, with the amount quoted as ranging from 0 to 0.075 percent by weight. Another EPA reference source (3) quotes the amount of sulfur in bark to range from 0.05 to 0.075 percent by weight.

Ultimate analysis of four Douglas Fir barks used in pyrolysis development work performed by Boucher, et al. (4), suggested sulfur content to range from 0.04 to 0.16 percent by dry weight. A summary contained in yet another reference (5) indicates the sulfur content for a variety of barks to range from a trace to 0.1 percent by weight.

The EPA's emission factor for wood waste-fired boilers, contained in Environmental Pollution Control, Pulp and Paper Industry, Part I, Air (6), is based on a range of 0 to 0.2 percent sulfur content, where an arbitrary average of 0.1 percent is selected. The value contained in this reference projects an emission level of 0.375 pounds SO_2 per million Btu (86 percent stoichiometric conversion of sulfur content). These values would further suggest gaseous concentrations of SO_2 on the order of 130 ppm, while the limited data available from the literature (7) indicate measured concentrations approaching about one tenth of these levels.

(2) Other Physical and Chemical Properties of Bark - There are other important properties of bark which should be considered in an investigation addressing the potential SO_2 emissions from the combustion of bark. One of these is the ash content of bark. Published data (11) show the ash content of bark to vary from 0.5 to 10.0 percent, with the greater portion of these values falling between 2.0 and 6.0 percent. However, the actual values encountered in the field will be somewhat higher due to varying wood composition, and the amount of dirt carried with the bark resulting from its contact with soil.

A second consideration is bark ash composition. Bark ashes are mainly composed of inorganic oxides, carbonates, and sulfates. The oxides of silica and calcium usually account for more than half of the ash content while oxides of iron, titanium, aluminum, magnesium, manganese, and carbonates of calcium are also present. The earlier cited reference data indicated ash sulfate (as SO_3) content ranging from 1.4 to 7.4 percent.

The properties of bark which have been discussed in this section will later be shown to have a substantial influence on the distribution of sulfur compounds in combustion products resulting from the burning of bark.

C. Need for Development of Sulfur Balance Around Boiler Systems in This Study

During the initial stages of this investigation, preliminary testing to determine SO_2 levels in flue gases resulted in much lower values than anticipated, based on the fuel sulfur content. Previous investigative work conducted by the NCASI (13) revealed that the ash products of combustion do indeed react with SO_2 generated during combustion. It is also not known how much of the sulfur content of the fuel was originally in a sulfate form and not available for SO_2 generation. Consequently, in order to enhance the validity of this investigative effort, it was deemed imperative to develop a sulfur balance around the boiler system studied at each site, by including the following elements:

(1) The SO_2 emission levels in boiler stack gases were continuously monitored for sufficient duration during a stable operating period.

(2) Samples of particulates emitted during these test periods were collected for analysis of sulfate content. Also, samples were collected from the particulate control device for the same purpose.

(3) Samples from the boiler ash hopper were also collected and analyzed for sulfates.

(4) A composite sample of the bark fired was collected and analyzed for total sulfur content.

(5) The pertinent boiler operating information was recorded during the test periods at each site.

D. Testing and Analytical Procedures Utilized

The testing and analytical procedures which were utilized to develop the required data will be summarized in this section.

(1) Stack Gas SO_2 Determinations - Testing was performed on boiler flue gases using a Barton coulometric titrator to determine SO_2 concentrations. The decision to thermally oxidize the gas sample prior to analysis with the Barton titrator was predicated on the possibility that organic constituents contained in the flue gases might generate a bromine demand, thus resulting in an erroneously high indication of SO_2 concentration. The tests were conducted for a minimum duration of four (4) hours and were performed in accordance with the equipment and procedures outlined in NCASI AQITB No. 89 (8).

(2) Analysis of Sulfur in Bark and Ash Samples - The sulfur analysis on all samples obtained during this investigation was performed in duplicate by an independent laboratory, which used a Leco DB-64 digital titrator for this purpose. The DB-64 Sulfur Titrator automates the familiar iodate titration used in the determination of sulfur by the combustion method, and is further described in Leco Bulletin No. 200-734 (9).

(3) Analysis of Sulfate in Ash Samples - In addition to having all ash samples analyzed by the Leco furnace method for sulfur, sulfate determinations were also performed in the NCASI Southern Regional laboratory using the gravimetric method (barium chloride precipitation) (10), as specified in Standard Methods.

In utilizing this procedure on the bark samples, the material was "ashed" in the laboratory. This step also provided information on the ash content for each of the bark samples.

IV RESULTS

The investigative efforts covered in this report resulted from the field testing, laboratory analysis, and data compilation associated with the operation of four different bark boilers.

A. Sulfur Content of Bark

The bark fuel supply at each of the mill sites consisted of a mixture from several sources such as that resulting from debarking of roundwood stored at the mill, and purchased bark from sawmills and other sources. Although the dominant specie was pine bark in all cases, there were substantial amounts of hardwood bark in the mixture as well. These barks were derived from wood harvested from the lower quadrant of the Southeastern United States (Alabama, Florida, and Georgia), the area essentially being a square of 400 miles (160,000 square miles).

Sulfur content of composite bark samples taken from each of the four study sites was 0.068, 0.010, 0.060, and 0.134 percent on a dry weight basis. These values are well within the ranges which have been reported in the literature surveyed.

B. Sulfur Contained in Ash Materials of Combustion

At each study site ash samples were taken at the points where these materials are purged from the system; e.g., boiler grate ash, primary collector hopper fly ash and fly ash discharged with flue gases. Analysis of these samples showed that 90 percent or more of the feed fuel sulfur content is contained in (or on) these ash materials, the actual values being 99.3, 90.4, 95.1, and 93.5 percent. In the case of the higher value (99.3 percent), a large portion of the primary collector hopper fly ash was reinjected into the boiler. This provided a finer ash with longer retention times to react with SO_2, consequently resulting in almost complete adsorption of SO_2 gases generated during combustion.

In the case of the lower value (90.4 percent), analysis indicates that the flue gas fly ash contained the lowest amount (31.0 percent) of total sulfur and the grate ash contained the highest (55.6 percent) amount, suggesting that the bark size or some other physical factor is responsible for this distribution shift. Since this source was a gas and bark-fired boiler, the NO_x emission levels were high, suggesting a high combustion temperature which inhibits SO_3 formation and the subsequent sulfate specie formation.

C. Sulfur Emitted as SO_2 in Stack Gases

As indicated in the above discussion, for the sources sampled, in the most extreme case, less than 10 percent of the total sulfur content of bark fuel was released as SO_2 via the stack gas. These values for the four sources concerned were 0.7, 9.6, 5.9, and 6.5 percent. The higher percentage value of 9.6 occurs at the source with lowest fuel sulfur content (0.01 percent), and the probable causes for this result are discussed in the previous section.

A summary of all the pertinent data relative to this investigation is contained in Table 1.

V DISCUSSION

A. Chemical and Physical Analysis of Bark and Wood Waste

The properties of wood residues and bark fuels can vary so greatly that a standard specification is not possible. The differences should be recognized and accounted for in the engineering and operation of wood-fueled systems. Table 2 summarizes the analyses for several properties of selected wood species.

The ash content of wood residues is generally low, but still is significant when large quantities are burned. The ash content of bark usually is greater than that of wood because handling and harvesting of logs frequently causes dirt and sand to cling to the bark. Saltwater transport and storage of logs also can add to the ash content by deposition of sea salt in the wood or bark.

B. Review of the Combustion Mechanism

The basic process of burning wood-refuse fuels requires the evaporation of moisture, the distillation and combustion of volatile components, and the combustion of the remaining carbon materials. These three steps are accomplished either separately or simultaneously depending on the type of equipment that is selected for the particular installation. Boiler emissions are affected by the size distribution of fuel, firing method, reinjection of fly carbon (ash), furnace vertical velocity and residence time, and overfire air.

C. Factors Affecting Sulfur Distribution in Combustion Products

The issues which have been raised generate further interest in the sulfur content of wood residues and in the distribution of the sulfur in the products of combustion. Earlier work by Kaiser (12) discusses the apparent effect of alkaline components of ash in uniting with sulfur oxides, and certainly the presence of sulfate sulfur in ash products of wood waste combustion has been established in the references quoted in this report, as well as that determined in our own laboratory.

The variables which affect the sulfur distribution are closely related to those cited in the previous section which also influence overall emission levels, i.e., size distribution of fuel, reinjection of fly ash, residence time and velocity, and combustion temperature. Also, the fuel composition such as sulfur content (amount as free sulfur or sulfate) and ash content (and composition) may exert an effect as well.

TABLE 1 SULFUR DISTRIBUTION IN DEDICATED BARK BOILER SYSTEMS

MILL NO.	BARK FEED Lbs/Hr Dry Wt.	PERCENT ASH IN BARK	SULFUR IN BARK		SULFUR RELEASED TO ATM. VIA STACK		HEAT INPUT MM Btu/Hr	LBS SO_2 Per MMBtu	PERCENT OF TOTAL		
			Percent	Lbs/Hr	Percent of Total	Lbs/Hr			Contained in Fly Ash	Contained in Hopper Ash	Discharged W/Grate Ash
1	28,090	1.3	0.068	19.1	0.7	0.134	257.6	0.104×10^{-2}	84.2	1.8	13.3
2	15,275	1.3	0.010	1.7	9.6	0.163	156.0	0.208×10^{-2}	31.0	3.8	55.6
3	18,000	2.5	0.060	10.4	5.9	0.614	144.8	0.84×10^{-2}	86.8	5.0	4.0
4	30,600	3.3	0.134	40.8	6.5	2.65	247.5	2.142×10^{-2}	---- 88.4 ----- (By Difference)		5.1

TABLE 2 ANALYSES OF SOME SELECTED WOOD REFUSE BURNED AS FUEL[a], (11)

ITEM	JACK PINE	BIRCH	MAPLE	WESTERN HEMLOCK
Proximate analysis, percent				
Ash	2.1	2.0	4.3	2.5
Volatile	74.3	78.5	76.1	72.0
Fixed carbon	23.6	19.2	19.6	25.5
Ultimate analysis, percent				
Carbon	53.4	57.4	50.4	53.6
Hydrogen	5.9	6.7	5.9	5.8
Sulfur	0	0	0	0
Nitrogen	0.1	0.3	0.5	0.2
Ash	2.0	1.8	4.1	2.5
Oxygen (by difference)	38.6	33.8	39.1	37.9
Heat value, Btu/lb (bone dry)	8930	8870	8190	8885
Ash analysis, ppm				
SiO_2	16.0	3.0	9.9	10.0
Al_2O_3	6.3	0	3.8	2.1
Fe_2O_3	5.0	2.9	1.7	1.3
CaO	51.6	58.2	55.5	53.6
$CaCO_3$	4.9	13.0	1.4	9.7
MgO	5.5	4.2	19.4	13.1
MnO	1.6	4.6	1.0	1.2
P_2O_5	2.8	2.9	1.1	2.1
K_2O	4.1	6.6	5.8	4.6
Mn_2O	3.1	1.3	2.2	1.1
TiO_2	0.2	Trace	Trace	Trace
SO_3	2.6	3.2	1.4	1.4
Fusion point of ash, F				
Initial	2450	2710	2650	2760
Softening	2750	2720	2820	2770
Fluid	2760	2730	2830	2780
Weight, lb/ft^3 (bone dry)	29	37-44	31-42	26-29

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[a] Average moisture of about 50 percent as received at firing equipment. Adapted from information compiled by the Steam Power Committee of the Canadian Pulp and Paper Association.

D. Factors Contributing to SO_2 Emission Levels from Combustion of Bark

The SO_2 emission levels from bark and wood waste boilers have been shown to be extremely low (10 ppm or less) because of two major reasons, (a) the initial sulfur content of fuel is extremely low (less than 0.2 percent) and (b) most of the sulfur (90 percent or more) is combined with the ash products of combustion.

VI CONCLUSIONS

(1) The sulfur content of the barks fired ranged from 0.01 to 0.134 percent by weight on a dry basis. This resulted in a sulfur input to the boilers ranging from 1.7 to 40.8 lbs per hour.

(2) The percentage of total sulfur fed which was released to the atmosphere via the stack as SO_2 ranged from 0.7 to 9.6 percent. Sulfur dioxide concentrations ranged from <1 to 10 ppm or 0.01×10^{-2} to 2.14×10^{-2} lbs of SO_2 per 10^6 Btu.

(3) The total sulfur accounted for, based on calculations from analysis and material flow ranged from 86 to 113 percent of that contained in the bark feed.

(4) In the case of the sources investigated only 10 percent or less with an average of just over 5 percent of the fuel sulfur content was emitted as SO_2. This fact is further substantiated by the sulfate content of the ash products of combustion, which are discharged at various points in the operation. Table 1 contains a summary of all pertinent data, and as indicated, all of the sulfur contained in the fuel is accounted for as SO_2, or as sulfate in ash released from the (a) boiler grate, (b) mechanical collector hoppers, and (c) the fly ash discharged with the exit gas.

(5) The reaction of sulfur, oxygen, and ash minerals to produce sulfates in the combustion process is responsible for preventing the full conversion of the bark and wood waste sulfur to SO_2 in the flue gases. Some of the sulfur may be in sulfate form in the bark and wood waste before combustion. That SO_2-SO_3 will unite with metal oxides in the gas phase is well known from the use of pulverized dolomite and other minerals to control sulfur oxide emissions from oil-fired power boilers. Sulfates of iron, magnesium, sodium, and calcium etc., are produced in the gas phase of such boilers.

(6) Based on work performed by others (12), it may be inferred that the sulfur content of boiler fly ash increases with time of contact with the flue gases, and possibly with the fineness of dust particles. Also, the alkali content of the fly ash is highest in the emitted fine ash. The greater time of contact and higher alkali content of the finer fly ash may have a combined effect in fixing sulfur, such as by reacting with SO_2 and SO_3 in the combustion gases.

VII LITERATURE REFERENCES

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Reference 4

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Extra

ncasi technical bulletin

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

A STUDY OF NITROGEN OXIDES EMISSIONS FROM LIME KILNS

ATMOSPHERIC QUALITY IMPROVEMENT
TECHNICAL BULLETIN No. 107

APRIL 1980

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ATMOSPHERIC QUALITY IMPROVEMENT
TECHNICAL BULLETIN NO. 107

April 28, 1980

A STUDY OF NITROGEN OXIDES EMISSIONS FROM LIME KILNS

The source emission estimates required for completion of the ambient air quality modelling requirements in satisfying the provisions of EPA's Prevention of Significant Deterioration regulations for new construction have identified the need for a reliable information base for estimating NO_x emissions from combustion sources in the forest products industry. During the past year an extensive field measurement program was initiated to generate information on NO_x emissions from wood residue-fired boilers, kraft recovery furnaces and lime kilns.

The attached technical bulletin reports on the findings of the first phase of a study of NO_x emissions from lime kilns. The field work was conducted under the direction of Kenneth T. Hood and Reid A. Miner, Research Engineers at the West Coast and Southern Regional Centers respectively, assisted by Thomas F. Briody, Russell J. Korvola and Michael E. Franklin, and C. M. Tipton, I. D. Lynch, D. B. Davenport and H. S. Oglesby at these centers. Mr. Hood assembled the sampling apparatus used in the study and assembled the report from which the technical bulletin was prepared.

The study showed that the three-hour mean NO_x emission rates from the five lime kilns studied ranged from 0.07 to 1.13 lbs NO_x per million Btu fired. The NO_x emission rates observed for lime kilns were highly variable and at one gas-fired kiln were found to be related to combustion zone temperature. Combustion zone temperature was measured at only one test site. In this case combustion zone temperatures of about 1850°C were required for minimum NO_x emissions.

Combustion zone temperature alone does not appear to be the sole reason for the range of NO_x emission factors observed, based on the data from one kiln. The temperature-NO_x emission relationships at this kiln suggest that temperatures unsatisfactory for producing CaO would not have been maintained in those two kilns producing NO_x emissions of about 0.2 lbs per million Btu. Further study is required to better understand the relationships of combustion zone temperature and NO_x emission potential. Planning for such work is underway and will be initiated soon.

This technical bulletin is the third of three reports on NO_x emissions from combustion sources in the forest products industry. The first, Atmospheric Quality Improvement Technical Bulletin No. 102, entitled "A Study of Nitrogen Oxides Emissions from Wood Residue Boilers," was distributed earlier. The second, Atmospheric Quality Improvement Technical Bulletin No. 105, entitled "A Study of Nitrogen Oxides Emissions from Kraft Recovery Furnaces" was also distributed earlier. Additional field studies are now underway to clarify kraft recovery furnace size-NO_x emission rates indicated for large furnaces in the earlier study.

Your questions and comments on this technical bulletin should be addressed to Mr. Kenneth T. Hood at the West Coast Regional Center, Mr. Reid Miner at the Southern Regional Center, or to me at the address above.

Yours very truly,

Russell O. Blosser
Technical Director

ROB:gs
Attach.

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A STUDY OF NITROGEN OXIDES EMISSIONS FROM LIME KILNS

I INTRODUCTION

The United States Environmental Protection Agency has designated nitrogen dioxide (NO_2) as a criteria pollutant. Reliable estimates of oxides of nitrogen (NOx) emissions are also required for carrying out the modelling of combustion source emissions necessary for satisfying Prevention of Significant Deterioration regulations. Since available information is limited relative to the potential for emission of NOx from combustion processes associated with the manufacture of pulp and paper and power generation from boilers fired on wood residue, the establishment of a larger data base is desirable.

The NCASI is currently conducting a national program in cooperation with individual member mills designed to provide information on oxides of nitrogen emissions from "kraft recovery units" (defined as both the recovery furnace and boiler sections) (115), lime kilns and wood residue-fired power boilers (114). This particular bulletin will discuss the emission rate of NOx from kraft mill lime kilns. The lime kiln sites sampled in the Northwest United States included two kilns firing oil and one kiln firing oil and natural gas during separate sampling intervals. Two test sites located in the Southeast United States represented one oil fired kiln and one natural gas fired kiln.

II BACKGROUND AND LITERATURE REVIEW

A comprehensive literature search representative of recent publications associated with NOx formation kinetic theory, measurement techniques, field sampling methodology, source control strategies, previously reported field results and the effects of these gases to the ambient was performed and is presented in NCASI Atmospheric Quality Improvement Technical Bulletin No. 102 (114) entitled, "A Study of Nitrogen Oxides Emissions from Wood Residue Boilers." The entire listing of literature references from the wood residue boiler bulletin are reproduced in the bibliography of this report for convenience.

Galeano and Leopold (43) reported on findings determined from EPA Method 7 oxides of nitrogen "grab sampling" conducted on a kraft mill lime kiln. The lime kiln was rated at 250 tons per day (assumed to be calcium oxide product) and operated at 23 percent excess air (approximately 3.9% oxygen in the flue gas). The combustion temperatures ranged between 2300°F to 2530°F as measured with a "Leeds and Northrup optical pyrometer" which "detected the hottest combustion zone temperatures". The NOx testing at this source was conducted both before and after a venturi scrubber.

The measurements were similar at each location and were found to average **188 ppm NOx** (157 to 213 ppm) and 200 ppm NOx (113 to 260 ppm) for the inlet and outlet of the scrubber, respectively.

Results from an unpublished mill report (124) indicated a range of roughly 50 to 100 ppm (0.15 to 0.35 pounds per million Btu) nitric oxide when adjusted to ten percent oxygen in the flue gas. These values were measured with a continuous chemiluminescence monitor during time intervals which approximated the normal range of the oil (No. 6) fired kiln's operating conditions. This included use of minimum primary air and the existing seven-hole burner tip. Abnormal kiln conditions such as a variety of primary and secondary air variations, high and low fuel firing levels, and use of a modified four-hole burner tip were also investigated to determine the influence on nitrogen oxide production. Varying these parameters produced either higher NOx emissions, in the case of alternate burner tips, or inconclusive results.

Based on the very limited oxides of nitrogen evaluations conducted previously on lime kiln oil and gas fired sources, there was evidence of significant variability in emission levels. As will be discussed, the use of optical and possibly radiation pyrometers to adjust combustion zone temperatures may offer, within the normal range of kiln operation, a potential NOx control mechanism. One such site study has been undertaken by NCASI personnel and is presented in this report. Future investigations into lime kiln NOx emissions will incorporate both optical and radiation pyrometers to measure flame temperature and determine the NOx emission level based on the mode of kiln operation.

III DESCRIPTION OF OXIDES OF NITROGEN MONITORING SYSTEM

A. General

The basic monitor was the Monitor Labs Nitrogen Oxides Analyzer Model 8440E. The unit was a gas phase device utilizing the chemiluminescence principle for continuous detection and reporting of Nitric Oxide (NO), Nitrogen Dioxide (NO_2), and Oxides of Nitrogen (NOx) on a ppm dry basis. The operation of the monitor was based on the chemiluminescence of an activated NO_2 species (NO_2^*) that was produced by a chemical reaction between ozone and NO (41).

The monitor was somewhat unique in that dual sub-atmospheric reaction cells (which resulted in minimal measurement error as described in recent investigations) (120,121), or detector systems were incorporated into the design with an independent cell for the measurement of NO and NOx. Thus, the data produced by the monitor was spontaneous and not averaged. Optical and electronic stability was insured through temperature controls and an optical chopper. An ISOFLO pneumatic system controls each gas stream's flow rate to the respective reaction cells. These flow controllers served to transport the gas sample through the reaction cells with the chemiluminescence emission from the reaction chambers halted and transmitted alternately to the photomultiplier tubes at the rate of 35 times per second by the optical chopper. A phase sensitive amplifier processed the photomultiplier signal which was then converted to a voltage output for recorder utilization.

The monitor was packaged as two separate modules connected electronically and physically with pneumatic flow lines. The Analyzer module consisted of the reaction cells and photomultiplier tube (PMT) assemblies, the ISOFLO flowrate control assembly, PMT power, signal processing electronics, the front panel readout display and recorder outputs. The Sample Conditioner module included the preliminary pneumatic network which employed a sample filter, sample and ozone scrubber, a reaction cell vacuum regulator, and vacuum pump. A schematic diagram of the two module monitor was presented in Figure 1 (57).

B. Principle of Operation of the Model 8440E NOx Monitor

The dual channel chemiluminescence analysis system included two detection assemblies, each of which employed a reaction cell, optical chopper, and a PMT unit. The reaction cell itself consisted of three functional subsystems. These subsystems corresponded to first, the concentric ozone and sample nozzles, second, the sub-atmospheric reaction chamber, and third, the exhaust ports. The operation of the monitor was dependent on the chemiluminescence of an activated molecular nitrogen dioxide species which was produced by the reaction between NO and O_3 in the evacuated reaction chamber (22). Gas containing the nitric oxide molecules entered the reaction chamber by way of a concentric nozzle while the ozone was directed to the reaction chamber via the center nozzle. A small portion of the NO molecules react with ozone to form the activated NO_2* species. A broad-band radiation, from 500 to 3000 nm with a maximum intensity at approximately 1100 nm, was emitted as activated NO_2* molecules decreased to a lower energy state (23). The manufacturer (57) indicated that the current produced by the photomultiplier tube was directly proportional to the intensity of the chemiluminescent emission.

The use of a MOLYCON (68) converter to chemically reduce the NO_2 fraction in the sample to NO was utilized in the monitor. This allowed a determination of the total oxides of nitrogen through a sample and detector system which was, except for the converter, identical to that used for the NO measurement. The NO_2 content was obtained by electronically subtracting the NO response from the total NOx response which represented the sum of the NO and NO_2 in the sampled gas.

C. Monitoring System Adaptation to Source NOx Measurements

The apparatus used for source NOx sampling is depicted in Figure 2. Several of the components noted as "optional" in the schematic were not found to be required for accurate sampling of

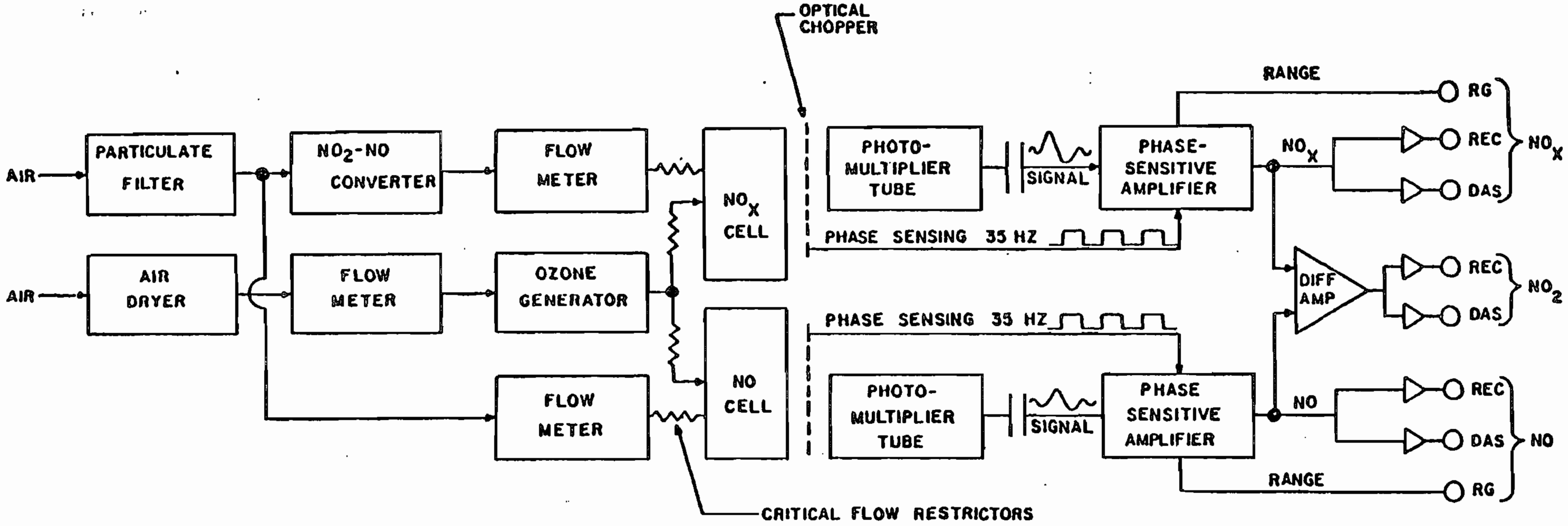

FIGURE 1. BLOCK DIAGRAM, DUAL CHANNEL NOx ANALYZER, MONITOR LABS INC. MODEL 8440E (57)

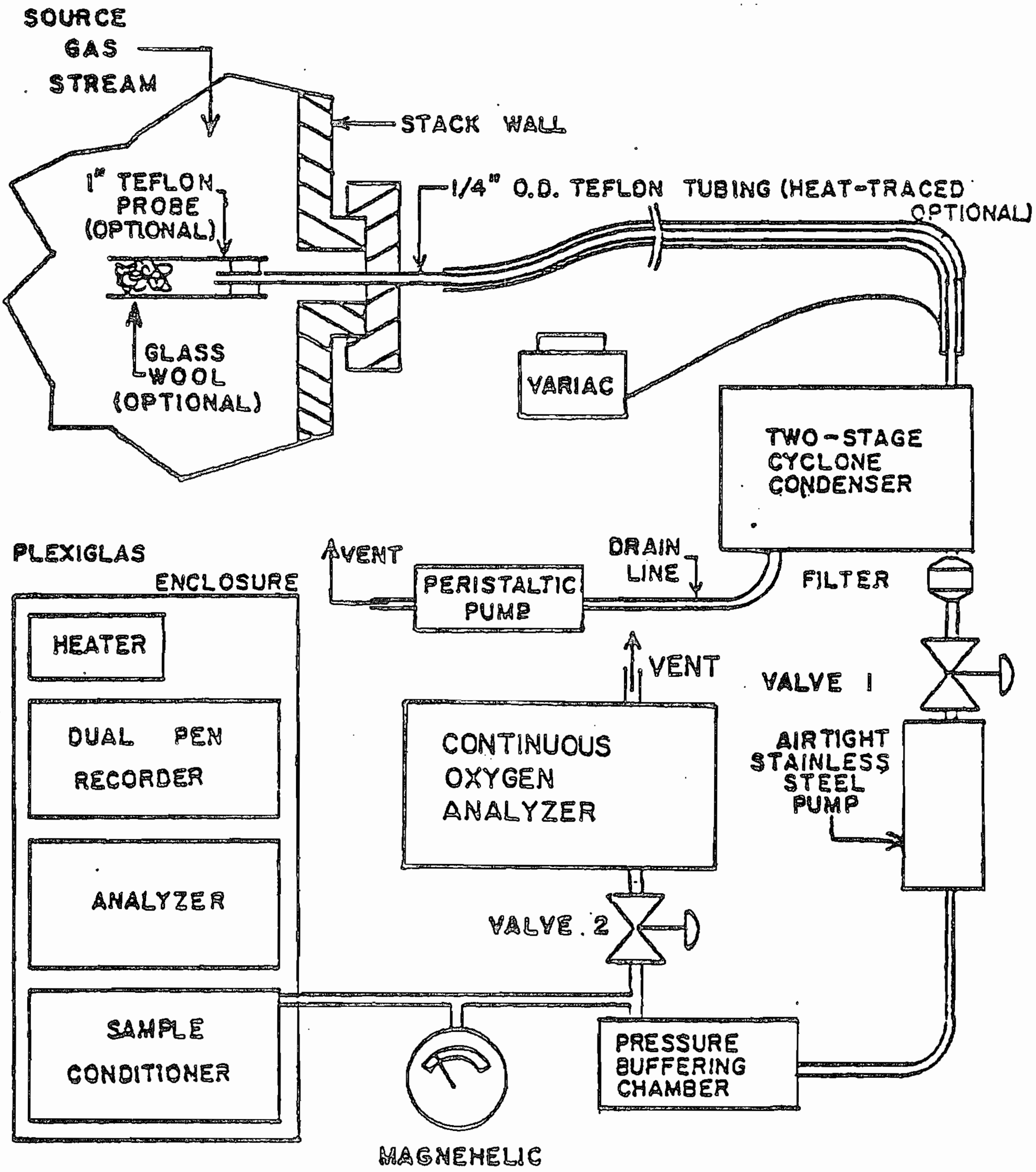

FIGURE 2. SCHEMATIC OF NOx SOURCE MEASUREMENT SYSTEM

some of the sources. The system was designed for consistent operation for vacuum or pressure source gas conditions through the use of a high flow sampling rate and a vented "buffering chamber." This was necessitated by the sensitivity of the monitor to swings in sampling pressure. A constant two inches water pressure was maintained in the inlet line to the Sample Conditioner module of the monitor through the use of the two valves depicted. The in-line filter located after the condenser eliminated the problem of particulate which might foul either valve No. 1 or the stainless steel pump. An additional pump was located on the cyclone condenser drop-out line to insure minimal water/gas contact and to protect the monitor against possible moisture carry-over. The two NOx monitor modules and a two-pen recorder were housed in a heated plexiglas enclosure to minimize dirt infiltration into the circuitry and to maintain monitor operation within the manufacturer specified temperature constraints of 50 to 104°F. The two-pen heat writing recorder allowed unattended data collection for both nitric oxide (NO) and total oxides of nitrogen (NOx).

Teflon probes, fittings and sample lines were used for all sections of the transport system preceding the condenser. Since the sample gas temperature dropped below 100°C at all sites tested within a short distance from the stack, no NO_2 to NO catalytic conversion was judged to occur at the 304 stainless steel condenser. The relatively high sample flow rate and limited time in the gas handling system served to minimize the potential for NO_2 absorption within the system. The stainless steel incorporated into the gas handling system after the condenser was limited to the No. 1 valve, the air-tight pump and three fittings. The balance of the transport system was teflon instead of stainless steel for convenience in making adjustments to the sampling network.

D. Calibration of Source NOx Monitor

The span gas employed for purposes of instrument calibration was obtained from Airco Industrial Gases and contained in aluminum cylinders. Two standards were used, one at 100 and the other at 500 ppm nitric oxide (NO) packed in dry nitrogen. These gases were considered equivalent to primary standards or standard reference materials (SRM's) by the National Bureau of Standards (NBS). If desired by the purchaser, three verification tests, which included chemiluminescent detection and the phenoldisulfonic acid method, were performed by Airco to determine the exact nitric oxide concentration in each cylinder.

Full sampling system spans were conducted through the use of calibrated cylinder gas equipped with a two-stage regulator connected to a valved flowmeter. Although the monitor operated with a one second time constant, the total time interval required for the system to purge and respond to the full calibration gas concentration was approximately 15 minutes. For purposes of quality assurance, the sample system calibration was also augmented with spiking trials at sometime during the testing at a majority of the sites.

These trials were carried out by pulling approximately half the usual combustion gas sample flow measured by the monitor with the balance of the flow supplied from calibrated cylinder span gas. Through careful attention to sample line pressures and the chronological measurement by the NOx monitor of (a) undiluted stack gas, (b) stack gas diluted with ambient air, (c) stack gas diluted with calibrated standard span gas, (d) undiluted calibration span gas, and (e) undiluted stack gas, the spike trials determined that the calibration span and stack gas oxides of nitrogen mixtures were conserved at each testing site through the sample conditioning system. As an example, this procedure was conducted at the site designated as No. 4A in the following manner. The NOx monitoring system was calibrated and placed on-line measuring exhaust gas from the oil fired lime kiln for about four hours. With the monitor indicating a steady level of NOx emissions corresponding to 155 ppm, the stack gas was diluted with 45 percent ambient air (as determined with calibrated flowmeters on the stack gas sample line and the dilution sample line) which produced an instrument response of 85 ppm NOx. The dilution line was then attached to a cylinder of calibrated nitric oxide (NO) span gas of 500 ppm and at the same 45 percent flow rate. The resulting instrument response was 295 ppm. The calculated response corresponded to 310 ppm for a difference of 4.8 percent based on the higher value between the calculated and measured concentration levels, respectively. Accuracy in flow measurements and data transposition were considered the primary reasons for the calculated NOx levels being higher than the measured values. The measurement of undiluted span gas insured instrument calibration stability, while detection of undiluted stack gas as the last step in the spiking procedure determined that there was no change in exhaust gas NOx concentration. In all cases the difference was less than ten percent of the higher value between the combined stack and span gas mixture NOx measurement and that value of NOx calculated from undiluted stack and span gas concentrations by knowing the percent flow rate of each.

IV DESCRIPTION OF INDIVIDUAL LIME KILN SYSTEMS STUDIED

A total of five lime kilns were sampled as part of the oxides of nitrogen study. Three of the kilns (Nos. 1, 2, and 4 as represented in Table 1) were located in the Northwest United States with the balance (Nos. 3 and 5) in the Southeast. Three of the lime kilns were fired on oil alone, one kiln fired natural gas and one utilized oil followed by natural gas during the study interval.

Limited operational and design characteristics found for the six lime kilns are presented in Table 1. This information includes the type of fuel fired at each site sampled for NOx. The design calcium oxide production rate, each kiln's physical dimensions, and the quantity of No. 6 fuel oil or natural gas fired at each source are parameters detailed for each NOx test interval. The particulate control device in service at each site is indicated with the position of the sample site with respect to the control device specified for each of the lime kiln systems.

TABLE 1. DESIGN AND OPERATING CHARACTERISTICS FOR LIME KILNS STUDIED

Location and Fuel Type	Rated CaO Capacity (TPD)	Kiln Length (feet)	Kiln Diameter (feet)	Mean Oil (gpm) or Natural Gas (SCFH) Fired	Sampling Site[1]
1: Oil	138	276	9	4.1	V.S.O.
2: Oil	250	262	12	8.1	P.S.O.
3: Oil	80	170	9	4.3	V.S.O.
4A: Oil	130	250	9	5.3	V.S.O.
4B: Gas	130	250	9	33,400	V.S.O.
5: Gas	125	175	11 to 10*	53,000	V.S.O.

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1. V.S.O. Venturi scrubber outlet.
   P.S.O. Peabody scrubber outlet.

* Diameter at cold end.

(1) Kiln No. 1 - Lime kiln No. 1 was fired on oil during the testing interval, manufactured by Traylor and began operation in September, 1948. The mean equivalent production rate for the testing period was 360 air dried tons of pulp per day. The kiln had a length of 275 feet, 7.5 inches with a diameter of 9 feet and a "pitch" of one-half inch per foot.

(2) Kiln No. 2 - The oil fired kiln identified as No. 2 was manufactured by Vulcan and started operation in December, 1970. The kiln had a mean equivalent production rate of 735 air dried tons of pulp per day. The pitch was 0.5183 inches per foot for the 12 foot diameter and 262 foot long kiln.

(3) Kiln No. 3 - The kiln labeled as No. 3 was an Allis-Chalmers oil fired rotary system that was installed in 1952. The equivalent pulp production during the sampling period for the rated 80 tons of calcium oxide product per day system was 350 tons of pulp per day. The kiln was 170 feet long and had a diameter of 9 feet.

(4) Kiln No. 4 - The rotary lime kiln represented as No. 4A and 4B was manufactured by Allis-Chalmers, installed by Sandwell International Inc. and began operation on oil and natural gas in 1968. The burner for the system was an Allis-Chalmers size 10 combustion gas or steam atomizing oil burner capable of a heat release of roughly 65 million Btu per hour when fired on either natural gas or No. 6 oil fuel. The oil pump and heater had a capacity of heating 11 gpm of oil from 120 to 140°F. The mean equivalent production rate for the study interval at this kiln was 348 tons of pulp per day.

(5) Kiln No. 5 - Lime kiln No. 5 was an Allis-Chalmers gas fired rotary kiln that was installed in 1958. The burning zone temperatures of this system were monitored by a flame pyrometer which enabled a temperature/NOx production relationship to be developed as will be subsequently detailed. An average of 430 tons of pulp per day was considered the equivalent production rate for this kiln during the NOx test period.

(6) Kiln Exhaust Gas Conditions - Exit gas conditions measured during the NOx kraft mill lime kiln sampling intervals are presented in Table 2. This information includes the number of hours sampled which averaged 42 hours for each of the sites studied. The parameter noted as the combustion gas temperature represented the hottest source position preceding the scrubbers used for particulate control, which could be measured and recorded for temperature continuously at each lime kiln site. These values were similar for the various sites with the exception of location No. 5. The average presented in the table for this site corresponded to the actual burning or combustion zone temperature and will be discussed at length later in this report. Exhaust gas flow, percent excess oxygen, and percent excess carbon dioxide are specified for all of the installations. In some cases the combustion exhaust gas flows were not measured during the actual NOx sampling time period which necessitated the use of estimates from previous measurements taken for similar fuel firing rates.

TABLE 2. LIME KILN EXHAUST GAS PARAMETERS MEASURED DURING SAMPLING INTERVAL

Location and Fuel Type	NOx Testing Interval (hours)	Mean Combustion Gas Temp. (°F)	Mean Combustion Gas Flow (SDCFM)	Mean Flue Gas Oxygen Percent	Mean Carbon Dioxide Percent
1: Oil	33	1077[1]	23,400	5.2	16.8
2: Oil	52	765[2]	19,370	5.1	17.7
3: Oil	38	N.A.	15,500	8.1	12.8
4A: Oil	69	891[3]	13,580	4.9	18.9
4B: Gas	19	893[3]	10,260	4.9	18.9
5: Gas	42	2053[4]	20,700[5]	8.5	12.4

N.A. Not available.
1. Chain section hot end temperature.
2. Cold end temperature.
3. Chain section middle temperature.
4. Combustion or burning zone temperature.
5. Based upon 10 tests made by the mill.

V. DISCUSSION AND PRESENTATION OF RESULTS FROM OXIDES OF NITROGEN FIELD MEASUREMENTS

A. General

EPA New Source Performance Standards (NSPS), (31,32,33,34) have specified fossil-fuel fired steam generator (for which construction was commenced after August 17, 1971) nitrogen oxide limits for various fuel types. The interval chosen for NOx averaging was "any three-hour period during which the average emission (the arithmetic average of three contiguous one-hour periods) exceed the applicable standards".

While there is no NOx NSPS for kraft mill lime kilns, the existing (34) liquid fossil fuel (oil) NOx standard for steam generators is 0.30 pounds per million Btu heat input (130 ng/J) with the gaseous fossil fuel standard being 0.20 pounds NOx per million Btu (86 ng/J). A level of 0.70 pounds NOx per million Btu (300 ng/J) was indicated for solid fossil fuel. Fuel such as lignite was related to a standard of 0.60 pounds NOx per million Btu (260 ng/J). Lignite derived from specific locations, given as North Dakota, South Dakota, or Montana and fired in a cyclone combustion system must meet a 0.80 pounds NOx per million Btu (340 ng/J) level regardless of auxiliary fuel use.

The EPA standards (117,118) (adopted June 11, 1979 without revisions) apply to "all electric utility steam generating units (a) capable of firing more than 73 MW (250 million Btu per hour) heat input of fossil fuel (approximately 25 MW of electrical energy output), and (b) for which construction was commenced after September 18, 1978" are as follows. The liquid fuel (except shale oil and liquid fuel derived from coal) NOx standard chosen is 0.30 pounds per million Btu heat input (130 ng/J) with the gaseous fuel (except gaseous fuel derived from coal) standard noted as 0.20 pounds NOx per million Btu (86 ng/J). A level of 0.50 pounds NOx per million Btu (210 ng/J) was indicated for the firing of subbituminous coal, shale oil, or any solid, liquid, or gaseous fuel derived from coal. Any fuel combusted in a slag tap furnace having more than 25 percent, by weight, lignite which has been mined in North Dakota, South Dakota or Montana was assigned a standard of 0.80 pounds NOx per million Btu (340 ng/J). The combustion of all other solid fuel was related to a standard of 0.60 pounds NOx per million Btu (260 ng/J).

The limitation of NOx as NO_2 (119) for the simultaneous combustion of any combination of the fuels mentioned above must follow a proration formula incorporating the applicable standard of all the fuels fired in a boiler.

$$E_{NO_2} = \frac{w(86) + x(130) + y(210) + z(260)}{100}$$

where:

E_{NO_2} = is the applicable standard for nitrogen oxides when multiple fuels are combusted simultaneously (ng/J heat input);

w = is the percentage of total heat input derived from the combustion of fuels subject to the 86 ng/J heat input standard;

x = is the percentage of total heat input derived from the combustion of fuels subject to the 130 ng/J heat input standard;

y = is the percentage of total heat input derived from the combustion of fuels subject to the 210 ng/J input standard; and

z = is the percentage of total heat input derived from the combustion of fuels subject to the 260 ng/J heat input standard.

Since the NOx emissions on any source are determined as nitrogen dioxide (NO_2) on a parts per million (ppm) concentration basis, the data must be converted to the appropriate units of pounds NOx as NO_2 per million Btu heat input. This can be accomplished through the measurement of (a) excess oxygen, (b) the combustion gas flow rate, and (c) the quantity and heat content of the fuel burned. As specified in the Federal Register (116), the TRS and particulate matter concentrations determined after a kraft mill lime kiln control device must be adjusted to ten percent excess oxygen content whether it is greater or less than ten percent. This adjustment addresses the need to normalize pollutant emission concentration data for various degrees of gas stream dilution through transport ducts, fans and control devices. For this reason, the NOx three-hour average concentration data in this bulletin is presented on both a measured stack concentration and also adjusted to ten percent oxygen. At all sites tested, the stack flue gas oxygen level at the point of measurement was less than ten percent oxygen.

B. Lime Kiln Sites

The oxides of nitrogen emission results for the five kilns sampled are presented in Table 3. As specified in the Federal Register (34), the data was compiled into first, hourly averages and then into three-hour averages. The mean and range for each site are noted in the table. The NOx concentration in parts per million, measured at stack conditions, is directly above the NOx concentration mean adjusted to ten percent excess oxygen. Both the three-hour mean and range are given in Table 3 with units of pounds NOx per million Btu heat input and nanograms NOx per Joule

TABLE 3 OXIDES OF NITROGEN FIELD MEASUREMENTS FOR LIME KILNS SAMPLED

Location & Fuel Type	NOx (3) Hour Average Mean (ppm)	NOx (3) Hour Average Mean ($lb/10^6$ Btu)	NOx (3) Hour Average Mean (ng/J)[1]	NOx (3) Hour Average Range (ppm)	NOx (3) Hour Average Range ($lb/10^6$ Btu)	NOx (3) Hour Average Range (ng/J)[1]
1: Oil	185 (130)*	0.850	365	165-215	0.750-0.990	325-425
2: Oil	80 (55)*	0.155	65	35-145	0.065-0.285	30-120
3: Oil	50 (45)*	0.160	70	25-65	0.085-0.215	35-90
4A: Oil	150 (100)*	0.310	135	110-260	0.230-0.545	100-235
4B: Gas	145 (100)*	0.290	125	95-195	0.195-0.390	85-165
5: Gas	310 (275)*	0.780	335	145-430	0.334-1.125	150-485

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[1] 1 $lb/10^6$ Btu = 430 nanograms per Joule heat input.

* Adjusted to 10 percent oxygen in the flue gas. The other ppm oxygen concentration data corresponds to actual stack oxygen levels shown in Table 2.

heat input for each of the five sites and six combustion modes studied. These NOx emission values correspond to the time testing interval noted in Table 2. The NOx mean and upper range found for each site in units of pounds NOx per million Btu are depicted in Figure 3. All of the lime kiln sources represented in this figure except Nos. 4B and 5 corresponded to 100 percent oil fuel firing. The two exceptions were kiln sites fired on 100 percent natural gas during the study period.

The dashed line at 0.30 pounds NOx per million Btu in Figure 3 indicates the standard for oil fired boilers. The lower dashed line at 0.20 pounds NOx per million Btu corresponds to the standard for natural gas fired boilers. As shown in the figure, three out of four of the kilns fired on oil had at least one three-hour interval over 0.30 pounds NOx per million Btu. Two of these three sites were found to have data means over the oil fired boiler standard. Both of the kilns which fired natural gas had a majority of their three-hour NOx averages which were above the standard for natural gas fired boilers.

The wide range and high three-hour average NOx emission levels found for the natural gas fired kiln at site No. 5 point toward a potential dependence of NOx concentrations over the normal range of this particular burner operation. A relationship between combustion zone temperature and NOx emission rate was obtained in a study by NCASI personnel with the use of an optical pyrometer and is presented in Figure 4. The relationship in the figure was based on a total of 37 data points. The solid portion of the curve indicates the use of linear regression techniques performed on 33 of these data points which were judged to follow a close linear distribution to give the following equation having a correlation coefficient, R, of 0.965:

$$\frac{\text{lb NOx}}{10^{6}\ \text{Btu}} = 2.17 \times 10^{-3}\ (\text{Temperature, °F}) - 3.58$$

The dashed portion of the center curve was a smooth fit approximation through the remaining four data points. Based on the data collected encompassing various modes of burner operation at this site, there was judged to be a potential for reduction of NOx emissions to less than 0.4 pounds per million Btu. Adjustment of the gas firing rate and the excess air levels supplied to the kiln's burner may enable the combustion zone temperature as measured by the optical pyrometer to be controlled at less than 1850°F. Below this temperature the NOx to combustion zone temperature relationship was judged to be insignificant for the limited amount of data collected. The normal combustion zone temperature for long kilns usually averages about 2000°F with as much as 2375°F required for short kilns. The minimum temperature at which calcium carbonate dissociates and the partial pressure of carbon dioxide reaches one atmosphere is 1670°F (123). Heat and radiation losses of up to 40% in combination with the energy required to evaporate 30 to 40% water carried in the lime mud charged to the kiln, makes the minimum combustion zone temperature somewhat higher than this value.

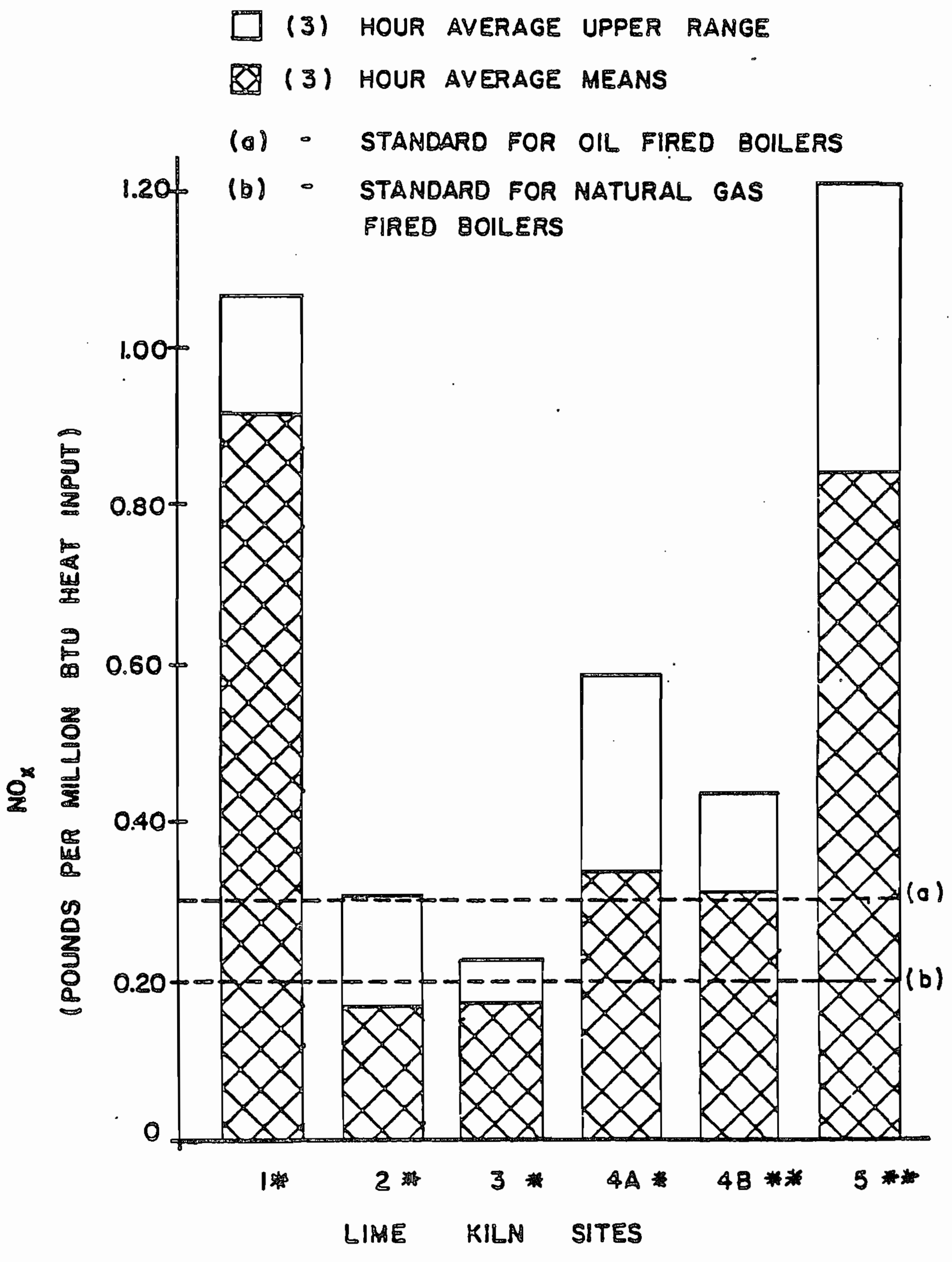

FIGURE 3. NOx EMISSION LEVELS FOR KRAFT MILL LIME KILNS SAMPLED

* OIL FIRED
** NATURAL GAS FIRED

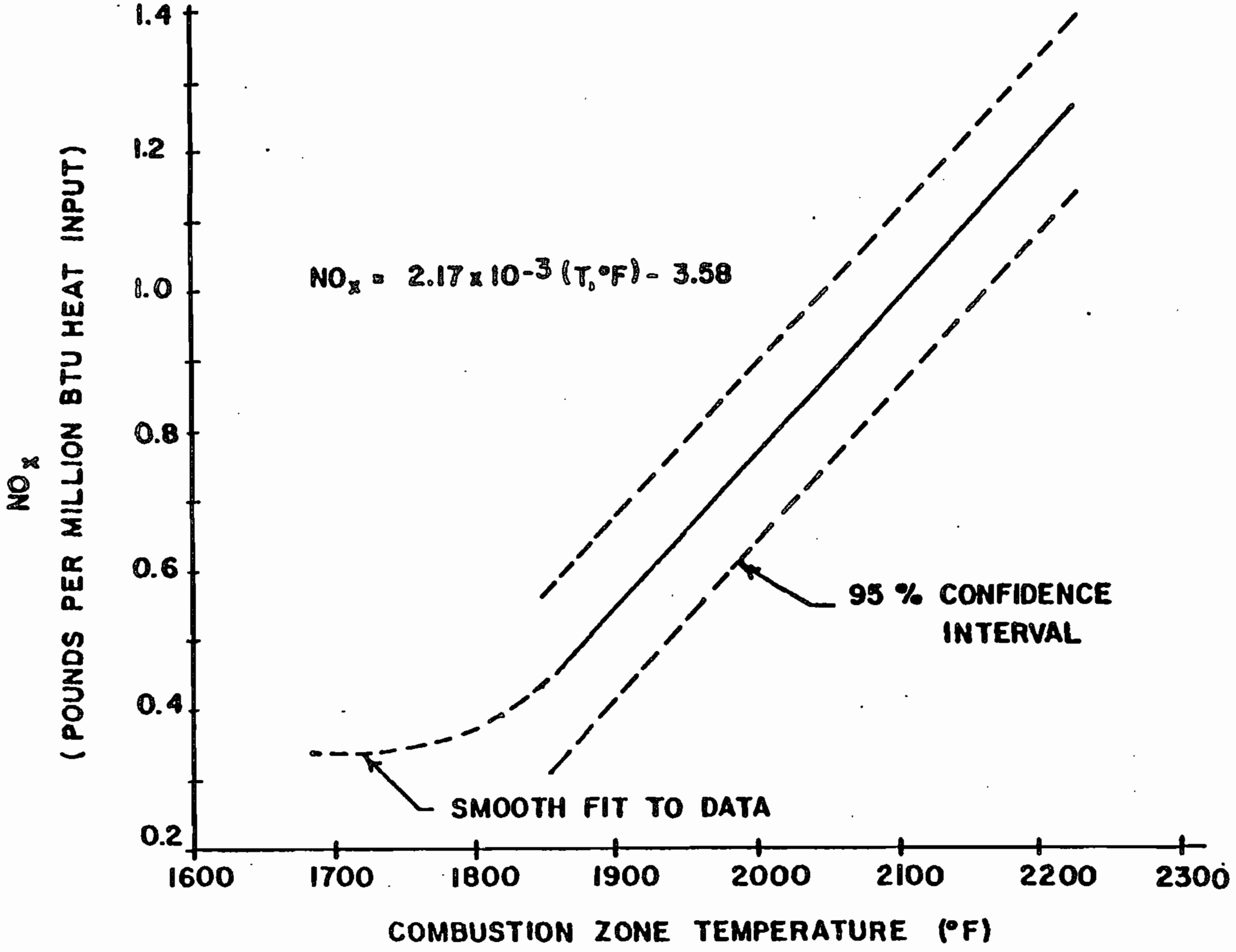

FIGURE 4. THE RELATIONSHIP BETWEEN COMBUSTION ZONE TEMPERATURE AND NOx EMISSIONS

Further work is needed to address the relationships between combustion zone temperatures and lime kiln NOx generation. The use of these temperature monitors may prove a useful tool in controlling kiln NOx emissions to consistent levels.

VI SUMMARY

(1) The information contained in this report includes oxides of nitrogen emission data generated at five kraft mill lime kiln sites in the Northwest and Southeast United States. A comprehensive literature search was performed and can be found in the NCASI Atmospheric Quality Improvement Technical Bulletin No. 102 entitled, "A Study of Nitrogen Oxides Emissions from Wood Residue Boilers." This literature search was representative of recent publications associated with NOx formation kinetic theory, measurement techniques, field sampling methodology, source control strategies, previously reported field results and the effects of these gases on the ambient.

(2) The chemiluminescence oxides of nitrogen measurement principle used in this study was discussed and presented in the literature as accurate and easily adapted to continuous sampling of combustion sources. This was in contrast to the widely accepted phenoldisulphonic acid (EPA Method 7) grab sampling method. The details of a gas handling system for use with existing, but slightly modified, chemiluminescent ambient NO/NOx monitors was also presented. The 100 percent (±10 percent) recovery of nitric oxide (NO) gas spiked into sampled combustion exhaust gas during the field trials was found to reaffirm that NOx sample line losses were insignificant for all site trials.

(3) Summarization of the data compiled in this report is presented in Table 4. This table contains a synopsis of NOx "emission factors" based on heat input and equivalent pulp production for the sites sampled. The mean and range found for the various kilns are indicated in this table based on a three contiguous hour average criteria.

(4) One natural gas fired lime kiln site afforded the opportunity to study the relationship between combustion or burner zone temperature and NOx emission levels. The data indicated that combustion zone temperatures below 1850°F were required to reduce NOx concentrations to less than 0.4 pounds per million Btu heat input. Further work is needed to address the relationships between combustion zone temperatures and lime kiln NOx generation potential.

(5) The emission of NOx from combustion sources is influenced by a number of factors including combustion temperature, instantaneous flame temperature, fuel bound nitrogen and operational parameters such as excess oxygen and the method of fuel firing. The data generated during this study indicated a three-hour mean emission rate ranging from 0.07 to 1.13 pounds of NOx per million Btu input

TABLE 4. NOx EMISSION RATE SUMMARY FOR LIME KILNS SAMPLED

Location & Fuel Type	Tons Pulp Per Day Mean	NOx (3) Hour Average Mean			NOx (3) Hour Average Range		
		($lb/10^6$ Btu)	(ng/J)	(lb/ton pulp)	($lb/10^6$ Btu)	(ng/J)	(lb/ton pulp)
1: Oil	360	0.85	365	2.1	0.75-0.99	325-425	1.8-2.4
2: Oil	735	0.16	65	0.4	0.07-0.28	30-120	0.2-0.7
3: Oil	350	0.16	70	0.4	0.08-0.21	35-90	0.2-0.5
4A: Oil	350	0.31	135	1.0	0.23-0.54	100-235	0.7-1.7
4B: Gas	350	0.29	125	0.7	0.19-0.39	85-165	0.7-1.3
5: Gas	430	0.78	335	2.6	0.34-1.12	150-485	1.1-3.7

for lime kilns firing either oil or gas fuel. This would correspond to emission rates of between 0.16 and 3.7 pounds NOx per ton of pulp.

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ncasi technical bulletin

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

A STUDY OF WOOD-RESIDUE FIRED POWER BOILER TOTAL GASEOUS NON-METHANE ORGANIC EMISSIONS IN THE PACIFIC NORTHWEST

ATMOSPHERIC QUALITY IMPROVEMENT
TECHNICAL BULLETIN No. 109

SEPTEMBER 1980

ncasi
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ATMOSPHERIC QUALITY IMPROVEMENT
TECHNICAL BULLETIN No. 109

September 22, 1980

A STUDY OF WOOD-RESIDUE FIRED POWER BOILER TOTAL GASEOUS NON-METHANE ORGANIC EMISSIONS IN THE PACIFIC NORTHWEST

Volatile organic compounds (VOC) are considered by EPA to be photo-oxidants which are involved in the formation of ozone. Volatile organic compounds, by EPA definition, are a subgroup of non-methane compounds, previously generally referred to as hydrocarbons. As a result of regulations governing the permitting of new sources or modified existing sources, estimates of VOC emissions are frequently needed for the new or modified source. In addition, VOC emissions from other sources at the manufacturing site must be known to calculate the net change in VOC emissions.

The available information on VOC emissions from sources in the forest products industry is not only sparse, that available is almost universally generated using a measurement procedure differing from that now proposed for use in most circumstances by EPA. For these reasons the National Council initiated a study of VOC emissions from several unit processes using the method of measurement advocated by EPA. This technical bulletin is the first of a series on the study of VOC source emissions. The investigative work and preparation of the report from which the technical bulletin was assembled was carried out by Victor J. Dallons, Research Engineer, under the direction of Andre L. Caron. Mr. Dallons was assisted by Dean R. Hoy, Ronald A. Messmer, and David R. Fyke.

This technical bulletin includes a description of the sampling and analytical method used and heretofore unidentified limitations of its use on combustion sources where carbon dioxide and significant amounts of moisture coexist. The bulletin contents describe the VOC emission levels found at four wood-fired boilers in the Pacific Northwest firing principally Douglas Fir. To the extent that VOC emissions may differ from wood residues derived from other wood species, the finding are qualified.

The study showed VOC emissions based on seven to ten duplicate samples collected simultaneously at each of four boilers to range from 0.04 to 0.10 lb/10^6 million Btu heat input with a mean for the four boilers of 0.07. This mean is one third that for hydrocarbons currently reported in EPA AP-42. Analysis of the emission and boiler operating data showed VOC emissions to generally be lower as the percent of overfire air increased. Simultaneous sampling at the inlet and outlet of an impingement type wet scrubber on one of the boilers showed insignificant changes in VOC levels. While this scrubber design is not a particularly effective gas-liquid contacter, it was felt that other factors would probably limit the effectiveness of any scrubber design in reducing VOC at this source.

This technical bulletin will be followed soon by two others; one on VOC emissions from kraft recovery furnace systems and the other on VOC emissions from lime kilns.

Already a major element of the National Council's program, the VOC emission study has recently made a substantial expansion. The investigative effort, previously staffed only at the West Coast Regional Center, has now been expanded to the East Coast, with staff support from the Northeast and Southern Regional Centers. The investigative activity now encompasses a study of VOC emissions and the effectiveness of existing control technology on wood veneer dryers and solvent emissions from surface coating and printing. The scope of the investigative program is expanding geographically and will be expanded to other sources as time permits.

Your questions and comments on the contents of this technical bulletin should be addressed to me, or to Mr. Victor Dallons or Mr. Andre L. Caron at the West Coast Regional Center.

Yours very truly,

Russell O. Blosser
Technical Director

ROB:gs
Attach.

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A STUDY OF WOOD-RESIDUE FIRED POWER BOILER TOTAL GASEOUS NON-METHANE ORGANIC EMISSIONS IN THE PACIFIC NORTHWEST

I INTRODUCTION

Volatile organic compounds are considered by the Environmental Protection Agency (EPA) to be photo-oxidants which are involved in the formation of ozone. Volatile organic compounds are a subgroup of non-methane hydrocarbons. Non-methane hydrocarbons have been designated as criteria pollutants by EPA, although the Agency has stated that the national primary and secondary ambient air quality standards for non-methane hydrocarbons (0.24 ppm 3 hour average between 6 and 9 a.m.) is only for use as a guide to achieve the ozone ambient air quality standard. Potential emissions of volatile organic compounds in amounts greater than a threshold tonnage per year results in classification of the source as major. Major new sources and existing source modifications must satisfy non-attainment (NA) or prevention of significant deterioration (PSD) regulations mandated by the 1977 Clean Air Amendments in order to obtain a construction permit.

Major sources locating in non-attainment areas must meet an emission offset policy where emissions from the new or altered source must be offset by a reduction in emissions from existing sources in the area. These sources must also achieve the lowest achievable emission rate (LAER) which is either (a) the lowest emission rate specified for the source class in any state implementation plan or (b) the lowest emission rate achieved in practice by a source of the same type.

Mills located in prevention of significant deterioration areas (PSD) are subject to best available control technology (BACT) emission limitations. Best available control technology is an emission limitation based on the maximum degree of reduction for the pollutant in question determined on a case-by-case basis. Mills located in PSD areas may choose to offset their emissions to avoid a PSD review. In either case, data from a one-year ambient monitoring program may be required and the impact of the source as determined by an approved modelling exercise determined prior to a major source applying for a permit.

To date, no definitive assessment has been made of total gaseous organic compounds emissions resulting from pulp and paper industry combustion and other process sources. Modelling to satisfy non-attainment and PSD regulations is unreliable with the information presently available on emissions and subsequent reactions which result in ambient ozone formation. Hence it is unknown which and what size pulp and paper mill processes are considered major sources with respect to gaseous organics.

Hydrocarbon emission factors expressed as methane for wood residue-fired boilers published in AP 42, 1979 (1) were 2 lbs hydrocarbon per ton of 50% moisture fuel fired. This value translates to 0.22 lb hydrocarbon per million Btu fired, assuming 9,000 Btu per pound wood residue heat value. The values published in the 1979 supplement are the same as published in the AP 1976 edition and no new references are listed. Consequently, little is known about the method used in obtaining this data or if the procedures used would yield data consistent with EPA Method 25. Any comparisons made between the data generated and presented in this text and the value presented in AP 42 should consider the difference in methods by which the data was generated.

The National Council is currently surveying total gaseous organic emissions from selected sources in the forest products industry to provide a data base on potential emissions to be expected from various sources. It is the aim of this project to produce data consistent with the EPA reference method to be selected for the measurement of total gaseous non-methane organic compounds (TGNMO). The sampling and analysis procedures used in this study were in accordance with proposed EPA Method 25, published in the Federal Register October 3, 1980 (Appendix A) (2).

The EPA proposed analytical procedure yields values for carbon monoxide, carbon dioxide, methane and total gaseous organics. The analytical procedure was altered to produce results for ethane and ethylene. Methane and ethane are not photoreactive and were not included in the results. The total gaseous photochemically reactive organics (TGPRO) results are reported as methane. The following presents and discusses the sampling equipment, the procedures used, and results obtained from the wood-residue fired power boiler portion of this study, carried out when burning western wood residues. The boilers sampled were considered as representative of current boiler design and operating practices.

II BOILER DESCRIPTIONS

During the course of the study four wood-residue fired power boilers were surveyed. Two boilers produced about 150,000 lb/hr steam, and the other two about 400,000 lb/hr steam. One of the larger boilers fired gas or oil as supplemental fuel. All of the boilers studied are located in the northwest United States.

Boiler A is a spreader-stoker unit rated at 180,000 lb/hr steam at 600 psi and 600°F while burning wood-residues derived from Douglas fir and some cedar. Hogged fuel is spread by four pneumatic stokers onto fixed grates. The boiler was manufactured by Riley Union and installed by the Bumstead and Woolford Company in 1975.

Primary combustion air enters the boiler through 3/16 inch diameter holes in the fixed grate, overfire air enters the boiler through the oil fire windbox on one side of the unit. During normal operation of the furnace most of the preheated combustion air enters through the grates. Overfire air, which represented about 12% the total air flow, is not preheated.

The combustion chamber has dimensions of 21 feet 6 inches wide, 22 feet 6 inches long, and 37 feet 1 inch high, with a volume of

17,940 cubic feet. There are 54 cubic feet of combustion volume for every million Btu/hr fired at rated conditions.

Combustion air is preheated to approximately 450°F. Cinders are removed from the flue gas by multiclones, and followed by wet scrubbers which follow the ID fan.

The boiler was designed to operate on wood residue with a moisture content of 45%, a dry composition of 3.4% H_2, 23.7% O_2, 47.7% C and 0.2% ash, and having a heating value of 4930 Btu/lb. The boiler efficiency is rated at 70%. This boiler is designed and operated to take swings in the mill steam demand. Swings in steam demand of 50,000 lb/hr representing in excess of 25% of the unit's design capacity were common during the sampling periods.

Power boiler B is a spreader-stoker unit rated at 600,000 lb/hr, 850 psig and 750°F, while burning hogged fuel derived from Douglas fir and some cedar plus supplemental fuel. Supplemental fuel, either oil or gas, normally makes up 10 to 35% of the boiler heat input. Hogged fuel 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 and is introduced so as to set up a swirling motion inside the fire box. Four oil/gas burners (and windboxes) are located above the stokers on the four corners of the boiler. Primary air comprises about 70% of the total air flow, while overfire and windbox air comprises the other 30%.

The combustion chamber has dimensions of 19 ft. 11 in. wide, 20 ft. 11 in. deep and 65 ft. 9 in. high, with a volume of 27,400 cu. ft. There is 23.5 cu. ft. of combustion volume for every million Btu fired at rated conditions. 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 Douglas fir bark with a dry composition of 6.3% H_2, 40.5% O_2, 52.3% C, 0.1% N, and 0.8% ash at a 50% moisture content along with supplemental fuel. The bark has a heating value of 4525 Btu/lb as fired. Supplemental fuel is #6 oil with a heat value of 18,500 Btu/lb oil or natural gas with a heat value of 1040 Btu/cu ft.

Large swings in steam demand are taken up by changing the firing rate of wood or supplemental fuel. The boiler steam output remains fairly constant over short periods of time (approximately 1 hour). Small changes in mill steam demand are taken up by other power boilers.

Power boiler C is a spreader-stoker unit rated at 150,000 lb/hr at 625 psig pressure and 600°F. Douglas fir mixed wood residue and bark is spread by four mechanical stokers onto moving grates. The boiler was built by Combustion Engineering in 1952.

Primary combustion air enters the boiler under the grates, and overfire air enters in several locations along the four corners of the boiler below the stokers. Primary air is about 75 to 80% of the total air flow. Four oil/gas burners and windboxes are located above the stokers in the four corners of the boiler. Combustion air is preheated to about 520°F. Cinders are removed from the flue gas with multiclones.

This boiler is fired at fairly constant rate. Changes in mill steam demand are taken up in steps.

Boiler D is a spreader-stoker unit rated at 400,000 lb/hr steam when burning fuel with a 55% moisture content and at 550,000 lb/hr steam at 1250 psig when burning fuel with a 30% moisture content. Fuel derived from Douglas fir residue 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 in several locations just above the stokers around the entire perimeter of the boiler. Overfire air can also be added about 10 ft. higher on the boiler. Opposite and above the stokers are six oil burners in two tiers. Primary air comprises about 60% of the total air flow, overfire and windbox air comprises about 40% of the total air flow.

The combustion chamber has dimensions of 33 ft. wide, 22 ft. deep and 66 ft. high, with a volume of 47,913 cu. ft. There is 102 cu. ft. of combustion volume for every million Btu fired at rated conditions.

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 Douglas fir residue with a dry composition of 6.0% H_2, 40.5% O_2, 52.5% C, and 1.0% ash. The wood residue has a heat value of 8900 Btu/lb bone dry. The boiler has a 64% efficiency when firing wood residue with a 55% moisture content, and a 75% efficiency when firing wood residue with a 30% moisture content.

This boiler is operated on a very steady basis, with mill steam demand swings being taken up by other power boilers.

A fixed orifice wet scrubber was sampled to determine any effect it had on TGNMO emissions. The scrubber was designed with a side inlet and directed the gas flow downward through a fixed restricted annular orifice causing solids to be impacted against a static liquid reservoir just below the orifice. After impingement a circular motion was imparted to the gases which flowed upward through a central duct to accomplish centrifugal de-entrainment of agglomerated dust particles. Figure 1 depicts a wet scrubber of this type. Water was sprayed onto the annular orifice to prevent plugging. Approximately 35 GPM uncontaminated water makeup was added to the scrubber, about 75% of which was evaporated and the remainder blow down.

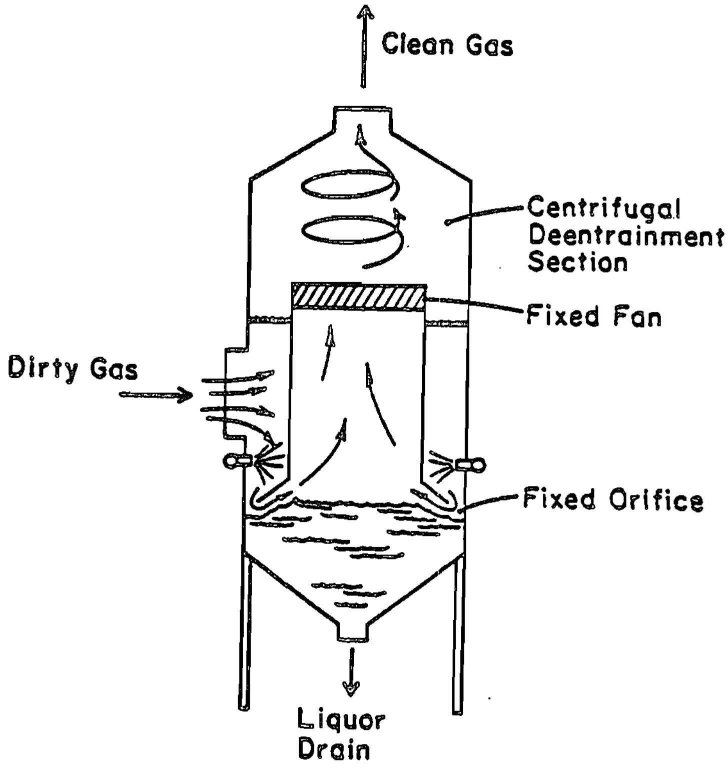

FIGURE 1

IMPINGEMENT TYPE WET SCRUBBER

III SAMPLING AND ANALYSIS METHOD

The procedure used for data collection was similar to the one developed by the Southern California Air Pollution Control District and Method 25 (Appendix A) procedures. The principle of the procedure is to separate the compounds at the time of collection into a high and low molecular weight fraction using a cold trap (-78°C). The light components are captured in an evacuated tank. The trap containing condensed organics is burned to convert organics to CO_2 for analysis in the laboratory. The light and unreactive organics captured in the evacuated tank are separated on a chromatographic column yielding concentrations for CO, CH_4, CO_2, C_2H_6 and C_2H_4. All other organics are eluted in one peak. Summation of the trap and tank organic results gives TGNMO stack concentrations. All results are reported as methane.

A. Sampling

Field samples were taken in duplicate through a single ¼ in. stainless steel probe fitted with a tee to split the flow to two sampling trains. The stack end of the probe was filled with glass wool before each sample was drawn to prevent collection of particulates in the traps. Six feet of 1/8 in. stainless steel tubing ran from the tee to each trap which was submerged in granular dry ice. Skematics of the trap construction and sampling assembly are presented in Figures 2 and 3, respectively. Condensible organics and water vapor were captured in the traps. From the traps the gas flowed through a rotometer, a flow control valve, and into a 17 liter evacuated stainless steel tank.

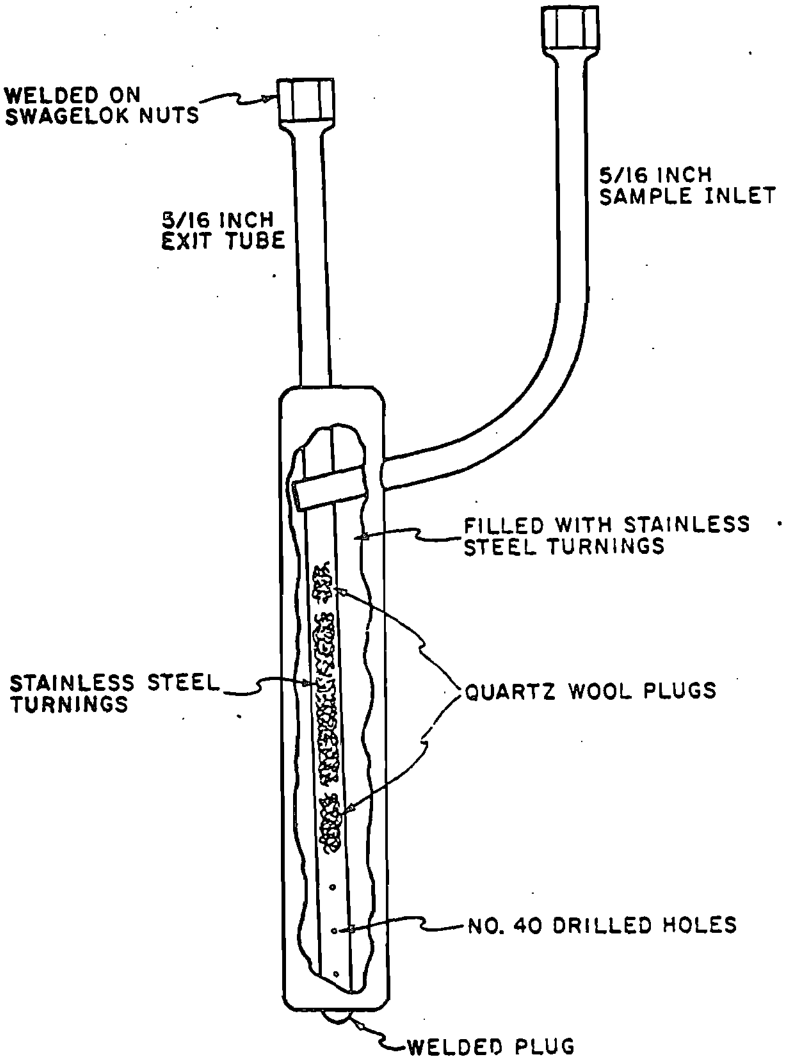

FIGURE 2

CONDENSATE TRAP

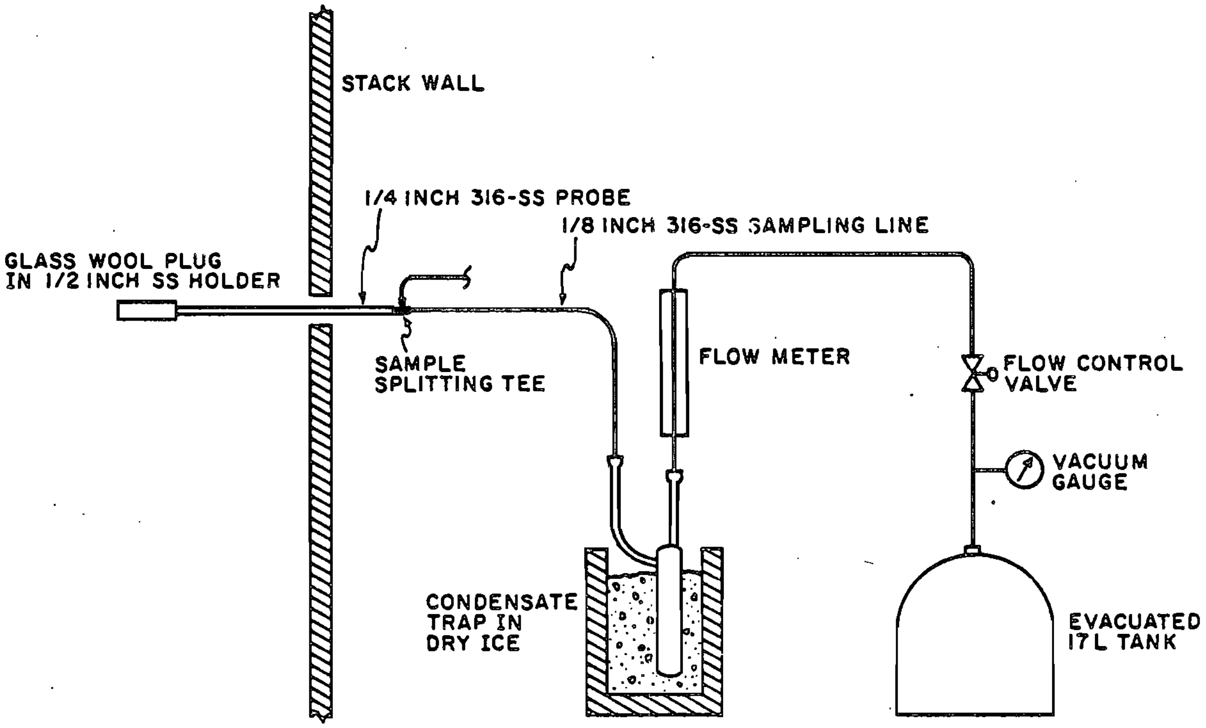

FIGURE 3

TGNMO SAMPLING TRAIN

All screw connections in the sampling system were checked for leaks in the field before sampling by pressurizing with air at 30 psi and soaking the joints individually with soapy water. Leaks detected were eliminated prior to sampling.

Sampling flow rates were set at about 180 ml/min so that about 10 liters of sample were collected in the one hour sampling period. When a trap froze due to condensation of stack moisture, the trap inlet was heated momentarily with a propane torch to melt the ice. The sampling system was watched closely to maintain the proper flow rate. At the end of the sampling period the tee and probe to the stack were heated gently with a propane torch to volatilize any organics condensed. After sampling, the trap and 6-foot section of line to the tee were capped and transported to the laboratory packed in dry ice. Tank pressures were measured before and after sampling to determine sample size. Orsat analyses were made for CO_2 and O_2 before and after sampling if only one sampling port was available, and during sampling if a second port was available.

Field data collected on boiler operating conditions included steam production rate, steam pressure and temperature, flue gas oxygen, flue gas temperature at the entrance and exit of the preheater, preheated air temperature, and auxiliary fuel usage. Any unusual operating conditions were noted.

B. Sample Preparation

When the samples were returned to the laboratory, each trap and sample tank combination used in the field was connected to the trap burning system in the sequence of trap, oxidation tube furnace, U-tube water trap packed in dry ice, and IR analyzer and sampling vessel as shown in Figure 4. The stack gases remaining in the trap were flushed into the tank with carbon compound free air (hereafter referred to as zero air) at a rate of 100 cc/min. When all of the CO_2 was flushed and into the tank as indicated by the IR detector response, the tank was pressurized with zero air via a trap bypass.

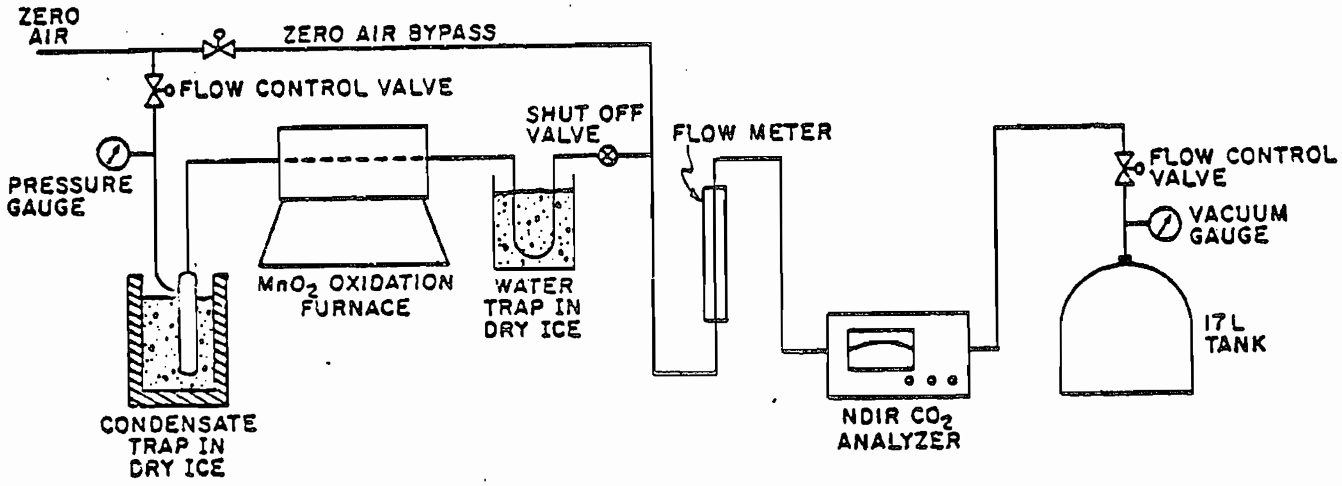

FIGURE 4

TRAP BURNOUT SYSTEM TRAP FLUSH MODE

Following sampling tank pressurization, a four liter stainless steel vessel evacuated to a minimum of 28 in. Hg was then attached in the tank's place. Zero air was passed through the sampling line and trap while they were heated to a dull red color with an acetylene torch. A metering valve in the zero air supply line controlled the pressure in the trap to 15 to 25 in Hg while flow was controlled by a valve on the evacuated vessel. Pressure in the trap can increase rapidly due to boiling of condensed water. The trap was monitored to avoid excess pressures that may result in leaks. Figure 5 shows the burn-out assembly.

Care was taken that the sampling line, trap, and lines to the oxidizer were heated sequentially so that incompletely oxidized organics that might recondense in the system would be revolatilized.

Each trap was burned until the CO_2 in the carrier gas, as shown by the IR analyzer, had returned to baseline. The vessel was then pressurized to less than 5 in. Hg. The volume of water in the water trap was measured and recorded. Stack moisture content was calculated from this data.

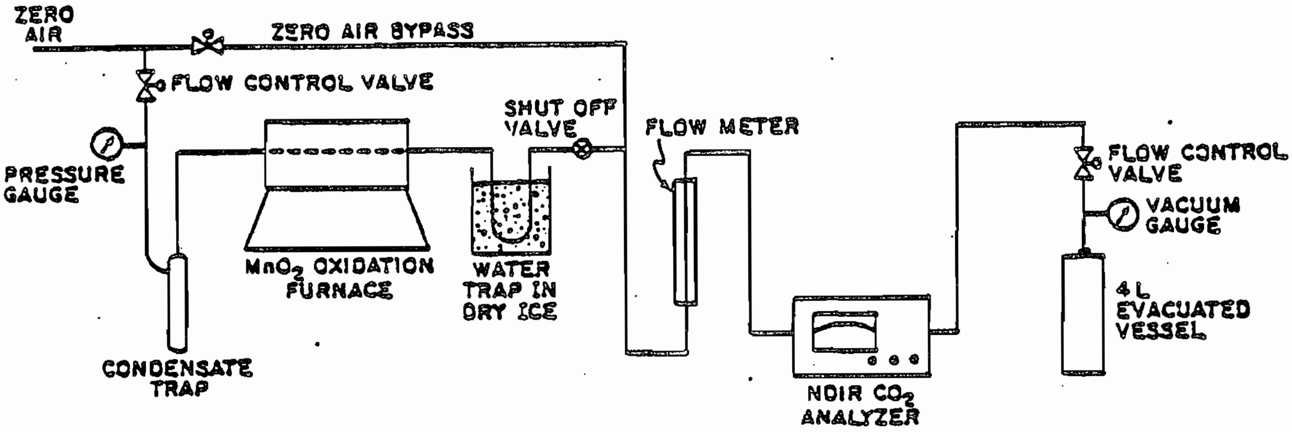

FIGURE 5

TRAP BURN OUT SYSTEM TRAP BURN MODE

Zero air was prepared by further purifying zero grade air from cylinders. Air from the cylinder way passed over air oxidation catalyst to oxidize organics to carbon dioxide and then passed through ascarite for carbon dioxide removal. The nitrogen carrier gas used for the chromatographic column was cleaned by passing through a molecular sieve and through a catalytic oxidation column. Trace quantities of carbon dioxide in the nitrogen carrier gas do not interfere with the analysis.

C. Sample Analysis

The analysis system components consisted of an injection port with an inert septum, a silicon SF-96 on Chromosorb W/Porapak Q column operated at -78°C, -30°C, 25°C, and 100°C with back flush capability, a MnO_2 oxidation furnace operated at 600°C for oxidation of the CH_4, CO, and organics to CO_2, and hydrogen addition to the nitrogen carrier at a rhodium catalyst methanator operated at 400°C to convert CO_2 to CH_4. The column was made of 1/8 O.D. stainless steel tubing packed with 3 feet of 10% methyl silicone on Supelcoport 80/100 mesh followed by 1.5 feet Porapak Q 60/80 mesh. The CH_4 was analyzed by a flame ionization detector (FID). The FID output was integrated with an integrator. A second inert injection port was placed just prior to the oxidation furnace for system checks. A skematic is shown in Figure 6.

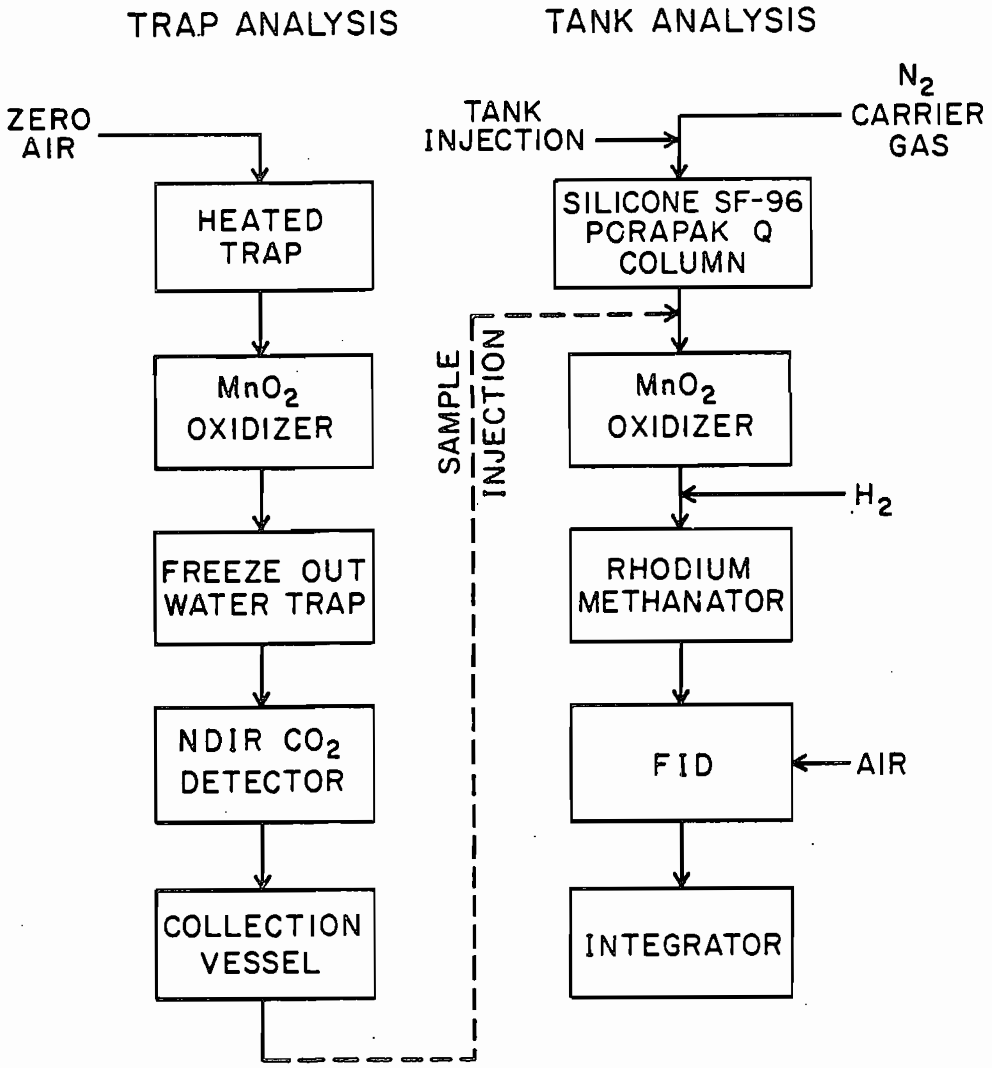

FIGURE 6

TGNMO ANALYTICAL SCHEME

Starting with the column submerged in a dry ice-isopropanol bath at -78°C, a 5 ml sample was drawn from the pressurized evacuated sampling tank and injected into the carrier gas to the column. Carbon monoxide and methane were separated. The column was then operated at room temperature for carbon dioxide elution. After the elution, the column was placed in a boiling water bath and the carrier gas flow through the column reversed. The volatile organics were released from the column. Each evacuated sampling tank was analyzed in triplicate. On the first injection of each duplicate pair, the column was placed in a $CaCl_2$-ice bath at -30°C to separate ethylene, ethane, and propane. If these compounds were not detected the samples were analyzed as above, but if present, the samples were analyzed with the -30°C column temperature step.

Analysis of the sampling tank for carbon dioxide required separate injections from that used for the organic analyses. The amount of carbon dioxide in a 5 ml injection was shown to overload the reduction catalyst causing a low carbon dioxide value to be reported. Carbon dioxide concentrations in the tanks were determined in triplicate using ½ ml injections directly to the oxidizer. Carbon monoxide and TGNMO concentrations were subtracted from the CO_2 value thus attained.

The trap burn-off vessel contents were analyzed by injecting 5 ml drawn from the vessel into the carrier gas bypassing the chromatographic column and entering the oxidation furnace. The results were reported as ppm CH_4.

D. Calculations

Laboratory results were in terms of ppm TGNMO as methane as found in the sampling tank or vessel. These were corrected to standard conditions in the stack. To obtain corrected stack values the tank and vessel volumes corrected to standard condition were divided by the sample volume corrected to standard conditions and multiplied by the tank or vessel TGPRO concentrations respectively. Summation of tank and vessel concentrations were presented as stack TGNMO concentration at standard conditions.

The sample volume at standard conditions was calculated by:

$$\text{Sample Vol.} = (9.124)\ (V_T)\ \left(\frac{P_2}{T_2} - \frac{P_1}{T_1}\right)$$

where: V_T = tank volume in liters

P_1 = absolute pressure in the tank prior to sampling, in. Hg

T_1 = absolute temperature in the tank at time of measurement of P_1, °K

P_2 = absolute pressure in the tank after sampling, in. Hg

T_2 = absolute temperature of the tank at time of P_2 measurement, °K.

The volume of the tank or vessel at the time of analysis was calculated by:

$$\text{Pressurized Container Volume} = \frac{(Vc)\ (Pc)\ (9.124)}{Tc}$$

where: V_c = container volume, liters

P_c = pressure of container when filling is completed, in. Hg

T_c = absolute temperature of container at time of measurement of Pc, °K

The TGNMO's in those containers were calculated by:

$$\text{Stack Concentration} = \left(\text{Container Concentration} - \text{Container Blank}\right)\left(\text{Pressurized Container Volume}\right)/\left(\text{Sample Volume}\right)$$

The container blanks are a column blank and the zero air total carbon concentration for the tank and vessel respectively. Both blanks were kept below 5 ppm. The steps taken to remedy a response of more than 5 ppm are enumerated in Section IV B 1. The blanks were run daily.

Stack TGNMO concentrations were converted to $lb/10^6$ Btu through use of conversion formulas published in 40 CR 121:1516, 60.45, Sections e and f. Conversion of concentrations to $lb/10^6$ Btu required use of either the stack percent O_2 or percent CO_2 in the calculations. Since CO_2 concentrations representing an average over the sampling period were available from the tank analysis and they were used in the calculations. It was found that orsat measurements may not give true averages since they were not taken frequently during sampling.

The conversion equation used was:

$$E = C \cdot F_c \; \frac{100}{\%\, CO_2}$$

where: E = pollutant emissions, $lb/10^6$ Btu (ng/J)

C = pollutant concentration, lb/dscf (ng/dscf)

The pollutant concentration in lb/dscf (ng/dscm) was found from the part per million concentration by:

$$C = (2.59 \times 10^{-9} \text{ lb/dscf})(\text{Conc. ppm})(\text{M.W.})$$

$$C = (4.15 \times 10^{-4} \text{ ng/dscm})(\text{Conc. ppm})(\text{M.W.})$$

where M.W. was the molecular weight of the pollutant, in this case the M.W. for methane is 16.

Fc is a factor representing a ratio of volume of carbon dioxide generated to the calorific value of the fuel combusted.

For wood residue, Fc = 1840 scf $CO_2/10^6$ Btu, for bark, Fc = 1860 csf $CO_2/10^6$ Btu.

IV QUALITY CONTROL

The TGNMO analysis system was checked for proper operation at frequent intervals. Daily checks were made for FID sensitivity, zero air purity, column carrier gas purity and system leaks. Weekly checks were made on all catalysts efficiencies. Bi-weekly checks were made for evacuated sampling tank leaks and tank contamination.

A. Catalyst Efficiency Checks

All catalyst efficiencies were checked at the beginning of each week.

(1) Oxidation Catalyst Efficiency Check - To check the oxidation catalyst, the reduction catalyst was bypassed while operating the TGNMO analyzer in an otherwise normal fashion. Triplicate injections of 5 ml each of standard methane gas were made. If the catalyst was operating properly, the only gas reaching the FID was carbon dioxide and no response was indicated. Any response was reported and the catalyst efficiency recorded. When the catalyst efficiency was found to be less than 95%, it was replaced.

(2) Reduction Catalyst Efficiency Check - With the TGNMO analysis system in its normal operating mode triplicate injections of a CO_2 standard were made directly to the reduction catalyst and the FID response recorded. Triplicate injections of a standard methane gas were made directly to the reduction catalyst to calibrate the FID. The usual calibration curve could not be used because reduction catalyst inefficiencies were included in it. When the catalyst efficiency was less than 95% it was replaced.

(3) Cryogenic Freeze-Out Trap Oxidation Catalyst Efficiency Check - The cryogenic trap oxidation catalyst was checked by connecting the methane calibration gas cylinder to the trap oxidation catalyst and venting to atmosphere a flow of 160 ml/min. Triplicate samples of the flow taken from an injection/withdrawal port following the catalyst were injected into the TGNMO analysis system while the carrier gas bypassed both the oxidizer and the methanator. A response from the FID detector indicated a faulty oxidizer catalyst in the cryogenic trap burnout system. At a catalyst efficiency of less than 95% it was replaced.

B. Carrier Gas Contaminate Check

The purity of the chromatographic column nitrogen carrier gas and the zero air used for cryogenic trap burning as well as for tank and vessel pressurization were checked daily. Impurities in either gas results in a positive bias in the results.

(1) Zero Air Check - Zero air was checked for its total carbon content by withdrawing a sample from a port in the zero air supply line when the trap burnout system was receiving a flow of 160 ml/min, and injecting it into the TGNMO analysis system prior to the oxidizer. A zero air total carbon content greater than 5 ppm indicated that replacement of the ascarite CO_2 filter, molecular seive, or zero air oxidation catalyst was required.

(2) Nitrogen Carrier Gas Contaminant Check - The nitrogen carrier gas was checked for contaminants daily as follows. The column was flushed of all carbon by placing it in boiling water while in the back flush mode. The column was then passed through the temperature sequence as if a sample had been injected starting with the dry ice-isoproponal bath in the forward mode. If the organic peak calculated was more than 5 ppm, the carrier gas cleanup system is regenerated with a new molecular sieve and oxidation catalyst. Organic peaks of less than 5 ppm are subtracted from that day's tank analyses.

C. Leak Checks

Leaks in the TGNMO analysis and sampling system are not readily apparent and the system must be diligently checked to assure integrity of the samples. Each section of the sampling and analysis system was checked for leaks daily prior to use.

(1) Tank Leaks - The evacuated sampling tanks were checked for leaks once every two weeks by evacuating them to more than 25 in. Hg measuring the vacuum with a mercury manometer, and remeasuring the vacuum 24 hours or more later. If the vacuum decreased, the tank was assumed to have leaked. The leak was located by pressurizing the tank to 30 in. Hg and submerging it in water. Once the leak was located and fixed, the tank was retested and returned to service.

(2) Sampling Assembly Leaks - The gauge assembly, connections between the gauge assembly, rotometer, traps, and sampling lines were checked daily at the sampling site for leaks. The sampling line was capped and a tank pressurized to 30 in. hg. was attached to the gauge assembly. All connections in the system were squirted with soapy water and inspected for bubbles. If a leak was found it was corrected before sampling.

(3) Trap Burnoff Assembly Leaks - This assembly was checked for leaks daily by plugging the trap burnoff system where the trap was connected and a vacuum of 20 in. Hg drawn on the system. Both the flow meter and the IR analyzer were monitored. A flow through the flow meter or a CO_2 response on the IR analyzer indicated a leak which was repaired prior to use of the system. The leak location can be found by tracing the system with dry ice wrapped in a towel. When the IR analyzer gives a response, the leak has been located. All trap connections to the burnout system were checked for leaks by squirting the joints with soapy water while the system was under pressure.

(4) Analytical-Field CO_2 Cross Check - Since the analysis system yields a stack CO_2 concentration, the values can be compared to check sample integrity. An unreasonably low analytical CO_2 value as compared to the Orsat CO_2 value indicated a possible leak in the sampling system during sample collection and the results were discarded.

D. FID Calibration

Daily calibration checks of the flame ionization detector (FID) were required to detect changes in gas flows and leaks which cause decreases in sensitivity. Two calibrations are needed, one through the catalyst and FID, and one through the column, catalyst, and FID.

Several criteria had to be satisfied by the calibration check namely: (a) calibration curve linearity, and (b) calibration curve drift from pre-set limits over the duration of the project.

(1) Linearity - Linearity of the detector was checked at the beginning of the project by multiple injections of standard methane gas. Different size injections were used to simulate six different concentrations of methane, between 20 ppm to 1035 ppm. A regression analysis yielded r^2 values of 1.000 and 0.995 for injections directly to the oxidizer and injections through the column, respectively, indicating good linearity. Figures 7 and 8 show the results of the linearity check for ranges 0-1000 ppm CH_4 and 0 through 5% CO_2, respectively.

Linearity was checked once a week. Three simulated concentrations of methane were injected both through the column and bypassing the column. A r^2 was calculated to show that linearity was maintained.

(2) FID Sensitivity Check - The day to day calibration curve will exhibit random variations due to differences in gas flows and other detector operating conditions. It is also possible for the calibration line (FID sensitivity) to drift from its average position. Such a drift would indicate gradual changes in gas flows, leaks in the analysis system, or catalyst inactivation. Any calibration line drift was detected from the normal random variations found.

Random variations at any point on the calibration line will give a normal distribution. The characteristics of that distribution was quantified at the beginning of the study. Once those distributions were quantified, any daily average calibration point falling outside 90% of the distribution indicated a possible problem with the system. When this occurred, septum conditions, connection leaks, and gas flow deviations were checked and the reason for the deviation identified and corrected.

A fixed portion of a population distribution can be found by $\bar{x} \pm Ks$, where K is a value found in tables (3) and depends upon

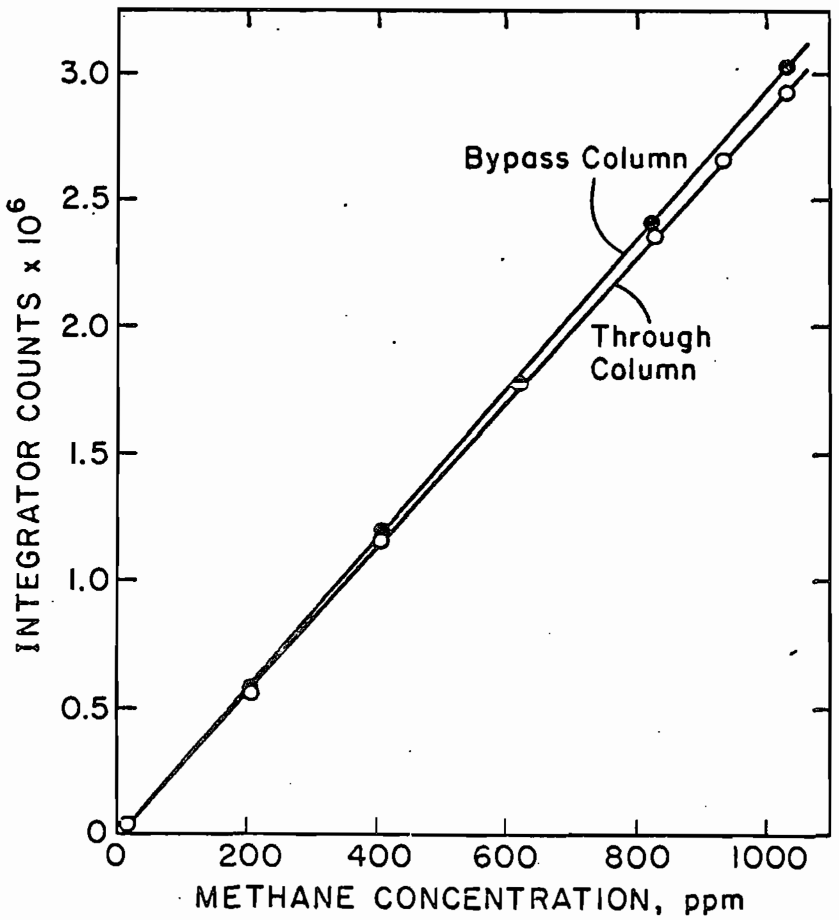

FIGURE 7

FID LINEARITY

FID RESPONSE VS. INPUT METHANE CONCENTRATION

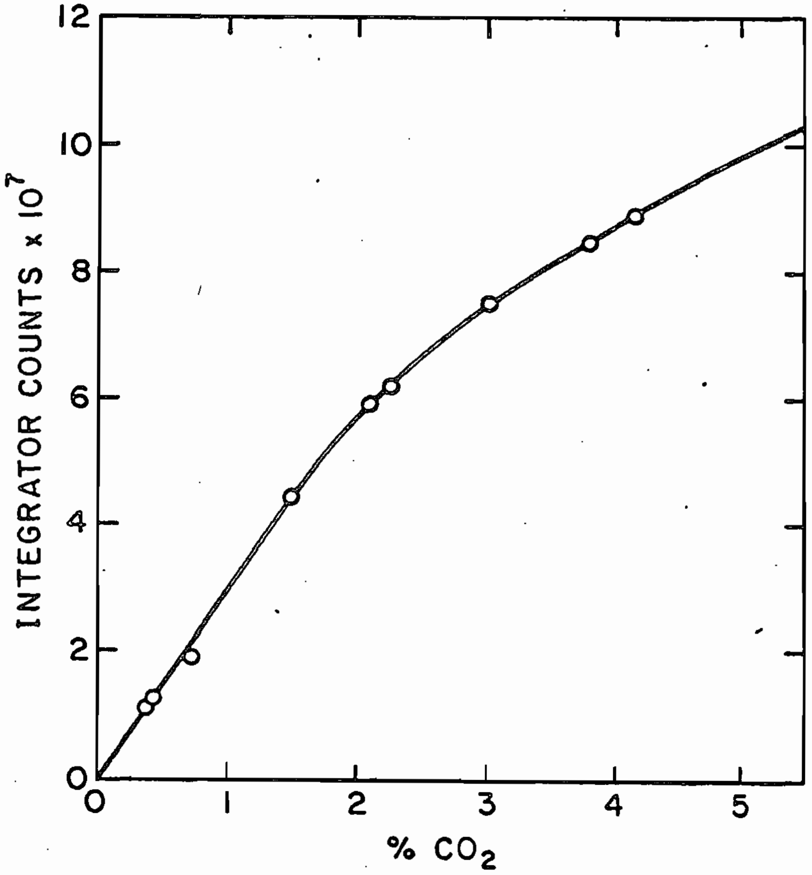

FIGURE 8

FID LINEARITY AT HIGH CO_2 CONCENTRATIONS
FID RESPONSE VS. INPUT CO_2 CONCENTRATION
AFTER CONVERSION TO METHANE

the number of samples taken, the confidence interval, and the percentage of the population to be included, $\bar{x}$ and s are the mean standard deviation of the population, respectively. For this work, 90% of the normal day to day variation will be accepted with 95% confidence. Ten calibrations were used to establish the distribution. The criteria is shown in Table 1.

TABLE 1 DEVELOPMENT OF CRITERIA FOR ACCEPTANCE OF FID CALIBRATION POINTS, EXAMPLE

Calibration Gas Concentration	Integrator Count $\bar{x}$	s	K	Integrator Count Lower Limit	Upper Limit
Direct to Oxidizer					
1033	3501,624	358,488	749,240	2,752,384	4,250,863
Through Column					
1033	3,569,880	339,768	710,115	2,859,764	4,279,995

(3) Calibration Accuracy - Establishment of a daily calibration line was made using 4 injections of 5 ml standard 1033 ppm methane gas in air. A calibration line was drawn between the 1033 ppm concentration and zero. Percent calibration accuracies at the 95% confidence level were calculated from the mean and standard deviation of the integrator counts by the equation:

$$\pm \% \text{ accuracy} = \frac{s}{\bar{x}\sqrt{n}} t$$

Where t is the value from the t distribution table with the probability of $\alpha/2$ and n-1 degrees of freedom. If the accuracy was better than ± 3%, the calibration points were accepted, if not, the system was checked for problems and more calibration injections were made until the ± 3% accuracy was achieved.

E. Data Rejection

Non-duplicated results from paired samples were an indication of errors either during the sampling or sample preparation portions of the procedure. Data was rejected when the analytical results from the duplicate samples did not agree with each other. A paired result was accepted when the absolute difference between the pair was not greater than two times the standard deviation of all the test data taken from a source.

V ACCURACY AND PRECISION

Evaluation of the TGNMO sampling results requires knowledge of the accuracy and precision of the test method. Accuracy is influenced by interferences, sample losses, and detection error. Possible interferences and losses for the test method were investigated. Confirmation of the sampling and analysis technique was established with recoveries of methanol injected into the trap both in field and laboratory situations. Precision of the TGNMO sampling and analysis methods on a source was determined by statistical analysis of the paired analytical results.

A. Interferences

The TGNMO analytical scheme passes each sample through oxidation and reduction catalysts for detection on an FID as methane. The FID is sensitive only to organic carbon. Carbon dioxide or monoxide that is not separated from the organics will constitute a positive interference. A chromatographic column is used to separate nonorganics from organic constituents in the evacuated tank portion of the sampling train. Proper operation of the column will minimize interferences due to carbon dioxide tailing.

In the cryogenic trap portion of the analysis, inorganic carbon gases are separated from the organics via freeze out of the organics. In theory, all inorganic carbonaceous gases pass through the trap, however, some of these gases and/or inorganic carbonaceous particulates can be captured in the trap. Interference results when retained inorganic carbon is released with organic carbonaceous material when the trap is heated. Each potential interference is discussed below.

(1) Carbon Dioxide Tailing on the GC Column - Carbon dioxide has a tendency to tail badly from the chromatographic column, especially at high flue gas CO_2 concentrations. Sufficient time must be allowed for the carbon dioxide to be completely eluted from the column before it is back flushed. If the column is heated and back flushed before the carbon dioxide has completely eluted, it will become part of the organic peak and constitute a positive interference. In this work CO_2 tailing was monitored at high attenuation to assure that all of the CO_2 was eluted from the column.

(2) Particulates - Particulates in pulp and paper combustion sources generally contain inorganic carbon. Wood-residue fired boiler flue gases contain unburned elemental carbon and carbonates in the fly ash. Kraft recovery furnace particulates are high in sodium carbonate. Lime kiln particulates contain calcium carbonate. If these materials pass the filter and enter the trap they become a potential source of carbon dioxide during the trap burnout.

Elemental carbon in the traps will burn to carbon dioxide. Particulate carbon must be removed from the gas stream during sampling. Particulates that are made up of carbonates may decompose when the cryogenic trap is being heated. The trap is heated to about 600°C. The decomposition temperatures of carbonates that may be present in pulp and paper mill combustion sources are listed in Table 2. (4)

TABLE 2 DECOMPOSITION TEMPERATURE OF CARBONATES

Carbonate	Decomposition Temperature
$CaCO_3$	898°C
K_2CO_3	891°C
$KHCO_3$	100-200°C
Na_2CO_3	851°C
$NaHCO_3$	270°C

Only the bicarbonates of sodium and potassium will decompose at 600°C. However, the other carbonates may react with organic acids captured in the trap to release carbon dioxide when the traps are heated. Therefore, it is imperative that good instack filtering of the gas stream be used when the presence of carbonates are suspected in the sampled source.

(3) Carbon Dioxide Absorption in Traps - Absorption of carbon dioxide in the TGNMO sampling equipment is the largest potential source of interference. Absorption of carbon dioxide can take place in both the sampling line and cryogenic trap. Any water condensed in the sampling line will absorb relatively large quantities of CO_2. Adsorption of CO_2 in the cryogenic trap occurs because of its large surface area and because its operating temperature is at the condensation temperature of CO_2. When the traps are heated during sample preparation, the CO_2 captured is desorbed from the traps and delivered to the collection vessel along with CO_2 from oxidation of the captured organics. The adsorbed CO_2 thus becomes an interference.

Flushing of traps and sampling lines with carbon dioxide-free air theoretically removes carbon dioxide. However, desorption of CO_2 from the water in the lines is slow. The NDIR detector will sometimes show as much as 10 ppm CO_2 in the air stream after a 1-hour flush; thus, a considerable amount of CO_2 remains in the system at the end of the flush period. Differing flush times will result in differing quantities of CO_2 retained. Desorption of CO_2 from internal trap surfaces has been shown to be rapid, and need not be considered further here.

Carbon dioxide can also be stripped when water condensed in the sampling lines enters the cryogenic trap and is suddenly frozen. Carbon dioxide frozen into the ice matrix cannot be removed from the trap by flushing.

Factors that may affect the quantity of CO_2 remaining in the trap after flushing are the flush time, the amount of water in the sampling system that becomes frozen, the total amount of water in the system, the water temperature prior to freezing, and the sample gas carbon dioxide concentration.

At combustion source stack sampling conditions, the amount of CO_2 captured by the trap can be significant. Table 3 shows the equilibrium concentration of carbon dioxide absorbed in water in terms of grams CO_2 per gram water at various water temperatures and carbon dioxide concentrations. To illustrate the potential interference due to CO_2 absorption in water condensed in the traps, Figure 9 shows the ppm interference possible at various stack moisture and carbon dioxide concentrations. The actual amount of CO_2 retained by the traps will depend upon conditions at which the samples are collected.

TABLE 3 EQUILIBRIUM ABSORPTION OF CARBON DIOXIDE IN 100 GRAMS OF WATER (5)

Temperature (°C)	Grams CO_2 Absorbed in 100 Grams of Water				
(%CO_2)	0.04	5	10	15	20
0	1.3×10^{-4}	0.017	0.033	0.050	0.067
10	0.93×10^{-5}	0.012	0.023	0.035	0.046
20	0.68×10^{-5}	0.0085	0.017	0.026	0.034
30	0.50×10^{-5}	0.0065	0.013	0.020	0.026
40	0.42×10^{-5}	0.0052	0.010	0.016	0.021

B. Laboratory CO_2 Absorption Interference Study

Adsorption characteristics of carbon dioxide in the cryogenic traps used in this study were determined in the laboratory using several different sample stream carbon dioxide and moisture concentrations. The test covered conditions of no CO_2 or moisture to 18% CO_2 and 50% moisture in the gas stream. Results from the tests are reported in a format that allowed correction of field sampling data for the interfering CO_2.

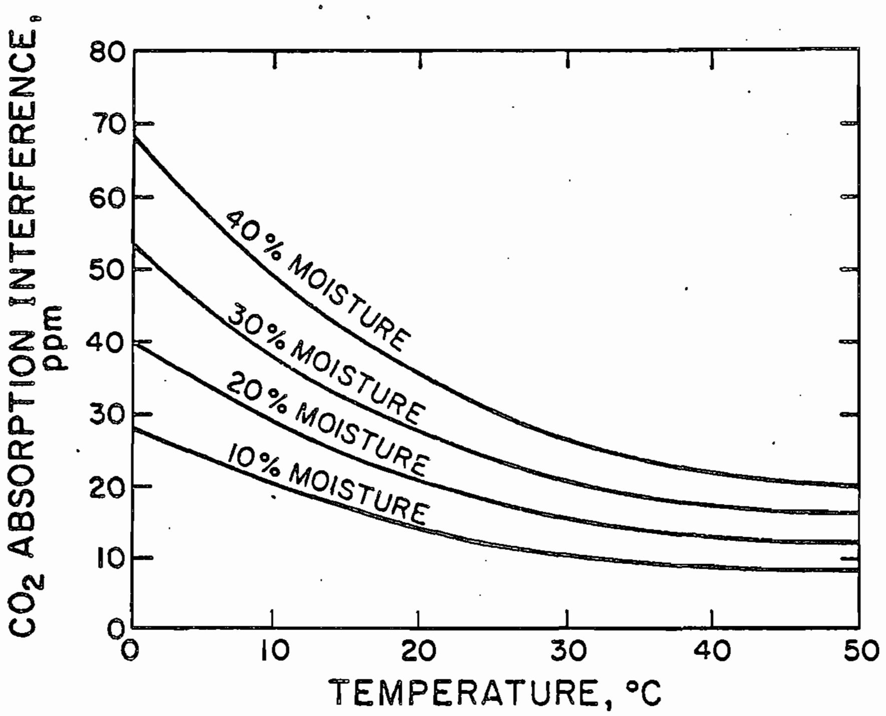

FIGURE 9

INTERFERENCE POSSIBLE DUE TO ABSORPTION OF CO_2 IN WATER CONDENSED IN SAMPLING TRAP AT VARIOUS STACK GAS % MOISTURES AND WATER TEMPERATURES AT 12 % CO_2

(1) Procedure - Carbon dioxide in air mixtures were directed to a heated U-tube containing water to add moisture to the air stream. The water added to the U-tube was passed through activated carbon to remove organics. The quantity of moisture added to the air stream was roughly controlled by adjusting the temperature of the U-tube. This moisturized air was passed through a MnO_2 oxidation catalyst at 600°C to insure that there were no organics delivered to the trap. After the oxidation catalyst the gas passed through a cryogenic trap set in dry ice, to a flowmeter and to a 17 l evacuated tank. This apparatus is the trap burnout system used in reverse but with a sample collected as in the field. Gas flow was controlled to 200 cc/min until 10 l of gas was collected.

The trap was then flushed with carbon dioxide free air flowing at 100 cc/min until the NDIR registered less than 10 ppm CO_2. Flushing of the traps took from 20 min. to 1 hr.

After flushing, the trap was heated with an acetylene torch with the CO_2 free sweep-gas passing through the oxidation furnace, a cold trap to remove moisture, the NDIR detector, and into an evacuated collection vessel. When all of the CO_2 was removed from the trap as indicated by the NDIR the collection vessel contents were analyzed with the TGNMO analyzer. The amount of water collected in the cold trap was used to determine the gas stream moisture content.

Vessel volumes, pressures, temperatures, and moisture collected in the trap were measured and recorded. Analysis of the collection vessel contents was according to the TGNMO procedures used on field samples.

(2) Calculations - The data was reduced to a common basis for consistency and ease of relating it to field samples. The weight of CO_2 caught in the traps can be expressed by:

$$\text{Weight} = (PV/RT)\ \text{M.W.}\ (\text{ppm})$$

For easier comparison to field samples, the data is presented as carbon dioxide found for a 10 l field sample. This is calculated by:

$$\text{ppm @ STPV} = \frac{(\text{ppm measured})(P\ V)(293)}{(T)(29.92)(10)} = \frac{(\text{weight})(293)(R)}{(29.92)(10)(\text{M.W.})}$$

where P, V, and T are the pressure, volume and temperature of the vessel at the time of measurement. M.W. is the molecular weight of methane. To find the CO_2 background for a specific sample size, the ppm @ STPV times 10 is divided by the sample size.

C. Results

Results of the carbon dioxide interference study are shown in Table 4 and Figures 10 and 11. Figure 10 shows a constant background carbon dioxide interference for all moisture levels when the sampled gas contained less than 5 ppm CO_2 or 659 ppm CO_2. After elimination of one data point from the 650 ppm CO_2 data, the log average CO_2 background was 8.0 ppm CO_2 for the 659 ppm CO_2 data, and 8.1 ppm for the 0% CO_2 data. The log average of all the data when no moisture was added to the traps was 7.4 ppm. These results show that when there is no water present in the trap, all of the carbon dioxide is successfully removed from the trap during flushing. The small background residual CO_2 may be due to small leaks, residual carbon left in the trap or oxidation furnace from earlier runs, carbon burned from the steel the trap is constructed of, or chemically adsorbed CO_2 or CO in the system.

TABLE 4 CO_2 INTERFERENCE STUDY DATA

0 % CO_2

ml H_2O in trap	% H_2O in air	Interference CO_2 ppm
0	0	10.1
0	0	9.3
1.0	10.7	4.2
2.5	24.3	9.7
2.5	25.1	8.5
2.5	33.0	8.5
3.3	27.9	9.5
3.6	32.4	5.3
6.1	45.1	7.7
8.6	52.6	8.0

658 ppm CO_2

ml H_2O in trap	% H_2O in air	Interference CO_2 ppm
0	0	7.1
0	0	8.4
0.9	10.4	6.0
1.7	17.5	5.1
2.9	29.4	14.2
4.3	38.0	3.9
5.0	40.7	40.0
5.1	39.8	17.7
5.7	44.3	13.6
6.6	46.7	7.9
8.6	54.0	3.5
8.7	53.5	13.0

8 % CO_2

ml H_2O in trap	% H_2O in air	Interference CO_2 ppm
0	0	9.4
0	0	2.5
0.6	6.9	6.3
1.4	14.7	6.3
3.0	27.9	5.1
4.0	32.7	27.7
5.0	38.6	61.7
8.6	53.0	62.9
9.3	52.8	23.4

12 % CO_2

ml H_2O in trap	% H_2O in air	Interference CO_2 ppm
0	0	5.1
0	0	8.4
.8	9.1	13.3
1.6	16.8	5.4
3.3	32.3	65.8
4.5	35.7	28.2
5.1	39.3	21.2
6.4	45.0	413.0
7.0	47.7	7.1

12% CO_2

ml H_2O in trap	% H_2O in air	Interference CO_2 ppm
0	0.0	13.6
1.2	13.1	30.8
1.3	16.6	31.3
1.7	14.5	71.1
1.7	20.9	37.7
1.8	19.3	62.7
2.4	16.5	49.9
3.8	29.3	21.0
3.8	25.5	14.0
3.9	24.4	24.4
4.2	29.7	81.8
4.4	29.4	106.1
5.5	32.2	128.9
5.6	32.7	96.6

15 % CO_2

ml H_2O in trap	% H_2O in air	Interference CO_2 ppm
0	0.0	6.8
0	0.0	10.0
1.1	12.4	7.8
2.7	28.5	35.7
2.8	-	65.2
3.7	33.6	15.3
5.4	42.0	13.0
5.6	-	117.0
5.7	44.6	22.0
6.3	45.5	72.0

18 % CO_2

ml H_2O in trap	% H_2O in air	Interference CO_2 ppm
0	0	8.3
0	0	10.5
1.3	15.2	14.0
2.8	29.3	70.9
4.4	35.1	51.2
4.5	39.1	23.4
7.9	51.3	170.0
9.3	54.6	146.0

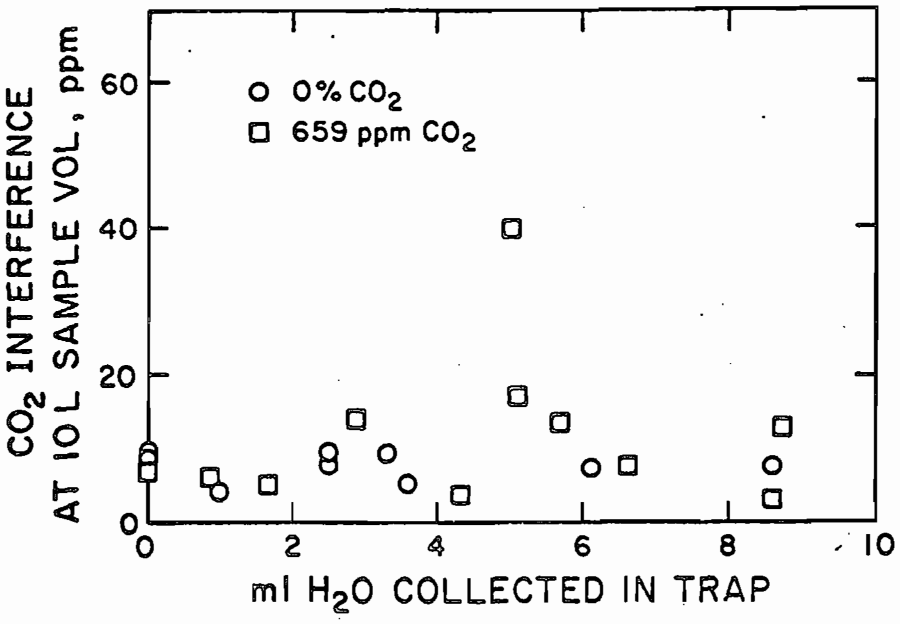

FIGURE 10

CO_2 INTERFERENCE AT LOW STACK GAS CARBON DIOXIDE CONCENTRATIONS

Figure 11 shows the CO_2 absorption interference as a function of sampled gas moisture content at carbon dioxide concentrations between 8 to 18%. Below 20% moisture there appears to be no significant interference above background. Above 20% flue moisture there appears to be a random interference that increases with sampled gas moisture and carbon dioxide content. The randomness of this data makes it difficult to predict the CO_2 interference encountered at high stack moistures. Figure 12 shows the same data in terms of ml H_2O caught in the trap. This data is representative of a 10 l sample volume with the NCASI sampling equipment.

A closer look at all the data collected for 12% CO_2, Figure 13, shows that the CO_2 interference tended to fall into two groups, that which grouped about a line with a slope of 18.5 ppm CO_2 interference per ml H_2O in the trap and that which fell below 30 ppm interference regardless of the amount of water collected in the trap. There is no apparent reason to explain the different groupings. Almost all of the interference data fell below the theoretical maximum interference which occurs when the water absorbing the CO_2 is at 0°C. The 18.5 ppm CO_2 interference per ml water corresponds to the theoretical interference at a water temperature of 3°C.

Most combustion sources have stack moisture contents above 20% and carbon dioxide concentrations above 10%. At these conditions the interference can be significant. A correction factor is needed

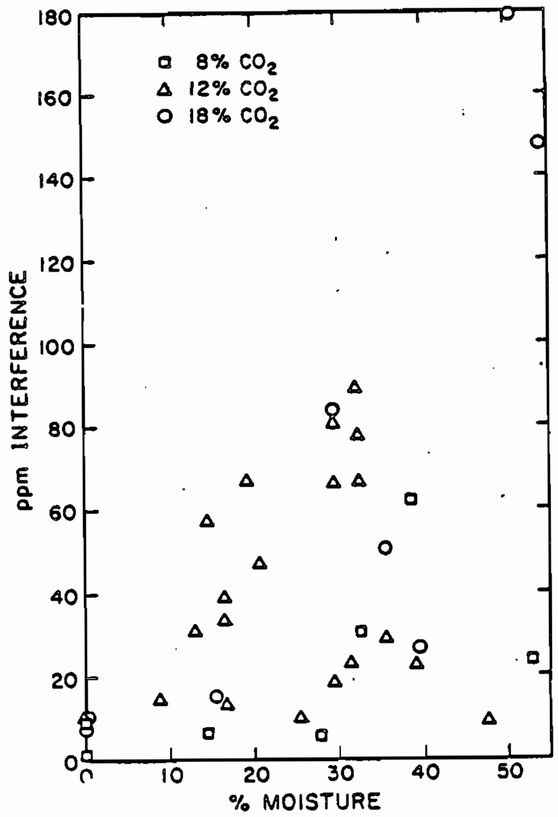

FIGURE 11

INTERFERNCE AT HIGH STACK GAS CO_2
CONCENTRATIONS AS A FUNCTION OF
STACK GAS % MOISTURES

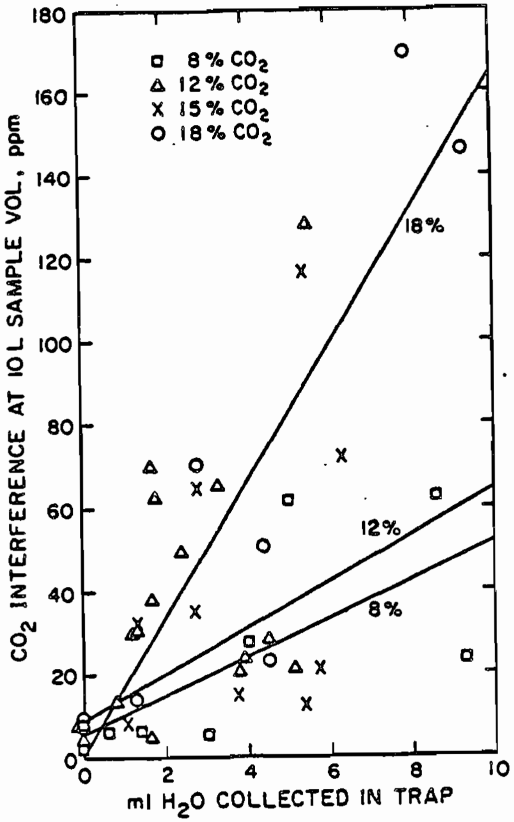

FIGURE 12

INTERFERENCE AT HIGH STACK GAS CO_2
CONCENTRATIONS AS A FUNCTION OF WATER
COLLECTED IN SAMPLING TRAP

to adjust TGNMO data collected from combustion sources to reflect the interference from CO_2 absorption in the traps. Because of the high variability of the interference the correction factor is applicable only for an average of a number of data points.

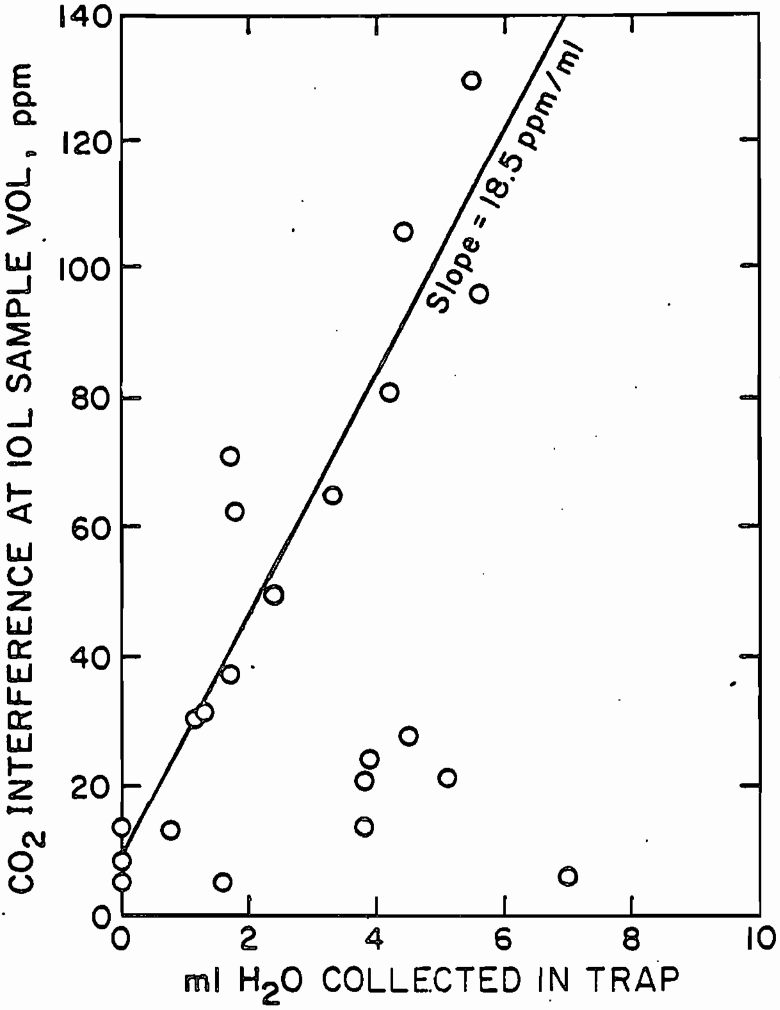

FIGURE 13

CARBON DIOXIDE INTERFERENCE AT 12% CO_2 IN STACK GAS

If it is assumed that the interference is proportional to the amount of water collected in a trap, the interference can be calculated by measurement of the water captured and CO_2 content of the gas stream. The interference data was plotted against ml H_2O collected in a trap and linear regression run for each CO_2 concentration studied. The slope of the lines is the amount of CO_2 adsorbed per ml water present. The slopes were plotted in Figure 14 and a linear regression run. From this regression data a formula was developed to estimate an average CO_2 interference at particular sampling conditions. The resulting formula was:

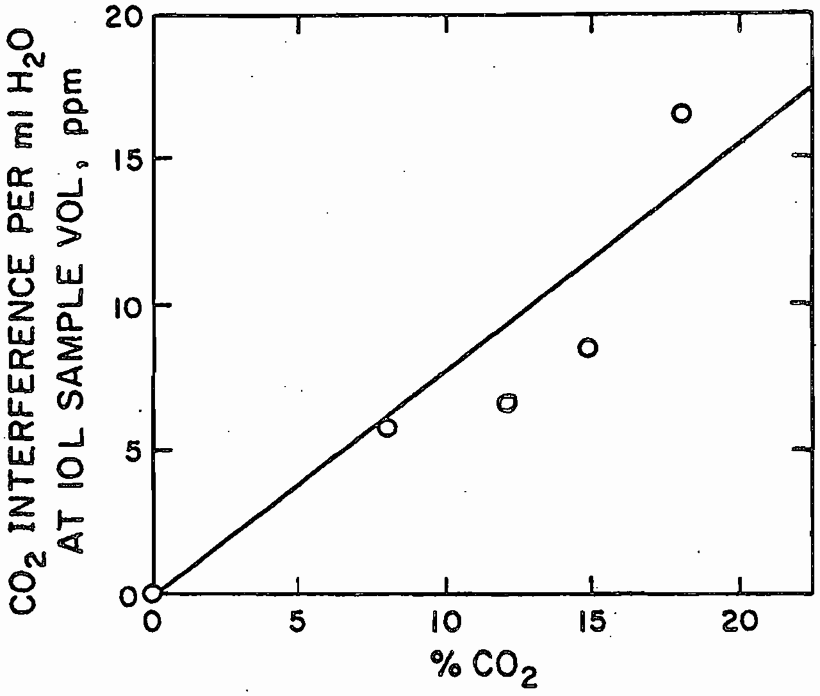

FIGURE 14

CO_2 INTERFERENCE PER ml H_2O IN SAMPLE TRAP AT 10 l SAMPLE VOLUME vs. SAMPLE GAS % CO_2

$$\text{Average Interference} = \frac{71 + [(98.1 \times \%CO_2) - 6.2](\text{ml } H_2O \text{ collected})}{\text{sample volume}}$$

This formula will give an average correction value for the amount of CO_2 and water present in the trap, but due to the high variability of the moisture data it can not be used to correct an individual piece of data.

To correct the raw TGNMO data collected in this study from wood-residue fired boilers for the random CO_2 interference, each piece of data is corrected for an average CO_2 interference.

Although the individual corrections on each piece of data can be in error to the extent of ± the correction value, the average of a sufficient number of data points should smooth the correction randomness resulting in a corrected average TGNMO emission value. The uncorrected data contains the randomness associated with CO_2 absorption. This randomness would need to be averaged whether or not the data is corrected for CO_2 absorption.

The minimum detectable level of the TGNMO sampling procedure is dependent upon the CO_2 and moisture content of the gas being sampled. At atmospheric carbon dioxide levels the minimum detectable TGNMO level is about 10 ppm. Below this level it is difficult to distinguish between the method background and what is in the sample. As the sampled gas carbon dioxide concentration increases, the moisture in the sample becomes an important factor in limiting minimum detection. High CO_2 and no moisture situations will set the minimum detectable TGNMO at the background level of 20 ppm. At 15% moisture and 12% CO_2, conditions typical of burning wood residue, the minimum detectable level is about 35 ppm. At 30% moisture and 15% CO_2, conditions typical of recovery furnaces, the minimum detectable level was shown to be about 70 ppm.

D. Trap Contamination

Cryogenic traps must be tightly capped when not in use or when filled with a sample. Experience in this study showed that uncapped, or loosely capped traps in storage adsorb carbonate materials from the air. This adsorbed material constitutes a variable background. As a precaution, any trap stored in the laboratory for periods greater than two weeks was burned prior to use.

E. Losses

Loss of organic compounds in the TGNMO sample and analysis procedures can occur in the sampling probe, through leaks, absorption of CO_2 in the trap burnout water removal system, adsorption or organics in the evacuated sampling tanks, hanging up on the chromatographic column, and incomplete oxidation while being burned out of the trap. Sample losses due to leaks and poor oxidation are minimized through the quality control procedures previously described.

(1) Probe Losses - Organic material can condense in the probe or adsorb onto the probe filter during sampling. The probe is kept at stack temperature to minimize this condensation.

(2) Adsorption Losses - Carbon dioxide produced from oxidation of the cryogenic trap contents can be adsorbed in any moisture condensing in the lines after the oxidation furnace. To eliminate this, adsorption water was frozen out of the gas stream immediately following the oxidation catalyst. Water will be condensed to the liquid phase before freezing and adsorbed CO_2 can be frozen into the ice.

The amount of CO_2 absorbed in the water before freezing is controlled by Henry's Law for CO_2 absorption. At 0°C the amount of adsorption in water is 3.36×10^{-3} grams times the mole fraction of CO_2 for each ml of water present, a maximum of 1.71×10^{-4} ppm CO_2 for each ppm CO_2 present when water is condensed during the burnout. This is a very small loss.

F. Recovery of Injected Compounds

The accuracy of the overall TGNMO analysis technique was demonstrated by recovery of known quantities of organic compounds injected into traps both in the laboratory and in the field. Laboratory methanol injections into the traps equivalent to 300 to

440 ppm methane showed an average recovery of 114%. Field recoveries were determined by injecting the equivalent of 250 to 410 ppm methanol into one of the duplicate pairs while sampling a wood residue fired boiler. The TGNMO determined from the sample without methanol injection was subtracted from the sample results into which methanol was injected to give the recovery. The average of the field recoveries was 88%. The data is shown in Table 5.

G. Precision of Data

The precision of data collected is established to evaluate the meaningfulness of the results. The data collected in this study was evaluated for precision via the statistical procedure called analysis of variance.

(1) Analysis of Variance - Differences in results from one sample to another can be due either to variations in the source being sampled or due to random error in the sampling and analysis technique. It is desirable to separate the variation in the data from that which results from the analytical procedure so as to gain a true indication of the source characteristics. The variation due to the source can then be tested for significance against the randomness resulting from the analytical procedure.

Many statistical texts contain discussions on analysis of variance (ANOVA). The procedure used in this work uses a single factor analysis and is as follows.

T = x where x is the value of each observation

x^2 = summation of squares of all observations

x^2 = summation of squares of all observations

Tc = total of the duplicate pairs

n = number of replications of each test

N = total number of samples taken

c = number of observations (N/n)

$$SSC = \frac{Tc^2}{n} - \frac{T^2}{N}$$

$$SSt = X^2 - \frac{T^2}{N}$$

$$SSr = SSt - SSc$$

TABLE 5 METHANOL RECOVERY DATA

Sample Number		Methanol Injected ppm as CH_4	TGNMO Analytical Result, ppm	Recovery ppm	Recovery %
Field Recoveries	**Source**				
11271[a]	W-R F	0	53	340	82
11272	Boiler	408	390		
11273[a]	W-R F	381	420	310	82
11274	Boiler	0	110		
12281	W-R F	236	300	220	95
12282	Boiler	0	81		
12283	W-R F	342	450	300	88
12284	Boiler	0	150		
01231	W-R F	245	240	200	81
01232	Boiler	0	42		
01233	W-R F	0	68	270	99
01234	Boiler	266	340		
03113	Kraft Rec'y	0	147	152	94
03114	Furnace	162	300		
03131	Kraft Rec'y	0	100	171	107
03132	Furnace	161	270		
03271	Kraft Rec'y	176	300	180	103
03272	Furnace	0	120		
12271	Laboratory	439	490	490	113
12272		379	440	440	115

table to calculate the mean squares and separate estimates of variance due to analytical or wood residue boiler sources.

Source of Variation	Squares (SS)	Freedom (DF)	Square, (MS) (MS=SS/DF)	Mean Square Ratio (MSR)	Parameters Estimated
Boilers	SSc	c-1		$\frac{MSc}{MSr}$	$\sigma^2 + n\sigma A^2$
Experimental	SSr	c(n-1)			σ^2

When the MSR is less than the appropriate F statistic from the F distribution tables, the variation appearing in the data is due to the randomness resulting from the analytical procedures and not necessarily from the source.

An estimate of the variance of the TGPRO from the boilers is calculated by:

$$Sn^2 - \frac{SSc/(c-1) - SSr/c(n-1)}{n}$$

An estimate of the variance of the analytical procedure is given by σ^2.

VI RESULTS

Wood-residue boiler A was sampled 11 times, 7 of which met data acceptance criteria. Samples from boiler A were taken after the ID fan and just prior to the scrubbers. Boiler B was sampled 9 times, 8 of which met data acceptance criteria. Samples from Boiler B were taken after the multiclones and prior to the ID fan. Wood-residue fired boiler C was sampled 9 times, 7 of which met data acceptance criteria. Samples from boiler C were taken after the multiclones and prior to the ID fan. Boiler D was sampled 8 times, all of which met data acceptance criteria. Samples from boiler D were taken from the stack after the dry scrubber and ID fans.

Boilers A and B were sampled under a variety of operating conditions and while operated by numerous operators. Boilers C and D ran at similar operating conditions and had the same operators each time they were sampled.

A. TGNMO Emissions from Boilers Sampled

TGNMO as methane, carbon monoxide, and other pertinent data for duplicated samples are shown in Table 6. The average uncorrected TGNMO's for each boiler was 0.12, 0.07, 0.09 and 0.05 lb as methane/10^6 Btu fired for boilers A through D respectively. Little or no ethane or ethylene were found in the samples.

During the early part of the work on wood-residue fired boilers, water collected in the burnout moisture removal trap was not measured. Calculation of an estimate of the CO_2 absorption interference for each piece of data could not be performed. Interference estimates were calculated for each source with the data that was available for that source. Wood-residue boilers C and D had complete information for estimating the CO_2 interference. Average corrections for the boilers were 0.016, 0.015, 0.014, and 0.015 lb/10^6 Btu representing a corrected TGNMO contribution of 0.10, 0.05, 0.07, and 0.04 lb/10^6 Btu for boilers A through D respectively.

The average 1 hour geometric mean of the carbon monoxide values were 0.90, 0.20, 2.52 and 0.22 lb/10^6 Btu were found to be log normal distributed. All analytical data generated is presented in Appendix B.

B. Precision

Two factors must be accounted for when considering the precision of this data. The hidden variation in the carbon dioxide interference correction factor and the variation found between the duplicate samples. It is difficult to predict the uncertainty contribution due to application of the interference factor because of the large variation in the data producing the correction factor. At best the correction factor variation is plus or minus the correction factor. The variation in the interference factor need not be considered when working with uncorrected data.

The precision of the data as indicated by duplicate samples is obtained from an analysis of variance. Results of analysis of variance on uncorrected lb/10^6 Btu data is shown in Table 7.

TABLE 7 ANALYSIS OF VARIANCE RESULTS

Boiler	n	S Sample	S Error	MSR	F	Significant?	95% Confidence About Average
A	12	0.066	0.019	28.9	2.8	yes	0.043
B	8	0.021	0.021	2.9	2.8	no	0.025
C	7	0.018	0.026	3.2	4.3	no	0.032
D	8	0.005	0.011	1.4	3.8	no	0.010

$\frac{lb}{10^6 Btu} \times 9 = \frac{lb}{ton}$ [illegible]

[illegible]

TABLE 6 WOOD RESIDUE FIRED BOILER TGNMO DATA

(uncorrected)

TGNMO as CH_4		CO as CO		Stack O_2	Stack Moisture	Average Steam Production
lb/10^6 Btu	ppm	lb/10^6 Btu	ppm	%	%	lb/hr
Boiler A						
0.06	100	3.25	3000	7.5	-	145,000
0.19	190	3.03	1750	11.2	-	75,000
0.22	310	-	3050	10.5	-	125,000
0.18	190	1.20	740	11.5	-	130,000
0.10	140	0.64	640	7.3	12.3	135,000
0.14	210	0.31	260	7.8	25.3	100,000
0.08	100	0.38	300	8.4	17.4	100,000
0.05	76	2.16	2230	8.0	11.7	130,000
0.21	316	1.45	5610	7.0	15.3	130,000
0.04	53	0.42	350	9.0	16.0	140,000
0.06	63	0.66	410	8.6	16.3	100,000
0.06	75	1.50	1010	11.5	12.6	105,000
Avg. 0.12		1.36				
Boiler B						
0.03	79	0.042	48	6.0	16.6	300,000
0.10	180	0.091	97	6.8	15.3	350,000
0.09	120	0.417	641	5.4	-	475,000
0.08	100	0	0	9.5	20.9	350,000
0.07	60	0.604	273	12.5	7.0	250,000
0.04	30	0.539	255	11.6	10.6	250,000
0.04	40	0.249	156	7.8	13.9	410,000
0.07	80	0.110	70	7.8	12.3	420,000
[illegible] 0.065		0.257				
Boiler C						
0.06	61	1.44	900	11.0	9.7	100,000
0.14	116	4.00	1900	12.1	15.0	80,000
0.08	74	2.92	1570	11.6	15.5	90,000
0.08	84	2.99	1460	11.3	15.9	100,000
0.08	77	2.71	1640	12.0	12.0	110,000
0.08	84	2.29	1420	11.3	16.8	100,000
[illegible] 0.057		2.73				
Boiler D						
0.03	41	0.117	87	8.9	13.9	300,000
0.05	70	0.151	116	8.9	13.3	300,000
0.05	78	0.224	217	7.4	17.7	340,000
0.04	71	0.144	148	7.2	18.7	350,000
0.06	99	0.242	230	6.6	13.9	350,000
0.06	84	0.291	252	8.8	13.3	340,000
0.04	61	0.243	212	9.3	19.4	300,000
0.05	71	0.537	410	10.2	11.9	275,000
[illegible]		[illegible]				

TABLE 7 ANALYSIS OF VARIANCE RESULTS

Boiler	n	S Sample	S Error	MSR	F	Significant?	95% Confidence About Average
A	12	0.066	0.019	28.9	2.8	yes	0.043
B	8	0.021	0.021	2.9	2.8	no	0.025
C	7	0.018	0.026	3.2	4.3	no	0.032
D	8	0.005	0.011	1.4	3.8	no	0.010

Figures 15 and 16 show the approximate 1-hour average lb/10^6 Btu of TGNMO and carbon monoxide, respectively, plotted against the probability of occurrence, for each boiler.

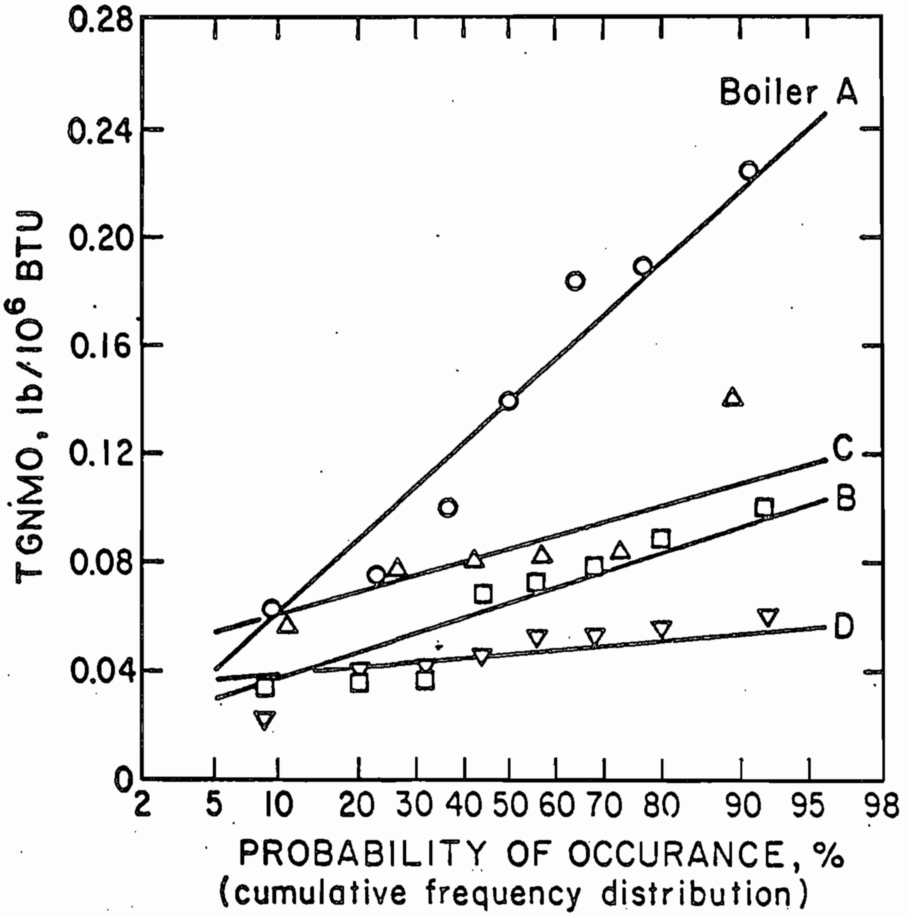

FIGURE 15

CUMULATIVE FREQUENCY DISTRIBUTION OF TGNMO's FROM WOOD-RESIDUE FIRED BOILERS

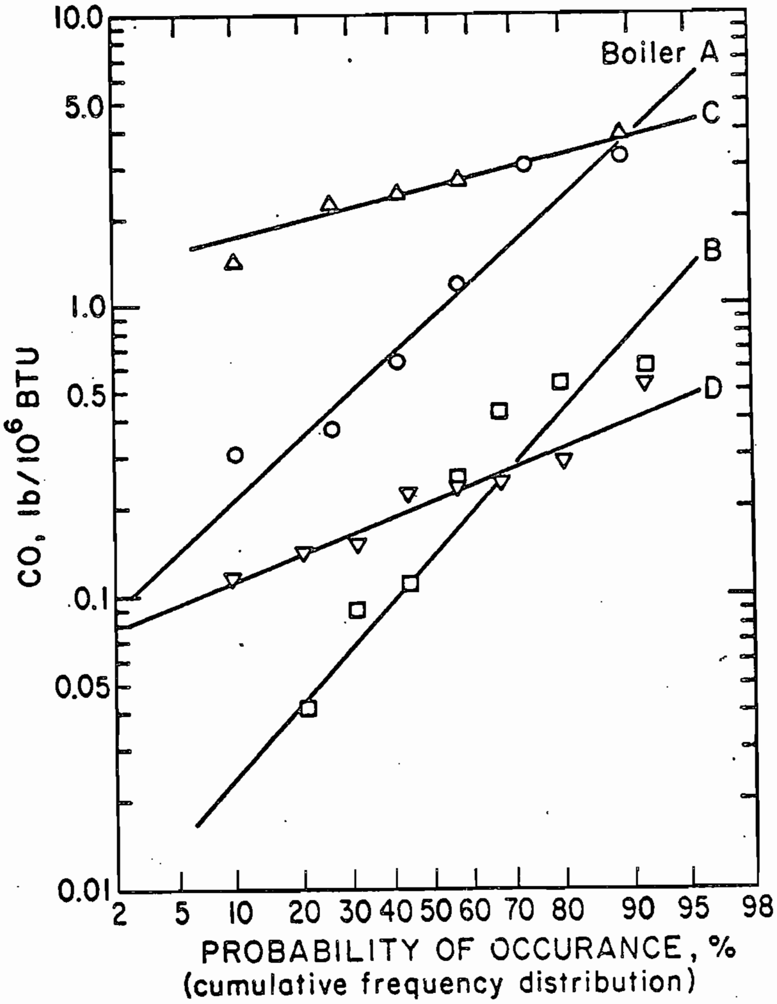

FIGURE 16

CUMULATIVE FREQUENCY DISTRIBUTION OF CO
FROM WOOD-RESIDUE FIRED BOILERS

These plots show that TGNMO lb/10^6 Btu emissions are normally distributed and CO emissions are log normally distributed. They also show that for 95% of the time the 1-hour average emissions will be less than 0.24, 0.10, 0.12 and 0.06 lb/10^6 Btu for boilers A, B, C and D, respectively. Also for 95% of the time, 1-hour average carbon monoxide emissions will be less than 5.8, 1.3, 4.3 and 0.5 lb/10^6 Btu for boilers A, B, C and D, respectively.

C. Correlation to Boiler Design

The boiler design feature to which average TGNMO emission rates were related was the percentage of total air used as overfire air. As illustrated in Figure 17, the greater the percentage of total air used as overfire, the lower the TGNMO emission rates were. Data corrected for CO_2 absorption interference was used for plotting Figure 17. When 12% overfire air was used, as in boiler A, an average TCNMO emission rate of 0.10 lb/10^6 was experienced. At 40% overfire air use, less than 0.03 lb/10^6 Btu TGNMO emissions result.

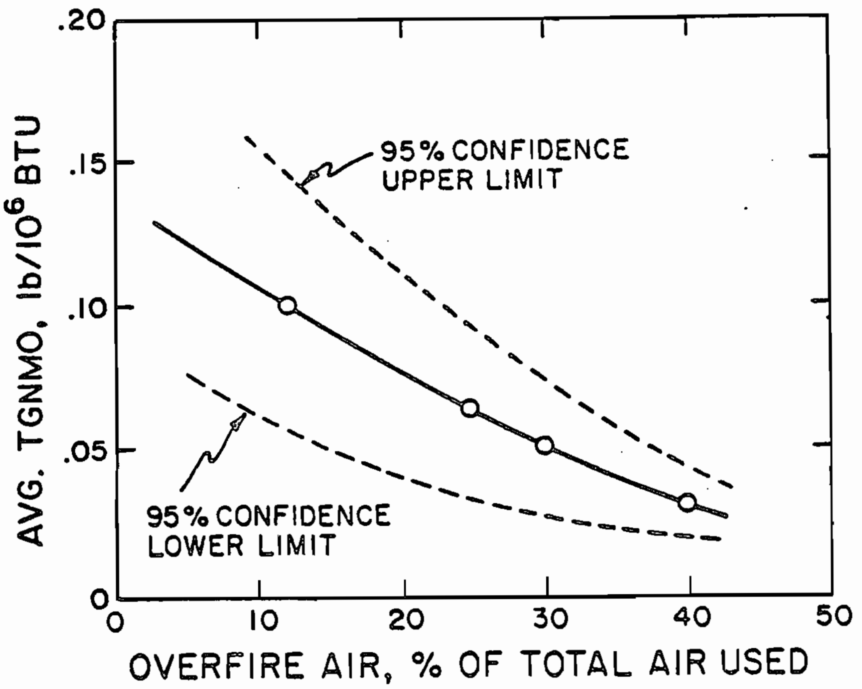

FIGURE 17

RELATIONSHIP BETWEEN TCNMO AND OVERFIRE AIR USE

No correlation between carbon monoxide emissions and boiler design or firing mode could be found. The two larger boilers had lower CO emissions than the smaller boilers, but the association could be coincidental. Data for more boilers and over longer periods of time would be required to confirm the association.

D. Correlation to Boiler Operation

The TGNMO emission data was searched for relationships to operating conditions such as steam production, flue gas moisture content and boiler flue gas exit temperature. No strong correlations could be found with any of the recorded operating parameters. Most of the boiler operations were over a narrow range of operating parameters.

Both boilers A and C showed a trend with higher TRNMO emissions higher stack oxygen levels as shown in Figures 18 and 19.

It is possible to postulate that in boilers A and C, where most of the combustion air was provided under the grates, uneven

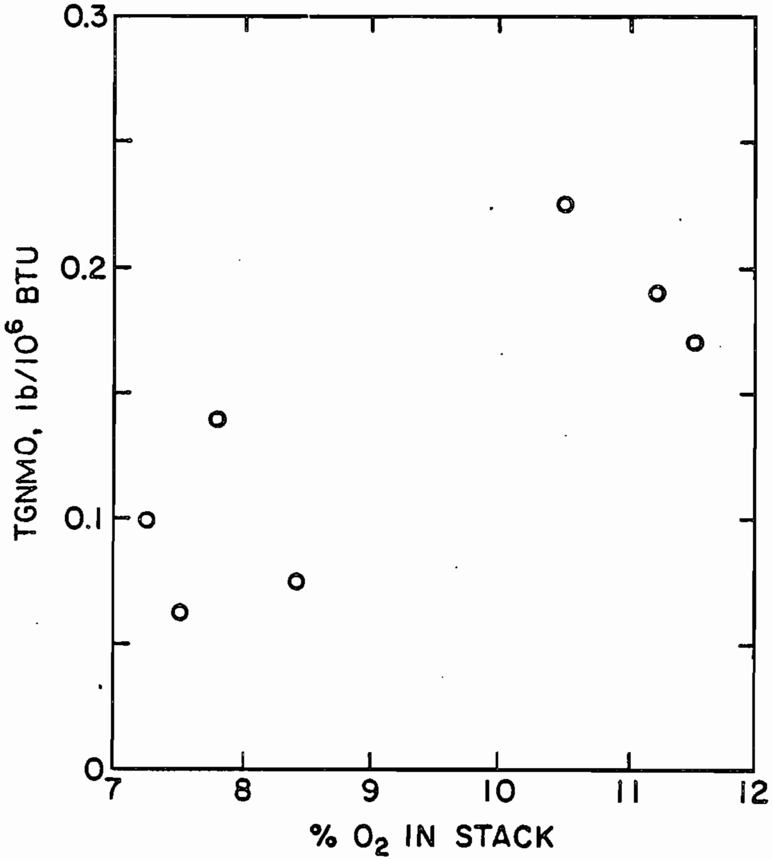

FIGURE 18

RELATIONSHIP BETWEEN TGNMO AND STACK % O_2 FOR BOILER A

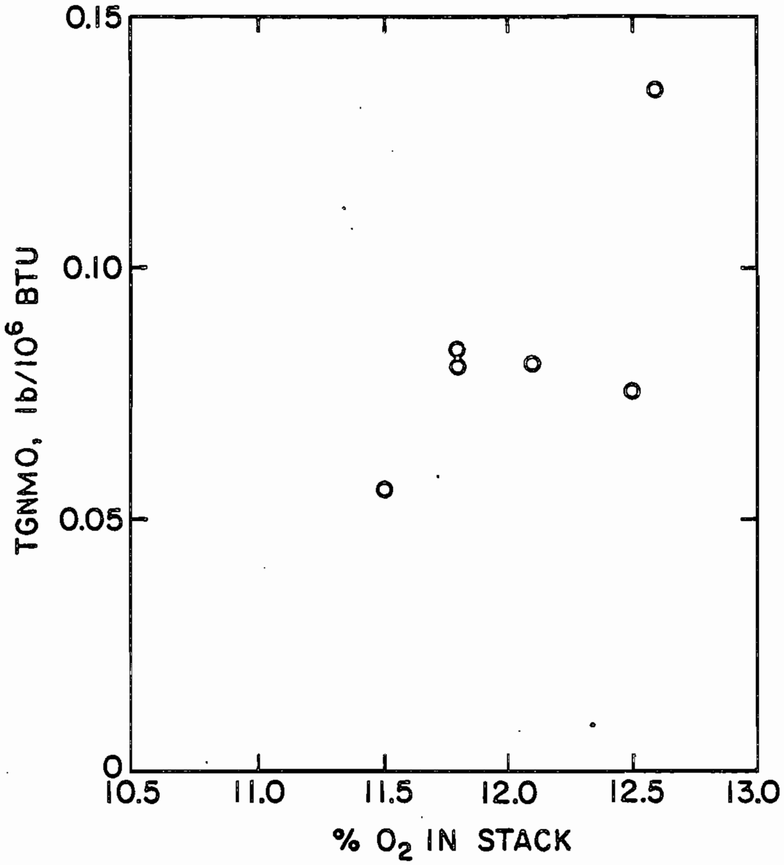

FIGURE 19

RELATIONSHIP BETWEEN TGNMO AND STACK % O_2 FOR BOILER C burning could result. An uneven fuel cover on the grate could allow combustion air to pass through some portions of the grate unreacted. High pressure drops elsewhere across the bed would prevent sufficient air to pass through the fuel for complete combustion. Inadequate gas turbulence would allow uncombusted organics to escape the combustion zone resulting in a TGNMO emission. Furnaces using overfire air are designed to induce turbulence for gas mixing and complete combustion. With low overfire air usage, evenness of the fuel on the grate would influence TGNMO emissions.

Mills B and D showed no relationship between TGNMO's and flue gas oxygen content.

Carbon monoxide emissions correlated with stack gas moisture content and auxiliary fuel type for boiler E and with O_2 for boiler C. Figures 20 and 21 show the relationship between carbon monoxide and stack gas moisture content for boiler B and between carbon monoxide and flue gas oxygen content for boiler C respectively. The high CO emissions for boiler B occurred when a large amount of oil was burned while flue gas oxygen content was high, indicating too short of a residence time for complete combustion of oil. Carbon monoxide emissions were always low when natural gas was burned as an auxiliary fuel in boiler B.

Both the carbon monoxide and TGNMO's for boiler C increased in proportion with flue gas oxygen content indicating a common mechanism and incomplete combustion of these materials.

E. Effect of a Wet Scrubber on TGNMO Emissions

Samples were taken simultaneously preceding and following an impingement type wet scrubber to determine if removal of TGNMO's occurred. The data in Table 8 shows that there was a small reduction in TGNMO's across the scrubber. The data was corrected for the CO_2 absorption interference so that the higher moisture content of the flue gas after the scrubber would not bias the results.

TABLE 8 TGNMO EMISSIONS BEFORE AND AFTER A WET SCRUBBER

	Before TGNMO $lb/10^6$ Btu	After TGNMO $lb/10^6$ Btu
	0.033	0.085
	0.190	0.083
	0.028	0.037
	0.041	0.036
	0.060	0.051
Average	0.0704	0.058

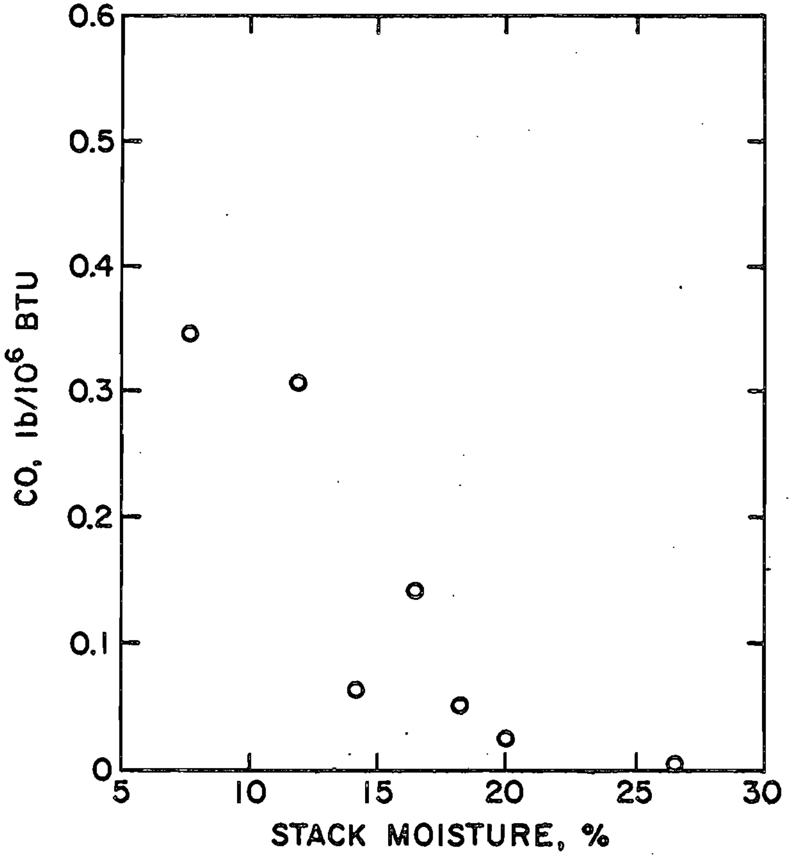

FIGURE 20

RELATIONSHIP BETWEEN CARBON MONOXIDE AND STACK MOISTURE FOR BOILER B

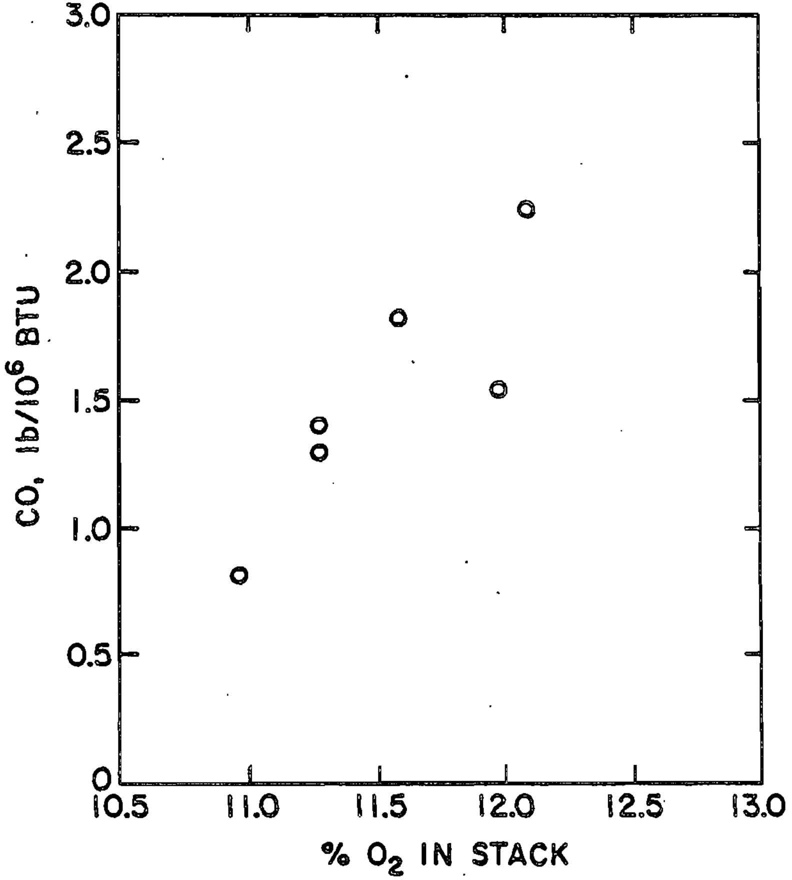

FIGURE 21

RELATIONSHIP BETWEEN CARBON MONOXIDE AND STACK % O_2 FOR BOILER C

No significant removal of TGNMO's should be expected from impingement type wet scrubbers used on wood-residue fired boilers. This type of scrubber is not designed for gas absorption and does not function well in that capacity. Any high boiling point organic compounds present in the flue gas may condense to form particulate when cooled by the scrubbers water sprays. Condensed particulate organics will be removed from the scrubber water along with other solids. Lower boiling point soluble organics such as alcohols removed by the scrubber would likely be stripped from the recirculated scrubber water into the gas stream. However, if a contaminated water makeup (i.e., evaporator condensate) is used in the scrubber, evaporation and stripping of the contaminated water could lead to an increase in TGNMO emissions.

VII SUMMARY

(1) Four wood-residue fired boilers operated on fuel derived from Douglas fir were sampled for TGNMO's and carbon monoxide. Sampling consisted of condensing volatile organics in a cryogenic trap while collecting ten liters of stack gas over an approximate 1-hour period. The samples were returned to the laboratory for analysis.

(2) Average TGNMO emission rates corrected for the interference were 0.10, 0.05, 0.07 and 0.04 lb/10^6 Btu for boilers A-D respectively.

(3) TGNMO emission rates were related to the percentage of total air used as overfire air. Larger percentages of overfire air use corresponded with lower TGNMO emissions.

(4) Average carbon monoxide emission rates were 0.47, 0.26, 2.~~6~~73 and 0.24 lb/10^6 Btu for boilers A-D respectively. Carbon monoxide showed considerable variation and appeared to be linked to flue gas oxygen content when oil was burned in boiler B, to flue gas oxygen content for boiler C, and was completely random for boiler A.

(5) An interference to the TGNMO sampling and analysis technique was investigated. This interference resulted from absorption of carbon dioxide in water condensed in the sample trap and the subsequent incorporation into the ice matrix in the cryogenic trap. This CO_2 was not removed from the trap when flushed with zero air. The resulting interference increased in variability and magnitude in proportion with CO_2 and increased moisture content of the sampled gas increased. For typical wood-residue fired boiler flue gases the interference was in the range of 15 to 30 ppm or 0.012 to 0.021 lb/10^6 Btu. The minimum detectable TGNMO for wood-residue fired boilers is 35 ppm with EPA Method 25.

(6) Little TGNMO emission reduction was observed across the wet impingement type scrubber on the wood-residue fired boiler samples.

Due to the design of these units, no significant reduction or contribution would be expected for units operated with a fresh water feed.

(7) Hydrocarbon emission factors expressed as methane for wood-residue fired boilers published in AP 42, Supplement 9 in 1979 (1) were 2 lbs hydrocarbon per ton of 50% moisture fuel fired. This value translates to 0.22 lb hydrocarbon per million Btu fired assuming 9,000 Btu per pound wood residue heat value. This is two to four times the contribution indicated by this study conducted on wood-residue fired boilers considered as representative of current design practices. The values published in the 1979 Supplement are the same as published in the 1976 AP 42 edition and no new references are listed. Consequently, little is known about the method used in obtaining this data or if the procedures used would yield data consistent with EPA Method 25. Any comparisons made between the data generated and presented in this text and the value presented in AP 42, Supplement 9 should consider the difference in methods by which the data was generated.

VIII REFERENCES

(1) "Compilation of Air Pollutant Emission Factors," 3rd Edition, Supplement 9, AP-42 (1977)

(2) Federal Register 45 (194) (October 3, 1980)

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

(4) Weast, B. and Hodgman, [Eds.], Handbook of Chemistry and Physics, 46 Edition, The Chemical Rubber Company (1965)

(5) Perry, J.H., Editor, Chemical Engineering Handbook, 4th Edition, McGraw-Hill Book Company, New York, New York (1969)

APPENDIX A

EPA METHOD 25

40 CFR Part 60

[FRL 1525-7]

Standards of Performance for New Stationary Sources; Addition of Reference Methods 24 and 25 to Appendix A

AGENCY: Environmental Protection Agency (EPA).

ACTION: Final rule.

SUMMARY: This action establishes two new reference methods to be added to Appendix A of 40 CFR Part 60, Standards of Performance for New Stationary Sources. Reference Method 24 will be used to determine the volatile organic compound (VOC) content of coating materials, and Reference Method 25 will be used to determine the percentage reduction of VOC emissions achieved by emission control devices. These reference methods will be used in several air pollution regulations for industrial surface coatings which are being developed for proposal and promulgation.

EFFECTIVE DATE: October 3, 1980.

ADDRESSES: *Background Information Document.* The Background Information Document (BID) for the promulgated test methods may be obtained from the U.S. EPA Library (MD-35), Research Triangle Park, North Carolina 27711, telephone number (919) 541-2777. Please refer to "Reference Methods 24 and 25—Background Information for Promulgated Test Methods," EPA-450/3-79-030c.

Docket. Docket No. A-79-05, containing all supporting information and public comments, is available for public inspection and copying between 8:00 a.m. and 4:00 pm., Monday through Friday, at EPA's Central Docket Section, Room 2902, Waterside Mall, 401 M Street SW., Washington, D.C. 20460.

FOR FURTHER INFORMATION CONTACT: Mr. Gene W. Smith, Standards Development Branch (MD-13), U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711, telephone number (919) 541-5421.

SUPPLEMENTARY INFORMATION:

Summary of Reference Methods

Reference Method 24, "Determination of Volatile Matter Content, Water Content, Density, Volume Solids, and Weight Solids of Surface Coatings," is used to determine the volatile matter content, water content, density, volume solids, and weight fraction solids of paint, varnish, or related surface coatings. Several ASTM standard methods which comprise Method 24 are used to make these determinations. All coatings are analyzed by the same procedure except for the additional step of measuring the water content of waterborne (water reducible) coatings. A data validation procedure is used to establish precision limits for the coating analysis. This verifies the ability of the analyst and the analytical procedure to obtain reproducible results for the coatings tested. In addition for waterborne coatings, the measured parameters are modified by the appropriate confidence limits based on between-laboratory precision statements.

Reference Method 25, "Determination of Total Gaseous Nonmethane Organic Emissions as Carbon," is used to measure the total gaseous nonmethane organics in source emissions. An evacuated cylinder is used to withdraw emission samples from the stack through a chilled condensate trap. After sampling is completed, the contents of the condensate trap and evacuated cylinder are analyzed separately. The organic content of the condensate trap is oxidized to CO_2 which is quantitatively collected in an intermediate collection vessel; a portion of the carbon dioxide is reduced to methane and measured by a flame ionization detector (FID). A portion of the sample collected in the gas sampling tank is injected into a gas chromatograph which separates the nonmethane organics from carbon monoxide, methane, and carbon dioxide; the nonmethane organics are oxidized to carbon dioxide, reduced to methane, and measured by FID. The results of the analyses are combined and reported as total gaseous nonemethane organics.

Background

On October 5, 1979, as an appendix to the proposed standards of performance for automobile and light-duty truck surface coating operations, EPA proposed reference methods for analyzing the volatile organic compound (VOC) content of coatings. These proposed methods were Reference Method 24 (Candidate 1) and (Candidate 2). Candidate 1 expresses the VOC content of surface coating in terms of mass of carbon. Candidate 2, based on the use of several ASTM methods, reports the mass of VOC. Both test methods were proposed to obtain public comment.

Reference Method 25 was proposed at the same time. It measures the volatile organic emissions in effluent streams from stationary sources. When used to measure the inlet and outlet streams of an emission control device, the efficiency of the device can be determined.

These methods would normally be promulgated with the standards of performance for automobile and light-duty truck surface coating operations which are scheduled to be promulgated in the fall of 1980. However, the methods are being promulgated earlier because several changes have been made to the proposed methods, and several regulations are being developed for proposal in the near future which will require the use of these methods. This will allow the public to have the opportunity to comment on the use of these final methods in their respective industries.

Public Participation

During development of the test methods, trade and professional associations and individual companies supplied information and data on these methods. After proposal on October 5, 1979, comments were received from coatings manufacturers and suppliers, trade and professional associations, and State air pollution control agencies. The methods were also discussed at a public hearing held on November 9, 1979. The public comment period was extended from October 5, 1979, to December 14, 1979.

Public Comments and Changes Made to Proposed Reference Methods

Fifteen comment letters were received on the proposed test methods. These comments have been carefully considered and, where determined to be appropriate by the Administrator, changes have been made in the proposed test methods. A detailed discussion of these comments is contained in the background document entitled, "Reference Methods 24 and 25—Background Information for Promulgated Test Methods," which is referred to in the ADDRESSES section of this preamble.

General

The Administrator has rejected proposed Reference Method 24 (Candidate 1) and selected proposed Reference Method 24 (Candidate 2) as the test method to be used to determine the volatile organic content of coatings. Conclusive data were presented by commenters showing that certain coatings representing a significant portion of those in use could not be distilled as required by proposed Method 24 (Candidate 1). For this reason, the Administrator concluded that proposed Method 24 (Candidate 1) is not applicable to all coatings and should not be selected as the reference method.

Several procedural and editorial changes have been made to Reference Method 24 (Candidate 2) and Reference Method 25 as proposed in order to clarify and to improve the sampling and analytical procedures. These changes are based on additional information obtained by EPA from experience with the methods and on the public comments received.

Reference Method 24

The following discussion summarizes the procedural changes made to proposed Reference Method 24, Candidate 2. The procedures were added to protect the source owner from invalid results that might result from poor analytical techniques, application of the method to a coating not suitable for analysis with Reference Method 24, or imprecision in Reference Method 24 resulting from a high percentage of water in the solvent.

The promulgated reference method requires the analyst to complete duplicate analyses on each sample tested. A comparison is then made between these results and the within-laboratory precision statements for each parameter. Duplicate analyses are made until the results fall within the range established for the within-laboratory precision statements. The purpose of the procedures is to verify that the analyst can achieve a level of precision for the coating under analysis equal to or better than the precision obtained by experienced analysts participating in the ASTM studies of the method. Because of the variety of coatings that may be subject to analysis, it is possible that certain coatings may not be amenable to analysis using Reference Method 24; that is, in certain cases it may not be possible to achieve results which meet the precision limits. In this case, the method provides for a case-by-case evaluation and development of a suitable procedure.

An additional procedure for waterborne coatings was added to the promulgated reference method to protect the source owner or operator from a determination of noncompliance when the owner is actually in compliance. This procedure is needed because the results of Reference Method 24 are dependent on the difference between the weight of total solvents and the weight of water. As the percent weight of water increases, the difference decreases. As a result, any imprecision in the measurement of the weight of total solvent in water is magnified in the calculation of organic solvent content. For example, if the total solvent of a coating is measured as 100±2 units and the water content is measured at 90±2 units, the organic solvent content would be in the range of 6 to 14 units. The magnitude of the range, as a percent of the true organic solvent content, increases with increasing water content and could, as shown in the example, lead to a conclusion of noncompliance even when the owner is in compliance. The procedure added to Reference Method 24 for waterborne coatings protects the owner or operator from this erroneous determination by minimizing the calculated value for VOC content. This is done, for example, by subtracting the between-laboratory precision statement from the average value of total solvent and adding the between-laboratory precision statement to the average value for water content. Thus, if a source owner is in compliance based on average coating values, the compliance method will automatically show a lower VOC content because of the adjustments made to the average values based on the between-laboratory precision statements.

Based on comments from manufacturers that ASTM 2697 has only been shown to be applicable to architectural coatings, the analytical procedure for determining volume solids has been eliminated from Reference Method 24. The commenters stated that this ASTM procedure was not applicable to all the coatings that Method 24 was intended to cover. Therefore, Method 24 requires that the volume solids be calculated from manufacturer's formulation data.

The coatings classifications step in the proposed method was eliminated because industry comments indicated that it was only necessary to separate waterborne (water reducible) and solvent-borne (solvent reducible) coatings. Therefore, the "Procedure" discussed in Section 4 of the proposed method has been simplified.

Several commenters recommended that the use of coatings manufacturers' data be allowed in calculating VOC content of coatings rather than required Method 24. Coatings manufacturers' data will be allowed in calculating VOC content of coatings because this will reduce the burden on the industry to measure all coatings with Method 24. Use of this method to calculate VOC content of coatings will require industries to closely monitor and record all organic solvents added to the coatings at the plant. Method 24 will be the reference method.

One commenter suggested that EPA should specify the volume fraction of solids for the various types of coatings similar to the way transfer efficiencies were listed. Based on comments from manufacturers that ASTM 2697 has only been shown to be applicable to architectural coatings, the volume fraction of solids determination in Method 24 has been removed. Method 24 specifies the use of manufacturer's formulation data for calculating volume fraction of solids.

Reference Method 25

The majority of the procedural changes made to Method 25 relate to calibration requirements and are meant to improve quality assurance and at the same time simplify the daily operation of the analytical equipment. This is accomplished by requiring performance tests on the analytical equipment (nonmethane organic analyzer and condensate recovery and conditioning apparatus) prior to initial use; specific criteria for the performance tests are provided. Routine daily calibrations (much less time consuming than previously required) are conducted and the results are compared to performance test reference values to determine whether the performance of the analytical equipment is still acceptable.

In the promulgated test method, several important system components are not specified; instead, minimum performance specifications for these components are provided. The method is written in this manner to allow individual preference in choosing components, as well as to encourage development and use of improved components. Therefore, Addendum I which lists specific information regarding system components found to be acceptable has been added to the method to provide guidance for users.

Specifics of the most important procedural changes that have been included in the promulgated test method are as follows:

1. Section 1.1. Applicability. This section was rewritten to clarify the applicability of Method 25 in relation to several other organic measurement methods.

2. Section 2.2.2 Nonmethane Organic Analyzer. The reference to the analyzer is changed from "total gaseous nonmethane organic analyzer" to nonmethane organic analyzer (NMO). The description is clarified to indicate that the NMO analyzer is also used to quantify CO_2 from trap condensate recovery. Furthermore, a requirement that the NMO analyzer meet an initial performance test with specific criteria is added. Previously, only demonstration of "proper separation, oxidation, reduction and measurement" was required.

3. Section 4.1.3 Pretest Leak Check. The leak check procedure is simplified. Instead of evacuating the sample train,

the sample probe is plugged and then the sample value is opened; the sample tank vacuum gauge is monitored for a change in vacuum.

4. Section 4.1.4 Sample Train Operation. This section is clarified to indicate that any probe extension used must be positioned totally in the stack effluent; any portion of the sample probe outside the stack wall must be analyzed as part of the condensate trap.

5. Section 4.1.5 Post Test Leak Check. The leak check procedure is simplified (see "3" above).

6. Section 4.3.3 Recovery of Condensate Trap Sample. A requirement for mixing auxiliary oxygen with the carrier gas just prior to the catalyst is added. The procedures are clarified to indicate that the condensate trap is placed in a muffle furnace at 500°C (changed from 600°C) and that the probe must be heated.

7. Section 5.1 Initial Performance Check for Condensate Recovery and Conditioning Apparatus. A requirement is added for an initial performance test of the system which includes a carrier gas blank value determination (section 5.1.1), and oxidation catalyst efficiency check (section 5.1.2), and an overall system performance check via liquid injections (section 5.1.3). Previously, only a catalyst efficiency check was required.

8. Section 5.2 Initial NMO Analyzer Performance Test. The calibration criteria for the NMO analyzer are changed to include an initial performance test. This performance test requires an oxidation catalyst check (5.2.1), and an analyzer linearity check (5.2.2), determination of a NMO calibration response factor (5.2.2), determination of a CO_2 calibration response factor (5.2.3), determination of a NMO blank value (5.2.4) and a system check using several gaseous organic compounds (5.2.5).

9. Section 5.3 NMO Daily Calibration. This section requires that a daily calibration of the NMO analyzer be conducted. The calibration involves one CO_2 calibration gas and one propane calibration gas. Response factors are determined for both CO_2 and NMO. and a NMO blank value is measured. This calibration is conducted with the oxidation and reduction catalysts in full operation. The results obtained are compared to the reference values obtained during the initial performance test in order to determine if the analyzer performance is acceptable. This daily calibration procedure is greatly simplified compared to the procedure previously required which included bypassing the oxidation and reduction catalysts and using several different concentration levels of methane, carbon dioxide and propane calibration gases.

10. Section 6.2 Noncondensible Organics. The calculation for the NMO concentration of the contents of each collection tank is changed by rewriting the equation to include the subtraction of the daily NMO blank value from the measured concentration.

11. Section 6.3 Condensible Organics. The calculation for the NMO concentration of the contents of each condensate trap is changed by rewriting the equation to include the substraction of the daily condensate recovery and conditioning system carrier blank value from the measured CO_2 concentration.

Other Comments

1. One commenter noted that the drying time was different for ASTM D-2369 and ASTM D-2697, and that these procedures were not consistent with each other. Since ASTM D-2697 has been deleted, this comment is no longer applicable.

2. Three commenters recommended that the direct use of a flame ionization detection (FID) system or similar instrumentation systems be allowed instead of Method 25. The specific comments made and EPA's responses are as follows:

a. *Direct FID is simpler and more precise.* While the direct use of an FID system is simpler than Method 25, it will not give accurate results in many situations because the instrument response varies with different compounds. Therefore, the FID system cannot be considered an adequate reference method, but may be acceptable as an alternative compliance procedure on a case-by-case basis as allowed in 40 CFR 60.8(b).

b. *The ability to conduct on-site analyses and DOT restrictions associated with shipping organic samples from a source location to a laboratory make the FID preferable.* The ability to use the FID system to conduct on-site analyses is not in itself sufficient justification to allow the use of direct flame ionization detection. DOT regulations regarding shipment of hazardous materials do require that great care be taken in shipping the test samples. The DOT regulations impose strict packaging requirements on flammable liquids and compressed flammable gases. However, exemptions for the strict packaging requirements are permitted for most liquids if less than one quart is shipped (see 49 CFR 172.101). In addition, the gas sample tanks likely to be shipped from an on-site location to a laboratory for analyses do not meet the DOT definition of a compressed flammable gas because the sample tanks are not under high pressure and, therefore, should not pose a shipping problem (see 49 CFR 173.300).

Miscellaneous

This final rulemaking is issued under the authority of Sections 111, 114, and 301(a) of the Clean Air Act as amended (42 U.S.C. 7411, 7414, and 7601(a)).

Dated: September 25, 1980.

Douglas M. Costle,
Administrator.

Appendix A of 40 CFR Part 60 is amended by adding Reference Methods 24 and 25 as follows:

Appendix A—Reference Methods

* * * * *

Method 24—Determination of Volatile Matter Content, Water Content, Density, Volume Solids, and Weight Solids of Surface Coatings

1. Applicability and Principle

1.1 Applicability. This method applies to the determination of volatile matter content, water content, density, volume solids, and weight solids of paint, varnish, lacquer, or related surface coatings.

1.2 Principle. Standard methods are used to determine the volatile matter content, water content, density, volume solids, and weight solids of the paint, varnish, lacquer, or related surface coatings.

2. Applicable Standard Methods

Use the apparatus, reagents, and procedures specified in the standard methods below:

2.1 ASTM D 1475–60. Standard Method of Test for Density of Paint, Lacquer, and Related Products.

2.2 ASTM D 2369–81. Provisional Method of Test for Volatile Content of Paints.

2.3 ASTM D 3792–79. Standard Method of Test for Water in Water Reducible Paint by Direct Injection into a Gas Chromatograph.

2.4 ASTM Provisional Method of Test for Water in Paint or Related Coatings by the Karl Fischer Titration Method.

3. Procedure

3.1 Volatile Matter Content. Use the procedure in ASTM D 2369–81 to determine the volatile matter content (may include water) of the coating. Record the following information:

W_1 = Weight of dish and sample before heating, g.
W_2 = Weight of dish and sample after heating, g.
W_3 = Sample weight, g.

Run analyses in pairs (duplicate sets) for each coating until the criterion in section 4.3 is met. Calculate the weight fraction of the volatile matter (W_v) for each analysis as follows:

$$W_v = \frac{W_1 - W_2}{W_3} \qquad \text{Eq. 24-1}$$

Record the arithmetic average (W_v).

3.2 Water Content. For waterborne (water reducible) coatings only, determine the weight fraction of water (W_w) using either "Standard Method of Test for Water in Water Reducible Paint by Direct Injection into a Gas Chromatograph" or "Provisional Method of Test for Water in Paint or Related Coatings by the Karl Fischer Titration Method." A waterborne coating is any coating which contains more than 5 percent water by weight in its volatile fraction. Run duplicate sets of determinations until the criterion in section 4.3 is met. Record the arithmetic average (W_w).

3.3 Coating Density. Determine the density (D_c, kg/liter) of the surface coating using the procedure in ASTM D 1475–60.

Run duplicate sets of determinations for each coating until the criterion in section 4.3 is met. Record the arithmetic average (D_c).

3.4 Solids Content. Determine the volume fraction (V_s) solids of the coating by calculation using the manufacturer's formulation.

4. Data Validation Procedure

4.1 Summary. The variety of coatings that may be subject to analysis makes it necessary to verify the ability of the analyst and the analytical procedures to obtain reproducible results for the coatings tested. This is done by running duplicate analyses on each sample tested and comparing results with the within-laboratory precision statements for each parameter. Because of the inherent increased imprecision in the determination of the VOC content of waterborne coatings as the weight percent water increases, measured parameters for waterborne coatings are modified by the appropriate confidence limits based on between-laboratory precision statements.

4.2 Analytical Precision Statements. The within-laboratory and between-laboratory precision statements are given below:

	Within-laboratory	Between-laboratory
Volatile matter content, W_v	1.5 pct W_v	4.7 pct W_v
Water content, W_w	2.9 pct W_w	7.5 pct W_w
Density, D_c	0.001 kg/liter	0.002 kg/liter.

4.3 Sample Analysis Criteria. For W_v and W_w, run duplicate analyses until the difference between the two values in a set is less than or equal to the within-laboratory precision statement for that parameter. For D_c run duplicate analyses until each value in a set deviates from the mean of the set by no more than the within-laboratory precision statement. If after several attempts it is concluded that the ASTM procedures cannot be used for the specific coating with the established within-laboratory precision, the Administrator will assume responsibility for providing the necessary procedures for revising the method or precision statements upon written request to: Director, Emission Standards and Engineering Division, (MD–13) Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711.

4.4 Confidence Limit Calculations for Waterborne Coatings. Based on the between-laboratory precision statements, calculate the confidence limits for waterborne coatings as follows:

To calculate the lower confidence limit, subtract the appropriate between-laboratory precision value from the measured mean value for that parameter. To calculate the upper confidence limit, add the appropirate between-laboratory precision value to the measured mean value for that parameter. For W_v and D_c, use the lower confidence limits, and for W_w, use the upper confidence limit. Because V_s is calculated, there is no adjustment for the parameter.

5. Calculations

5.1 Nonaqueous Volatile Matter.

5.1.1 Solvent-borne Coatings.

$W_o = W_v$ Eq. 24–2

Where:

W_o = Weight fraction nonaqueous volatile matter, g/g.

5.1.2 Waterborne Coatings.

$W_o = W_v - W_w$ Eq. 24–3

5.2 Weight fraction solids.

$W_s = 1 - W_v$ Eq. 24–4

Where: W_s = Weight solids, g/g.

6. Bibliography

6.1 Provisional Method Test for Volatile Content of Paints. Available from: Chairman, Committee D–1 on Paint and Related Coatings and Materials, American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103. ASTM Designation D 2369–81.

6.2 Standard Method of Test for Density of Paint, Varnish, Lacquer, and Related Products. In: 1980 Book of ASTM Standards, Part 27. Philadelphia, Pennsylvania, ASTM Designation D 1475–60. 1980.

6.3 Standard Method of Test for Water in Water Reducible Paint by Direct Injection into a Gas Chromatograph. Available from: Chairman, Committee D–1 on Paint and Related Coatings and Materials, American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103. ASTM Designation D 3792–79.

6.4 Provisional Method of Test Water in Paint or Related Coatings by the Karl Fischer Titration Method. Available from: Chairman, Committee D–1 on Paint and Related Coatings and Materials, American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103.

Method 25—Determination of Total Gaseous Nonmethane Organic Emissions as Carbon

1. Applicability and Principle

1.1 Applicability. This method applies to the measurement of volatile organic compounds (VOC) as total gaseous nonmethane organics (TGNMO) as carbon in source emissions. Organic particulate matter will interfere with the analysis and therefore, in some cases, an in-stack particulate filter is required. This method is not the only method that applies to the measurement of TGNMO. Costs, logistics, and other practicalities of source testing may make other test methods more desirable for measuring VOC of certain effluent streams. Proper judgment is required in determining the most applicable VOC test method. For example, depending upon the molecular weight of the organics in the effluent stream, a totally automated semi-continuous nonmethane organic (NMO) analyzer interfaced directly to the source may yield accurate results. This approach has the advantage of providing emission data semi-continuously over an extended time period.

Direct measurement of an effluent with a flame ionization detector (FID) analyzer may be appropriate with prior characterization of the gas stream and knowledge that the detector responds predictably to the organic compounds in the stream. If present, methane will, of course, also be measured. In practice, the FID can be applied to the determination of the mass concentration of the total molecular structure of the organic emissions under the following limited conditions: (1) Where only one compound is known to exist; (2) when the organic compounds consist of only hydrogen and carbon; (3) where the relative percentage of the compounds is known or can be determined, and the FID response to the compounds is known; (4) where a consistent mixture of compounds exists before and after emission control and *only* the relative concentrations are to be assessed; or (5) where the FID can be calibrated against mass standards of the compounds emitted (solvent emissions, for example).

Another example of the use of a direct FID is as a screening method. If there is enough information available to provide a rough estimate of the analyzer accuracy, the FID analyzer can be used to determine the VOC content of an uncharacterized gas stream. With a sufficient buffer to account for possible inaccuracies, the direct FID can be a useful tool to obtain the desired results without costly exact determination.

In situations where a qualitative/quantitative analysis of an effluent stream is desired or required, a gas chromatographic FID system may apply. However, for sources emitting numerous organics, the time and expense of this approach will be formidable.

1.2 Principle. An emission sample is withdrawn from the stack at a constant rate through a chilled condensate trap by means of an evacuated sample tank. TGNMO are determined by combining the analytical results obtained from independent analyses of the condensate trap and sample tank fractions. After sampling is completed, the organic contents of the condensate trap are oxidized to carbon dioxide (CO_2) which is quantitatively collected in an evacuated vessel; then a portion of the CO_2 is reduced to methane (CH_4) and measured by a FID. The organic content of the sample fraction collected in the sampling tank is measured by injecting a portion into a gas chromatographic (GC) column to achieve separation of the nonmethane organics from carbon monoxide (CO), CO_2 and CH_4; the nonmethane organics (NMO) are oxidized to

CO_2, reduced to CH_4, and measured by a FID. In this manner, the variable response of the FID associated with different types of organics is eliminated.

2. Apparatus

The sampling system consists of a condensate trap, flow control system, and sample tank (Figure 1). The analytical system consists of two major sub-systems: an oxidation system for the recovery and conditioning of the condensate trap contents and a NMO analyzer. The NMO analyzer is a GC with backflush capability for NMO analysis and is equipped with an oxidation catalyst, reduction catalyst, and FID. (Figures 2 and 3 are schematics of a typical NMO analyzer.) The system for the recovery and conditioning of the organics captured in the condensate trap consists of a heat source, oxidation catalyst, nondispersive infrared (NDIR) analyzer and an intermediate collection vessel (Figure 4 is a schematic of a typical system.) TGNMO sampling equipment can be constructed from commercially available components and components fabricated in a machine shop. NMO analyzers are available commercially or can be constructed from available components by a qualified instrument laboratory.

2.1 Sampling. The following equipment is required:

2.1.1 Probe. 3.2-mm OD (⅛-in.) stainless steel tubing.

2.1.2 Condensate Trap. Constructed of 316 stainless steel; construction details of a suitable trap are shown in Figure 5.

2.1.3 Flow Shut-off Valve. Stainless steel control valve for starting and stopping sample flow.

2.1.4 Flow Control System. Any system capable of maintaining the sampling rate to within ±10 percent of the selected flow rate (50 to 100 cc/min range).

2.1.5 Vacuum Gauge. Gauge for monitoring the vacuum of the sample tank during leak checks and sampling.

2.1.6 Sample Tank. Stainless steel or aluminum tank with a volume of 4 to 8 liters, equipped with a stainless steel female quick connect for assembly to the sample train and analytical system.

2.1.7 Mercury Manometer. U-tube mercury manometer capable of measuring pressure to within 1 mm Hg in the 0–900 mm range.

2.1.8 Vacuum Pump. Capable of evacuating to an absolute pressure of 10 mm Hg.

2.2 Analysis. The following equipment is required:

2.2.1 Condensate Recovery and Conditioning Apparatus. An apparatus for recovering and catalytically oxidizing the condensate trap contents is required. Figure 4 is a schematic of such a system. The analyst must demonstrate prior to initial use that the analytical system is capable of proper oxidation and recovery, as specified in section 5.1. The condensate recovery and conditioning apparatus consists of the following major components.

2.2.1.1 Heat Source. A heat source sufficient to heat the condensate trap (including probe) to a temperature where the trap turns a "dull red" color. A system using both a propane torch and an electric muffle-type furnace is recommended.

2.2.1.2 Oxidation Catalyst. A catalyst system capable of meeting the catalyst efficiency criteria of this method (section 5.1.2). Addendum I of this method lists a catalyst system found to be acceptable.

2.2.1.3 Water Trap. Any leak-proof moisture trap capable of removing moisture from the gas stream.

2.2.1.4 NDIR Detector. A detector capable of indicating CO_2 concentration in the zero to 1 percent range. This detector is required for monitoring the progress of combustion of the organic compounds from the condensate trap.

2.2.1.5 Pressure Regulator. Stainless steel needle valve required to maintain the trap conditioning system at a near constant pressure.

2.2.1.6 Intermediate Collection Vessel. Stainless steel or aluminum collection vessel equipped with a female quick connect. Tanks with nominal volumes in the 1 to 4 liter range are recommended.

2.2.1.7 Mercury Manometer. U-tube mercury manometer capable of measuring pressure to within 1 mm Hg in the 0–900 mm range.

2.2.1.8 Gas Purifiers. Gas purification systems sufficient to maintain CO_2 and organic impurities in the carrier gas and auxiliary oxygen at a level of less than 10 ppm (may not be required depending on quality of cylinder gases used).

2.2.2 NMO Analyzer. Semi-continuous GC/FID analyzer capable of: (1) separating CO, CO_2, and CH_4 from nonmethane organic compounds, (2) reducing the CO_2 to CH_4 and quantifying as CH_4 and (3) oxidizing the nonmethane organic compounds to CO_2, reducing the CO_2 to CH_4 and quantifying as CH_4. The analyst must demonstrate prior to initial use that the analyzer is capable of proper separation, oxidation, reduction, and measurement (section 5.2). The analyzer consists of the following major components:

2.2.2.1 Oxidation Catalyst. A catalyst system capable of meeting the catalyst efficiency criteria of this method (section 5.2.1). Addendum I of this method lists a catalyst system found to be acceptable.

2.2.2.2 Reduction Catalyst. A catalyst system capable of meeting the catalyst efficiency criteria of this method (section 5.2.3). Addendum I of this method lists a catalyst system found to be acceptable.

2.2.2.3 Separation Column(s). Gas chromatographic column(s) capable of separating CO, CO_2, and CH_4 from NMO compounds as demonstrated according to the procedures established in this method (section 5.2.5). Addendum I of this method lists a column found to be acceptable.

2.2.2.4 Sample Injection System. A GC sample injection valve fitted with a sample loop properly sized to interface with the NMO analyzer (1 cc loop recommended).

2.2.2.5 FID. A FID meeting the following specifications is required.

2.2.2.5.1 Linearity. A linear response (± 5%) over the operating range as demonstrated by the procedures established in section 5.2.2.

2.2.2.5.2 Range. Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale for a full scale range of 10 to 50000 ppm CH_4.

2.2.2.6 Data Recording System. Analog strip chart recorder or digital intergration system compatible with the FID for permanently recording the analytical results.

2.2.3 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 1 mm Hg.

2.2.4 Thermometer. Capable of measuring the laboratory temperature within 1°C.

2.2.5 Vacuum Pump. Capable of evacuating to an absolute pressure of 10 mm Hg.

2.2.6 Syringe (2). 10 µl and 100 µl liquid injection syringes.

2.2.7 Liquid Sample Injection Unit. 316 SS U-tube fitted with a Teflon injection septum, see Figure 6.

3. Reagents

3.1 Sampling. Crushed dry ice is required during sampling.

3.2 Analysis.

3.2.1 NMO Analyzer. The following gases are needed:

3.2.1.1 Carrier Gas. Zero grade gas containing less than 1 ppm C. Addendum I of this method lists a carrier gas found to be acceptable.

3.2.1.2 Fuel Gas. Pure hydrogen, containing less than 1 ppm C.

3.2.1.3 Combustion Gas. Zero grade air or oxygen as required by the detector.

3.2.2 Condensate Recovery and Conditioning Apparatus.

3.2.2.1 Carrier Gas. Five percent O_2 in N_2, containing less than 1 ppm C.

3.2.2.2 Auxiliary Oxygen. Zero grade oxygen containing less than 1 ppm C.

3.2.2.3 Hexane. ACS grade, for liquid injection.

3.2.2.4 Toluene. ACS grade, for liquid injection.

3.3 Calibration. For all calibration gases, the manufacturer must recommend a maximum shelf life for each cylinder (i.e., the length of time the gas concentration is not expected to change more than ± 5 percent from its certified value). The date of gas cylinder preparation, certified organic concentration and recommended maximum shelf life must be affixed to each cylinder before shipment from the gas manufacturer to the buyer. The following calibration gases are required.

3.3.1 Oxidation Catalyst Efficiency Check Calibration Gas. Gas mixture standard with nominal concentration of 1 percent methane in air.

3.3.2 Flame Ionization Detector Linearity and Nonmethane Organic Calibration Gases (3). Gas mixture standards with nominal propane concentrations of 20 ppm, 200 ppm, and 3000 ppm, in air.

3.3.3 Carbon Dioxide Calibration Gases (3). Gas mixture standards with nominal CO_2 concentrations of 50 ppm, 500 ppm, and 1 percent, in air. Note: total NMO less than 1 ppm required for 1 percent mixture.

3.3.4 NMO Analyzer System Check Calibration Gases (4).

3.3.4.1 Propane Mixture. Gas mixture standard containing (nominal) 50 ppm CO, 50 ppm CH_4, 2 percent CO_2, and 20 ppm C_3H_8, prepared in air.

3.3.4.2 Hexane. Gas mixture standard containing (nominal) 50 ppm hexane in air.

3.3.4.3 Toluene. Gas mixture standard containing (nominal) 20 ppm toluene in air.

3.3.4.4 Methanol. Gas mixture standard containing (nominal) 100 ppm methanol in air.

4. Procedure

4.1 Sampling.

4.1.1 Sample Tank Evacuation and Leak Check. Either in the laboratory or in the field, evacuate the sample tank to 10 mm Hg absolute pressure or less (measured by a mercury U-tube manometer) then leak check the sample tank by isolating the tank from the vacuum pump and allowing the tank to sit for 10 minutes. The tank is acceptable if no change in tank vacuum is noted.

4.1.2 Sample Train Assembly. Just prior to assembly, measure the tank vaccuum using a mercury U-tube manometer. Record this vaccum (P_{ti}), the ambient temperature (T_{ti}), and the barometric pressure (P_{bi}) at this time. Assuring that the flow shut-off valve is in the closed position, assemble the sampling system as shown in Figure 1. Immerse the condensate trap body in dry ice to within 2.5 or 5 cm of the point where the inlet tube joins the trap body.

4.1.3. Pretest Leak Check. A pretest leak check is required. After the sampling train is assembled, record the tank vacuum as indicated by the vaccum gauge. Wait a *minimum* period of 10 minutes and recheck the indicated vacuum. If the vacuum has not changed, the portion of the sampling train behind the shut-off valve does not leak and is considered acceptable. To check the front portion of the sampling train, assure that the probe tip is tightly plugged and then open the sample train flow shut-off valve. Allow the sample train to sit for a minimum period of 10 minutes. The leak check is acceptable if no visible change in the tank vacuum gauge occurs. Record the pretest leak rate (cm/Hg per 10 minutes). At the completion of the leak check period, close the sample flow shut-off valve.

4.1.4. Sample Train Operation. Place the probe into the stack such that the probe is perpendicular to the direction of stack gas flow; locate the probe tip at a single preselected point. If a probe extension which will not be analyzed as part of the condensate trap is being used, assure that at least a 15 cm section of the probe which will be analyzed with the trap is in the stack effluent. For stacks having a negative static pressure, assure that the sample port is sufficiently sealed to prevent air in-leakage around the probe. Check the dry ice level and add ice if necessary. Record the clock time and sample tank gauge vacuum. To begin sampling, open the flow shut-off valve and adjust (if applicable) the control valve of the flow control system used in the sample train; maintain a constant flow rate (±10 percent) throughout the duration of the sampling period. Record the gauge vacuum and flowmeter setting (if applicable) at 5-minute intervals. Select a total sample time greater than or equal to the minimum sampling time specified in the applicable subpart of the regulation; end the sampling when this time period is reached or when a constant flow rate can no longer be maintained due to reduced sample tank vacuum. When the sampling is completed, close the flow shut-off valve and record the final sample time and guage vacuum readings. Note: If the sampling had to be stopped before obtaining the minimum sampling time (specified in the applicable subpart) because a constant flow rate could not be maintained, proceed as follows: After removing the probe from the stack, remove the used sample tank from the sampling train (without disconnecting other portions of the sampling train) and connect another sample tank to the sampling train. Prior to attaching the new tank to the sampling train, assure that the tank vacuum (measured on-site by the U-tube manometer) has been recorded on the data form and that the tank has been leak-checked (on-site). After the new tank is attached to the sample train, proceed with the sampling until the required minimum sampling time has been exceeded.

4.1.5 Post Test Leak Check. A leak check is mandatory at the conclusion of each test run. After sampling is completed, remove the probe from the stack and plug the probe tip. Open the sample train flow shut-off valve and monitor the sample tank vacuum gauge for a period of 10 minutes. The leak check is acceptable if no visible change in the tank vacuum gauge occurs. Record the post test leak rate (cm Hg per 10 minutes). If the sampling train does not pass the post leak check, invalidate the run or use a procedure acceptable to the Administrator to adjust the data.

4.2 Sample Recovery. After the post test leak check is completed, disconnect the condensate trap at the flow metering system and tightly seal both ends of the condensate trap. Keep the trap packed in dry ice until the samples are returned to the laboratory for analysis. Remove the flow metering system from the sample tank. Attach the U-tube manometer to the tank (keep length of connecting line to a minimum) and record the final tank vacuum (P_t); record the tank temperature (T_t) and barometric pressure at this time. Disconnect the manometer from the tank. Assure that the test run number is properly identified on the condensate trap and the sample tank(s).

4.3 Condensate Recovery and Conditioning. Prepare the condensate recovery and conditioning apparatus by setting the carrier gas flow rate and heating the catalyst to its operating temperature. Prior to initial use of the condensate recovery and conditioning apparatus, a system performance test must be conducted according to the procedures established in section 5.1 of this method. After successful completion of the initial performance test, the system is routinely used for sample conditioning according to the following procedures:

4.3.1 System Blank and Catalyst Efficiency Check. Prior to and immediately following the conditioning of each set of sample traps, or on a daily basis (whichever occurs first) conduct the carrier gas blank test and catalyst efficiency test as specified in sections 5.1.1 and 5.1.2 of this method. Record the carrier gas initial and final blank values, B_{ti} and B_{tf}, respectively. If the criteria of the tests cannot be met, make the necessary repairs to the system before proceeding.

4.3.2 Condensate Trap Carbon Dioxide Purge and Sample Tank Pressurization. The first step in analysis is to purge the condensate trap of any CO_2 which it may contain and to simultaneously pressurize the sample tank. This is accomplished as follows: Obtain both the sample tank and condensate trap from the test run to be analyzed. Set up the condensate recovery and conditioning apparatus so that the carrier flow bypasses the condensate trap hook-up terminals, bypasses the oxidation catalyst, and is vented to the atmosphere. Next, attach the condensate trap to the apparatus and pack the trap in dry ice. Assure that the valves isolating the collection vessel connection from the atmospheric vent and the vacuum pump are closed and then attach the sample tank to the system as if it were the intermediate collection vessel. Record the tank vacuum on the laboratory data form. Assure that the NDIR analyzer indicates a zero output level and then switch the carrier flow through the condensate trap; immediately switch the carrier flow from vent to collect. The condensate trap recovery and conditioning apparatus should now be set up as indicated in Figure 8. Monitor the NDIR; when CO_2 is no longer being passed through the system, switch the carrier flow so that it once again bypasses the condensate trap. Continue in this manner until the gas sample tank is pressurized to a nominal gauge pressure of 800 mm Hg. At this time, isolate the tank, vent the carrier flow, and record the sample tank pressure (P_{tf}), barometric pressure (P_{bf}), and ambient temperature (T_{tf}). Remove the sample tank from the system.

4.3.3 Recovery of Condensate Trap Sample. Oxidation and collection of the sample in the condensate trap is now ready to begin. From the step just completed in section 4.3.1.2 above, the system should be set up so that the carrier flow bypasses the condensate trap, bypasses the oxidation catalyst, and is vented to the atmosphere. Attach an evacuated intermediate collection vessel to the system and then switch the carrier so that it flows through the oxidation catalyst. Switch the carrier from vent to collect and open the valve to the collection vessel; remove the dry ice from the trap and then switch the carrier flow through the trap. The system should now be set up to operate as indicated in Figure 9. During oxidation of the condensate trap sample, monitor the NDIR to determine when all the sample has been removed and oxidized (indicated by return to baseline of NDIR analyzer output). Begin heating the condensate trap and probe with a propane torch. The trap should be heated to a temperature at which the trap glows a "dull red" (approximately 500°C). During the early part of the trap "burn out," adjust the carrier and auxiliary oxygen flow rates so that an excess of oxygen is being fed to the catalyst system. Gradually increase the flow of carrier gas through the trap. After the NDIR indicates that most of the organic matter has been purged, place the trap in a muffle furnance (500°C). Continue to heat the probe with a torch or some other procedure (e.g., electrical resistance heater). Continue this procedure for at least 5 minutes after the NDIR has returned to baseline. Remove the heat from the trap but continue the carrier flow until the intermediate collection vessel is pressurized to a gauge pressure of 800 mm

Hg (nominal). When the vessel is pressurized, vent the carrier; measure and record the final intermediate collection vessel pressure (P_f) as well as the barometric pressure (P_{bv}), ambient temperature (T_v), and collection vessel volume (V_v).

4.4 Analysis. Prior to putting the NMO analyzer into routine operation, an initial performance test must be conducted. Start the analyzer and perform all the necessary functions in order to put the analyzer in proper working order, then conduct the performance test according to the procedures established in section 5.2. Once the performance test has been successfully completed and the CO_2 and NMO calibration response factors determined, proceed with sample analysis as follows:

4.4.1 Daily operations and calibration checks. Prior to and immediately following the analysis of each set of samples or on a daily basis (whichever occurs first) conduct a calibration test according to the procedures established in section 5.3. If the criteria of the daily calibration test cannot be met, repeat the NMO analyzer performance test (section 5.2) before proceeding.

4.4.2 Analysis of Recovered Condensate Sample. Purge the sample loop with sample and then inject a preliminary sample in order to determine the appropriate FID attenuation. Inject triplicate samples from the intermediate collection vessel and record the values obtained for the condensible organics as CO_2 (C_{cm}).

4.4.3 Analysis of Sample Tank. Purge the sample loop with sample and inject a preliminary sample in order to determine the appropriate FID attenuation for monitoring the backflushed non-methane organics. Inject triplicate samples from the sample tank and record the values obtained for the nonmethane organics (C_{tm}).

5. Calibration and Operational Checks

Maintain a record of performance of each item.

5.1 Initial Performance Check of Condensate Recovery and Conditioning Apparatus.

5.1.1 Carrier Gas and Auxiliary Oxygen Blank. Set equal flow rates for both the carrier gas and auxiliary oxygen. With the trap switching valves in the bypass position and the catalyst in-line, fill an evacuated intermediate collection vessel with carrier gas. Analyze the collection vessel for CO_2; the carrier blank is acceptable if the CO_2 concentration is less than 10 ppm.

5.1.2 Catalyst Efficiency Check. Set up the condensate trap recovery system so that the carrier flow bypasses the trap inlet and is vented to the atmosphere at the system outlet. Assure that the valves isolating the collection system from the atmospheric vent and vacuum pump are closed and then attach an evacuated intermediate collection vessel to the system. Connect the methane standard gas cyclinder (section 3.3.1) to the system's condensate trap connector (probe end, Figure 4). Adjust the system valving so that the standard gas cylinder acts as the carrier gas and adjust the flow rate to the rate normally used during trap sample recovery. Switch off the auxiliary oxygen flow and then switch from vent to collect in order to begin collecting a sample. Continue collecting a sample in a normal manner until the intermediate vessel is filled to a nominal gauge pressure of 300 mm Hg. Remove the intermediate vessel from the system and vent the carrier flow to the atmosphere. Switch the valving to return the system to its normal carrier gas and normal operating conditions. Analyze the collection vessel for CO_2; the catalyst efficiency is acceptable if the CO_2 concentration is within ±5 percent of the expected value.

5.1.3 System Performance Check. Construct a liquid sample injection unit similar in design to the unit shown in Figure 6. Insert this unit into the condensate recovery and conditioning system in place of a condensate trap and set the carrier gas and auxiliary oxygen flow rates to normal operating levels. Attach an evacuated intermediate collection vessel to the system and switch from system vent to collect. With the carrier gas routed through the injection unit and the oxidation catalyst, inject a liquid sample (see. 5.1.3.1 to 5.1.3.4) via the injection septum. Heat the injection unit with a torch while monitoring the oxidation reaction on the NDIR. Continue the purge until the reaction is complete. Measure the final collection vessel pressure and then analyze the vessel to determine the CO_2 concentration. For each injection, calculate the percent recovery using the equation in section 6.6.

The performance test is acceptable if the average percent recovery is 100±10 percent with a relative standard deviation (section 6.7) of less than 5 percent for each set of triplicate injections as follows:

5.1.3.1 100 μl hexane.
5.1.3.2 10 μl hexane.
5.1.3.3 100 μl toluene.
5.1.3.4 10 μl toluene.

5.2 Initial NMO Analyzer Performance Test.

5.2.1 Oxidation Catalyst Efficiency Check. Turn off or bypass the NMO analyzer reduction catalyst. Make triplicate injections of the high level methane standard (section 3.3.1). The oxidation catalyst operation is acceptable if no FID response is noted.

5.2.2 Analyzer Linearity Check and NMO Calibration. Operating both the oxidation and reduction catalysts, conduct a linearity check of the analyzer using the propane standards specified in section 3.3. make triplicate injections of each calibration gas and then calculate the average response factor (area/ppm C) for each gas, as well as the overall mean of the response factor values. The instrument linearity is acceptable if the average response factor of each calibration gas is within ±5 percent of the overall mean value and if the relative standard deviation (section 6.7) for each set of triplicate injections is less than ±5 percent. Record the overall mean of the propane response factor values as the NMO calibration response factor (RF_{NMO}).

5.2.3 Reduction Catalyst Efficiency Check and CO_2 Calibration. An exact determination of the reduction catalyst efficiency is not required. Instead, proper catalyst operation is indirectly checked and continuously monitored by establishing a CO_2 response factor and comparing it to the NMO response factor. Operating both the oxidation and reduction catalysts make triplicate injections of each of the CO_2 calibration gases (section 3.3.3). Calculate the average response factor (area/ppm) for each calibration gas, as well as the overall mean of the response factor values. The reduction catalyst operation is acceptable if the average response factor of each calibration gas is within ±5 percent of the overall mean value and if the relative standard deviation (section 6.7) for each set of triplicate injections is less than ±5 percent. Additionally, the CO_2 overall mean response factor must be within ±10 percent of the NMO calibration response factor (RF_{NMO}) calculated in section 5.2.2. Record the overall mean of the response factor values as the CO_2 calibration response factor (RF_{CO_2}).

5.2.4 NMO System Blank. For the high level CO_2 calibration gas (section 3.3.3) record the NMO value measured during the CO_2 calibration conducted in section 5.2.3. This value is the NMO blank value for the analyzer (B_a) and should be less than 10 ppm.

5.2.5 System Performance Check. Check the column separation and overall performance of the analyzer by making triplicate injections of the calibration gases listed in section 3.3.4. The analyzer performance is acceptable if the measured NMO value for each gas (average of triplicate injections) is within ±12 percent of the expected value.

5.3 NMO Analyzer Daily Calibration.

5.3.1 NMO Blank and CO_2. Inject triplicate samples of the high level CO_2 calibration gas (section 3.3.3) and calculate the average response factor. The system operation is adequate if the calculated response factor is within ±10 percent of the RF_{CO_2} calculated during the initial performance test (section 5.2.2). Use the daily response factor (DRF_{CO_2}) for analyzer calibration and the calculation of measured CO_2 concentrations in the collection vessel samples. In addition, record the NMO blank value (B_a); this value should be less than 10 ppm.

5.3.2 NMO Calibration. Inject triplicate samples of the mixed propane calibration cylinder (section 3.3.4.1) and calculate the average NMO response factor. The system operation is adequate if the calculated response factor is within ±10 percent of the RF_{NMO} calculated during the initial performance test (section 5.2.1). Use the daily response factor (DRF_{NMO}) for analyzer calibration and calculation of NMO concentrations in the sample tanks.

5.4 Sample Tank. The volume of the gas sampling tanks used must be determined. Prior to putting each tank in service, determine the tank volume by weighing the tanks empty and then filled with deionized distilled water; weigh to the nearest 5 gm and record the results. Alternatively, measure the volume of water used to fill the tanks to the nearest 5 ml.

5.5 Intermediate Collection Vessel. The volume of the intermediate collection vessels used to collect CO_2 during the analysis of the condensate traps must be determined. Prior to putting each vessel into service, determine the volume by weighing the vessel empty and then filled with deionized distilled water; weigh to the nearest 5 gm and record the results. Alternatively, measure the volume of water used to fill the tanks to the nearest 5 ml.

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6. Calculations

Note: All equations are written using absolute pressure; absolute pressures are determined by adding the measured barometric pressure to the measured gauge pressure.

6.1 Sample Volume. For each test run, calculate the gas volume sampled:

$$V_s = 0.386\ V \left(\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}}\right)$$

6.2 Noncondensible Organics. For each sample tank, determine the concentration of nonmethane organics (ppm C):

$$C_t = \left[\frac{\frac{P_{tf}}{T_{tf}}}{\frac{P_t}{T_t} \quad \frac{P_{ti}}{T_{ti}}}\right] \left[\frac{1}{r} \sum_{j=1}^{r} C_{tm_j} - B_a\right]$$

6.3 Condensible Organics. For each condensate trap determine the concentration of organics (ppm C):

$$C_c = 0.386 \frac{V_v}{V_s} \frac{P_f}{T_f} \left[\frac{1}{q} \sum_{k=1}^{q} C_{cm_k} - B_t\right]$$

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6.4 Total Gaseous Nonmethane Organics (TGNMO). To determine the TGNMO concentration for each test run, use the following equation:

$$C = C_t + C_c$$

6.5 Total Gaseous Nonmethane Organics (TGNMO) Mass Concentration. To determine the TGNMO mass concentration as carbon for each test run, use the following equation:

$$M_c = 0.498\ C$$

6.6 Percent Recovery. To calculate the percent recovery for the liquid injections to the condensate recovery and conditioning system use the following equation:

$$\text{percent recovery} = 1.6 \frac{M}{L} \frac{V_v}{\rho} \frac{P_f}{T_f} \frac{C_{cm}}{N}$$

6.7 Relative Standard Deviation.

$$RSD = \frac{100}{\bar{X}} \sqrt{\frac{\Sigma (x_i - \bar{x})^2}{n - 1}}$$

Where:

B_e = Measured NMO blank value for NMO analyzer, ppm C.
B_t = Measured CO_2 blank value for condensate recovery and conditioning system carrier gas, ppm CO_2.
C = total gaseous nonmethane organic (TGNMO) concentration of the effluent, ppm C equivalent.
C_c = Calculated condensible organic (condensate trap) concentration of the effluent, ppm C equivalent.
C_{cm} = Measured concentration (NMO analyzer) for the condensate trap (intermediate collection vessel), ppm CO_2.
C_t = Calculated noncondensible organic concentration (sample tank) of the effluent, ppm C equivalent.
C_{tm} = Measured concentration (NMO analyzer) for the sample tank, ppm NMO.
L = Volume of liquid injected, microliters.
M = Molecular weight of the liquid injected, g/g-mole.
M_c = total gaseous non-methane organic (TGNMO) mass concentration of the effluent, mg C/dscm.
N = Carbon number of the liquid compound injected (N=7 for toluene, N=6 for hexane).
P_f = Final pressure of the intermediate collection vessel, mm Hg absolute.
P_{ti} = Gas sample tank pressure prior to sampling, mm Hg absolute.
P_t = Gas sample tank pressure after sampling, but prior to pressurizing, mm Hg absolute.
P_{tf} = Final gas sample tank pressure after pressurizing, mm Hg absolute.
T_f = Final temperature of intermediate collection vessel, °K.
T_{ti} = Sample tank temperature prior to sampling, °K.
T_t = Sample tank temperature at completion of sampling, °K.
T_{tf} = Sample tank temperature after pressurizing °K.
V = Sample tank volume, cm.
V_v = Intermediate collection vessel volume, cm.
V_s = Gas volume sampled, dscm.
n = Number of data points.
q = Total number of analyzer injections of intermediate collection vessel during analysis (where k = injection number, 1 . . . q).
r = Total number of analyzer injections of sample tank during analysis (where j = injection number, 1 . . . r).
x_i = Individual measurements.
X = Mean value.
p = Density of liquid injected, g/cc.

7. Bibliography

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7.2 Salo, Albert E., William L. Oaks, and Robert D. MacPhee. Measuring the Organic Carbon Content of Source Emissions for Air Pollution Control. Paper No. 74–190. (Presented at the 67th Annual Meeting of the Air Pollution Control Association. Denver, CO. June 9–13, 1974.) 25 p.

Method 25

Addendum I. System Components

In test Method 25 several important system components are not specified; instead minimum performance specifications are provided. The method is written in this manner to permit individual preference in choosing components, as well as to encourage development and use of improved components. This addendum is added to the method in order to provide users with some specific information regarding components which have been found satisfactory for use with the method. This listing is given only for the purpose of providing information and does not constitute an endorsement of any product by the Environmental Protection Agency. This list is not meant to imply that other components not listed are not acceptable.

1. Condensate Recovery and Conditioning System Oxidation Catalyst. ⅜" OD×14" inconel tubing packed with 8 inches of hopcalite* oxidizing catalyst and operated at 800°C in a tube *furnace. Note: At this* temperature, this catalyst must be purged with carrier gas at all times to prevent catalyst damage.

2. NMO Analyzer Oxidation Catalyst. ⅛" OD×14" inconel tubing packed with 6 inches of hopcalite oxidizing catalyst and operated at 800°C in a tube furnace. (See note above.)

3. NMO Analyzer Reduction Catalyst. Reduction Catalyst Module; Byron Instruments, Raleigh, N.C.

4. Gas Chromatographic Separation Column. ⅛ inch OD stainless steel packed with 3 feet of 10 percent methyl silicone, Sp 2100 (or equivalent) on Supelcoport (or equivalent), 80/100 mesh, followed by 1.5 feet Porapak Q (or equivalent) 60/80 mesh. The inlet side is to the silicone. Condition the column for 24 hours at 200°C with 20 cc/min N_2 purge.

During analysis for the nonmethane organics the separation column is operated as follows: First, operate the column at −78°C (dry ice bath) to elute CO and CH_4. After the CH_4 peak operate the column at 0°C to elute CO_2. When the CO_2 is completely eluted, switch the carrier flow to backflush the column and simultaneously raise the column temperature to 100°C in order to elute all nonmethane organics (exact timings for column operation are determined from the calibration standard).

Note.—The dry ice operating condition may be deleted if separation of CO and CH_4 is unimportant.

Note.—Ethane and ethylene may or may not be measured using this column; whether or not ethane and ethylene are quantified will depend on the CO_2 concentration in the gas sample. When high levels of CO_2 are present, ethane and ethylene will elute under the tail of the CO_2 peak.

5. Carrier Gas. Zero grade nitrogen or helium or zero air.

BILLING CODE 6560-01-M

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*MSA registered trademark.

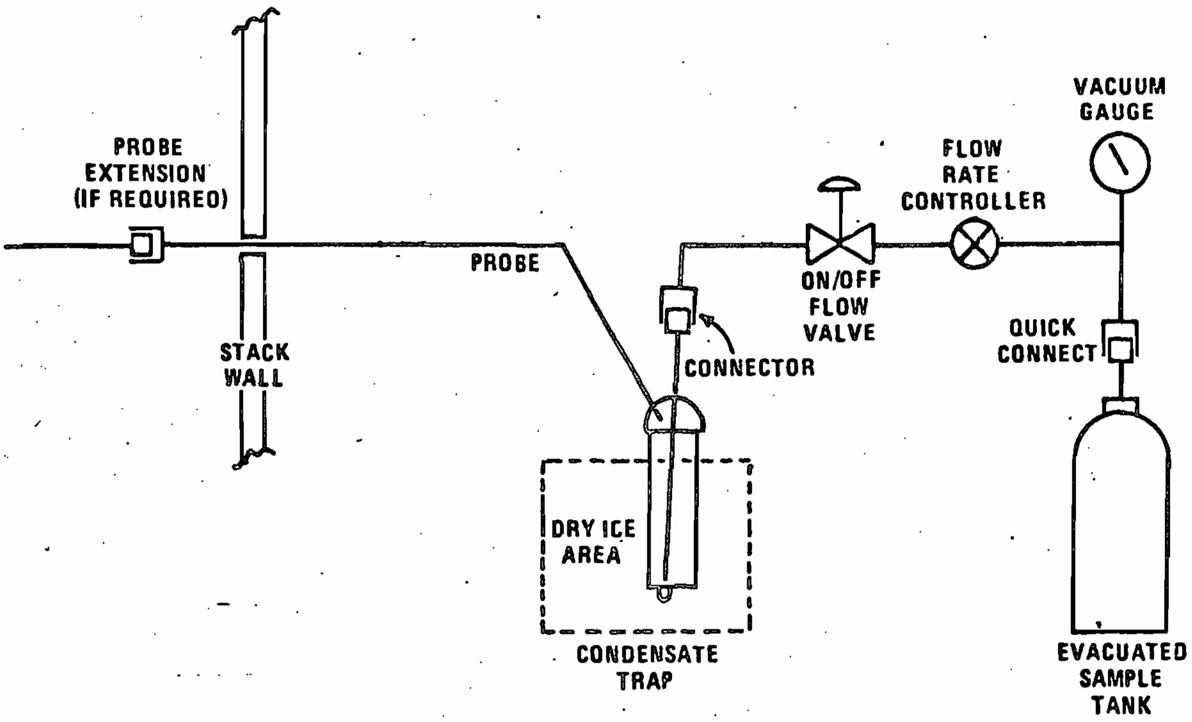

Figure 1. Sampling apparatus.

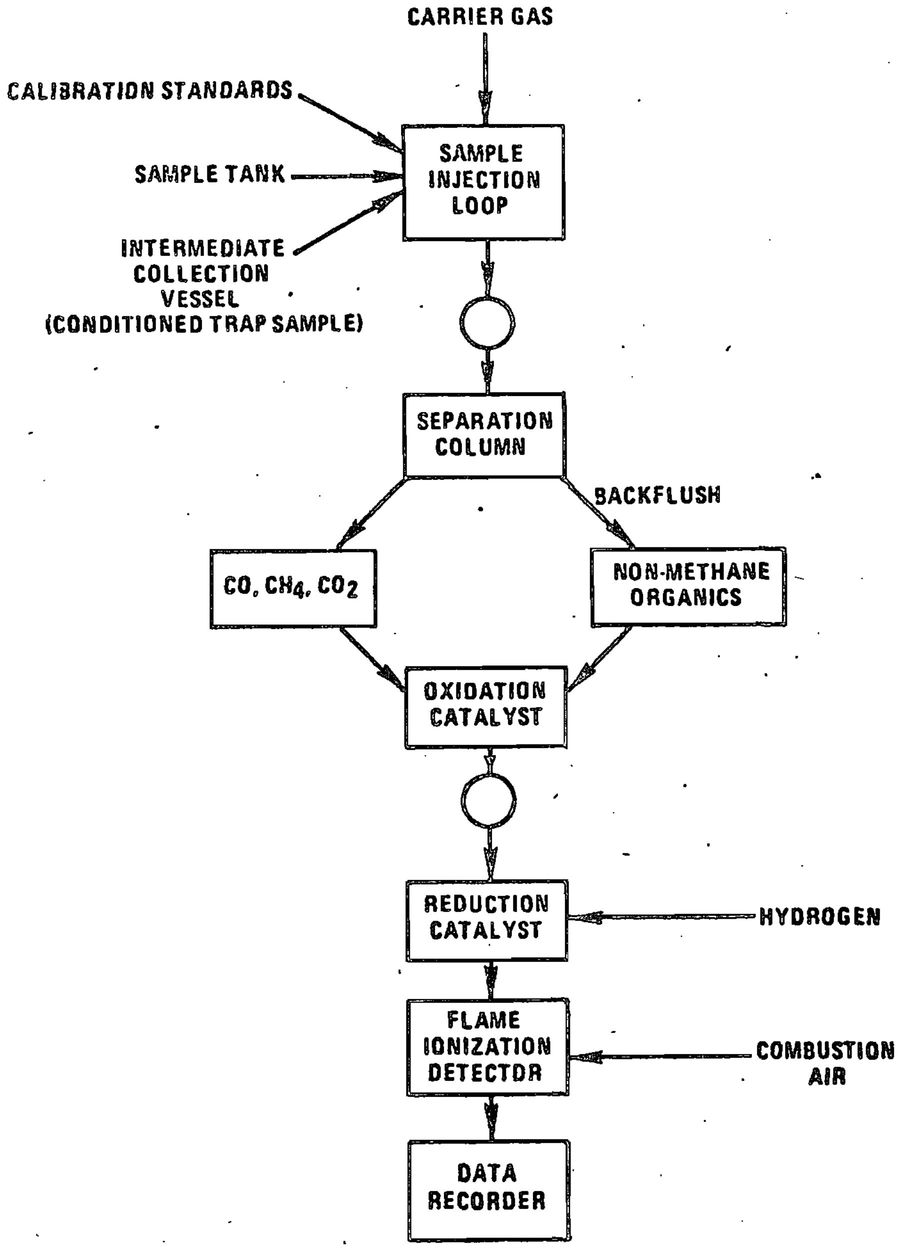

Figure 2. Simplified schematic of non-methane organic (NMO) analyzer.

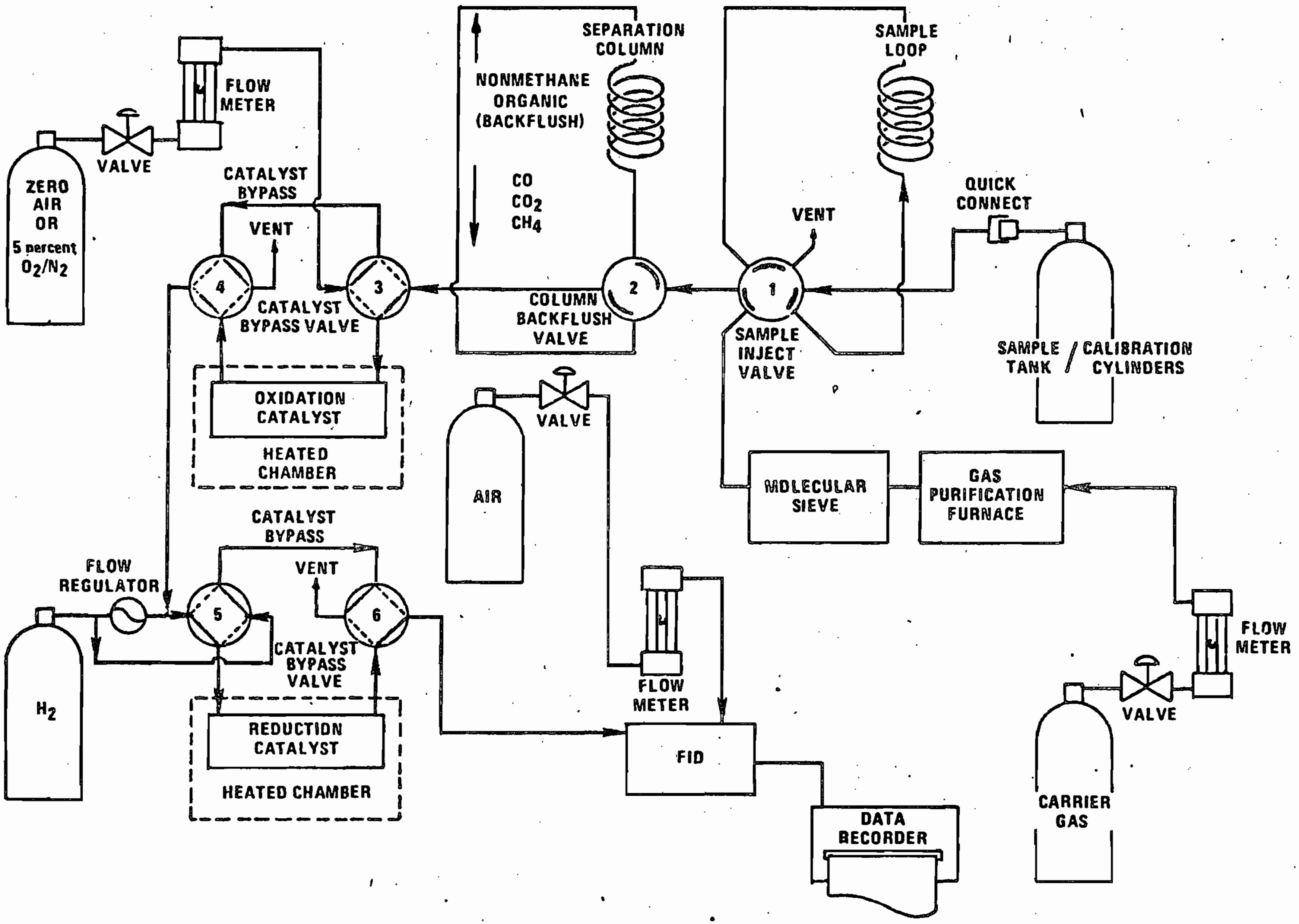

Figure 3. Nonmethane organic (NMO) analyzer.

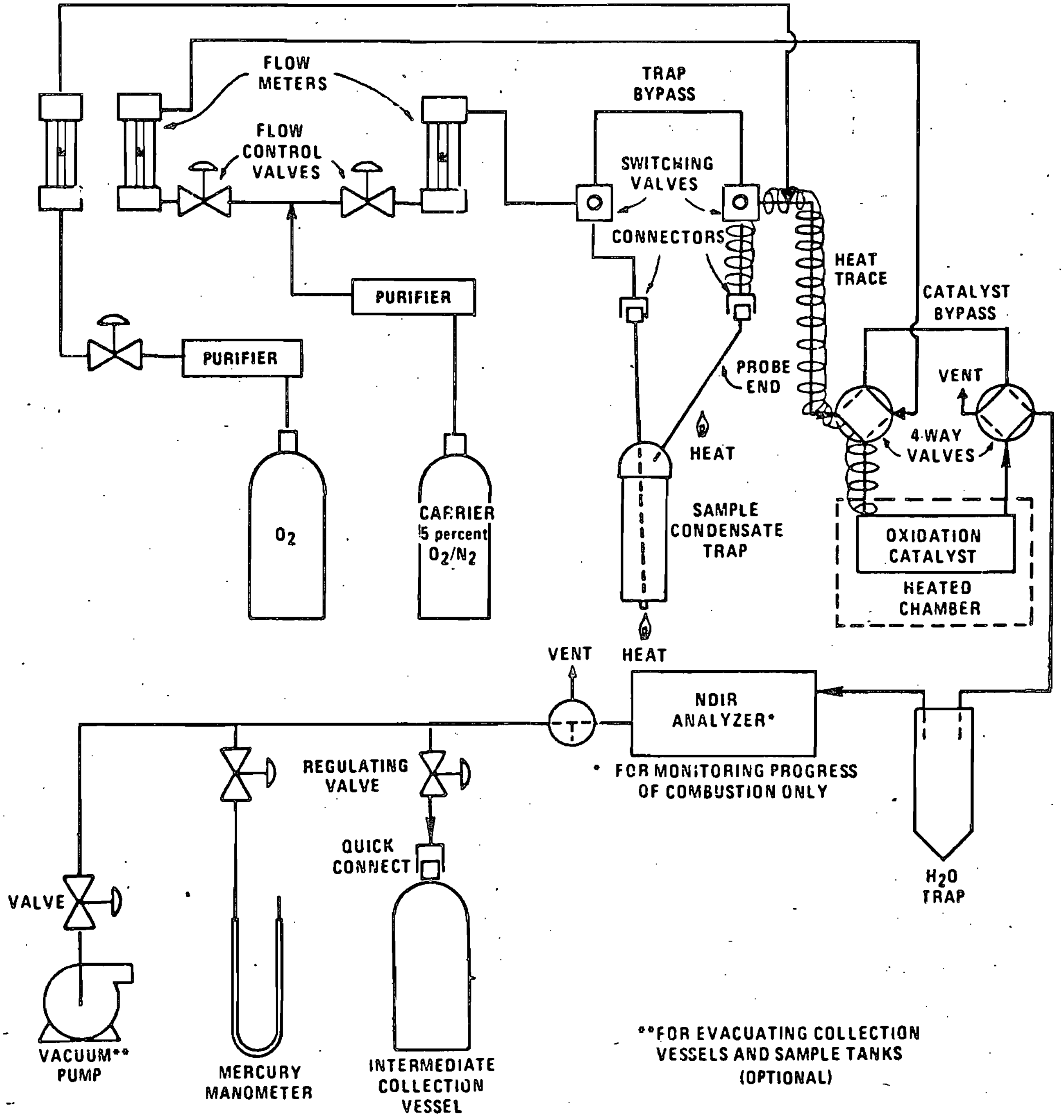

Figure 4. Condensate recovery and conditioning apparatus.

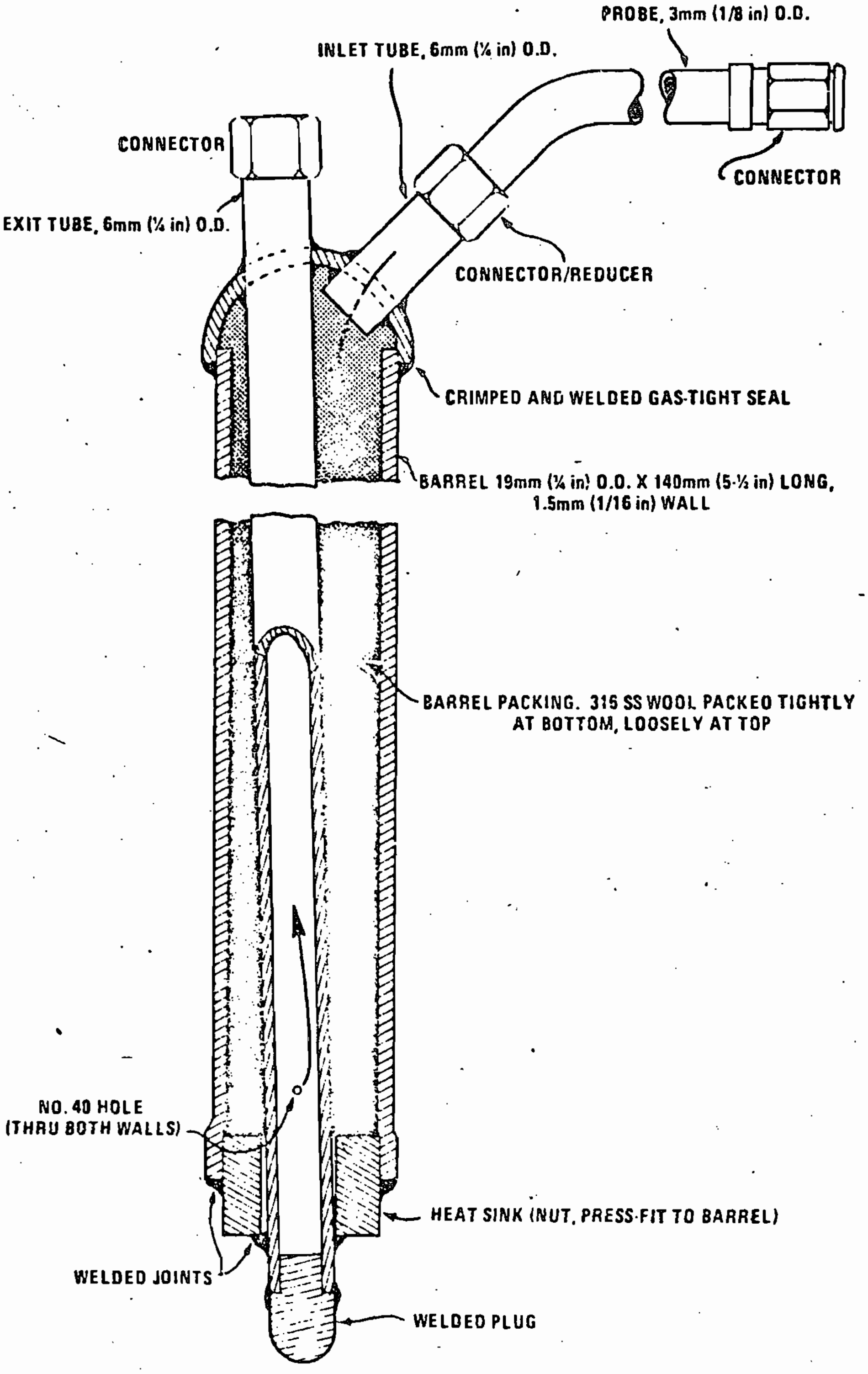

Figure 5. Condensate trap[2].

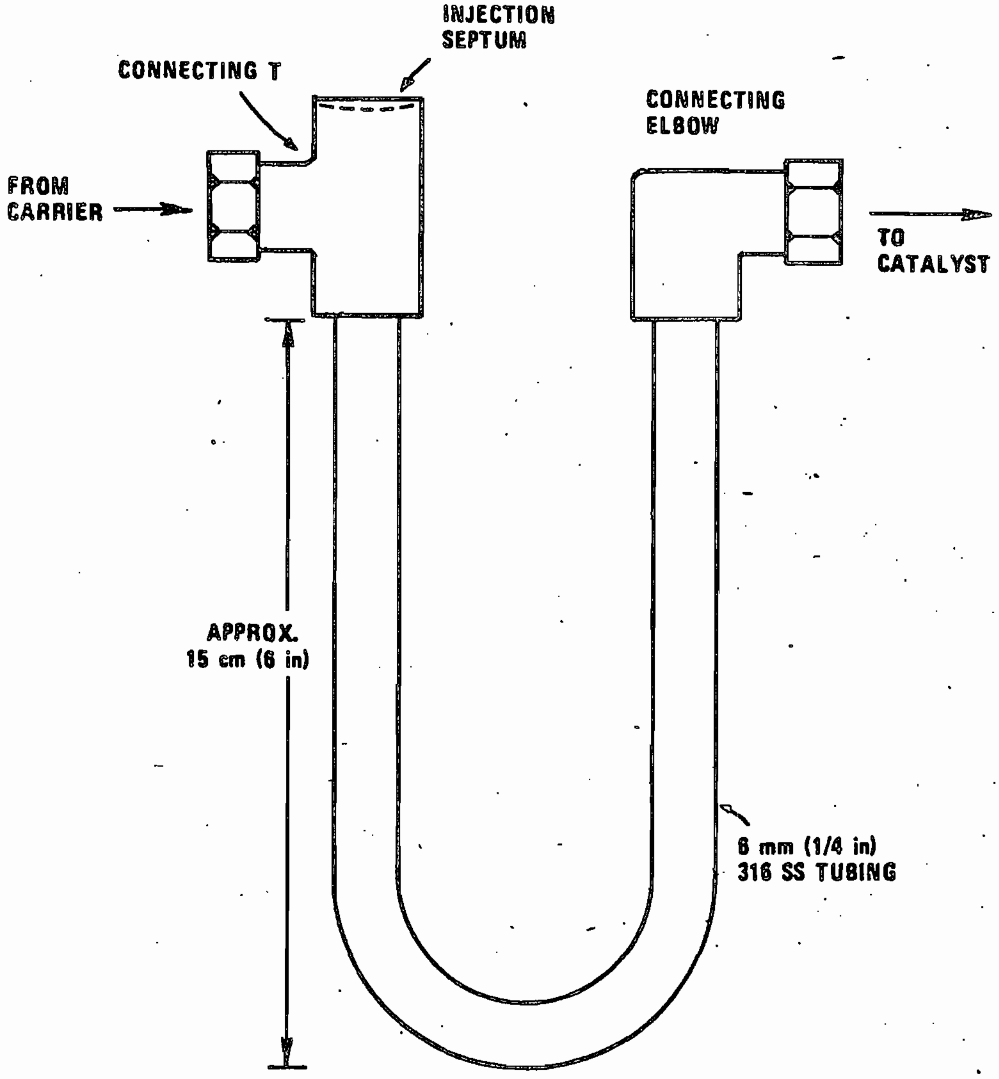

Figure 6. Liquid sample injection unit.

VOLATILE ORGANIC CARBON

FACILITY__________ SAMPLE LOCATION__________

LOCATION__________ OPERATOR__________

DATE__________ RUN NUMBER__________

TANK NUMBER__________ TRAP NUMBER__________ SAMPLE ID NUMBER__________

	TANK VACUUM, mm Hg	TANK VACUUM, cm Hg	BAROMETRIC PRESSURE, mm Hg	AMBIENT TEMPERATURE, °C
PRETEST (MANOMETER)		(GAUGE)		
POST TEST (MANOMETER)		(GAUGE)		

LEAK RATE cm Hg / 10 min

PRETEST__________

POST TEST__________

TIME CLOCK/SAMPLE	GAUGE VACUUM, cm Hg	FLOWMETER SETTING	COMMENTS

Figure 7. Example Field Data Form.

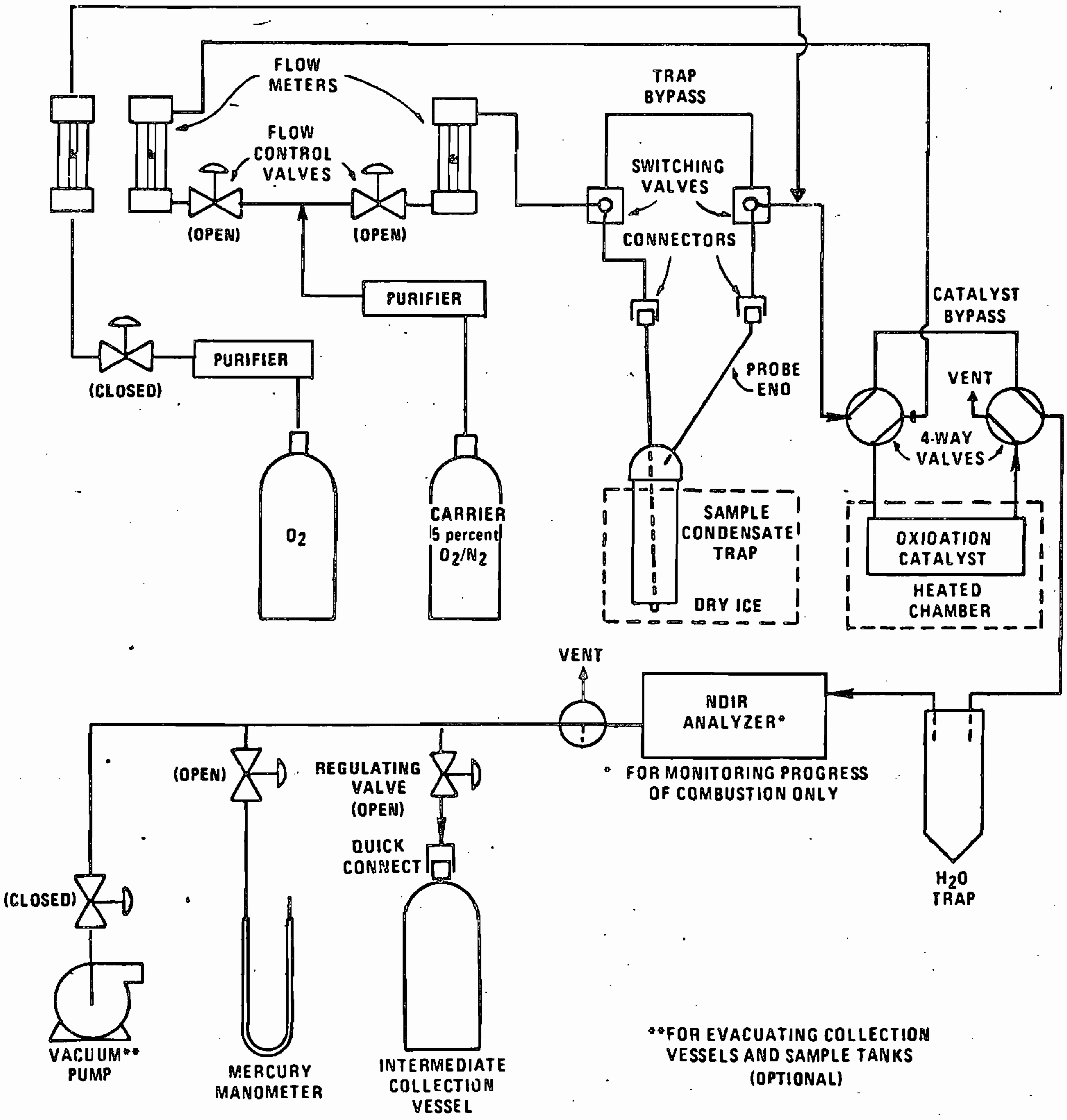

Figure 8. Condensate recovery and conditioning apparatus, carbon dioxide purge.

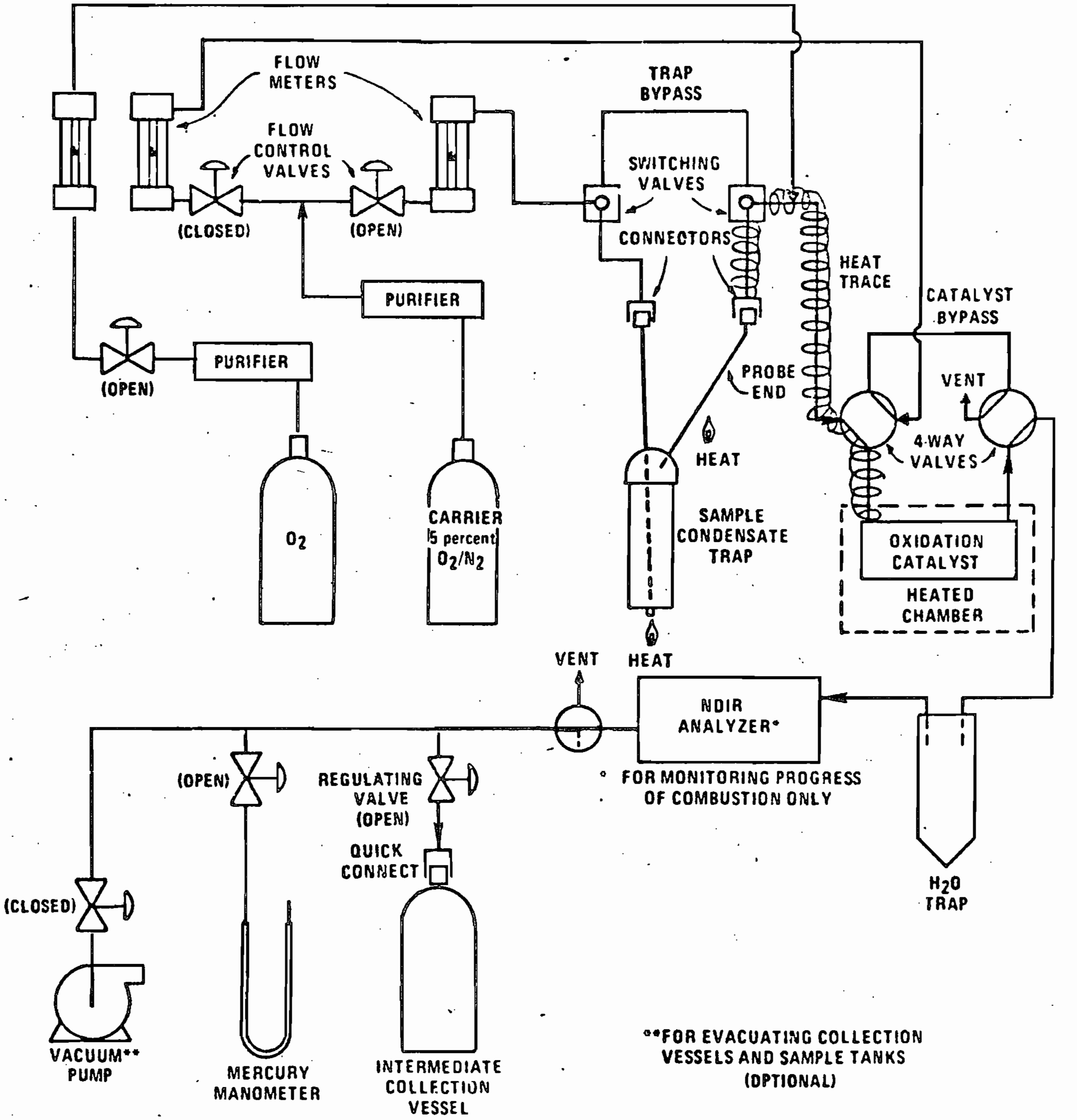

Figure 9. Condensate recovery and conditioning apparatus, collection of trap organics.

[FR Doc. 80-30718 Filed 10-2-80; 8:45 am]

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APPENDIX B

ANALYTICAL DATA

TABLE 7 ANALYTICAL DATA - BOILER A

Sample #	TGNMO	TGNMO	CO	CO	CH_4	C_2H_6	Analytical CO_2	Orsat CO_2	Orsat O_2	Flue Gas Moisture	Steam Production
	lb/10^6Btu as CH_4	ppm as CH_4	lb/10^6Btu as CO	ppm as CO	ppm as CH_4	ppm as CH_4	%	%	%	%	lb/hr
08281	0.078	124	3.44	3136	290	-	-	12.6	7.5	-	145,000
08282	0.049	78	3.10	2866	257	-	-				
08291	0.22	292	2.85	2269	207	-	-	10.4	8.7		60,000-140,000
08292	0.12	160	1.92	1527	109	-	-				
09041	0.17	182	3.03	1837	60	-	7.9	7.7	11.2	-	75,000
09042	0.21	194	3.03	1663	43	-	7.2				
09043	0.23	321	3.25	2682	71	-	10.2	8.3	10.5		100,000-150,000
09044	0.22	300	4.36	3408	127	-	10.2				
09051	0.20	264	1.28	986	91	-	10.0	11.8	8.0	15.9	50,000
09052	0.07	88	1.35	1052	94	-	10.2				
09053	0.18	187	1.22	787	0	-	8.4	8.1	11.5	15.9	125,000-135,000
09054	0.17	184	1.18	697	0	-	7.7				
09261	0.20	223	0.16	106	0	-	8.6	8.9	10.0	33.6	75,000-125,000
09262	0.12	136	1.47	943	0	-	8.4				
10101	0.18	332	0.60	646	12	0	14.0	10.8	8.4	-	100,000-120,000
10102	0.07	92	0.71	540	29	0	10.0				
10103	0.11	118	0.80	770	0	0	12.6	12.4	7.2	12.3	125,000-150,000
10104	0.09	156	0.49	511	10	0	13.6				
10111	0.15	225	0.35	274	0	0	10.3	11.1	7.8	25.3	100,000
10112	0.13	201	0.27	250	2	0	11.9				
10113	0.09	116	0.33	253	0	0	9.9	10.3	8.4	17.4	100,000
10114	0.06	84	0.43	336	0	0	10.3				

TABLE 8 ANALYTICAL DATA - BOILER B

Sample #	TGNMO	TGNMO	CO	CO	CH_4	C_2H_6	Analytical CO_2	Orsat CO_2	Orsat O_2	Mill O_2	Flue Gas Moisure	Steam Production	Aux. Fuel Use
	lb/10^6Btu as CH_4	ppm as CH_4	lb/10^6Btu as CO	ppm as CO	ppm as CH_4	ppm as CH_4	%	%	%	%	%	1000 lb/hr	% of total
09111	sample lost												
09112	.155	237	0.0	0	0	0	-	11.2	6.8		32.6	300-400	14
09113	.143	215	0.005										
09114	sample lost												
09131	.032	65	0.042	49	0	16	6.4	-	-	6	19.9	300-400	22
09132	.036	78	0.040	47	0	0	6.7	-	-	6	19.9		22
09133	.091	161	0.091	98	0	0	7.2	-	-	6.4-7.2	18.1	300	11
09134	.113	200	0.089	96	0	0	6.8	-	-	6.4-7.2	18.1		11
10041	.095	132	0.348	565	0	0	9.6	12.7	5.4		-	450-500	41
10042	.080	112	0.483	781	0	0	9.7	12.7	5.4		-		41
10043	.055	68	0.0	0	0	0	7.3	8.3	9.5		26.4	300-400	26
10044	.101	124	0.0	0	0	0	7.8	8.3	9.5		26.4		26
10231	.093	72	0.625	275	4	0	5.5	0.0	12.5	12	7.5	250	32
10232	.051	42	0.585	271	7	0	5.7		12.5		7.5		32
10233	.044	35	0.541	246	0	0	5.8	7.9	11.6	10	11.8	250	21
10234	.031	27	0.537	264	0	0	6.3		11.6	10	11.8		21
11011	0.027	30	0.242	153	2	0	8.2	11.8	7.8	6	16.2	410	11
11012	0.046	51	0.254	158	0	0	8.1		7.8		16.2		11
11013	0.093	105	0.100	64	0	0	8.4	11.9	7.8	4.2-5.0	14.0	420	11
11014	0.046	51	0.121	77	0	0	8.4		7.8		14.0		11

TABLE 9 ANALYTICAL DATA - BOILER C

Sample #	TGNMO	TGNMO	CO	CO	CH_4	C_2H_6	Analytical CO_2	Orsat CO_2	Orsat O_2	Mill O_2	Flue Gas Moisture	Steam Production
	$lb/10^6$Btu as CH_4	ppm as CH_4	$lb/10^6$Btu as CO	ppm as CO	ppm as CH_4	ppm as CH_4	%	%	%	%	%	1000 lb/hr
11131	0.147	70	4.02	1222	20	0	3.64	6.7	12.5	10.0	7.3	100
11132	1.133	15	0.10	30	0	0	0.10					
11133	0.048	55	1.34	983	0	0	8.62	7.5	11.0	10.5	10.8	150
11134	0.063	67	1.51	926	5	0	8.07					
11141	0.101	93	2.97	1559	22	1	7.04	8.8	11.6	10.0	18.3	90
11142	0.062	57	2.97	1586	27	0	6.97					
11151	0.129	107	3.70	1794	21	0	6.32	8.5	12.1	10.5	17.6	80
11152	0.151	124	4.19	2007	22	0	6.25					
11153	0.062	47	3.17	1420	15	0	5.85	7.4	11.6	10.0	16.5	85
11154	0.122	87	3.20	1323	15	0	5.46					
11281	0.104	103	2.57	1464	21	0	7.45	-	11.3	9.5	18.9	110
11282	0.064	66	2.42	1465	19	0	7.87					
11283	0.092	89	2.91	1647	20	5	7.40	-	12.0	10.0	13.6	150
11284	0.058	65	2.53	1639	20	0	8.40					
11291	0.099	105	2.32	1434	30	0	8.09	8.7	11.3	10.5	20.2	105
11292	0.066	63	2.25	1409	38	0	8.18					
11293	0.130	128	4.53	2600	41	0	7.49	6.5	12.0	7-11	13.9	90
11294	0.345	345	4.81	2816	47	0	7.64					

TABLE 10 ANALYTICAL DATA - BOILER D

Sample #	TGNMO	TGNMO	CO	CO	CH_4	C_2H_6	Analytical CO_2	Orsat CO_2	Orsat O_2	Mill O_2	Flue Gas Moisture	Steam Production	Stack Temp.
	$lb/10^6$ Btu as CH_4	ppm as CH_4	$lb/10^6$ Btu as CO	ppm as CO	ppm as CH_4	ppm as CH_4	%	%	%	%	%	1000 lb/hr	°F
10161	0.025	32	0.096	70	0	0	9.6	11.5	8.9	6	16.2	300	296
10162	0.038	50	0.138	104	0	0	10.1						
10163	0.042	60	0.045	119	0	0	10.8	11.5	8.9	3.5	15.3	300	296
10164	0.062	80	0.145	114	0	0	9.8						
02071	0.058	101	0.217	214	1	0	13.2	12.2	7.4	4.6	21.5	340	420
02072	0.031	55	0.231	220	2	0	13.4						
02073	0.034	59	0.228	147	1	0	13.4	12.9	7.2	3.8	23.0	350	400
02074	0.045	83	0.256	149	0	0	14.0						
02121	0.062	107	0.289	224	2	0	13.1	12.3	6.6	4.5	16.2	350	410
02122	0.056	91	0.291	237	1	0	12.4						
02123	0.047	71	0.236	251	1	0	11.6	11.6	8.8	5.5	15.4	340	410
02124	0.063	96	0.291	253	2	0	11.6						
02141	0.043	67	0.236	209	0	0	11.8	10.8	9.3	5-10	24.0	270-340	375
02142	0.036	54	0.250	215	0	0	11.5						
02143	0.044	60	0.527	410	1	0	10.4	9.8	10.2	9.5	13.5	250-350	375
02144	0.062	81	0.548	410	0	0	10.0						

ncasi

NATIONAL COUNCIL OF THE PAPER INDUSTRY FOR AIR AND STREAM IMPROVEMENT, INC.
260 MADISON AVE. NEW YORK, N.Y. 10016 (212) 532-9000

Russell O. Blosser
Technical Director
(212) 532 9001

done KAC 9/16/81

August 17, 1981

TO: Recipients of NCASI Technical Bulletins

FROM: Russell O. Blosser

SUBJECT: Errata to Atmospheric Quality Improvement Technical Bulletin No. 109

Attached are corrected copies of pages 12, 17, 20, 27, 31 and 39, all of which contained typographical errors in the original text mailed to you.

Would you please arrange to have these placed in the original bulletin mailed to you.

Copies made for our supply of 109.

ROB:gs
Encl.

Reference 6

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ncasi technical bulletin

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

A STUDY OF KRAFT PROCESS LIME KILN TOTAL GASEOUS NON-METHANE ORGANIC EMISSIONS

TECHNICAL BULLETIN NO. 358

SEPTEMBER 1981

NATIONAL COUNCIL OF THE PAPER INDUSTRY FOR AIR AND STREAM IMPROVEMENT, INC.
260 MADISON AVE. NEW YORK, N.Y. 10016 (212) 532-9000

Russell O. Blosser
Technical Director
(212) 532-9001

September 29, 1981

TECHNICAL BULLETIN NO. 358

A STUDY OF KRAFT PROCESS LIME KILN TOTAL GASEOUS NON-METHANE ORGANIC EMISSIONS

Volatile organic compounds (VOC) are considered by EPA to be photo-oxidants which are involved in the formation of ozone. Volatile organic compounds, by EPA definition, are a subgroup of non-methane compounds, previously generally referred to as hydrocarbons. As a result of regulations governing the permitting of new sources or modified existing sources, estimates of VOC emissions are frequently needed for the new or modified source. In addition, VOC emissions from other sources at the manufacturing site must be known to calculate the net change in VOC emissions.

The available information on VOC emissions from sources in the forest products industry is not only sparse, but that available is almost universally generated using a measurement procedure differing from that now proposed for use in most circumstances by EPA. For these reasons the National Council is carrying out a study of VOC emissions from several unit processes using the method of measurement advocated by EPA. This technical bulletin is the third of a series on the study of VOC source emissions. The investigative work and preparation of the report from which the technical bulletin was assembled was carried out at the West Coast Regional Center by Victor J. Dallons, Research Engineer, under the direction of Andre L. Caron, Regional Manager. Mr. Dallons was assisted by Dean R. Hoy, Ronald A. Messmer, and David R. Fyke.

This technical bulletin includes a description of the sampling and analytical method used and heretofore unidentified limitations of its use on combustion sources where carbon dioxide and significant amounts of moisture coexist. This is a particularly troublesome problem at lime kilns. The bulletin contents describe the VOC emission levels found at lime kilns.

The study showed VOC emissions based on four to eight duplicate samples collected simultaneously at three lime kilns to range from 0.024 to 0.30 lb/10^6 Btu heat input and 0.24 to 1.6 lb/ton calcium oxide produced. These values would have been substantially greater had they not been corrected for the CO_2 interference occurring with the use of EPA Method 25 when used on combustion sources. More kilns will have to be sampled to determine if these values are representative.

Based on samples collected simultaneously before and after wet scrubbers it was found that the composition of the scrubbing liquid, e.g., condensates versus fresh water, had no effect on TGNMO emissions. Laboratory work indicated, however, that organic components associated with the presence of green liquor dregs on the lime mud may be a contributing factor in the amount of TGNMO material emitted from a lime kiln.

The VOC investigative activity now encompasses a study of VOC emissions and the effectiveness of existing control technology on wood veneer dryers and solvent emissions from surface coating and printing. The scope of the investigative program is expanding geographically and will involve other sources as time permits.

Your questions and comments on the contents of this technical bulletin should be addressed to me, or to Mr. Victor Dallons or Mr. Andre L. Caron at the West Coast Regional Center.

Yours very truly,

Russell O. Blosser
Technical Director

ROB:mh
Att.

TABLE OF CONTENTS

A STUDY OF KRAFT PROCESS LIME KILN TOTAL GASEOUS NON-METHANE ORGANIC EMISSIONS

I INTRODUCTION

Volatile organic compounds are considered by the Environmental Protection Agency (EPA) to be photo-oxidants which are involved in the formation of ozone. Volatile organic compounds are a subgroup of non-methane hydrocarbons. Non-methane hydrocarbons have been designated as criteria pollutants by EPA, although the Agency has stated that the national primary and secondary ambient air quality standards for non-methane hydrocarbons (0.24 ppm 3-hour average between 6 and 9 a.m.) is only for use as a guide to achieve the ozone ambient air quality standard. Potential emissions of volatile organic compounds in amounts greater than a 100 tons per year results in classification of the source as major. Major new sources and existing source modifications must satisfy non-attainment (NA) or prevention of significant deterioration (PSD) regulations mandated by the 1977 Clean Air Amendments in order to obtain a construction permit.

Major sources locating in non-attainment areas must meet an emission offset policy where emissions from the new or altered source must be offset by a reduction in emissions from existing sources in the area. These sources must also achieve the lowest achievable emission rate (LAER) which is either (a) the lowest emission rate specified for the source class in any state implementation plan or (b) the lowest emission rate achieved in practice by a source of the same type.

Mills located in prevention of significant deterioration areas (PSD) are subject to best available control technology (BACT) emission limitations. Best available control technology is an emission limitation based on the maximum degree of reduction for the pollutant in question determined on a case-by-case basis. Mills located in PSD areas may choose to offset their emissions to avoid a PSD review. If the emission is not offset, data from a 1-year ambient monitoring program is required and the impact of the source as determined by an approved modelling exercise determined prior to a major source applying for a permit for an increase in emissions.

To date, no definitive assessment has been made of total non-methane gaseous organic emissions resulting from pulp and paper industry combustion and other process sources. Modelling to satisfy non-attainment and PSD regulations is unreliable with the information presently available on emissions and subsequent reactions which result in ambient ozone formation. Hence, it is unknown which and what size pulp and paper mill processes are considered major sources with respect to gaseous organics.

The National Council is currently surveying total gaseous non-methane organic emissions from selected sources in the forest products industry to provide a data base on potential emissions to be expected from various sources. It is the aim of this project to produce data consistent with the EPA reference method to be selected for the measurement of total gaseous non-methane organic compounds (TGNMO). The sampling and analysis procedures used in this study were in accordance with proposed EPA Method 25, published in the Federal Register October 3, 1980 (Appendix A) (2).

The EPA analytical procedure yields values for carbon monoxide, carbon dioxide, methane and total gaseous non-methane organics. The analytical procedure was altered to produce results for ethane and ethylene. Methane and ethane are not photoreactive and were not included in the results. The total gaseous non-methane organics (TGNMO) results are reported as methane. The following presents and discusses the sampling equipment, the procedures used, and results obtained from the kraft process lime kiln portion of this study. The kilns sampled were considered as representative of current kiln design and operating practices.

II KILN DESCRIPTIONS

Three lime kilns were sampled for TGNMO emissions both before and after wet scrubbers.

Kiln A is a rotary kiln manufactured by Allis Chalmers and began operation in 1968. The kiln is 9 ft. in diameter and 250 ft. long and can be fired on either gas or oil. Noncondensible gases from the pulp mill are not burned in the kiln. The kiln was designed to produce lime for production of 106 tons per day CaO (425 TPD of unbleached pulp). Fresh water was used throughout the causticizing system. Particulate emissions were controlled with a Chemico venturi type scrubber, which used fresh water for makeup.

Kiln B is a rotary kiln manufactured by Allis Chalmers and began operation in 1964. The kiln is 8 ft. in diameter and 250 ft. long and can be fired with either gas or oil. Noncondensible gases from the pulp mill were burned in the kiln. The kiln was designed to produce 90 tons per day CaO (360 tons pulp per day) but normally operated at 120 to 140 tons per day CaO. Evaporator condensates are used as makeup water throughout the causticizing system and in the scrubber. Particulate emissions were controlled with a Peabody bubble tray falling film scrubber.

Kiln C is a rotary kiln manufactured by Taylor Co. and began operation in 1980. The kiln is 11 ft. 6 in. in diameter and 330 ft. long. Combustion air was preheated by flowing over the outside of the hot end of the kiln. Noncondensible gases were burned in the kiln. The kiln was designed to produce 245 tons per day product (980 tons pulp per day). Fresh water was used for makeup throughout the causticizing system. Particulate emissions were controlled by an Air Pollution Industries venturi scrubber operating at a 30 to 32 in. pressure drop. Fresh water was used throughout the causticizing system for makeup.

III SAMPLING AND ANALYSIS METHOD

The procedure used for data collection was similar to the one developed by the Southern California Air Pollution Control District and EPA method 25 (Appendix A) procedures. The principle of the procedure is to separate organic compounds at the time of collection into high and low molecular weight fractions using a cold trap (-78°C). The light components are captured in an evacuated tank. The trap containing condensed organics is burned to convert organics to CO_2 for analysis in the laboratory. The light organics captured in the evacuated tank are separated on a chromatographic column yielding concentrations for CO, CH_4, CO_2, C_2H_6 and C_2H_4. All other organics are eluted in one peak. Summation of the trap and tank organic results gives TGNMO stack concentrations. All results are reported as methane.

A. Sampling

Field samples were taken simultaneously in duplicate through separate 1/2 in. stainless steel probes. The stack end of the probes were filled with glass wool before each sample was drawn to prevent collection of particulates in the traps. Six feet of 1/8 in. stainless steel tubing ran from the probes to the traps which were submerged in granular dry ice. The connection between the probe and sampling line was kept inside the stack during sampling. Skematics of the trap construction and sampling assembly are presented in Figures 1 and 2, respectively. Condensible organics and water vapor were captured in the traps. From the traps the gas flowed through a rotometer, a flow control valve, and into a 17-liter evacuated stainless steel tank.

All screw connections in the sampling system were checked for leaks in the field before sampling by pressurizing with air at 30 psi and soaking the joints individually with soapy water. Leaks detected were eliminated prior to sampling.

Sampling flow rates were set at about 230 ml/min so that about 13 liters of sample were collected in the one hour sampling period. When a trap froze due to condensation of stack moisture, the trap inlet was heated momentarily with a propane torch to melt the ice. The sampling system was watched closely to maintain the proper flow rate. After sampling, the trap and 6-foot section of line to the probe were capped and transported to the laboratory packed in dry ice. Tank pressures were measured before and after sampling to determine sample size. Orsat analyses were made for CO_2 and O_2 during sampling.

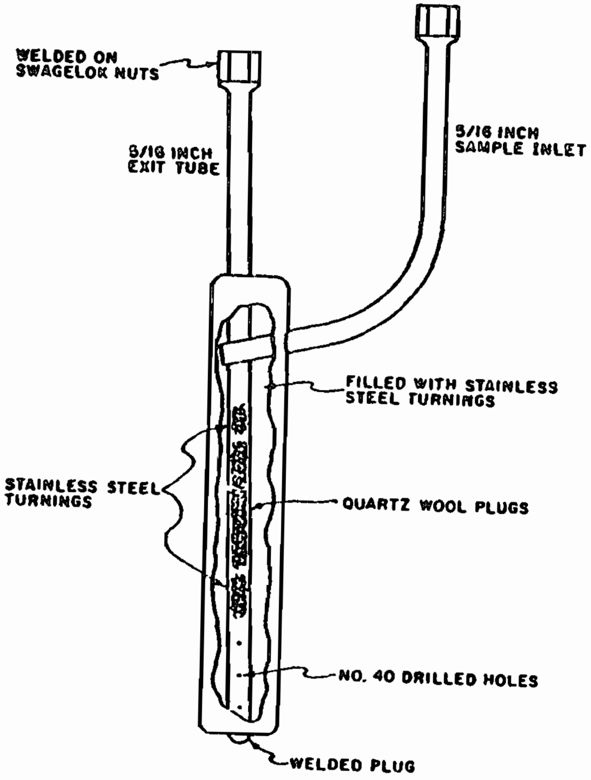

FIGURE 1

CONDENSATE TRAP

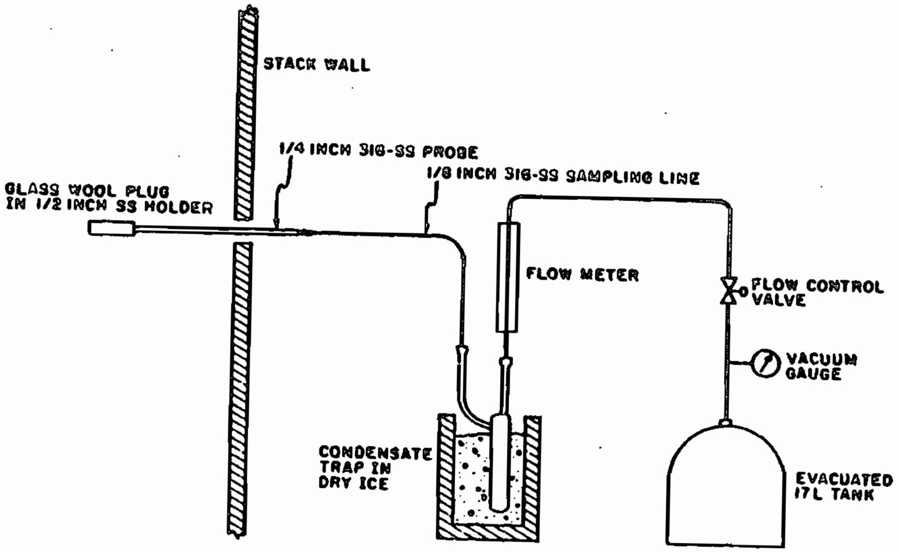

FIGURE 2

TGNMO SAMPLING TRAIN

B. Sample Preparation

When the samples were returned to the laboratory, each trap and sample tank combination used in the field was connected to the trap burning system in the sequence of trap, oxidation tube furnace, U-tube water trap packed in dry ice, and IR analyzer and sampling vessel as shown in Figure 3. The stack gases remaining in the trap were flushed into the tank with carbon compound free air (hereafter referred to as zero air) at a rate of 100 cc/min. When all of the CO_2 was flushed and into the tank as indicated by the IR detector response, the tank was pressurized with zero air via a trap bypass.

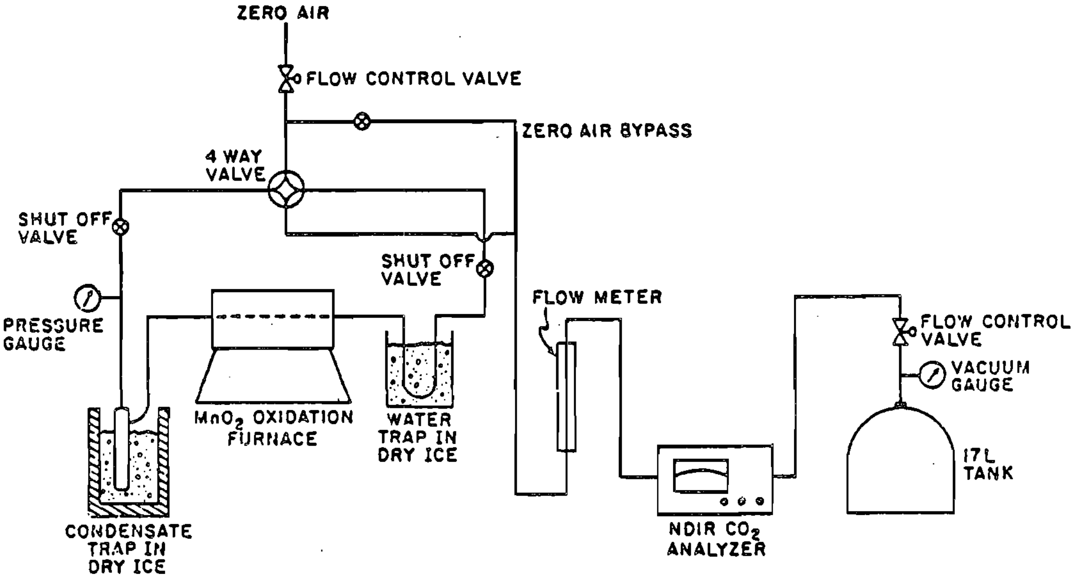

FIGURE 3

TRAP BURNOUT SYSTEM, FLUSH MODE

Following sampling tank pressurization, a 4-liter stainless steel vessel evacuated to a minimum of 28 in. Hg was then attached in the tank's place. Zero air was passed through the sampling line and trap while they were heated to a dull red color with an acetylene torch. A metering valve in the zero air supply line controlled the pressure in the trap to 15 to 25 in. Hg while flow was controlled by a valve on the evacuated vessel. Pressure in the trap can increase rapidly due to boiling of condensed water. The trap was monitored to avoid excess pressures that may result in leaks. Figure 4 shows the burnout assembly.

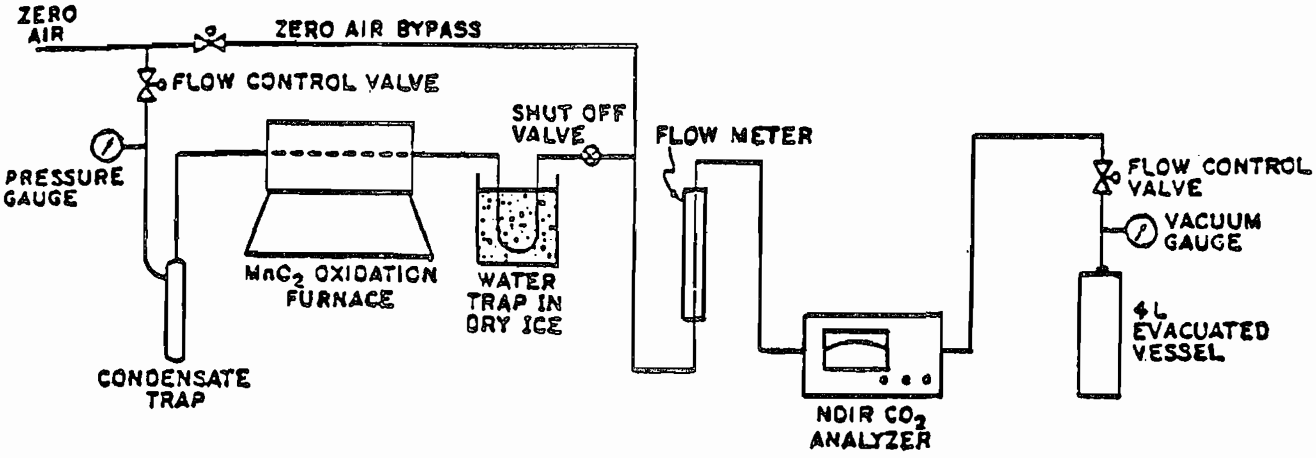

FIGURE 4

TRAP BURNOUT SYSTEM TRAP BURN MODE

Care was taken that the sampling line, trap, and lines to the oxidizer were heated sequentially so that incompletely oxidized organics that might recondense in the system would be revolatilized. Each trap was burned until the CO_2 in the carrier gas, as shown by the IR analyzer, had returned to baseline. The vessel was then pressurized to less than 5 in. Hg. The volume of water in the water trap was measured and recorded. Stack moisture content was calculated from this data.

Zero air was prepared by further purifying zero grade air from cylinders. Air from the cylinder was passed over air oxidation catalyst to oxidize organics to carbon dioxide and then passed through ascarite for carbon dioxide removal. The nitrogen carrier gas used for the chromatographic column was cleaned by passing through a molecular sieve and through a catalytic oxidation column. Trace quantities of carbon dioxide in the nitrogen carrier gas do not interfere with the analysis.

C. Sample Analysis

The analysis system components consisted of an injection port with an inert septum, a silicon SF-96 on Chromosorb W/Porapak Q column operated at -78°C, -30°C, 25°C, and 100°C with back flush capability, a MnO_2 oxidation furnace operated at 600°C for oxidation of the CH_4, CO, and organics to CO_2, and hydrogen addition to the nitrogen carrier at a rhodium catalyst methanator operated at 400°C to convert CO_2 to CH_4. The column was made of 1/8 O.D. stainless steel tubing packed with 3 ft. of 10% methyl silicone on Supelcoport 80/100 mesh followed by 1.5 ft. Porapak Q 60/80 mesh. The CH_4 was analyzed by a flame ionization detector (FID). The FID output was integrated with an integrator. A second inert injection port was placed just prior to the oxidation furnace for system checks. A skematic is shown in Figure 5.

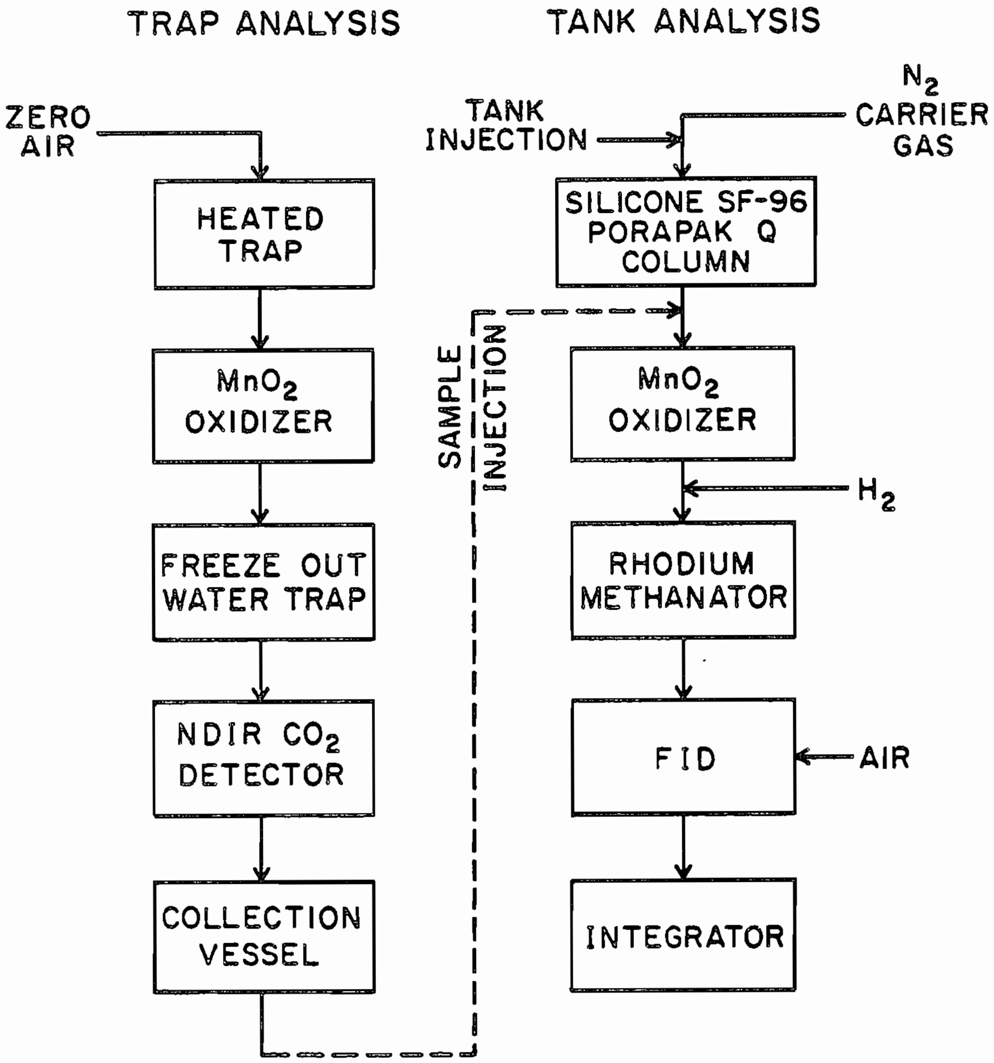

FIGURE 5

TGNMO ANALYTICAL SCHEME

Starting with the column submerged in a dry ice-isopropanol bath at -78°C, a 5 ml sample was drawn from the pressurized evacuated sampling tank and injected into the carrier gas to the column. Carbon monoxide and methane were separated. The column was then operated at room temperature for carbon dioxide elution. After the elution, the column was placed in a boiling water bath and the carrier gas flow through the column reversed. The volatile organics were released from the column. Each evacuated sampling tank was analyzed in triplicate. On the first injection of each duplicate pair, the column was placed in a $CaCl_2$-ice bath at -30°C to separate ethylene, ethane, and propane. If these compounds were not detected the samples were analyzed as above, but if present, the samples were analyzed with the -30°C column temperature step.

Analysis of the sampling tank for carbon dioxide required separate injections from that used for the organic analyses. The amount of carbon dioxide in a 5 ml injection was shown to overload the reduction catalyst causing a low carbon dioxide value to be reported. Carbon dioxide concentrations in the tanks were determined in triplicate using 1/2 ml injections directly to the oxidizer. Carbon monoxide and TGNMO concentrations were subtracted from the CO_2 value thus attained.

D. Calculations

Laboratory results were in terms of ppm TGNMO as methane as found in the sampling tank or vessel. These were corrected to standard conditions in the stack. To obtain corrected stack values the tank and vessel volumes corrected to standard condition were divided by the sample volume corrected to standard conditions and multiplied by the tank or vessel TGPRO concentrations respectively. Summation of tank and vessel concentrations were presented as stack TGNMO concentration at standard conditions.

The sample volume at standard conditions was calculated by:

$$\text{Sample Vol.} = (9.124)\ (V_T)\ \left(\frac{P_2}{T_2} - \frac{P_1}{T_1}\right)$$

where: V_T = tank volume in liters

P_1 = absolute pressure in the tank prior to sampling, in. Hg

T_1 = absolute temperature in the tank at time of measurement of P_1, °K

P_2 = absolute pressure in the tank after sampling, in. Hg

T_2 = absolute temperature of the tank at time of P_2 measurement, °K.

The volume of the tank or vessel at the time of analysis was calculated by:

$$\text{Pressurized Container Volume} = \frac{(Vc)\ (Pc)\ (9.124)}{Tc}$$

where: Vc = container volume, liters

Pc = pressure of container when filling is completed, in. Hg

Tc = absolute temperature of container at time of measurement of Pc, °K.

The TGNMO's in those containers were calculated by:

$$\begin{matrix}\text{Stack}\\ \text{Concentration}\end{matrix} = \left(\begin{matrix}\text{Container}\\ \text{Concentration}\end{matrix} - \begin{matrix}\text{Container}\\ \text{Blank}\end{matrix}\right) \cdot \left(\begin{matrix}\text{Pressurized}\\ \text{Container}\\ \text{Volume}\end{matrix}\right) / \left(\begin{matrix}\text{Sample}\\ \text{Volume}\end{matrix}\right)$$

The container blanks are a column blank and the zero air total carbon concentration for the tank and vessel respectively. Both blanks were kept below 5 ppm. The steps taken to remedy a response of more than 5 ppm are enumerated in Section IV B. 1. The blanks were run daily.

Stack gas TGNMO concentrations, after correction for the CO_2 interference, were converted to lb/ton CaO and lb/ton unbleached pulp production. Pounds TGNMO as methane per ton CaO produced was calculated by multiplying the stack TGNMO concentration, the stack gas flow rate and a units conversion factor and dividing by the CaO production. The lb TGNMO per ton unbleached pulp value was calculated by multiplying the lb/ton CaO by an assumed 0.3 tons CaO/ton pulp conversion factor. Stack flow rates were obtained by S type Pitot tube traverses across the stack after the scrubbers.

IV QUALITY CONTROL

The TGNMO analysis system was checked for proper operation at frequent intervals. Daily checks were made for FID sensitivity, zero air purity, column carrier gas purity and system leaks. Weekly checks were made on all catalysts efficiencies. Bi-weekly checks were made for evacuated sampling tank leaks and tank contamination.

A. Catalyst Efficiency Checks

All catalyst efficiencies were checked at the beginning of each week.

(1) Oxidation Catalyst Efficiency Check - To check the oxidation catalyst, the reduction catalyst was bypassed while operating the TGNMO analyzer in an otherwise normal fashion. Triplicate injections of 5 ml each of standard methane gas were made. If the catalyst was operating properly, the only gas reaching the FID was carbon dioxide and no response was indicated. Any response was

reported and the catalyst efficiency recorded. When the catalyst efficiency was found to be less than 95%, it was replaced.

(2) Reduction Catalyst Efficiency Check - With the TGNMO analysis system in its normal operating mode triplicate injections of a CO_2 standard were made directly to the reduction catalyst and the FID response recorded. Triplicate injections of a standard methane gas were made directly to the reduction catalyst to calibrate the FID. The usual calibration curve could not be used because reduction catalyst inefficiencies were included in it. When the catalyst efficiency was less than 95% it was replaced.

(3) Cryogenic Freeze-Out Trap Oxidation Catalyst Efficiency Check - The cryogenic trap oxidation catalyst was checked by connecting the methane calibration gas cylinder to the trap oxidation catalyst and venting to atmosphere a flow of 160 ml/min. Triplicate samples of the flow taken from an injection/withdrawal port following the catalyst were injected into the TGNMO analysis system while the carrier gas bypassed both the oxidizer and the methanator. A response from the FID detector indicated a faulty oxidizer catalyst in the cryogenic trap burnout system. At a catalyst efficiency of less than 95% it was replaced.

B. Carrier Gas Contaminate Check

The purity of the chromatographic column nitrogen carrier gas and the zero air used for cryogenic trap burning as well as for tank and vessel pressurization were checked daily. Impurities in either gas results in a positive bias in the results.

(1) Zero Air Check - Zero air was checked for its total carbon content by withdrawing a sample from a port in the zero air supply line when the trap burnout system was receiving a flow of 160 ml/min, and injecting it into the TGNMO analysis system prior to the oxidizer. A zero air total carbon content greater than 5 ppm indicated that replacement of the ascarite CO_2 filter, molecular sieve, or zero air oxidation catalyst was required.

(2) Nitrogen Carrier Gas Contaminant Check - The nitrogen carrier gas was checked for contaminants daily as follows. The column was flushed of all carbon by placing it in boiling water while in the back flush mode. The column was then passed through the temperature sequence as if a sample had been injected starting with the dry ice-isopropanal bath in the forward mode. If the organic peak calculated was more than 5 ppm, the carrier gas cleanup system was regenerated with a new molecular sieve and oxidation catalyst. Organic peaks of less than 5 ppm were subtracted from that day's tank analyses.

C. Leak Checks

Leaks in the TGNMO analysis and sampling system are not readily apparent and the system must be diligently checked to assure integrity of the samples. Each section of the sampling and analysis system was checked for leaks daily prior to use.

(1) Tank Leaks - The evacuated sampling tanks were checked for leaks once every two weeks by evacuating them to more than 25 in. Hg measuring the vacuum with a mercury manometer, and remeasuring the vacuum 24 hours or more later. If the vacuum decreased, the tank was assumed to have leaked. The leak was located by pressurizing the tank to 30 in. Hg and submerging it in water. Once the leak was located and fixed, the tank was retested and returned to service.

(2) Sampling Assembly Leaks - The gauge assembly, connections between the gauge assembly, rotometer, traps, and sampling lines were checked daily at the sampling site for leaks. The sampling line was capped and a tank pressurized to 30 in. Hg was attached to the gauge assembly. All connections in the system were squirted with soapy water and inspected for bubbles. If a leak was found it was corrected before sampling.

(3) Trap Burnoff Assembly Leaks - This assembly was checked for leaks daily by plugging the trap burnoff system where the trap was connected and a vacuum of 20 in. Hg drawn on the system. Both the flow meter and the IR analyzer were monitored. A flow through the flow meter or a CO_2 response on the IR analyzer indicated a leak which was repaired prior to use of the system. The leak location can be found by tracing the system with dry ice wrapped in a towel. When the IR analyzer gives a response, the leak has been located. All trap connections to the burnout system were checked for leaks by squirting the joints with soapy water while the system was under pressure.

(4) Analytical-Field CO_2 Cross Check - Since the analysis system yields a stack CO_2 concentration, the values can be compared to check sample integrity. An unreasonably low analytical CO_2 value as compared to the Orsat CO_2 value indicated a possible leak in the sampling system during sample collection and the results were discarded.

D. Flame Ionization Detector Calibration

Daily calibration checks of the flame ionization detector (FID) were required to detect changes in gas flow and leaks which can decrease sensitivity. Two calibrations are needed, one through the catalyst and FID, and one through the column, catalyst, and FID.

Several criteria had to be satisfied by the calibration check namely: (a) calibration curve linearity, and (b) calibration curve drift from pre-set limits over the duration of the project.

(1) Linearity - Linearity of the detector was checked at the beginning of the project by multiple injections of standard methane gas. Different size injections were used to simulate six different concentrations of methane, between 20 ppm to 1035 ppm. A regression analysis yielded r^2 values of 1.000 and 0.995 for injections directly to the oxidizer and injections through the column, respectively, indicating good linearity. Figures 6 and 7 show the results of the linearity check for ranges 0-1000 ppm CH_4 and 0 through 5% CO_2, respectively.

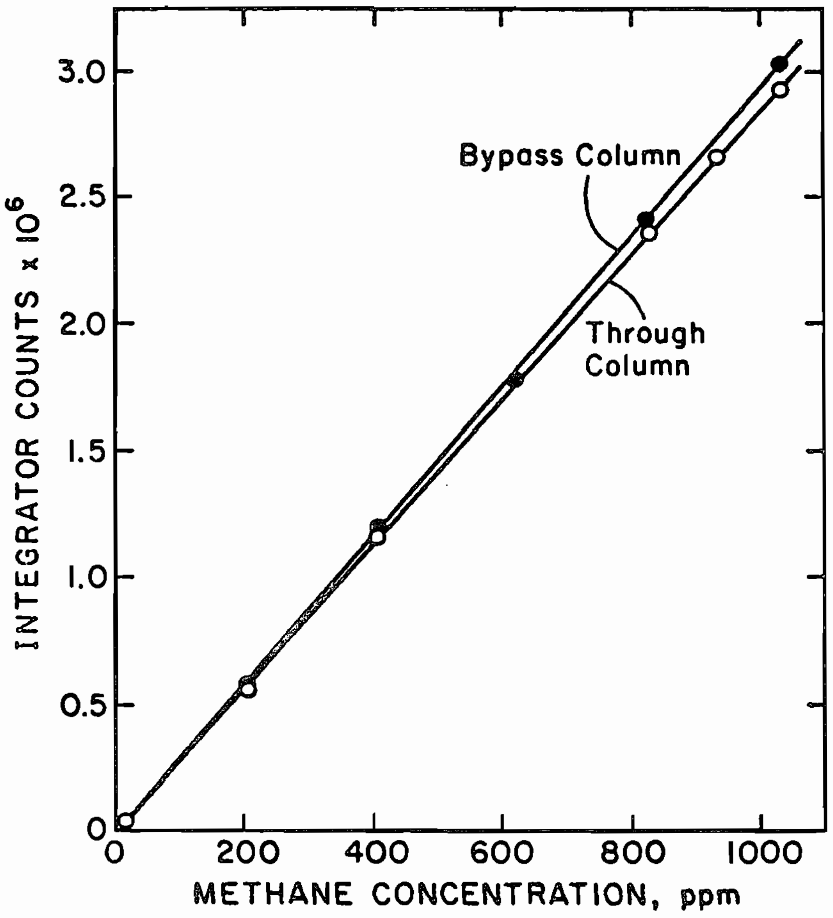

FIGURE 6

FID LINEARITY
FID RESPONSE VS. INPUT METHANE CONCENTRATION

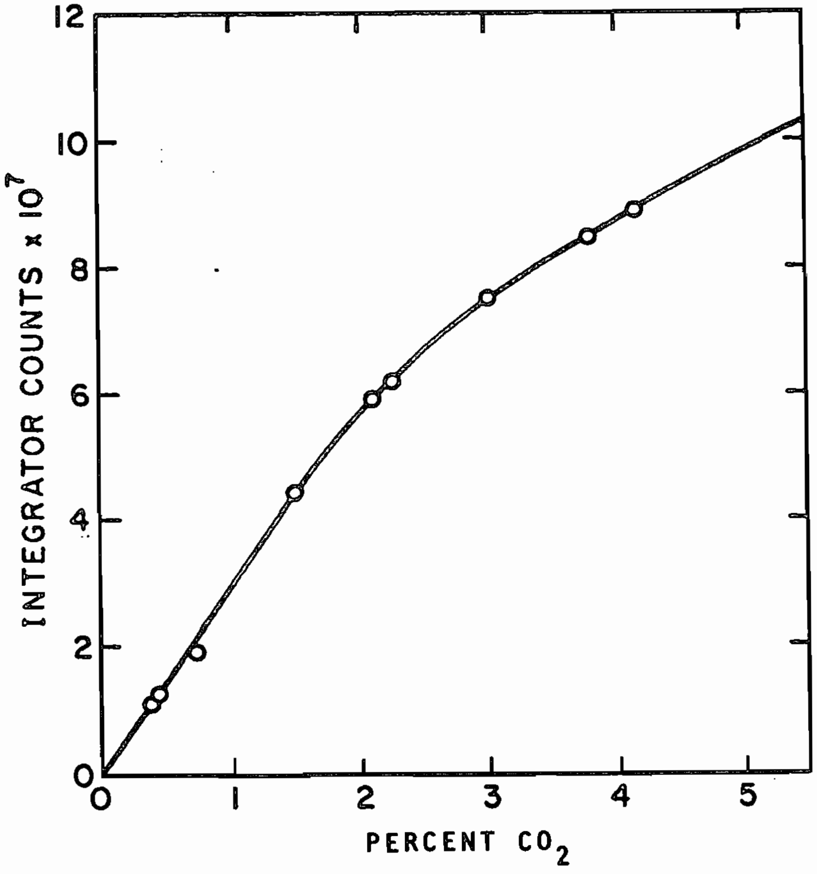

FIGURE 7

FID LINEARITY AT HIGH CO_2 CONCENTRATIONS
FID RESPONSE VS. INPUT CO_2 CONCENTRATION
AFTER CONVERSION TO METHANE

Linearity was checked once a week. Three simulated concentrations of methane were injected both through the column and bypassing the column. An r^2 was calculated to determine if linearity was maintained.

(2) FID Sensitivity Check - The day-to-day calibration curve will exhibit random variations due to differences in gas flows and other detector operating conditions. It is also possible for the calibration line (FID sensitivity) to drift from its average position. Such a drift would indicate gradual changes in gas flows, leaks in the analysis system, or catalyst inactivation. Any calibration line drift was detected from the normal random variations found.

Random variations at any point on the calibration line will give a normal distribution. The characteristics of that distribution was quantified at the beginning of the study. Once those distributions were quantified, any daily average calibration point falling outside 90% of the distribution indicated a possible problem with the system. When this occurred, septum conditions, connection leaks, and gas flow deviations were checked and the reason for the deviation identified and corrected.

A fixed portion of a population distribution can be found by $\bar{x} \pm K \cdot s$, where K is a value found in a statistical table (3), and depends upon the number of samples taken, the confidence interval, and the percentage of the population to be included, $\bar{x}$ and s are the mean standard deviation of the population, respectively. For this work, 90% of the normal day-to-day variation will be accepted with 95% confidence. Ten calibrations were used to establish the distribution. The criteria is shown in Table 1.

TABLE 1 DEVELOPMENT OF CRITERIA FOR ACCEPTANCE OF FID CALIBRATION POINTS, EXAMPLE

Calibration Gas Concentration	Integrator Count $\bar{x}$	s	K·s	Integrator Count Lower Limit	Integrator Count Upper Limit
Direct to Oxidizer					
1033	3,501,624	358,488	749,240	2,752,384	4,250,863
Through Column					
1033	3,569,880	339,768	710,115	2,859,764	4,279,995

(3) Calibration Accuracy - Establishment of a daily calibration line was made using 4 injections of 5 ml standard 1033 ppm methane gas in air. A calibration line was drawn between the 1033 ppm concentration and zero. Percent calibration accuracies at the 95% confidence level were calculated from the mean and standard deviation of the integrator counts by the equation:

$$\pm \text{ \% accuracy} = \frac{s}{\bar{x}\sqrt{n}} \; t_{\alpha/2:n-1} \times 100$$

If the accuracy was better than ± 3%, the calibration points were accepted, if not, the system was checked for problems and more calibration injections were made until the ± 3% accuracy was achieved.

E. Data Rejection

Non-duplicated results from paired samples were an indication of errors either during the sampling or sample preparation portions of the procedure. Data was rejected when the analytical results from the duplicate samples did not agree with each other. A paired result was accepted when the absolute difference between the pair was not greater than two times the standard deviation of all the test data taken from a source.

V ACCURACY AND PRECISION

Evaluation of the TGNMO sampling results requires knowledge of the accuracy and precision of the test method. Accuracy is influenced by interferences, sample losses, and detection error. Possible interferences and losses for the test method were investigated. Confirmation of the sampling and analysis technique was established with recoveries of methanol injected into the trap both in field and laboratory situations. Precision of the TGNMO sampling and analysis methods on a source was determined by statistical analysis of the paired analytical results.

A. Interferences

The TGNMO analytical scheme passes each sample through oxidation and reduction catalysts for detection on an FID as methane. The FID is sensitive only to organic carbon. Carbon dioxide or monoxide that is not separated from the organics will constitute a positive interference. A chromatographic column is used to separate nonorganics from organic constituents in the evacuated tank portion of the sampling train. Proper operation of the column will minimize interferences due to carbon dioxide tailing.

In the cryogenic trap portion of the analysis, inorganic carbon gases are separated from the organics via freeze out of the organics. In theory, all inorganic carbonaceous gases pass through the trap, however, some of these gases and/or inorganic carbonaceous particulates can be captured in the trap. Interference results when retained inorganic carbon is released with organic carbonaceous material when the trap is heated. Each potential interference is discussed below.

(1) Carbon Dioxide Tailing on the GC Column - Carbon dioxide has a tendency to tail badly from the chromatographic column, especially at high flue gas CO_2 concentrations. Sufficient time must be allowed for the carbon dioxide to be completely eluted from the column before it is back flushed. If the column is heated and back flushed before the carbon dioxide has completely eluted, it will become part of the organic peak and constitute a positive interference. In this work CO_2 tailing was monitored at high attenuation to assure that all of the CO_2 was eluted from the column.

(2) Particulates - Particulates in pulp and paper combustion sources generally contain inorganic carbon. Wood-residue fired boiler flue gases contain unburned elemental carbon and carbonates in the fly ash. Kraft recovery furnace particulates are high in sodium carbonate. Lime kiln particulates contain calcium carbonate. If these materials pass the filter and enter the trap they become a potential source of carbon dioxide during the trap burnout.

Elemental carbon in the traps will burn to carbon dioxide. Particulate carbon must be removed from the gas stream during sampling. Particulates that are made up of carbonates may decompose when the cryogenic trap is being heated. The trap is heated to about 600°C. The decomposition temperatures of carbonates that may be present in pulp and paper mill combustion sources are listed in Table 2 (4).

TABLE 2 DECOMPOSITION TEMPERATURE OF CARBONATES

Carbonate	Decomposition Temperature
$CaCO_3$	898°C
K_2CO_3	891°C
$KHCO_3$	100-200°C
Na_2CO_3	851°C
$NaHCO_3$	270°C

Only the bicarbonates of sodium and potassium will decompose at 600°C. However, the other carbonates may react with organic acids captured in the trap to release carbon dioxide when the traps are heated. Therefore, it is imperative that good instack filtering of the gas stream be used when the presence of carbonates are suspected in the sampled source.

(3) Carbon Dioxide Absorption in Traps - Absorption of carbon dioxide in the TGNMO sampling equipment is the largest potential source of interference. Absorption of carbon dioxide can take place in both the sampling line and cryogenic trap. Any water condensed in the sampling line will absorb relatively large quantities of CO_2. Adsorption of CO_2 in the cryogenic trap occurs because of its large surface area and because its operating temperature is at the condensation temperature of CO_2. When the traps are heated during sample preparation, the CO_2 captured is desorbed from the traps and delivered to the collection vessel along with CO_2 from oxidation of the captured organics. The adsorbed CO_2 thus becomes an interference.

Flushing of traps and sampling lines with carbon dioxide-free air theoretically removes carbon dioxide. However, desorption of CO_2 from the water in the lines is slow. The NDIR detector will sometimes show as much as 10 ppm CO_2 in the air stream after a 1-hour flush; thus, a considerable amount of CO_2 remains in the system at the end of the flush period. Differing flush times will result in differing quantities of CO_2 retained. Desorption of CO_2 from internal trap surfaces has been shown to be rapid, and need not be considered further here.

Carbon dioxide can also be stripped when water condensed in the sampling lines enters the cryogenic trap and is suddenly frozen. Carbon dioxide frozen into the ice matrix cannot be removed from the trap by flushing.

Factors that may affect the quantity of CO_2 remaining in the trap after flushing are the flush time, the amount of water in the sampling system that becomes frozen, the total amount of water in the system, the water temperature prior to freezing, and the sample gas carbon dioxide concentration.

At combustion source stack sampling conditions, the amount of CO_2 captured by the trap can be significant. Table 3 shows the equilibrium concentration of carbon dioxide absorbed in water in terms of grams CO_2 per gram water at various water temperatures and carbon dioxide concentrations. To illustrate the potential interference due to CO_2 absorption in water condensed in the traps, Figure 8 shows the ppm interference possible at various stack moisture and carbon dioxide concentrations. The actual amount of CO_2 retained by the traps will depend upon conditions at which the samples are collected.

TABLE 3 EQUILIBRIUM ABSORPTION OF CARBON DIOXIDE IN ONE HUNDRED GRAMS OF WATER (5)

Temperature (°C)	Grams CO_2 Absorbed in 100 Grams of Water				
(% CO_2)	0.04	5	10	15	20
0	1.3×10^{-4}	0.017	0.033	0.050	0.067
10	0.93×10^{-5}	0.012	0.023	0.035	0.046
20	0.68×10^{-5}	0.0085	0.017	0.026	0.034
30	0.50×10^{-5}	0.0065	0.013	0.020	0.026
40	0.42×10^{-5}	0.0052	0.010	0.016	0.021

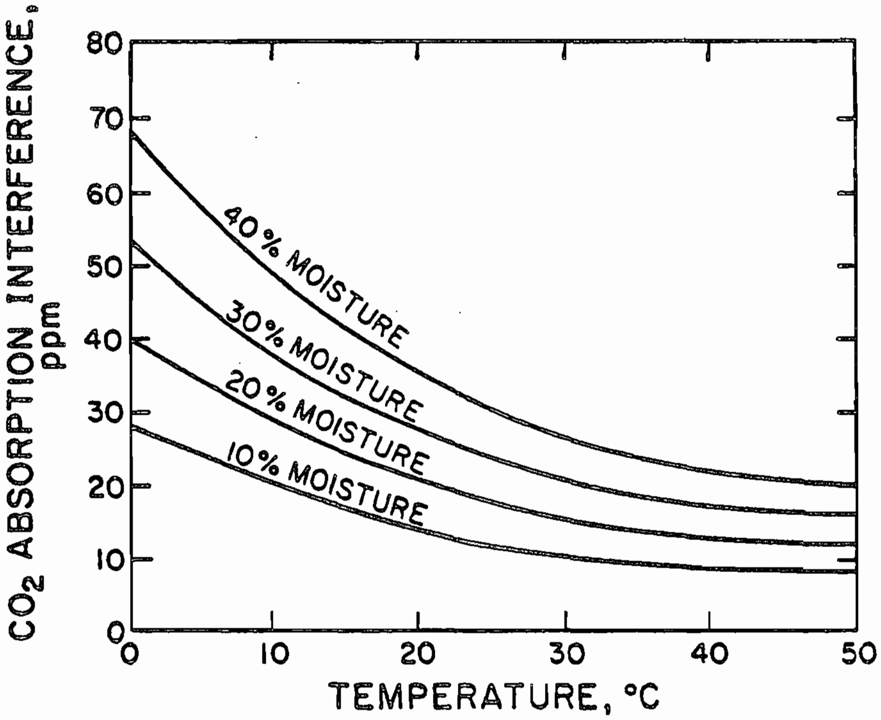

FIGURE 8

INTERFERENCE POSSIBLE DUE TO ABSORPTION OF CO_2 IN WATER CONDENSED IN SAMPLING TRAP AT VARIOUS STACK GAS % MOISTURES AND WATER TEMPERATURES AT 8% CO_2

B. Laboratory CO_2 Absorption Interference Study

Adsorption characteristics of carbon dioxide in the cryogenic traps used in this study were determined in the laboratory using several different sample stream carbon dioxide and moisture concentrations. The test covered conditions of no CO_2 or moisture to 18% CO_2 and 50% moisture in the gas stream. Results from the tests are reported in a format that allowed correction of field sampling data for the interfering CO_2.

(1) Procedure - Carbon dioxide in air mixtures were directed to a heated U-tube containing water to add moisture to the air stream. The water added to the U-tube was passed through activated carbon to remove organics. The quantity of moisture added to the air stream was roughly controlled by adjusting the temperature of the U-tube. This moisturized air was passed through a MnO_2 oxidation catalyst at 600°C to insure that there were no organics delivered to the trap. After the oxidation catalyst the gas passed through a cryogenic trap set in dry ice, to a flowmeter and to a 17-l evacuated tank. This apparatus is the trap burnout system used in reverse but with a sample collected as in the field. Gas flow was controlled to 200 cc/min until 10-l of gas was collected.

The trap was then flushed with carbon dioxide free air flowing at 100 cc/min until the NDIR registered less than 10 ppm CO_2. Flushing of the traps took from 20 min. to 1 hr.

After flushing, the trap was heated with an acetylene torch with the CO_2 free sweep-gas passing through the oxidation furnace, a cold trap to remove moisture, the NDIR detector, and into an evacuated collection vessel. When all of the CO_2 was removed from the trap as indicated by the NDIR the collection vessel contents were analyzed with the TGNMO analyzer. The amount of water collected in the cold trap was used to determine the gas stream moisture content.

Vessel volumes, pressures, temperatures, and moisture collected in the trap were measured and recorded. Analysis of the collection vessel contents was according to the TGNMO procedures used on field samples.

(2) Calculations - The data was reduced to a common basis for consistency and ease of relating it to field samples. The weight of CO_2 caught in the traps can be expressed by:

$$\text{Weight} = (PV/RT)\ \text{M.W.}\ (\text{ppm})$$

For easier comparison to field samples, the data is presented as carbon dioxide found for a 10-l field sample. This is calculated by:

$$\text{ppm @ STPV} = \frac{(\text{ppm measured})(P\ V)(293)}{(T)(29.92)(10)} = \frac{(\text{weight})(293)(R)}{(29.92)(10)(\text{M.W.})}$$

where P, V, and T are the pressure, volume and temperature of the vessel at the time of measurement. M.W. is the molecular weight of methane. To find the CO_2 background for a specific sample size, the ppm @ STPV times 10 is divided by the sample size.

C. Results

Results of the carbon dioxide interference study are shown in Table 4 and Figures 9 and 10. Figure 9 shows a constant background carbon dioxide interference for all moisture levels when the sampled gas contained less than 5 ppm CO_2 or 659 ppm CO_2. After elimination of one data point from the 650 ppm CO_2 data, the log average CO_2 background was 8.0 ppm CO_2 for the 659 ppm CO_2 data, and 8.1 ppm for the 0% CO_2 data. The log average of all the data when no moisture was added to the traps was 7.4 ppm. These results show that when there is no water present in the trap, all of the carbon dioxide is successfully removed from the trap during flushing. The small background residual CO_2 may be due to small leaks, residual carbon left in the trap or oxidation furnace from earlier runs, carbon burned from the steel the trap is constructed of, or chemically adsorbed CO_2 or CO in the system.

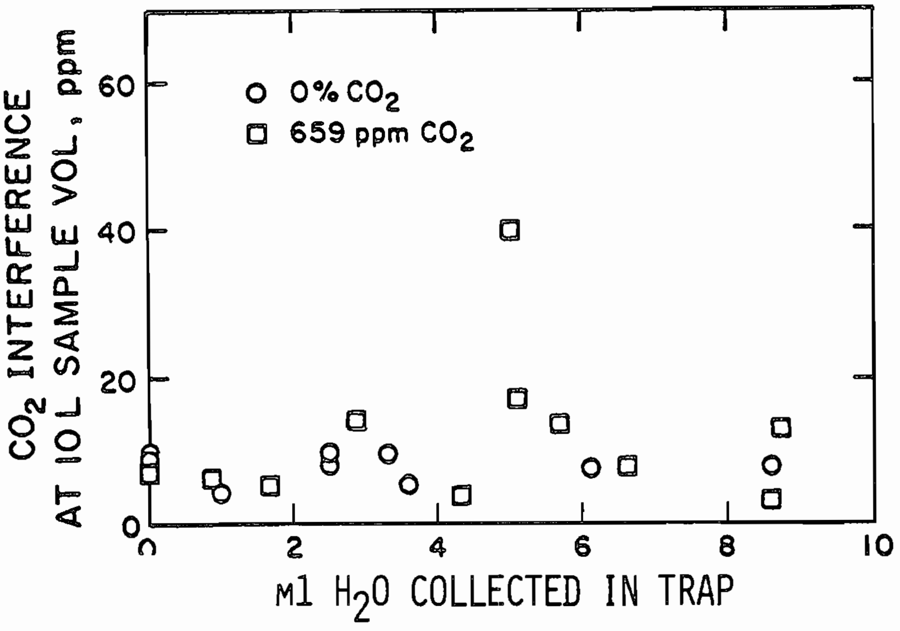

FIGURE 9

CO_2 INTERFERENCE AT LOW STACK GAS CARBON DIOXIDE CONCENTRATIONS

TABLE 4 CO_2 INTERFERENCE STUDY DATA

0 % CO_2		
ml H_2O in trap	% H_2O in air	Interference CO_2 ppm
0	0	10.1
0	0	9.3
1.0	10.7	4.2
2.5	24.3	9.7
2.5	25.1	8.5
2.5	33.0	8.5
3.3	27.9	9.5
3.6	32.4	5.3
6.1	45.1	7.7
8.6	52.6	8.0

658 ppm CO_2		
ml H_2O in trap	% H_2O in air	Interference CO_2 ppm
0	0	7.1
0	0	8.4
0.9	10.4	6.0
1.7	17.5	5.1
2.9	29.4	14.2
4.3	38.0	3.9
5.0	40.7	40.0
5.1	39.8	17.7
5.7	44.3	13.6
6.6	46.7	7.9
8.6	54.0	3.5
8.7	53.5	13.0

8 % CO_2		
ml H_2O in trap	% H_2O in air	Interference CO_2 ppm
0	0	9.4
0	0	2.5
0.6	6.9	6.3
1.4	14.7	6.3
3.0	27.9	5.1
4.0	32.7	27.7
5.0	38.6	61.7
8.6	53.0	62.9
9.3	52.8	23.4

12 % CO_2		
ml H_2O in trap	% H_2O in air	Interference CO_2 ppm
0	0	5.1
0	0	8.4
.8	9.1	13.3
1.6	16.8	5.4
3.3	32.3	65.8
4.5	35.7	28.2
5.1	39.3	21.2
6.4	45.0	413.0
7.0	47.7	7.1

12% CO_2		
ml H_2O in trap	% H_2O in air	Interference CO_2 ppm
0	0.0	13.6
1.2	13.1	30.8
1.3	16.6	31.3
1.7	14.5	71.1
1.7	20.9	37.7
1.8	19.3	62.7
2.4	16.5	49.9
3.8	29.3	21.0
3.8	25.5	14.0
3.9	24.4	24.4
4.2	29.7	81.8
4.4	29.4	106.1
5.5	32.2	128.9
5.6	32.7	96.6

15 % CO_2		
ml H_2O in trap	% H_2O in air	Interference CO_2 ppm
0	0.0	6.8
0	0.0	10.0
1.1	12.4	7.8
2.7	28.5	35.7
2.8	-	65.2
3.7	33.6	15.3
5.4	42.0	13.0
5.6	-	117.0
5.7	44.6	22.0
6.3	45.5	72.0

18 % CO_2		
ml H_2O in trap	% H_2O in air	Interference CO_2 ppm
0	0	8.3
0	0	10.5
1.3	15.2	14.0
2.8	29.3	70.9
4.4	35.1	51.2
4.5	39.1	23.4
7.9	51.3	170.0
9.3	54.6	146.0

Figure 10 shows the CO_2 absorption interference as a function of sampled gas moisture content at carbon dioxide concentrations between 8 to 18%. Below 10% moisture there appears to be no significant interference above background. Above 10% flue moisture there appears to be a random intereference that increases with sampled gas moisture and carbon dioxide content. The randomness of this data makes it difficult to predict the CO_2 interference encountered at high stack moisture content. Figure 11 shows the same data in terms of ml H_2O caught in the trap. This data is representative of a 10-l sample volume with the NCASI sampling equipment.

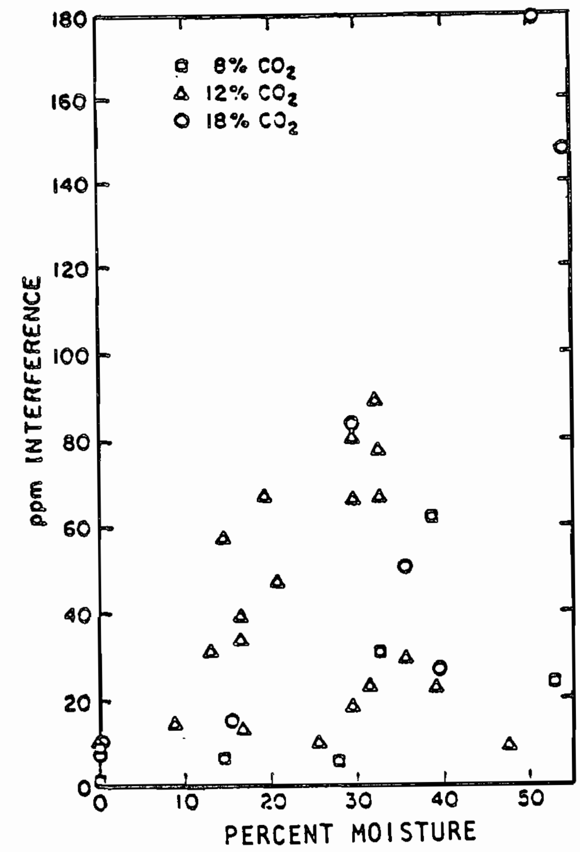

FIGURE 10

INTERFERENCE AT HIGH STACK GAS CO_2 CONCENTRATIONS AS A FUNCTION OF STACK GAS MOISTURE CONTENT

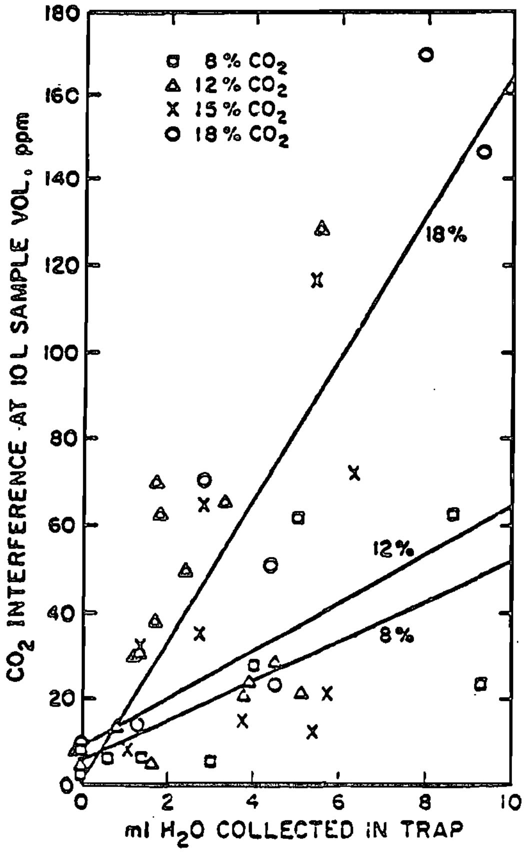

FIGURE 11

INTERFERENCE AT HIGH STACK GAS CO_2 CONCENTRATIONS AS A FUNCTION OF WATER COLLECTED IN SAMPLING TRAP

A closer look at all the data collected for 12% CO_2, Figure 12, shows that the CO_2 interference tended to fall into two groups, that which grouped about a line with a slope of 18.5 ppm CO_2 interference per ml H_2O in the trap and that which fell below 30 ppm interference regardless of the amount of water collected in the trap. There is no apparent reason to explain the different groupings. Almost all of the interference data fell below the theoretical maximum interference which occurs when the water absorbing the CO_2 is at 0°C. The 18.5 ppm CO_2 interference per ml water corresponds to the theoretical interference at a water temperature of 3°C.

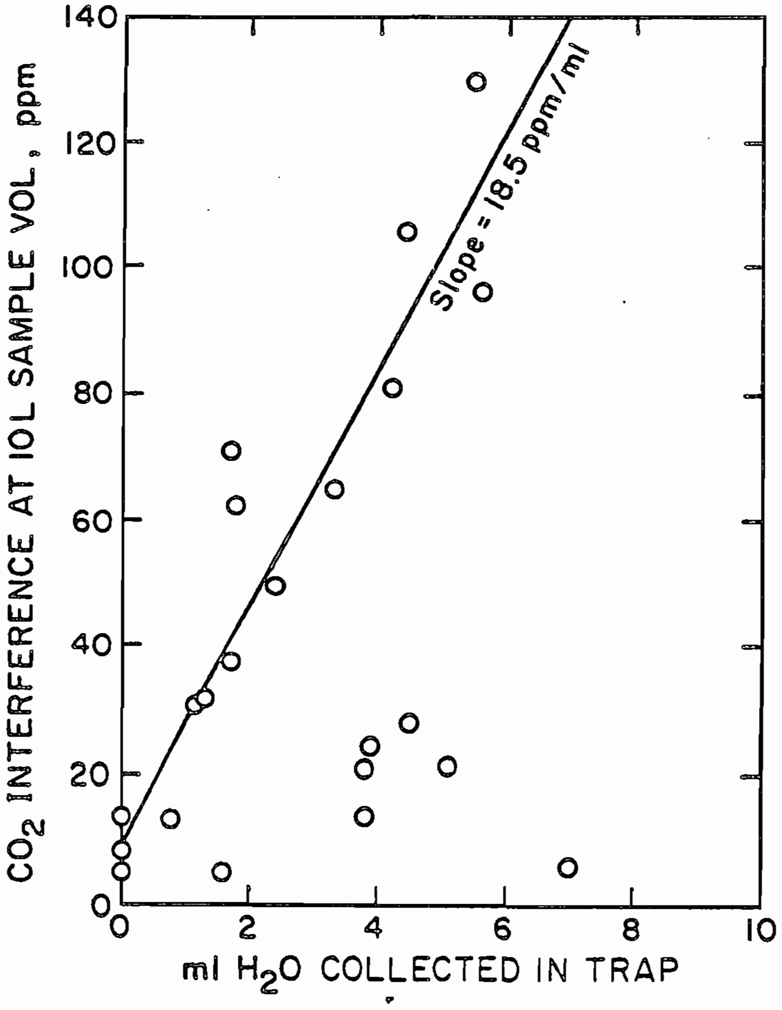

FIGURE 12

CARBON DIOXIDE INTERFERENCE AT 12% CO_2 IN STACK GAS

Most lime kilns have a stack gas moisture content above 30% and carbon dioxide concentations above 15%. At these conditions the interference can be significant. A correction factor is needed to adjust TGNMO data collected from combustion sources to reflect the interference from CO_2 absorption in the traps. Because of the high variability of the interference the correction factor is applicable only for an average of a number of data points.

If it is assumed that the interference is proportional to the amount of water collected in a trap, the interference can be calculated by measurement of the water captured and CO_2 content of the gas stream. The interference data was plotted against ml H_2O collected in a trap and linear regression run for each CO_2 concentration studied. The slope of the lines is the amount of CO_2 adsorbed per ml water present. The slopes were plotted in Figure 13 and a linear regression run. From this regression data a formula was developed to estimate an average CO_2 interference at particular sampling conditions. The resulting formula was:

$$\text{Average Interference} = \frac{71 + [(9.8 \text{ x } \%CO_2) - 6.2]\ (\text{ml } H_2O \text{ collected})}{\text{sample volume}}$$

This formula will give an average correction value for the amount of CO_2 and water present in the trap, but due to the high variability of the moisture data it can not be used to correct an individual piece of data.

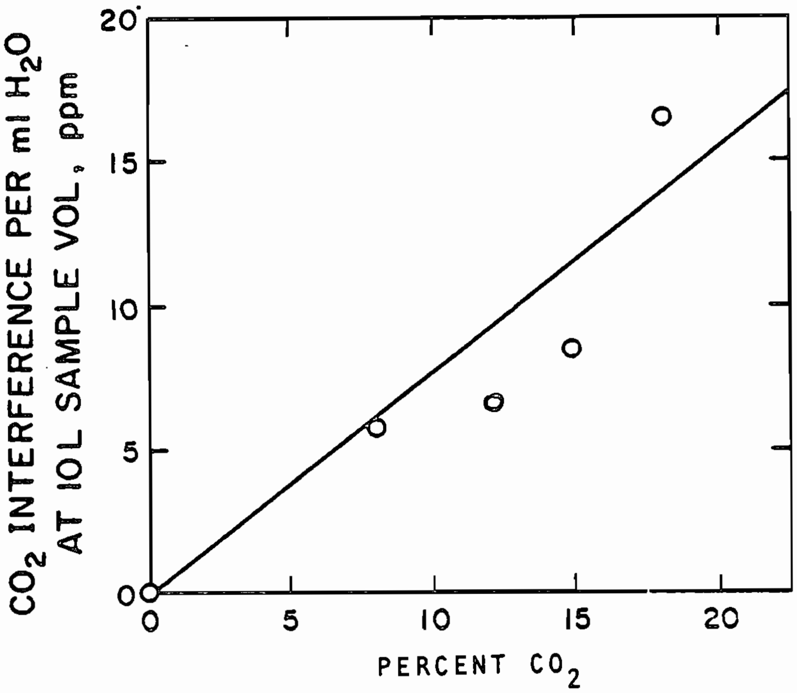

FIGURE 13

CO_2 INTERFERENCE PER ml H_2O IN SAMPLE TRAP AT 10-l SAMPLE VOLUME vs. SAMPLE GAS PERCENT CO_2

To correct the raw TGNMO data collected in this study for the random CO_2 interference, each piece of data is corrected for an average CO_2 interference. Although the individual corrections on each piece of data can be in error to the extent of ± the correction value, the average of a sufficient number of data points should smooth the correction randomness resulting in a corrected average TGNMO emission value. The uncorrected data contains the randomness associated with CO_2 absorption. This randomness would need to be averaged whether or not the data is corrected for CO_2 absorption.

The minimum detectable level of the TGNMO sampling procedure is dependent upon the CO_2 and moisture content of the gas being sampled. At atmospheric carbon dioxide levels the minimum detectable TGNMO level is about 10 ppm. Below this level it is difficult to distinguish between the method background and what is in the sample. As the sampled gas carbon dioxide concentration increases, the moisture in the sample becomes an important factor in limiting minimum detection. High CO_2 and no moisture situations will set the minimum detectable TGNMO at the background level of 20 ppm. At 30% moisture and 15% CO_2, conditions typical of lime kilns, the minimum detectable level was shown to be about 70 ppm.

D. Trap Contamination

Cryogenic traps must be tightly capped when not in use or when filled with a sample. Experience in this study showed that uncapped, or loosely capped traps in storage adsorb carbonaceous materials from the air. This adsorbed material constitutes a variable background. As a precaution, any trap stored in the laboratory for periods greater than two weeks was burned prior to use.

E. Losses

Loss of organic compounds in the TGNMO sample and analysis procedures can occur in the sampling probe through leaks, absorption of CO_2 in the trap burnout water removal system, adsorption or organics in the evacuated sampling tanks, hanging up on the chromatographic column, and incomplete oxidation while being burned out of the trap. Sample losses due to leaks and poor oxidation are minimized through the quality control procedures previously described.

(1) Probe Losses - Organic material can condense in the probe or adsorb onto the probe filter during sampling. The probe is kept at stack temperature to minimize this condensation.

(2) Adsorption Losses - Carbon dioxide produced from oxidation of the cryogenic trap contents can be adsorbed in any moisture condensing in the lines after the oxidation furnace. To eliminate this, adsorption water was frozen out of the gas stream immediately following the oxidation catalyst. Water will be condensed to the liquid phase before freezing and adsorbed CO_2 can be frozen into the ice.

The amount of CO_2 absorbed in the water before freezing is controlled by Henry's Law for CO_2 absorption. At 0°C the amount of adsorption in water is 3.36×10^{-3} grams times the mole fraction of CO_2 for each ml of water present, a maximum of 1.71×10^{-4} ppm CO_2 for each ppm CO_2 present when water is condensed during the burnout. This is a very small loss.

F. Recovery of Injected Compounds

The accuracy of the overall TGNMO analysis technique was demonstrated by recovery of known quantities of organic compounds injected into traps both in the laboratory and in the field. Laboratory methanol injections into the traps equivalent to 300 to 440 ppm methane showed an average recovery of 114%. Field recoveries were determined by injecting the equivalent of 250 to 410 ppm methanol into one of the duplicate pairs while sampling a wood-residue fired boiler. The TGNMO determined from the sample without methanol injection was subtracted from the sample results into which methanol was injected to give the recovery. The average of the field recoveries was 88%. The data is shown in Table 5.

G. Precision of Data

The precision of data collected is established to evaluate the meaningfulness of the results. The data collected in this study was evaluated for precision via the statistical procedure called analysis of variance.

(1) Analysis of Variance - Differences in results from one sample to another can be due either to variations in the source being sampled or due to random error in the sampling and analysis technique. It is desirable to separate the variation in the data due to changes in the source from that which results from the analytical procedure so as to gain a true indication of the source characteristics. The variation due to the source can then be tested for significance against the randomness resulting from the analytical procedure.

Many statistical texts contain discussions on analysis of variance (ANOVA). The procedure used in this work uses a single factor analysis and is as follows:

T = Σx where x is the value of each observation

Σx^2 = summation of squares of all observations

Tc = total of the duplicate pairs

n = number of replications of each test

N = total number of samples taken

c = number of observations (N/n)

TABLE 5 METHANOL RECOVERY DATA

Sample Number		Methanol Injected ppm as CH_4	TGNMO Analytical Result, ppm	Recovery ppm	Recovery Percent
Field Recoveries	**Source**				
11271	W-R F	0	53	340	82
11272	Boiler	408	390		
11273	W-R F	381	420	310	82
11274	Boiler	0	110		
12281	W-R F	236	300	220	95
12282	Boiler	0	81		
12283	W-R F	342	450	300	88
12284	Boiler	0	150		
01231	W-R F	245	240	200	81
01232	Boiler	0	42		
01233	W-R F	0	68	270	99
01234	Boiler	266	340		
03113	Kraft Rec'y	0	147	152	94
03114	Furnace	162	300		
03131	Kraft Rec'y	0	100	171	107
03132	Furnace	161	270		
03271	Kraft Rec'y	176	300	180	103
03272	Furnace	0	120		
12271	Laboratory	439	490	490	113
12272		379	440	440	115

$$SSc = \frac{Tc^2}{n} - \frac{T^2}{N}.$$

$$SSt = \Sigma x^2 - \frac{T^2}{N}$$

$$SSr = SSt - SSc$$

Shown below is a table to calculate the mean squares and separate estimates of variance due to analytical or wood-residue boiler sources.

Source of Variation	Squares (SS)	Freedom (DF)	Square, (MS) (MS=SS/DF)	Mean Square Ratio (MSR)	Parameters Estimated
Boilers	SSc	c-1		$\frac{MSc}{MSr}$	$\sigma^2 + n\sigma_a^2$
Experimental	SSr	c(n-1)			σ^2

When the MSR is less than the appropriate F statistic from the F distribution tables, the variation appearing in the data is due to the randomness resulting from the analytical procedures and not necessarily from the source.

An estimate of the variance of the TGNMO from the boilers is calculated by:

$$S_a^2 = \frac{SSc/(c-1) - SSr/c(n-1)}{n}$$

An estimate of the variance of the analytical procedure (S_r^2) is given by σ^2.

VI RESULTS

All the TGNMO ppm results were corrected for the CO_2 interference as shown in Appendix B. Average CO_2 interferences were 73, 62, and 34 ppm, which represented 75%, 19%, and 109% of the corrected TGNMO for kilns A-C, respectively. The subsequent data presented in this report has been corrected for the CO_2 interference.

Table 6 presents TGNMO emission data in terms of ppm CH_4, lb/ton lime produced, and lb/ton unbleached pulp, along with kiln operation information. The TGNMO emissions expressed as lb/ton unbleached pulp was calculated by assuming 0.3 tons of lime are required to produce 1 ton of pulp. Average TGNMO emissions from the kilns were 0.41, 1.6, and 0.24 lb/ton CaO produced or 0.12, 0.48, and 0.07 lb/ton pulp produced for kilns A-C, respectively. In terms of energy input to the kilns, the TGNMO emissions were 0.060, 0.30, and 0.037 lb/10^6 Btu, respectively.

Kiln B produced the highest emissions. The high TGNMO emission rate from this kiln likely resulted from organics introduced to the lime mud by the use of evaporator condensates in the lime mud washing system and at the scrubber. These organics were driven into the gas stream at the cold end of the kiln where the lime mud is dried at the scrubber.

Fresh water was being used in sprays to further wash the mud on the lime mud filter for the first 5 data entries for lime kiln B in Table 6. The TGNMO emissions were higher when fresh water was being used than when evaporator condensates were being used on the lime mud filter sprays. This result is contrary to what may be expected if the organic compounds emitted were introduced to the process through the wash water.

The TGNMO emissions from kiln A could also be due in part to organic compounds contained in the water associated with the lime mud rather than from uncombusted fuel. This kiln and causticizing system was operating over capacity and there were green liquor dregs in the lime mud. Dregs are composed of unburned carbon and products of corrosion contained in the smelt from the recovery furnace. Between 40 to 56% of dregs are lost upon ignition (6). It is possible that the unburned carbon contained volatile organic compounds and were emitted at the cold end of the kiln during drying.

To assess if the TGNMO emissions were associated with the lime mud or a product of combustion, a laboratory study on the lime mud organic content was performed. A measured quantity of lime mud from kiln A was heated to drive off water and organic compounds into the sample preparation system in the TGNMO analysis procedure. Results showed a potential emission rate of 0.44 lb TGNMO per ton lime produced when heated. Corrected field sampling results showed emissions of 0.37 lb/ton lime produced at the time the lime mud sample was collected.

It appears that organics present in the lime mud may be responsible for a significant portion of TGNMO emissions from this kiln. More studies of a similar nature on other lime kilns and a variety of lime muds are advisable to better define this potential relationship.

TGNMO emissions from kiln C were the lowest of the three kilns studied. This kiln burned noncondensible gases. It is not known whether burning of noncondensible gases contributes to TGNMO

TABLE 6 LIME KILN TGNMO EMISSIONS AND OPERATING PARAMETERS

	TGNMO		Stack Flow DSCFM	Lime Produced Tons/hr	Gas Burned cfm	Oil Burned gpm	10^6 Btu Input Ton CaO	TGNMO lb/10^6 Btu
ppm CH_4	lb/Ton CaO	lb/Ton Pulp						
Kiln A								
112	0.52	0.16	10,700	7.0	650		5.7	0.091
214	0.96	0.29	12,200	8.2	-	-		
82	0.37	0.11	12,200	8.2	-	-		
126	0.49	0.15	9,400	7.2		4.4	5.5	0.089
62	0.24	0.07	9,400	7.2		4.4	5.5	0.043
1	0.01	0.00	13,200	4.8		4.5	8.5	0.001
121	0.52	0.16	8,000	5.6	550		6.1	0.086
56	0.20	0.06	10,300	8.6		3.8	4.0	0.050
Avg. 97	0.41	0.12						0.060
Kiln B								
570	2.5	0.75	8,600	5.9	500		5.2	0.48
360	2.0	0.60	9,700	5.4	470		5.4	0.37
340	1.8	0.54	9,700	5.4	470		5.4	0.33
180	0.8	0.24	8,700	6.0	546		5.6	0.14
360	1.6	0.49	9,000*	6.0	460		4.7	0.34
250	1.6	0.49	10,400*	4.8	470		6.0	0.26
320	1.2	0.36	8,600	6.8	495		4.5	0.27
240	0.9	0.27	7,300	6.2	500		5.0	0.18
Avg. 328	1.6	0.48						0.30
Kiln C								
38	0.35	0.11	16,800	6.1		5.0	7.4	0.047
26	0.15	0.04	22,000	9.9		5.4	4.9	0.031
43	0.33	0.10	17,800	7.4		4.6	5.6	0.045
18	0.14	0.04	18,600	7.4		4.8	5.9	0.024
Avg. 31	0.24	0.07						

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* Flow rates calculated from material balance

emissions. Possible contribution to TGNMO emission from lime mud contaminants was not investigated at this kiln.

TGNMO emission changes across the scrubbers on each lime kiln were monitored by simultaneous sampling before and after the scrubber. Table 7 shows the results. All three kilns showed a slight increase in emissions across the scrubber. The increases found, however, were not statistically significant. A large number of samples would be required to show a definite trend.

TABLE 7 CHANGE IN TGNMO EMISSIONS ACROSS SCRUBBER

	TGNMO Before Scrubber ppm	TGNMO After Scrubber ppm	TGNMO Change
Kiln A	1	63	+62
	122	163	+41
	56	90	+34
Avg.	60	105	+45
Kiln B	195	225	+30
	361	264	-97
	246	263	+17
	198	272	+74
Avg.	250	206	+ 6
Kiln C	20	40	+20
	44	57	+13
Avg.	32	48	+16

The precision of the data as indicated by duplicate samples was obtained from an analysis of variance. Results of the analysis of variance on the TGNMO data in terms of lb/ton CaO produced are listed in Table 8. These results indicated: (1) significant variation in the results not caused by random sampling and analysis error exist in the data from kilns A and B, (2) that the average of a single paired sample is within ±0.14, ±0.64, and ±0.19 lb/ton CaO produced of the true value at the 95% confidence level for kilns A-C respectively, and (3) that the average TGNMO emissions reported for each lime kiln are within ±0.22, ±1.33, and ±0.08 lb/ton lime produced of the true average at the 95% confidence level for kilns A-C respectively.

TABLE 8 ANALYSIS OF VARIANCE RESULTS ON POUND TGNMO/ton LIME

Kiln	C	S Sample	S Error	MSR	F at 90% Confidence	Significant
A Before Scrubber	8	026	0.17	5.3	2.6	yes
A After Scrubber	5	0	0.14	0.6	3.5	no
B Before Scrubber	8	1.61	0.77	9.7	2.6	yes
B After Scrubber	4	1.67	0.65	14.2	3.5	yes
C Before Scrubber	4	0.05	0.12	1.4	4.2	no
C After Scrubber	2	0.02	0.11	1.1	49.5	no

The precision of the data was poorer than experienced when sampling wood-residue fired boilers and kraft recovery furnaces. Lime kiln stack gases contain higher levels of CO_2 and moisture than previous sources tested. These high CO_2 and moisture levels resulted in random high CO_2 interferences and poor precision. The TGNMO values reported for kiln C were at or below the level of detection.

The range of the data collected is illustrated in Figure 14. This figure shows the frequency of occurrence of TGNMO emissions from the lime kilns. Variations in TGNMO emissions could not be related to the kiln operating parameters.

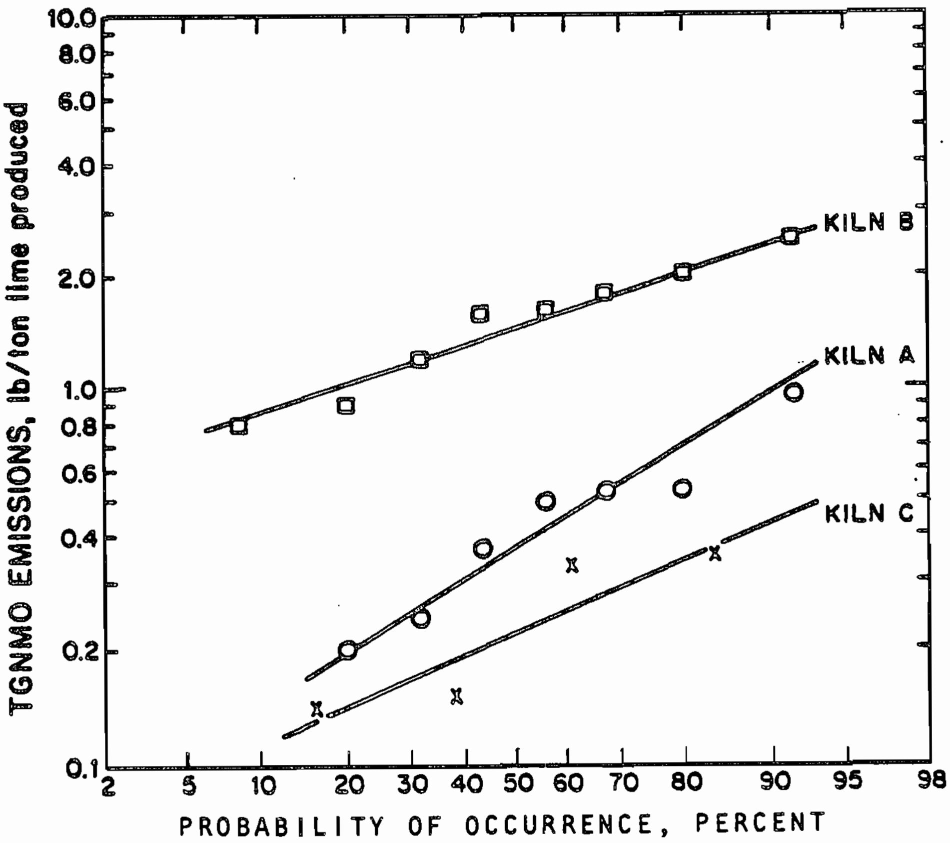

FIGURE 14

TGNMO CUMULATIVE FREQUENCY DISTRIBUTION DATA CORRECTED FOR CO_2 INTERFERENCE

VII SUMMARY

(1) TGNMO emissions were measured from three lime kilns. Average TGNMO emissions were 0.41, 1.6, and 0.24 lb/ton CaO produced. A greater number of kilns will need to be sampled to determine if these emission values are representative.

(2) The higher TGNMO emissions appeared to be related to organic contaminants in the lime mud. More study will be required to establish a relationship between TGNMO emissions and lime mud contaminants.

(3) Wet scrubbers used to control particulate emissions from lime kilns can contribute to TGNMO emissions, especially if contaminated makeup water is used. During this study, TGNMO contribution from the scrubber was not found to be significant.

(4) The high water and CO_2 levels in lime kiln exhaust gas result in high CO_2 interferences in EPA Method 25 and in poor measurement precision at the emission concentrations experienced.

VIII LITERATURE REFERENCES

(1) "Compilation of Air Pollutant Emission Factors," 3rd Edition, Supplement 9, AP-42 (1977).

(2) Federal Register 45 (194) (October 3, 1980).

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

(4) Weast, B. and Hodgman, [Eds.], Handbook of Chemistry and Physics, 46th Edition, The Chemical Rubber Company (1965).

(5) Perry, J.H., [Ed.], Chemical Engineering Handbook, 4th Edition, McGraw-Hill Book Company, New York, New York (1969).

(6) Whitney, R.P., [Ed.], Chemical Recovery in Alkaline Pulping Processes, TAPPI Monograph Series No. 32 (1968).

APPENDIX A

EPA METHOD 25

40 CFR Part 60

[FRL 1525-7]

Standards of Performance for New Stationary Sources; Addition of Reference Methods 24 and 25 to Appendix A

AGENCY: Environmental Protection Agency (EPA).

ACTION: Final rule.

SUMMARY: This action establishes two new reference methods to be added to Appendix A of 40 CFR Part 60, Standards of Performance for New Stationary Sources. Reference Method 24 will be used to determine the volatile organic compound (VOC) content of coating materials, and Reference Method 25 will be used to determine the percentage reduction of VOC emissions achieved by emission control devices. These reference methods will be used in several air pollution regulations for industrial surface coatings which are being developed for proposal and promulgation.

EFFECTIVE DATE: October 3, 1980.

ADDRESSES: *Background Information Document.* The Background Information Document (BID) for the promulgated test methods may be obtained from the U.S. EPA Library (MD-35), Research Triangle Park, North Carolina 27711, telephone number (919) 541-2777. Please refer to "Reference Methods 24 and 25—Background Information for Promulgated Test Methods," EPA-450/3-79-030c.

Docket. Docket No. A-79-05, containing all supporting information and public comments, is available for public inspection and copying between 8:00 a.m. and 4:00 pm., Monday through Friday, at EPA's Central Docket Section, Room 2902, Waterside Mall, 401 M Street SW., Washington, D.C. 20460.

FOR FURTHER INFORMATION CONTACT: Mr. Gene W. Smith, Standards Development Branch (MD-13), U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711, telephone number (919) 541-5421.

SUPPLEMENTARY INFORMATION:

Summary of Reference Methods

Reference Method 24, "Determination of Volatile Matter Content, Water Content, Density, Volume Solids, and Weight Solids of Surface Coatings," is used to determine the volatile matter content, water content, density, volume solids, and weight fraction solids of paint, varnish, or related surface coatings. Several ASTM standard methods which comprise Method 24 are used to make these determinations. All coatings are analyzed by the same procedure except for the additional step of measuring the water content of waterborne (water reducible) coatings. A data validation procedure is used to establish precision limits for the coating analysis. This verifies the ability of the analyst and the analytical procedure to obtain reproducible results for the coatings tested. In addition for waterborne coatings, the measured parameters are modified by the appropriate confidence limits based on between-laboratory precision statements.

Reference Method 25, "Determination of Total Gaseous Nonmethane Organic Emissions as Carbon," is used to measure the total gaseous nonmethane organics in source emissions. An evacuated cylinder is used to withdraw emission samples from the stack through a chilled condensate trap. After sampling is completed, the contents of the condensate trap and evacuated cylinder are analyzed separately. The organic content of the condensate trap is oxidized to CO_2 which is quantitatively collected in an intermediate collection vessel; a portion of the carbon dioxide is reduced to methane and measured by a flame ionization detector (FID). A portion of the sample collected in the gas sampling tank is injected into a gas chromatograph which separates the nonmethane organics from carbon monoxide, methane, and carbon dioxide; the nonmethane organics are oxidized to carbon dioxide, reduced to methane, and measured by FID. The results of the analyses are combined and reported as total gaseous nonemethane organics.

Background

On October 5, 1979, as an appendix to the proposed standards of performance for automobile and light-duty truck surface coating operations, EPA proposed reference methods for analyzing the volatile organic compound (VOC) content of coatings. These proposed methods were Reference Method 24 (Candidate 1) and (Candidate 2). Candidate 1 expresses the VOC content of surface coating in terms of mass of carbon. Candidate 2, based on the use of several ASTM methods, reports the mass of VOC. Both test methods were proposed to obtain public comment.

Reference Method 25 was proposed at the same time. It measures the volatile organic emissions in effluent streams from stationary sources. When used to measure the inlet and outlet streams of an emission control device, the efficiency of the device can be determined.

These methods would normally be promulgated with the standards of performance for automobile and light-duty truck surface coating operations which are scheduled to be promulgated in the fall of 1980. However, the methods are being promulgated earlier because several changes have been made to the proposed methods, and several regulations are being developed for proposal in the near future which will require the use of these methods. This will allow the public to have the opportunity to comment on the use of these final methods in their respective industries.

Public Participation

During development of the test methods, trade and professional associations and individual companies supplied information and data on these methods. After proposal on October 5, 1979, comments were received from coatings manufacturers and suppliers, trade and professional associations, and State air pollution control agencies. The methods were also discussed at a public hearing held on November 9, 1979. The public comment period was extended from October 5, 1979, to December 14, 1979.

Public Comments and Changes Made to Proposed Reference Methods

Fifteen comment letters were received on the proposed test methods. These comments have been carefully considered and, where determined to be appropriate by the Administrator, changes have been made in the proposed test methods. A detailed discussion of these comments is contained in the background document entitled, "Reference Methods 24 and 25—Background Information for Promulgated Test Methods," which is referred to in the ADDRESSES section of this preamble.

General

The Administrator has rejected proposed Reference Method 24 (Candidate 1) and selected proposed Reference Method 24 (Candidate 2) as the test method to be used to determine the volatile organic content of coatings. Conclusive data were presented by commenters showing that certain coatings representing a significant portion of those in use could not be distilled as required by proposed Method 24 (Candidate 1). For this reason, the Administrator concluded that proposed Method 24 (Candidate 1) is not applicable to all coatings and should not be selected as the reference method.

Several procedural and editorial changes have been made to Reference Method 24 (Candidate 2) and Reference Method 25 as proposed in order to clarify and to improve the sampling and analytical procedures. These changes are based on additional information obtained by EPA from experience with the methods and on the public comments received.

Reference Method 24

The following discussion summarizes the procedural changes made to proposed Reference Method 24, Candidate 2. The procedures were added to protect the source owner from invalid results that might result from poor analytical techniques, application of the method to a coating not suitable for analysis with Reference Method 24, or imprecision in Reference Method 24 resulting from a high percentage of water in the solvent.

The promulgated reference method requires the analyst to complete duplicate analyses on each sample tested. A comparison is then made between these results and the within-laboratory precision statements for each parameter. Duplicate analyses are made until the results fall within the range established for the within-laboratory precision statements. The purpose of the procedures is to verify that the analyst can achieve a level of precision for the coating under analysis equal to or better than the precision obtained by experienced analysts participating in the ASTM studies of the method. Because of the variety of coatings that may be subject to analysis, it is possible that certain coatings may not be amenable to analysis using Reference Method 24; that is, in certain cases it may not be possible to achieve results which meet the precision limits. In this case, the method provides for a case-by-case evaluation and development of a suitable procedure.

An additional procedure for waterborne coatings was added to the promulgated reference method to protect the source owner or operator from a determination of noncompliance when the owner is actually in compliance. This procedure is needed because the results of Reference Method 24 are dependent on the difference between the weight of total solvents and the weight of water. As the percent weight of water increases, the difference decreases. As a result, any imprecision in the measurement of the weight of total solvent in water is magnified in the calculation of organic solvent content. For example, if the total solvent of a coating is measured as 100±2 units and the water content is measured at 90±2 units, the organic solvent content would be in the range of 6 to 14 units. The magnitude of the range, as a percent of the true organic solvent content, increases with increasing water content and could, as shown in the example, lead to a conclusion of noncompliance even when the owner is in compliance. The procedure added to Reference Method 24 for waterborne coatings protects the owner or operator from this erroneous determination by minimizing the calculated value for VOC content. This is done, for example, by subtracting the between-laboratory precision statement from the average value of total solvent and adding the between-laboratory precision statement to the average value for water content. Thus, if a source owner is in compliance based on average coating values, the compliance method will automatically show a lower VOC content because of the adjustments made to the average values based on the between-laboratory precision statements.

Based on comments from manufacturers that ASTM 2697 has only been shown to be applicable to architectural coatings, the analytical procedure for determining volume solids has been eliminated from Reference Method 24. The commenters stated that this ASTM procedure was not applicable to all the coatings that Method 24 was intended to cover. Therefore, Method 24 requires that the volume solids be calculated from manufacturer's formulation data.

The coatings classifications step in the proposed method was eliminated because industry comments indicated that it was only necessary to separate waterborne (water reducible) and solvent-borne (solvent reducible) coatings. Therefore, the "Procedure" discussed in Section 4 of the proposed method has been simplified.

Several commenters recommended that the use of coatings manufacturers' data be allowed in calculating VOC content of coatings rather than required Method 24. Coatings manufacturers' data will be allowed in calculating VOC content of coatings because this will reduce the burden on the industry to measure all coatings with Method 24. Use of this method to calculate VOC content of coatings will require industries to closely monitor and record all organic solvents added to the coatings at the plant. Method 24 will be the reference method.

One commenter suggested that EPA should specify the volume fraction of solids for the various types of coatings similar to the way transfer efficiencies were listed. Based on comments from manufacturers that ASTM 2697 has only been shown to be applicable to architectural coatings, the volume fraction of solids determination in Method 24 has been removed. Method 24 specifies the use of manufacturer's formulation data for calculating volume fraction of solids.

Reference Method 25

The majority of the procedural changes made to Method 25 relate to calibration requirements and are meant to improve quality assurance and at the same time simplify the daily operation of the analytical equipment. This is accomplished by requiring performance tests on the analytical equipment (nonmethane organic analyzer and condensate recovery and conditioning apparatus) prior to initial use; specific criteria for the performance tests are provided. Routine daily calibrations (much less time consuming than previously required) are conducted and the results are compared to performance test reference values to determine whether the performance of the analytical equipment is still acceptable.

In the promulgated test method, several important system components are not specified; instead, minimum performance specifications for these components are provided. The method is written in this manner to allow individual preference in choosing components, as well as to encourage development and use of improved components. Therefore, Addendum I which lists specific information regarding system components found to be acceptable has been added to the method to provide guidance for users.

Specifics of the most important procedural changes that have been included in the promulgated test method are as follows:

1. Section 1.1. Applicability. This section was rewritten to clarify the applicability of Method 25 in relation to several other organic measurement methods.

2. Section 2.2.2 Nonmethane Organic Analyzer. The reference to the analyzer is changed from "total gaseous nonmethane organic analyzer" to nonmethane organic analyzer (NMO). The description is clarified to indicate that the NMO analyzer is also used to quantify CO_2 from trap condensate recovery. Furthermore, a requirement that the NMO analyzer meet an initial performance test with specific criteria is added. Previously, only demonstration of "proper separation, oxidation, reduction and measurement" was required.

3. Section 4.1.3 Pretest Leak Check. The leak check procedure is simplified. Instead of evacuating the sample train,

the sample probe is plugged and then the sample value is opened; the sample tank vacuum gauge is monitored for a change in vacuum.

4. Section 4.1.4 Sample Train Operation. This section is clarified to indicate that any probe extension used must be positioned totally in the stack effluent; any portion of the sample probe outside the stack wall must be analyzed as part of the condensate trap.

5. Section 4.1.5 Post Test Leak Check. The leak check procedure is simplified (see "3" above).

6. Section 4.3.3 Recovery of Condensate Trap Sample. A requirement for mixing auxiliary oxygen with the carrier gas just prior to the catalyst is added. The procedures are clarified to indicate that the condensate trap is placed in a muffle furnace at 500°C (changed from 600°C) and that the probe must be heated.

7. Section 5.1 Initial Performance Check for Condensate Recovery and Conditioning Apparatus. A requirement is added for an initial performance test of the system which includes a carrier gas blank value determination (section 5.1.1), and oxidation catalyst efficiency check (section 5.1.2), and an overall system performance check via liquid injections (section 5.1.3). Previously, only a catalyst efficiency check was required.

8. Section 5.2 Initial NMO Analyzer Performance Test. The calibration criteria for the NMO analyzer are changed to include an initial performance test. This performance test requires an oxidation catalyst check (5.2.1), and an analyzer linearity check (5.2.2), determination of a NMO calibration response factor (5.2.2), determination of a CO_2 calibration response factor (5.2.3), determination of a NMO blank value (5.2.4) and a system check using several gaseous organic compounds (5.2.5).

9. Section 5.3 NMO Daily Calibration. This section requires that a daily calibration of the NMO analyzer be conducted. The calibration involves one CO_2 calibration gas and one propane calibration gas. Response factors are determined for both CO_2 and NMO, and a NMO blank value is measured. This calibration is conducted with the oxidation and reduction catalysts in full operation. The results obtained are compared to the reference values obtained during the initial performance test in order to determine if the analyzer performance is acceptable. This daily calibration procedure is greatly simplified compared to the procedure previously required which included bypassing the oxidation and reduction catalysts and using several different concentration levels of methane, carbon dioxide and propane calibration gases.

10. Section 6.2 Noncondensible Organics. The calculation for the NMO concentration of the contents of each collection tank is changed by rewriting the equation to include the subtraction of the daily NMO blank value from the measured concentration.

11. Section 6.3 Condensible Organics. The calculation for the NMO concentration of the contents of each condensate trap is changed by rewriting the equation to include the substraction of the daily condensate recovery and conditioning system carrier blank value from the measured CO_2 concentration.

Other Comments

1. One commenter noted that the drying time was different for ASTM D-2369 and ASTM D-2697, and that these procedures were not consistent with each other. Since ASTM D-2697 has been deleted, this comment is no longer applicable.

2. Three commenters recommended that the direct use of a flame ionization detection (FID) system or similar instrumentation systems be allowed instead of Method 25. The specific comments made and EPA's responses are as follows:

a. *Direct FID is simpler and more precise.* While the direct use of an FID system is simpler than Method 25, it will not give accurate results in many situations because the instrument response varies with different compounds. Therefore, the FID system cannot be considered an adequate reference method, but may be acceptable as an alternative compliance procedure on a case-by-case basis as allowed in 40 CFR 60.8(b).

b. *The ability to conduct on-site analyses and DOT restrictions associated with shipping organic samples from a source location to a laboratory make the FID preferable.* The ability to use the FID system to conduct on-site analyses is not in itself sufficient justification to allow the use of direct flame ionization detection. DOT regulations regarding shipment of hazardous materials do require that great care be taken in shipping the test samples. The DOT regulations impose strict packaging requirements on flammable liquids and compressed flammable gases. However, exemptions for the strict packaging requirements are permitted for most liquids if less than one quart is shipped (see 49 CFR 172.101). In addition, the gas sample tanks likely to be shipped from an on-site location to a laboratory for analyses do not meet the DOT definition of a compressed flammable gas because the sample tanks are not under high pressure and, therefore, should not pose a shipping problem (see 49 CFR 173.300).

Miscellaneous

This final rulemaking is issued under the authority of Sections 111, 114, and 301(a) of the Clean Air Act as amended (42 U.S.C. 7411, 7414, and 7601(a)).

Dated: September 25, 1980.

Douglas M. Costle,
Administrator.

Appendix A of 40 CFR Part 60 is amended by adding Reference Methods 24 and 25 as follows:

Appendix A—Reference Methods

* * * * *

Method 24—Determination of Volatile Matter Content, Water Content, Density, Volume Solids, and Weight Solids of Surface Coatings

1. Applicability and Principle

1.1 Applicability. This method applies to the determination of volatile matter content, water content, density, volume solids, and weight solids of paint, varnish, lacquer, or related surface coatings.

1.2 Principle. Standard methods are used to determine the volatile matter content, water content, density, volume solids, and weight solids of the paint, varnish, lacquer, or related surface coatings.

2. Applicable Standard Methods

Use the apparatus, reagents, and procedures specified in the standard methods below:

2.1 ASTM D 1475–60. Standard Method of Test for Density of Paint, Lacquer, and Related Products.

2.2 ASTM D 2369–81. Provisional Method of Test for Volatile Content of Paints.

2.3 ASTM D 3792–79. Standard Method of Test for Water in Water Reducible Paint by Direct Injection into a Gas Chromatograph.

2.4 ASTM Provisional Method of Test for Water in Paint or Related Coatings by the Karl Fischer Titration Method.

3. Procedure

3.1 Volatile Matter Content. Use the procedure in ASTM D 2369–81 to determine the volatile matter content (may include water) of the coating. Record the following information:

W_1 = Weight of dish and sample before heating, g.

W_2 = Weight of dish and sample after heating, g.

W_3 = Sample weight, g.

Run analyses in pairs (duplicate sets) for each coating until the criterion in section 4.3 is met. Calculate the weight fraction of the volatile matter (W_v) for each analysis as follows:

$$W_v = \frac{W_1 - W_2}{W_3} \qquad \text{Eq. 24-1}$$

Record the arithmetic average (W_v).

1. Applicability and Principle

1.1 Applicability. This method applies to the measurement of volatile organic compounds (VOC) as total gaseous nonmethane organics (TGNMO) as carbon in source emissions. Organic particulate matter will interfere with the analysis and therefore, in some cases, an in-stack particulate filter is required. This method is not the only method that applies to the measurement of TGNMO. Costs, logistics, and other practicalities of source testing may make other test methods more desirable for measuring VOC of certain effluent streams. Proper judgment is required in determining the most applicable VOC test method. For example, depending upon the molecular weight of the organics in the effluent stream, a totally automated semi-continuous nonmethane organic (NMO) analyzer interfaced directly to the source may yield accurate results. This approach has the advantage of providing emission data semi-continuously over an extended time period.

Direct measurement of an effluent with a flame ionization detector (FID) analyzer may be appropriate with prior characterization of the gas stream and knowledge that the detector responds predictably to the organic compounds in the stream. If present, methane will, of course, also be measured. In practice, the FID can be applied to the determination of the mass concentration of the total molecular structure of the organic emissions under the following limited conditions: (1) Where only one compound is known to exist; (2) when the organic compounds consist of only hydrogen and carbon; (3) where the relative percentage of the compounds is known or can be determined, and the FID response to the compounds is known; (4) where a consistent mixture of compounds exists before and after emission control and *only* the relative concentrations are to be assessed; or (5) where the FID can be calibrated against mass standards of the compounds emitted (solvent emissions, for example).

Another example of the use of a direct FID is as a screening method. If there is enough information available to provide a rough estimate of the analyzer accuracy, the FID analyzer can be used to determine the VOC content of an uncharacterized gas stream. With a sufficient buffer to account for possible inaccuracies, the direct FID can be a useful tool to obtain the desired results without costly exact determination.

In situations where a qualitative/quantitative analysis of an effluent stream is desired or required, a gas chromatographic FID system may apply. However, for sources emitting numerous organics, the time and expense of this approach will be formidable.

1.2 Principle. An emission sample is withdrawn from the stack at a constant rate through a chilled condensate trap by means of an evacuated sample tank. TGNMO are determined by combining the analytical results obtained from independent analyses of the condensate trap and sample tank fractions. After sampling is completed, the organic contents of the condensate trap are oxidized to carbon dioxide (CO_2) which is quantitatively collected in an evacuated vessel; then a portion of the CO_2 is reduced to methane (CH_4) and measured by a FID. The organic content of the sample fraction collected in the sampling tank is measured by injecting a portion into a gas chromatographic (GC) column to achieve separation of the nonmethane organics from carbon monoxide (CO), CO_2 and CH_4; the nonmethane organics (NMO) are oxidized to

CO_2, reduced to CH_4, and measured by a FID. In this manner, the variable response of the FID associated with different types of organics is eliminated.

2. Apparatus

The sampling system consists of a condensate trap, flow control system, and sample tank (Figure 1). The analytical system consists of two major sub-systems: an oxidation system for the recovery and conditioning of the condensate trap contents and a NMO analyzer. The NMO analyzer is a GC with backflush capability for NMO analysis and is equipped with an oxidation catalyst, reduction catalyst, and FID. (Figures 2 and 3 are schematics of a typical NMO analyzer.) The system for the recovery and conditioning of the organics captured in the condensate trap consists of a heat source, oxidation catalyst, nondispersive infrared (NDIR) analyzer and an intermediate collection vessel (Figure 4 is a schematic of a typical system.) TGNMO sampling equipment can be constructed from commercially available components and components fabricated in a machine shop. NMO analyzers are available commercially or can be constructed from available components by a qualified instrument laboratory.

2.1 Sampling. The following equipment is required:

2.1.1 Probe. 3.2-mm OD (⅛-in.) stainless steel tubing.

2.1.2 Condensate Trap. Constructed of 316 stainless steel; construction details of a suitable trap are shown in Figure 5.

2.1.3 Flow Shut-off Valve. Stainless steel control valve for starting and stopping sample flow.

2.1.4 Flow Control System. Any system capable of maintaining the sampling rate to within ±10 percent of the selected flow rate (50 to 100 cc/min range).

2.1.5 Vacuum Gauge. Gauge for monitoring the vacuum of the sample tank during leak checks and sampling.

2.1.6 Sample Tank. Stainless steel or aluminum tank with a volume of 4 to 8 liters, equipped with a stainless steel female quick connect for assembly to the sample train and analytical system.

2.1.7 Mercury Manometer. U-tube mercury manometer capable of measuring pressure to within 1 mm Hg in the 0–900 mm range.

2.1.8 Vacuum Pump. Capable of evacuating to an absolute pressure of 10 mm Hg.

2.2 Analysis. The following equipment is required:

2.2.1 Condensate Recovery and Conditioning Apparatus. An apparatus for recovering and catalytically oxidizing the condensate trap contents is required. Figure 4 is a schematic of such a system. The analyst must demonstrate prior to initial use that the analytical system is capable of proper oxidation and recovery, as specified in section 5.1. The condensate recovery and conditioning apparatus consists of the following major components.

2.2.1.1 Heat Source. A heat source sufficient to heat the condensate trap (including probe) to a temperature where the trap turns a "dull red" color. A system using both a propane torch and an electric muffle-type furnace is recommended.

2.2.1.2 Oxidation Catalyst. A catalyst system capable of meeting the catalyst efficiency criteria of this method (section 5.1.2). Addendum I of this method lists a catalyst system found to be acceptable.

2.2.1.3 Water Trap. Any leak-proof moisture trap capable of removing moisture from the gas stream.

2.2.1.4 NDIR Detector. A detector capable of indicating CO_2 concentration in the zero to 1 percent range. This detector is required for monitoring the progress of combustion of the organic compounds from the condensate trap.

2.2.1.5 Pressure Regulator. Stainless steel needle valve required to maintain the trap conditioning system at a near constant pressure.

2.2.1.6 Intermediate Collection Vessel. Stainless steel or aluminum collection vessel equipped with a female quick connect. Tanks with nominal volumes in the 1 to 4 liter range are recommended.

2.2.1.7 Mercury Manometer. U-tube mercury manometer capable of measuring pressure to within 1 mm Hg in the 0–900 mm range.

2.2.1.8 Gas Purifiers. Gas purification systems sufficient to maintain CO_2 and organic impurities in the carrier gas and auxiliary oxygen at a level of less than 10 ppm (may not be required depending on quality of cylinder gases used).

2.2.2 NMO Analyzer. Semi-continuous GC/FID analyzer capable of: (1) separating CO, CO_2, and CH_4 from nonmethane organic compounds, (2) reducing the CO_2 to CH_4 and quantifying as CH_4 and (3) oxidizing the nonmethane organic compounds to CO_2, reducing the CO_2 to CH_4 and quantifying as CH_4. The analyst must demonstrate prior to initial use that the analyzer is capable of proper separation, oxidation, reduction, and measurement (section 5.2). The analyzer consists of the following major components:

2.2.2.1 Oxidation Catalyst. A catalyst system capable of meeting the catalyst efficiency criteria of this method (section 5.2.1). Addendum I of this method lists a catalyst system found to be acceptable.

2.2.2.2 Reduction Catalyst. A catalyst system capable of meeting the catalyst efficiency criteria of this method (section 5.2.3). Addendum I of this method lists a catalyst system found to be acceptable.

2.2.2.3 Separation Column(s). Gas chromatographic column(s) capable of separating CO, CO_2, and CH_4 from NMO compounds as demonstrated according to the procedures established in this method (section 5.2.5). Addendum I of this method lists a column found to be acceptable.

2.2.2.4 Sample Injection System. A GC sample injection valve fitted with a sample loop properly sized to interface with the NMO analyzer (1 cc loop recommended).

2.2.2.5 FID. A FID meeting the following specifications is required.

2.2.2.5.1 Linearity. A linear response (± 5%) over the operating range as demonstrated by the procedures established in section 5.2.2.

2.2.2.5.2 Range. Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale for a full scale range of 10 to 50000 ppm CH_4.

2.2.2.6 Data Recording System. Analog strip chart recorder or digital intergration system compatible with the FID for permanently recording the analytical results.

2.2.3 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 1 mm Hg.

2.2.4 Thermometer. Capable of measuring the laboratory temperature within 1°C.

2.2.5 Vacuum Pump. Capable of evacuating to an absolute pressure of 10 mm Hg.

2.2.6 Syringe (2). 10 μl and 100 μl liquid injection syringes.

2.2.7 Liquid Sample Injection Unit. 316 SS U-tube fitted with a Teflon injection septum, see Figure 6.

3. Reagents

3.1 Sampling. Crushed dry ice is required during sampling.

3.2 Analysis.

3.2.1 NMO Analyzer. The following gases are needed:

3.2.1.1 Carrier Gas. Zero grade gas containing less than 1 ppm C. Addendum I of this method lists a carrier gas found to be acceptable.

3.2.1.2 Fuel Gas. Pure hydrogen, containing less than 1 ppm C.

3.2.1.3 Combustion Gas. Zero grade air or oxygen as required by the detector.

3.2.2 Condensate Recovery and Conditioning Apparatus.

3.2.2.1 Carrier Gas. Five percent O_2 in N_2, containing less than 1 ppm C.

3.2.2.2 Auxiliary Oxygen. Zero grade oxygen containing less than 1 ppm C.

3.2.2.3 Hexane. ACS grade, for liquid injection.

3.2.2.4 Toluene. ACS grade, for liquid injection.

3.3 Calibration. For all calibration gases, the manufacturer must recommend a maximum shelf life for each cylinder (i.e., the length of time the gas concentration is not expected to change more than ± 5 percent from its certified value). The date of gas cylinder preparation, certified organic concentration and recommended maximum shelf life must be affixed to each cylinder before shipment from the gas manufacturer to the buyer. The following calibration gases are required.

3.3.1 Oxidation Catalyst Efficiency Check Calibration Gas. Gas mixture standard with nominal concentration of 1 percent methane in air.

3.3.2 Flame Ionization Detector Linearity and Nonmethane Organic Calibration Gases (3). Gas mixture standards with nominal propane concentrations of 20 ppm, 200 ppm, and 3000 ppm, in air.

3.3.3 Carbon Dioxide Calibration Gases (3). Gas mixture standards with nominal CO_2 concentrations of 50 ppm, 500 ppm, and 1 percent, in air. Note: total NMO less than 1 ppm required for 1 percent mixture.

3.3.4 NMO Analyzer System Check Calibration Gases (4).

3.3.4.1 Propane Mixture. Gas mixture standard containing (nominal) 50 ppm CO, 50 ppm CH_4, 2 percent CO_2, and 20 ppm C_3H_8, prepared in air.

3.3.4.2 Hexane. Gas mixture standard containing (nominal) 50 ppm hexane in air.

3.3.4.3 Toluene. Gas mixture standard containing (nominal) 20 ppm toluene in air.

3.3.4.4 Methanol. Gas mixture standard containing (nominal) 100 ppm methanol in air.

4. Procedure

4.1 Sampling.

4.1.1 Sample Tank Evacuation and Leak Check. Either in the laboratory or in the field, evacuate the sample tank to 10 mm Hg absolute pressure or less (measured by a mercury U-tube manometer) then leak check the sample tank by isolating the tank from the vacuum pump and allowing the tank to sit for 10 minutes. The tank is acceptable if no change in tank vacuum is noted.

4.1.2 Sample Train Assembly. Just prior to assembly, measure the tank vaccuum using a mercury U-tube manometer. Record this vaccum (P_{ti}), the ambient temperature (T_{ti}), and the barometric pressure (P_{bi}) at this time. Assuring that the flow shut-off valve is in the closed position, assemble the sampling system as shown in Figure 1. Immerse the condensate trap body in dry ice to within 2.5 or 5 cm of the point where the inlet tube joins the trap body.

4.1.3 Pretest Leak Check. A pretest leak check is required. After the sampling train is assembled, record the tank vacuum as indicated by the vaccum gauge. Wait a minimum period of 10 minutes and recheck the indicated vacuum. If the vacuum has not changed, the portion of the sampling train behind the shut-off valve does not leak and is considered acceptable. To check the front portion of the sampling train, assure that the probe tip is tightly plugged and then open the sample train flow shut-off valve. Allow the sample train to sit for a minimum period of 10 minutes. The leak check is acceptable if no visible change in the tank vacuum gauge occurs. Record the pretest leak rate (cm/Hg per 10 minutes). At the completion of the leak check period, close the sample flow shut-off valve.

4.1.4 Sample Train Operation. Place the probe into the stack such that the probe is perpendicular to the direction of stack gas flow; locate the probe tip at a single preselected point. If a probe extension which will not be analyzed as part of the condensate trap is being used, assure that at least a 15 cm section of the probe which will be analyzed with the trap is in the stack effluent. For stacks having a negative static pressure, assure that the sample port is sufficiently sealed to prevent air in-leakage around the probe. Check the dry ice level and add ice if necessary. Record the clock time and sample tank gauge vacuum. To begin sampling, open the flow shut-off valve and adjust (if applicable) the control valve of the flow control system used in the sample train; maintain a constant flow rate (±10 percent) throughout the duration of the sampling period. Record the gauge vacuum and flowmeter setting (if applicable) at 5-minute intervals. Select a total sample time greater than or equal to the minimum sampling time specified in the applicable subpart of the regulation; end the sampling when this time period is reached or when a constant flow rate can no longer be maintained due to reduced sample tank vacuum. When the sampling is completed, close the flow shut-off valve and record the final sample time and guage vacuum readings. Note: If the sampling had to be stopped before obtaining the minimum sampling time (specified in the applicable subpart) because a constant flow rate could not be maintained, proceed as follows: After removing the probe from the stack, remove the used sample tank from the sampling train (without disconnecting other portions of the sampling train) and connect another sample tank to the sampling train. Prior to attaching the new tank to the sampling train, assure that the tank vacuum (measured on-site by the U-tube manometer) has been recorded on the data form and that the tank has been leak-checked (on-site). After the new tank is attached to the sample train, proceed with the sampling until the required minimum sampling time has been exceeded.

4.1.5 Post Test Leak Check. A leak check is mandatory at the conclusion of each test run. After sampling is completed, remove the probe from the stack and plug the probe tip. Open the sample train flow shut-off valve and monitor the sample tank vacuum gauge for a period of 10 minutes. The leak check is acceptable if no visible change in the tank vacuum gauge occurs. Record the post test leak rate (cm Hg per 10 minutes). If the sampling train does not pass the post leak check, invalidate the run or use a procedure acceptable to the Administrator to adjust the data.

4.2 Sample Recovery. After the post test leak check is completed, disconnect the condensate trap at the flow metering system and tightly seal both ends of the condensate trap. Keep the trap packed in dry ice until the samples are returned to the laboratory for analysis. Remove the flow metering system from the sample tank. Attach the U-tube manometer to the tank (keep length of connecting line to a minimum) and record the final tank vacuum (P_t); record the tank temperature (T_t) and barometric pressure at this time. Disconnect the manometer from the tank. Assure that the test run number is properly identified on the condensate trap and the sample tank(s).

4.3 Condensate Recovery and Conditioning. Prepare the condensate recovery and conditioning apparatus by setting the carrier gas flow rate and heating the catalyst to its operating temperature. Prior to initial use of the condensate recovery and conditioning apparatus, a system performance test must be conducted according to the procedures established in section 5.1 of this method. After successful completion of the initial performance test, the system is routinely used for sample conditioning according to the following procedures:

4.3.1 System Blank and Catalyst Efficiency Check. Prior to and immediately following the conditioning of each set of sample traps, or on a daily basis (whichever occurs first) conduct the carrier gas blank test and catalyst efficiency test as specified in sections 5.1.1 and 5.1.2 of this method. Record the carrier gas initial and final blank values, B_{ti} and B_{tf}, respectively. If the criteria of the tests cannot be met, make the necessary repairs to the system before proceeding.

4.3.2 Condensate Trap Carbon Dioxide Purge and Sample Tank Pressurization. The first step in analysis is to purge the condensate trap of any CO_2 which it may contain and to simultaneously pressurize the sample tank. This is accomplished as follows: Obtain both the sample tank and condensate trap from the test run to be analyzed. Set up the condensate recovery and conditioning apparatus so that the carrier flow bypasses the condensate trap hook-up terminals, bypasses the oxidation catalyst, and is vented to the atmosphere. Next, attach the condensate trap to the apparatus and pack the trap in dry ice. Assure that the valves isolating the collection vessel connection from the atmospheric vent and the vacuum pump are closed and then attach the sample tank to the system as if it were the intermediate collection vessel. Record the tank vacuum on the laboratory data form. Assure that the NDIR analyzer indicates a zero output level and then switch the carrier flow through the condensate trap; immediately switch the carrier flow from vent to collect. The condensate trap recovery and conditioning apparatus should now be set up as indicated in Figure 8. Monitor the NDIR; when CO_2 is no longer being passed through the system, switch the carrier flow so that it once again bypasses the condensate trap. Continue in this manner until the gas sample tank is pressurized to a nominal gauge pressure of 800 mm Hg. At this time, isolate the tank, vent the carrier flow, and record the sample tank pressure (P_{tf}), barometric pressure (P_{bf}), and ambient temperature (T_{tf}). Remove the sample tank from the system.

4.3.3 Recovery of Condensate Trap Sample. Oxidation and collection of the sample in the condensate trap is now ready to begin. From the step just completed in section 4.3.1.2 above, the system should be set up so that the carrier flow bypasses the condensate trap, bypasses the oxidation catalyst, and is vented to the atmosphere. Attach an evacuated intermediate collection vessel to the system and then switch the carrier so that it flows through the oxidation catalyst. Switch the carrier from vent to collect and open the valve to the collection vessel; remove the dry ice from the trap and then switch the carrier flow through the trap. The system should now be set up to operate as indicated in Figure 9. During oxidation of the condensate trap sample, monitor the NDIR to determine when all the sample has been removed and oxidized (indicated by return to baseline of NDIR analyzer output). Begin heating the condensate trap and probe with a propane torch. The trap should be heated to a temperature at which the trap glows a "dull red" (approximately 500°C). During the early part of the trap "burn out," adjust the carrier and auxiliary oxygen flow rates so that an excess of oxygen is being fed to the catalyst system. Gradually increase the flow of carrier gas through the trap. After the NDIR indicates that most of the organic matter has been purged, place the trap in a muffle furnance (500°C). Continue to heat the probe with a torch or some other procedure (e.g., electrical resistance heater). Continue this procedure for at least 5 minutes after the NDIR has returned to baseline. Remove the heat from the trap but continue the carrier flow until the intermediate collection vessel is pressurized to a gauge pressure of 800 mm

Hg (nominal). When the vessel is pressurized, vent the carrier; measure and record the final intermediate collection vessel pressure (P_f) as well as the barometric pressure (P_{bv}), ambient temperature (T_v), and collection vessel volume (V_v).

4.4 Analysis. Prior to putting the NMO analyzer into routine operation, an initial performance test must be conducted. Start the analyzer and perform all the necessary functions in order to put the analyzer in proper working order, then conduct the performance test according to the procedures established in section 5.2. Once the performance test has been successfully completed and the CO_2 and NMO calibration response factors determined, proceed with sample analysis as follows:

4.4.1 Daily operations and calibration checks. Prior to and immediately following the analysis of each set of samples or on a daily basis (whichever occurs first) conduct a calibration test according to the procedures established in section 5.3. If the criteria of the daily calibration test cannot be met, repeat the NMO analyzer performance test (section 5.2) before proceeding.

4.4.2 Analysis of Recovered Condensate Sample. Purge the sample loop with sample and then inject a preliminary sample in order to determine the appropriate FID attenuation. Inject triplicate samples from the intermediate collection vessel and record the values obtained for the condensible organics as CO_2 (C_{rm}).

4.4.3 Analysis of Sample Tank. Purge the sample loop with sample and inject a preliminary sample in order to determine the appropriate FID attenuation for monitoring the backflushed non-methane organics. Inject triplicate samples from the sample tank and record the values obtained for the nonmethane organics (C_{tm}).

5. Calibration and Operational Checks

Maintain a record of performance of each item.

5.1 Initial Performance Check of Condensate Recovery and Conditioning Apparatus.

5.1.1 Carrier Gas and Auxiliary Oxygen Blank. Set equal flow rates for both the carrier gas and auxiliary oxygen. With the trap switching valves in the bypass position and the catalyst in-line, fill an evacuated intermediate collection vessel with carrier gas. Analyze the collection vessel for CO_2; the carrier blank is acceptable if the CO_2 concentration is less than 10 ppm.

5.1.2 Catalyst Efficiency Check. Set up the condensate trap recovery system so that the carrier flow bypasses the trap inlet and is vented to the atmosphere at the system outlet. Assure that the valves isolating the collection system from the atmospheric vent and vacuum pump are closed and then attach an evacuated intermediate collection vessel to the system. Connect the methane standard gas cyclinder (section 3.3.1) to the system's condensate trap connector (probe end, Figure 4). Adjust the system valving so that the standard gas cylinder acts as the carrier gas and adjust the flow rate to the rate normally used during trap sample recovery. Switch off the auxiliary oxygen flow and then switch from vent to collect in order to begin collecting a sample. Continue collecting a sample in a normal manner until the intermediate vessel is filled to a nominal gauge pressure of 300 mm Hg. Remove the intermediate vessel from the system and vent the carrier flow to the atmosphere. Switch the valving to return the system to its normal carrier gas and normal operating conditions. Analyze the collection vessel for CO_2; the catalyst efficiency is acceptable if the CO_2 concentration is within ±5 percent of the expected value.

5.1.3 System Performance Check. Construct a liquid sample injection unit similar in design to the unit shown in Figure 6. Insert this unit into the condensate recovery and conditioning system in place of a condensate trap and set the carrier gas and auxiliary oxygen flow rates to normal operating levels. Attach an evacuated intermediate collection vessel to the system and switch from system vent to collect. With the carrier gas routed through the injection unit and the oxidation catalyst, inject a liquid sample (see. 5.1.3.1 to 5.1.3.4) via the injection septum. Heat the injection unit with a torch while monitoring the oxidation reaction on the NDIR. Continue the purge until the reaction is complete. Measure the final collection vessel pressure and then analyze the vessel to determine the CO_2 concentration. For each injection, calculate the percent recovery using the equation in section 6.6.

The performance test is acceptable if the average percent recovery is 100 ± 10 percent with a relative standard deviation (section 6.7) of less than 5 percent for each set of triplicate injections as follows:

5.1.3.1 100 µl hexane.
5.1.3.2 10 µl hexane.
5.1.3.3 100 µl toluene.
5.1.3.4 10 µl toluene.

5.2 Initial NMO Analyzer Performance Test.

5.2.1 Oxidation Catalyst Efficiency Check. Turn off or bypass the NMO analyzer reduction catalyst. Make triplicate injections of the high level methane standard (section 3.3.1). The oxidation catalyst operation is acceptable if no FID response is noted.

5.2.2 Analyzer Linearity Check and NMO Calibration. Operating both the oxidation and reduction catalysts, conduct a linearity check of the analyzer using the propane standards specified in section 3.3. make triplicate injections of each calibration gas and then calculate the average response factor (area/ppm C) for each gas, as well as the overall mean of the response factor values. The instrument linearity is acceptable if the average response factor of each calibration gas is within ±5 percent of the overall mean value and if the relative standard deviation (section 6.7) for each set of triplicate injections is less than ±5 percent. Record the overall mean of the propane response factor values as the NMO calibration response factor (RF_{NMO}).

5.2.3 Reduction Catalyst Efficiency Check and CO_2 Calibration. An exact determination of the reduction catalyst efficiency is not required. Instead, proper catalyst operation is indirectly checked and continuously monitored by establishing a CO_2 response factor and comparing it to the NMO response factor. Operating both the oxidation and reduction catalysts make triplicate injections of each of the CO_2 calibration gases (section 3.3.3). Calculate the average response factor (area/ppm) for each calibration gas, as well as the overall mean of the response factor values. The reduction catalyst operation is acceptable if the average response factor of each calibration gas is within ±5 percent of the overall mean value and if the relative standard deviation (section 6.7) for each set of triplicate injections is less than ±5 percent. Additionally, the CO_2 overall mean response factor must be within ±10 percent of the NMO calibration response factor (RF_{NMO}) calculated in section 5.2.2. Record the overall mean of the response factor values as the CO_2 calibration response factor (RF_{CO_2}).

5.2.4 NMO System Blank. For the high level CO_2 calibration gas (section 3.3.3) record the NMO value measured during the CO_2 calibration conducted in section 5.2.3. This value is the NMO blank value for the analyzer (B_s) and should be less than 10 ppm.

5.2.5 System Performance Check. Check the column separation and overall performance of the analyzer by making triplicate injections of the calibration gases listed in section 3.3.4. The analyzer performance is acceptable if the measured NMO value for each gas (average of triplicate injections) is within ±12 percent of the expected value.

5.3 NMO Analyzer Daily Calibration.

5.3.1 NMO Blank and CO_2. Inject triplicate samples of the high level CO_2 calibration gas (section 3.3.3) and calculate the average response factor. The system operation is adequate if the calculated response factor is within ±10 percent of the RF_{CO_2} calculated during the initial performance test (section 5.2.2). Use the daily response factor (DRF_{CO_2}) for analyzer calibration and the calculation of measured CO_2 concentrations in the collection vessel samples. In addition, record the NMO blank value (B_s); this value should be less than 10 ppm.

5.3.2 NMO Calibration. Inject triplicate samples of the mixed propane calibration cylinder (section 3.3.4.1) and calculate the average NMO response factor. The system operation is adequate if the calculated response factor is within ±10 percent of the RF_{NMO} calculated during the initial performance test (section 5.2.1). Use the daily response factor (DRF_{NMO}) for analyzer calibration and calculation of NMO concentrations in the sample tanks.

5.4 Sample Tank. The volume of the gas sampling tanks used must be determined. Prior to putting each tank in service, determine the tank volume by weighing the tanks empty and then filled with deionized distilled water; weigh to the nearest 5 gm and record the results. Alternatively, measure the volume of water used to fill the tanks to the nearest 5 ml.

5.5 Intermediate Collection Vessel. The volume of the intermediate collection vessels used to collect CO_2 during the analysis of the condensate traps must be determined. Prior to putting each vessel into service, determine the volume by weighing the vessel empty and then filled with deionized distilled water; weigh to the nearest 5 gm and record the results. Alternatively, measure the volume of water used to fill the tanks to the nearest 5 ml.

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6. Calculations

Note: All equations are written using absolute pressure; absolute pressures are determined by adding the measured barometric pressure to the measured gauge pressure.

6.1 Sample Volume. For each test run, calculate the gas volume sampled:

$$V_s = 0.386\ V \left(\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}} \right)$$

6.2 Noncondensible Organics. For each sample tank, determine the concentration of nonmethane organics (ppm C):

$$C_t = \left[\frac{\frac{P_{tf}}{T_{tf}}}{\frac{P_t}{T_t} - \frac{P_{ti}}{T_{ti}}} \right] \left[\frac{1}{r} \sum_{j=1}^{r} C_{tm_j} - B_a \right]$$

6.3 Condensible Organics. For each condensate trap determine the concentration of organics (ppm C):

$$C_c = 0.386\ \frac{V_v}{V_s} \frac{P_f}{T_f} \left[\frac{1}{q} \sum_{k=1}^{q} C_{cm_k} - B_t \right]$$

6.4 Total Gaseous Nonmethane Organics (TGNMO). To determine the TGNMO concentration for each test run, use the following equation:

$$C = C_t + C_c$$

6.5 Total Gaseous Nonmethane Organics (TGNMO) Mass Concentration. To determine the TGNMO mass concentration as carbon for each test run, use the following equation:

$$M_c = 0.498\ C$$

6.6 Percent Recovery. To calculate the percent recovery for the liquid injections to the condensate recovery and conditioning system use the following equation:

$$\text{percent recovery} = 1.6\ \frac{M}{L} \frac{V_v}{\rho} \frac{P_f}{T_f} \frac{C_{cm}}{N}$$

6.7 Relative Standard Deviation.

$$RSD = \frac{100}{\bar{X}} \sqrt{\frac{\Sigma (x_i - \bar{x})^2}{n - 1}}$$

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Where:

B_a = Measured NMO blank value for NMO analyzer, ppm C.
B_t = Measured CO_2 blank value for condensate recovery and conditioning system carrier gas, ppm CO_8.
C = total gaseous nonmethane organic (TGNMO) concentration of the effluent, ppm C equivalent.
C_c = Calculated condensible organic (condensate trap) concentration of the effluent, ppm C equivalent.
C_{cm} = Measured concentration (NMO analyzer) for the condensate trap (intermediate collection vessel), ppm CO_2.
C_t = Calculated noncondensible organic concentration (sample tank) of the effluent, ppm C equivalent.
C_{tm} = Measured concentration (NMO analyzer) for the sample tank, ppm NMO.
L = Volume of liquid injected, microliters.
M = Molecular weight of the liquid injected, g/g-mole.
M_c = total gaseous non-methane organic (TGNMO) mass concentration of the effluent, mg C/dscm.
N = Carbon number of the liquid compound injected (N=7 for toluene, N=8 for hexane).
P_f = Final pressure of the intermediate collection vessel, mm Hg absolute.
P_{ti} = Gas sample tank pressure prior to sampling, mm Hg absolute.
P_t = Gas sample tank pressure after sampling, but prior to pressurizing, mm Hg absolute.
P_{tf} = Final gas sample tank pressure after pressurizing, mm Hg absolute.
T_f = Final temperature of intermediate collection vessel, °K.
T_{ti} = Sample tank temperature prior to sampling, °K.
T_t = Sample tank temperature at completion of sampling, °K.
T_{tf} = Sample tank temperature after pressurizing °K.
V = Sample tank volume, cm.
V_v = Intermediate collection vessel volume, cm.
V_s = Gas volume sampled, dscm.
n = Number of data points.
q = Total number of analyzer injections of intermediate collection vessel during analysis (where k = injection number, 1 . . . q).
r = Total number of analyzer injections of sample tank during analysis (where j = injection number, 1 . . . r).
x_i = Individual measurements.
X = Mean value.
p = Density of liquid injected, g/cc.

7. Bibliography

7.1 Salo, Albert E., Samuel Witz, and Robert D. MacPhee. Determination of Solvent Vapor Concentrations by Total Combustion Analysis: A Comparison of Infrared with Flame Ionization Detectors. Paper No. 75–33.2 (Presented at the 68th Annual Meeting of the Air Pollution Control Association. Boston, MA. June 15–20, 1975.) 14 p.

7.2 Salo, Albert E., William L. Oaks, and Robert D. MacPhee. Measuring the Organic Carbon Content of Source Emissions for Air Pollution Control. Paper No. 74–190. (Presented at the 67th Annual Meeting of the Air Pollution Control Association. Denver, CO. June 9–13, 1974.) 25 p.

Method 25

Addendum I. System Components

In test Method 25 several important system components are not specified; instead minimum performance specifications are provided. The method is written in this manner to permit individual preference in choosing components, as well as to encourage development and use of improved components. This addendum is added to the method in order to provide users with some specific information regarding components which have been found satisfactory for use with the method. This listing is given only for the purpose of providing information and does not constitute an endorsement of any product by the Environmental Protection Agency. This list is not meant to imply that other components not listed are not acceptable.

1. Condensate Recovery and Conditioning System Oxidation Catalyst. ⅜" OD×14" Inconel tubing packed with 8 inches of hopcalite* oxidizing catalyst and operated at 800°C in a tube furnace. Note: At this temperature, this catalyst must be purged with carrier gas at all times to prevent catalyst damage.

2. NMO Analyzer Oxidation Catalyst. ¼" OD×14" inconel tubing packed with 6 inches of hopcalite oxidizing catalyst and operated at 800°C in a tube furnace. (See note above.)

3. NMO Analyzer Reduction Catalyst. Reduction Catalyst Module; Byron Instruments, Raleigh, N.C.

4. Gas Chromatographic Separation Column. ⅛ inch OD stainless steel packed with 3 feet of 10 percent methyl silicone, Sp 2100 (or equivalent) on Supelcoport (or equivalent), 80/100 mesh, followed by 1.5 feet Porapak Q (or equivalent) 60/80 mesh. The inlet side is to the silicone. Condition the column for 24 hours at 200°C with 20 cc/min N_2 purge.

During analysis for the nonmethane organics the separation column is operated as follows: First, operate the column at −78°C (dry ice bath) to elute CO and CH_4. After the CH_4 peak operate the column at 0°C to elute CO_2. When the CO_2 is completely eluted, switch the carrier flow to backflush the column and simultaneously raise the column temperature to 100°C in order to elute all nonmethane organics (exact timings for column operation are determined from the calibration standard).

Note.—The dry ice operating condition may be deleted if separation of CO and CH_4 is unimportant.

Note.—Ethane and ethylene may or may not be measured using this column; whether or not ethane and ethylene are quantified will depend on the CO_2 concentration in the gas sample. When high levels of CO_2 are present, ethane and ethylene will elute under the tail of the CO_2 peak.

5. Carrier Gas. Zero grade nitrogen or helium or zero air.

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*MSA registered trademark.

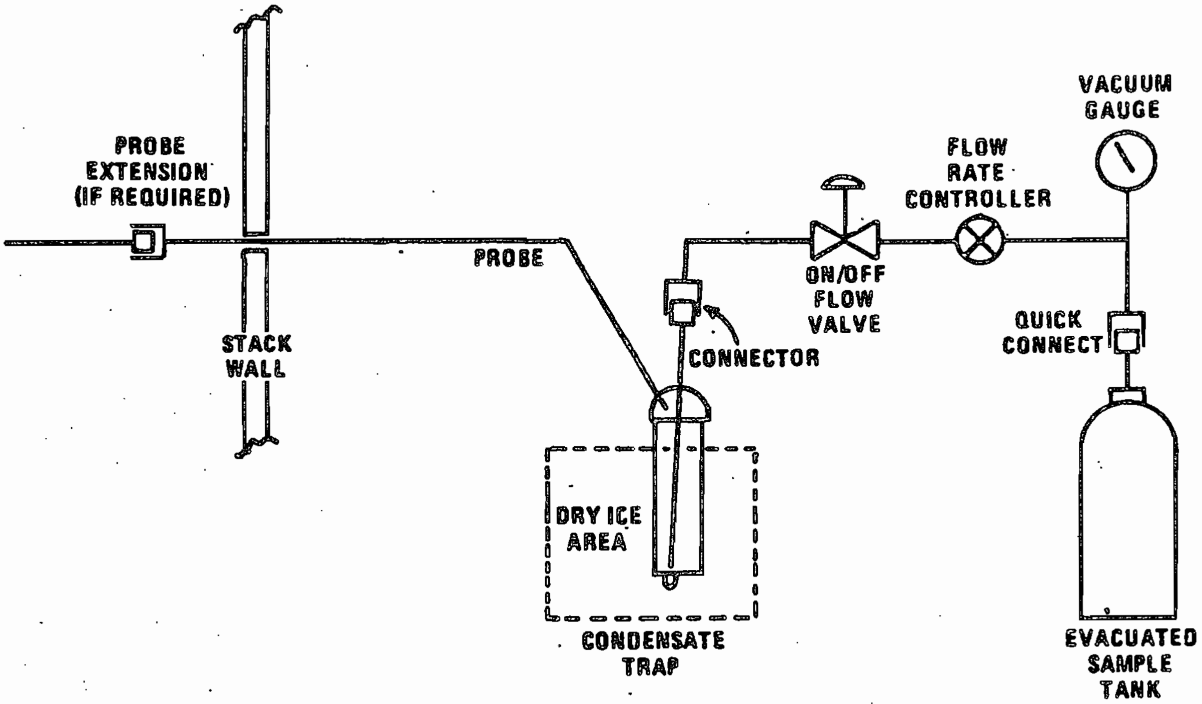


Figure 1. Sampling apparatus.

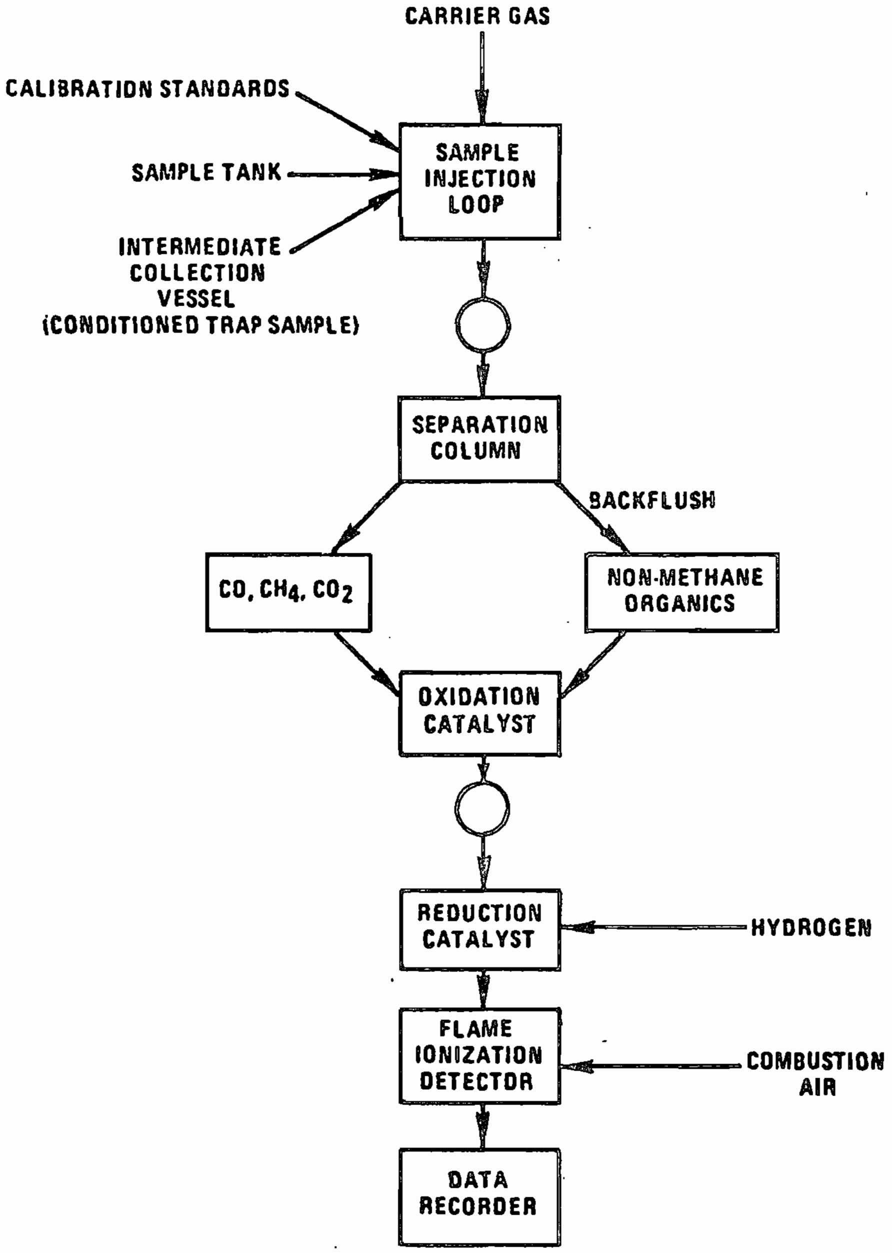


Figure 2. Simplified schematic of non-methane organic (NMO) analyzer.

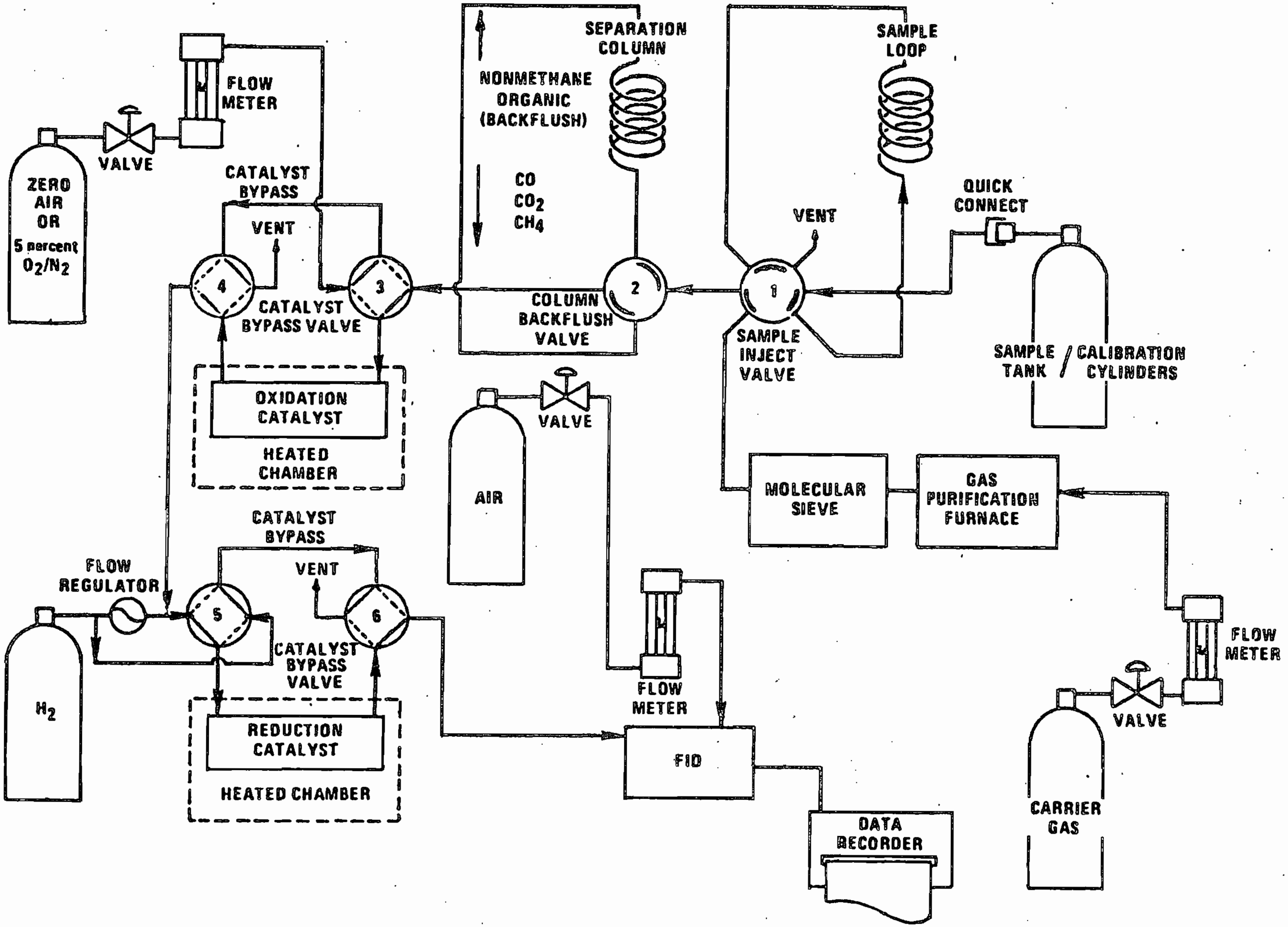


Figure 3. Nonmethane organic (NMO) analyzer.

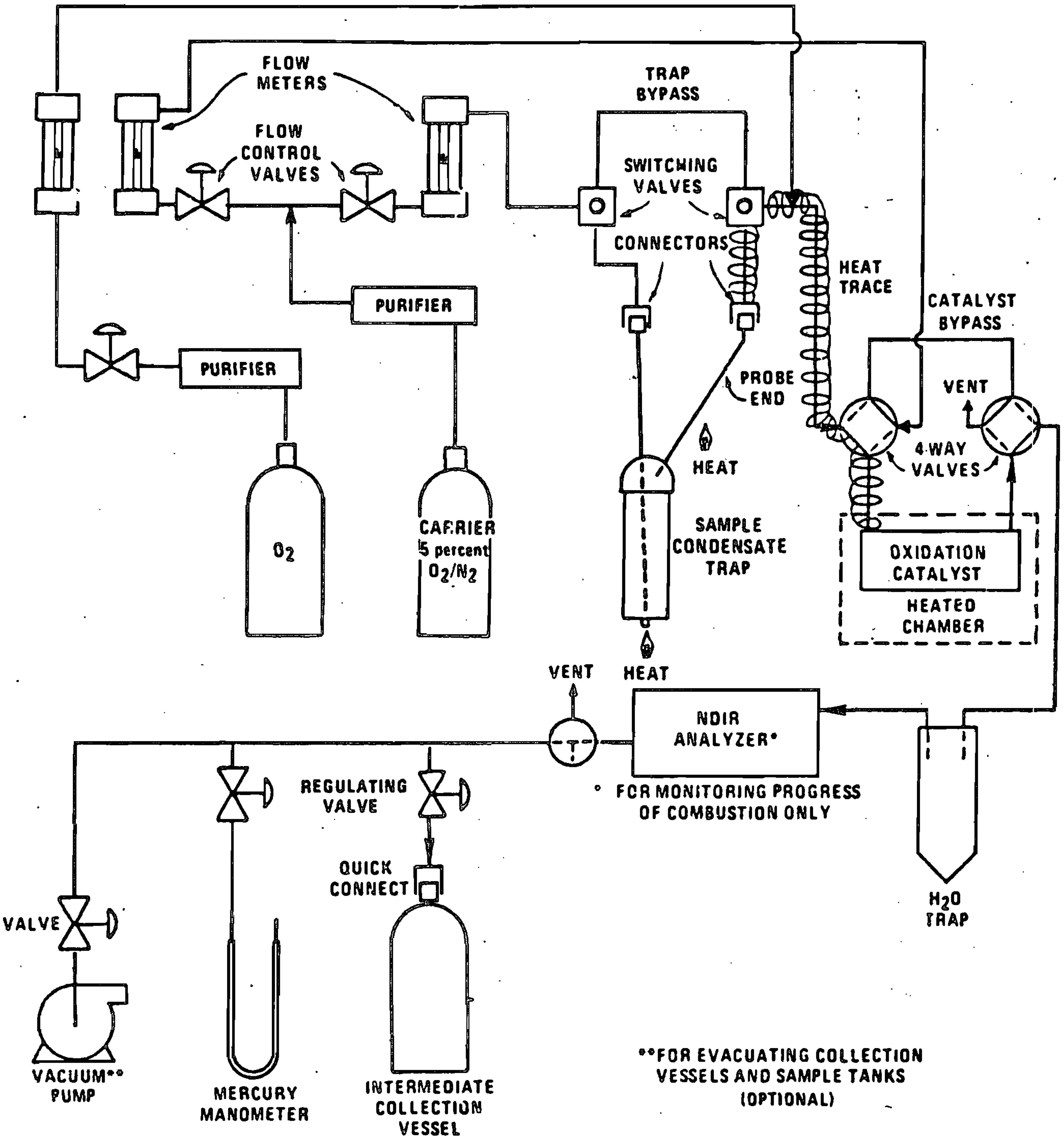
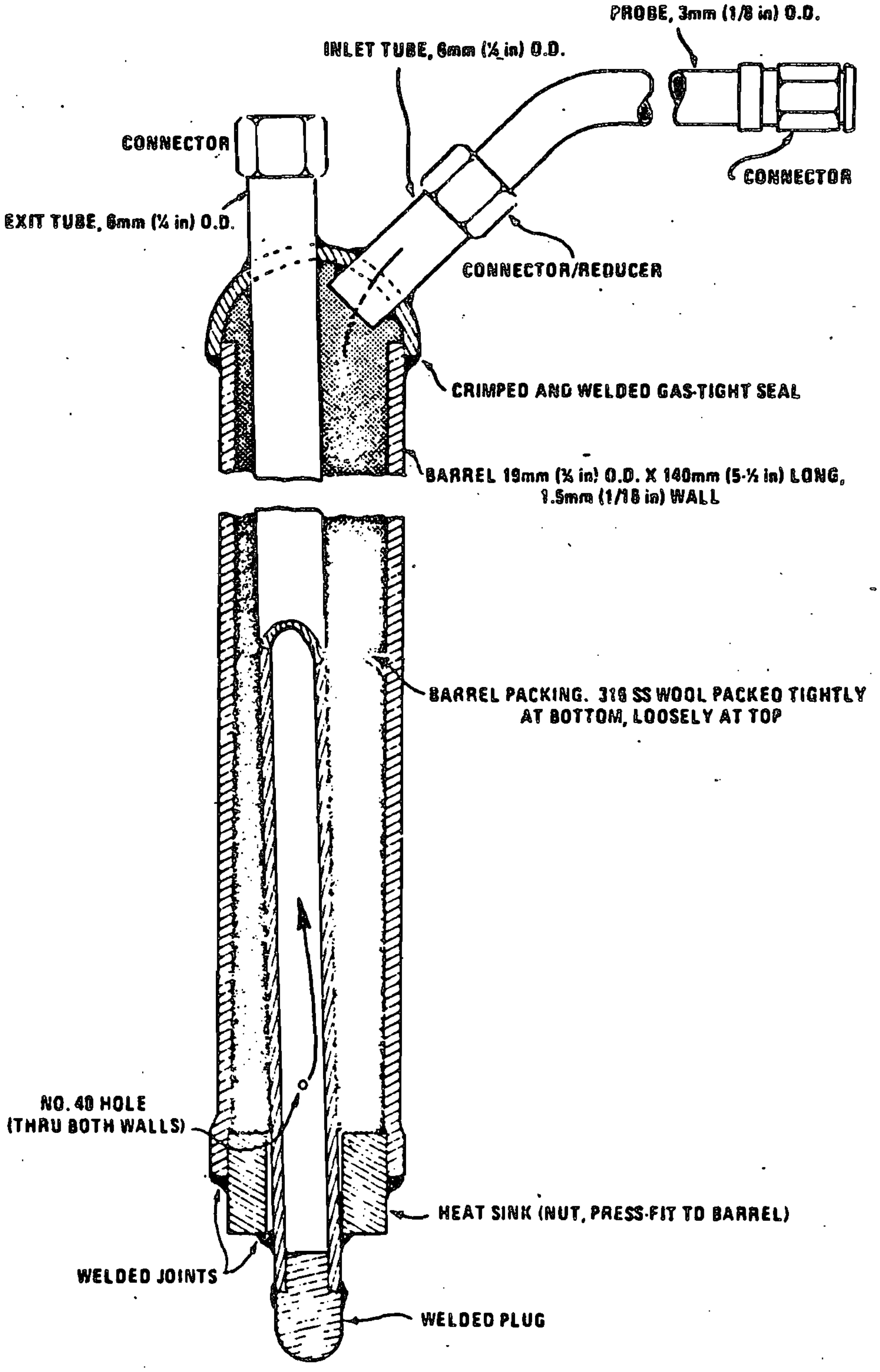


Figure 4. Condensate recovery and conditioning apparatus.



MATERIAL: TYPE 316 STAINLESS STEEL

Figure 5. Condensate trap[2].

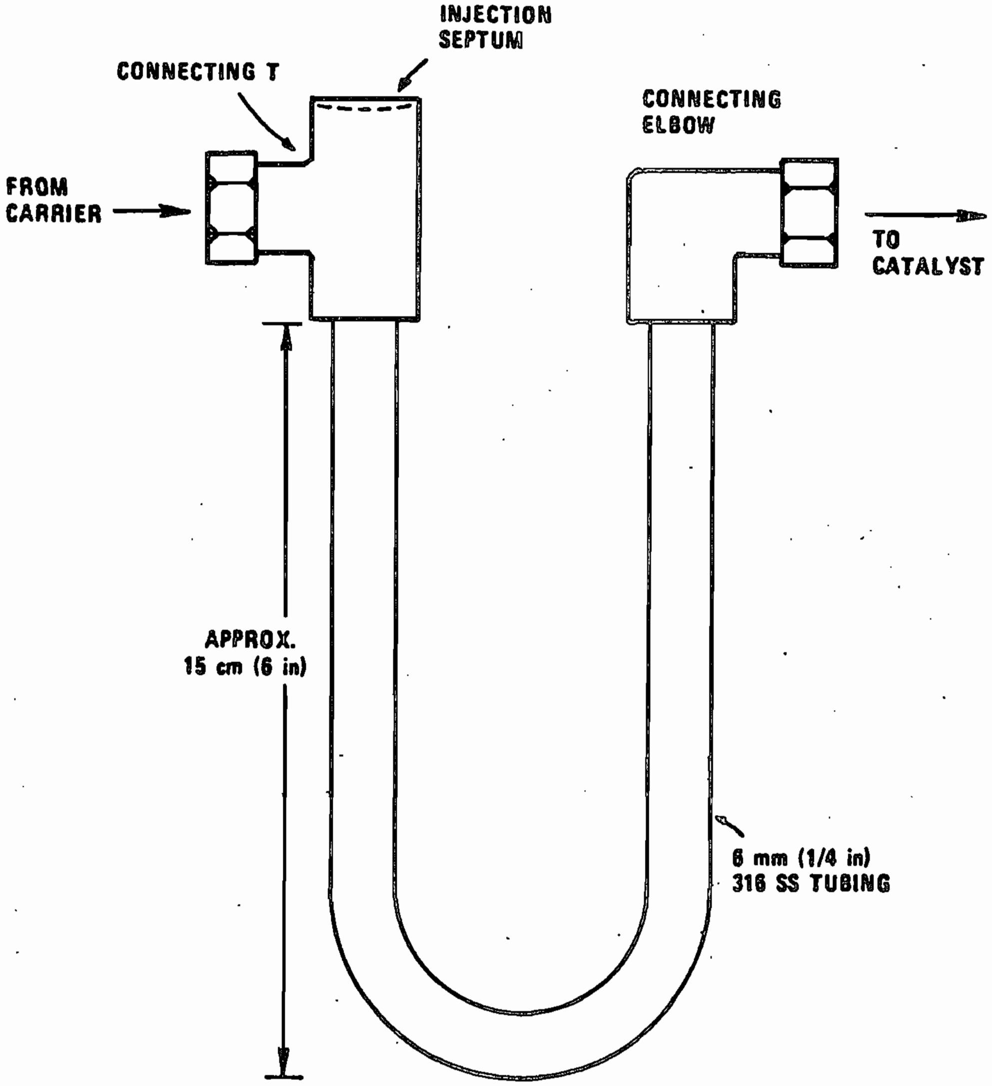


Figure 6. Liquid sample injection unit.

VOLATILE ORGANIC CARBON

FACILITY__________ SAMPLE LOCATION__________
LOCATION__________ OPERATOR__________
DATE__________ RUN NUMBER__________
TANK NUMBER__________ TRAP NUMBER__________ SAMPLE ID NUMBER__________

	TANK VACUUM, mm Hg	cm Hg	BAROMETRIC PRESSURE, mm Hg	AMBIENT TEMPERATURE, °C
PRETEST (MANOMETER)		(GAUGE)		
POST TEST (MANOMETER)		(GAUGE)		

LEAK RATE cm Hg / 10 min

PRETEST__________
POST TEST__________

TIME CLOCK/SAMPLE	GAUGE VACUUM, cm Hg	FLOWMETER SETTING	COMMENTS

Figure 7. Example Field Data Form.

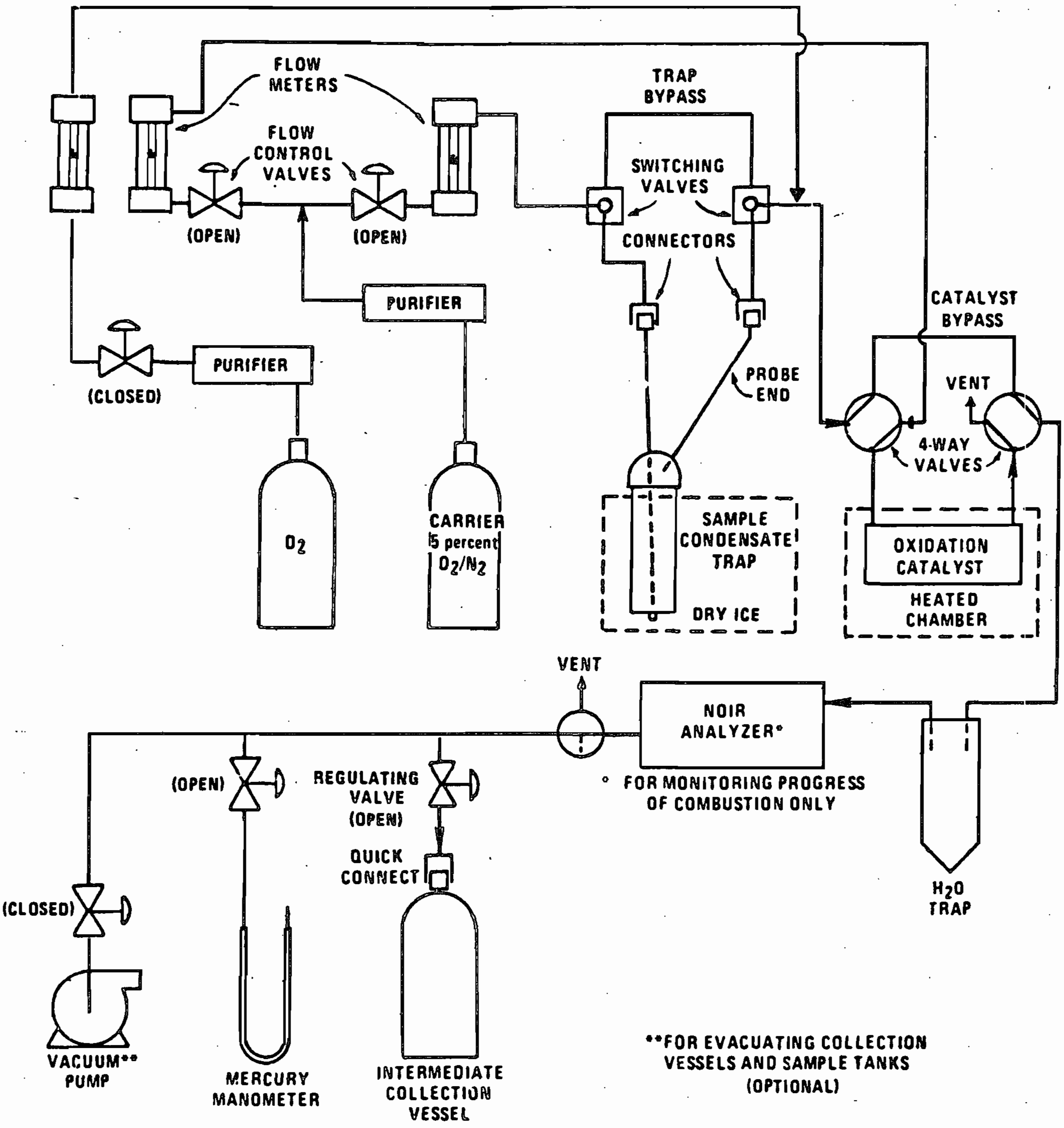


Figure 8. Condensate recovery and conditioning apparatus, carbon dioxide purge.

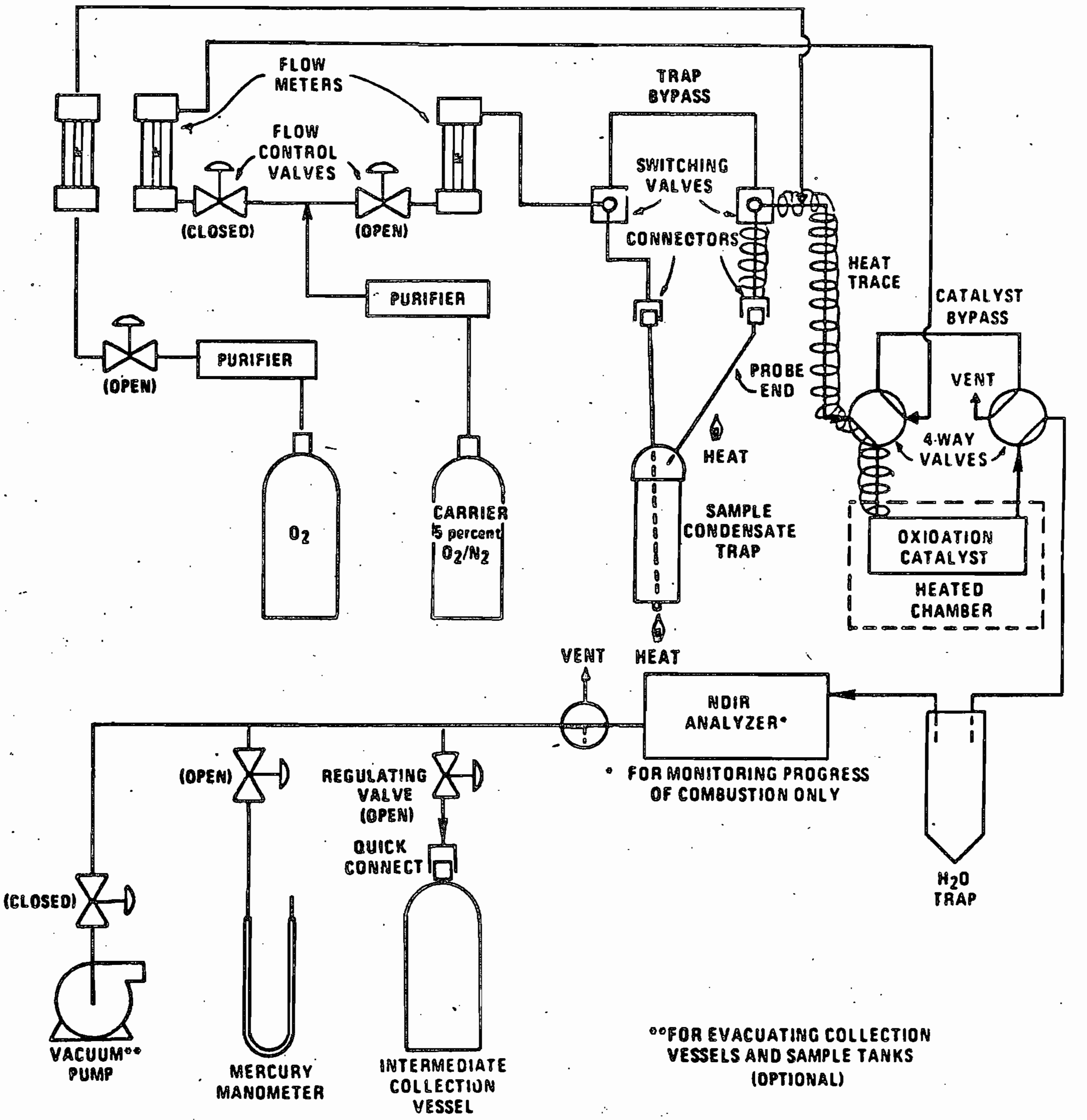


Figure 9. Condensate recovery and conditioning apparatus, collection of trap organics.

[FR Doc. 80-30716 Filed 10-2-80; 8:45 am]
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APPENDIX B

CALCULATION OF INTERFERENCE

TABLE B-1 CALCULATION OF CO_2 INTERFERENCE

KILN A

Sample #	TGNMO ppm	CO_2 %	H_2O collected ml	Sample volume l	CO_2 interference ppm	corrected TGNMO ppm	CH_4 ppm	CO ppm	C_2H_6 ppm
3181	163	16.9	5.3	13.71	56	107	0	6	0
2	183	16.7	6.5	13.86	66	117	0	6	1
3	311	17.0	1.1	3.23	67	244	0	49	2
4	496	19.2	0.9	3.08	7	489	0	45	0
3261	264	19.5	7.2	12.55	93	171	0	10	2
2	352	18.2	8.4	13.17	95	257	0	8	1
3	163	21.3	8.0	14.20	99	64	0	17	0
4	224	20.1	10.4	13.69	124	100	0	17	0
4011	245	22.0	5.9	12.12	90	155	0	56	0
2	184	20.7	7.3	14.61	86	198	2	52	0
3	102	19.2	5.4	14.21	62	40	0	10	0
4	122	22.1	2.7	13.92	39	84	0	15	0
4232	52	20.5	4.7	15.18	55	-2	0	10	0
3	273	20.0	9.2	11.18	135	139	2	16	0
4	120	20.0	2.9	12.79	41	78	0	7	0
4301	96	21.8	8.0	14.11	102	-6	28	2800	0
2	97	22.5	6.4	13.46	89	8	25	2500	0
3	152	19.2	7.2	13.28	89	63	34	2400	0
4	148	20.0	6.1	12.02	85	63	25	2100	0
7091	110	11.5	1.0	5.0	32	79	0	1	0
2	211	11.5	1.5	4.3	47	164	6	20	0
3	230	9.0	7.0	12.0	45	185	1	14	0
4	183	9.0	8.0	14.4	42	141	14	20	0
6121	69	18.4	4.5	13.5	53	17	0	10	0
2	143	18.4	4.3	14.6	47	96	0	9	0
3	170	16.7	5.7	14.1	57	113	0	12	0
4	133	17.0	5.9	13.0	65	68	0	11	0
7233	169	18.0	5.6	12.8	70	99	0	7200	0
7234	141	17.9	5.8	13.5	65	76	0	7100	0
7231	324	17.7	9.8	11.04	155	169	-	--	--
2	73	17.1	7.5	13.30	96	-23	-	--	--

TABLE B-1 (Cont'd)

KILN B

Sample #	TGNMO ppm	CO_2 %	H_2O collected ml	Sample volume l	CO_2 interference ppm	corrected TGNMO ppm	CH_4 ppm	CO ppm	C_2H_6 ppm
3201	649	16.5	4.3	9.67	64	585	2	45	0
2	624	16.4	4.6	9.70	61	562	1	41	0
3251	622	17.6	7.9	13.23	87	535	0	46	2
2	241	15.7	4.7	13.32	48	193	8	55	0
3	441	17.2	4.6	11.54	59	381	4	49	0
4	371	16.1	5.7	11.10	70	300	2	51	0
4291	236	14.1	3.3	11.12	38	197	0	42	0
2	209	12.3	4.8	14.43	36	173	2	34	0
3	237	13.6	4.0	10.67	46	191	1	35	0
4	327	16.4	3.7	9.81	68	259	2	41	0
5061	363	15.8	6.5	12.44	69	293	1	40	0
2	487	15.0	6.6	14.46	58	430	1	41	0
3	290	16.2	6.4	12.32	71	219	0	46	0
4	365	15.7	5.6	13.56	55	310	1	42	0
5201	296	10.6	5.1	12.36	39	257	1	46	0
2	275	10.4	5.1	12.10	39	236	1	58	0
3	306	11.2	5.9	12.50	46	261	1	42	0
4	306	10.9	6.2	14.20	41	266	0	42	0
6101	343	17.7	5.9	11.10	79	264	4	81	0
2	458	17.8	5.7	11.20	77	381	2	7	0
3	432	18.8	5.2	12.50	66	366	1	73	0
4	619	18.4	5.9	12.80	71	548	4	70	0
7151	163	19.0	4.6	11.30	66	97	2	156	0
2	448	18.3	4.5	11.86	60	388	1	163	0
3	495	18.6	6.2	12.70	76	419	2	157	0
4	200	18.5	5.7	11.80	75	125	3	154	0
7221	370	--	3.3	11.0	--	--	--	---	--
2	--	--	--	--	--	--	0	---	--
4	730	12.0	7.2	13.5	65	665	--	---	--
8201	--	20.6	5.7	12.6	--	---	--	---	--
2	--	22.0	6.2	13.3	--	---	--	---	--
3	217	23.2	5.8	13.1	103	114	0	1000	0
4	639	23.2	5.9	13.2	104	535	0	1000	0

KILN C

Sample #	TGNMO ppm	CO_2 %	H_2O collected ml	Sample volume l	CO_2 interference ppm	corrected TGNMO ppm	CH_4 ppm	CO ppm	C_2H_6 ppm
5081	61	10.0	3.3	14.3	26	35	0	11	0
2	57	9.6	2.9	13.7	24	33	0	12	0
3	64	9.0	1.4	11.7	16	48	0	15	0
4	50	8.9	2.0	10.5	22	28	0	11	0
5221	59	16.2	4.7	13.5	58	1	0	10	0
2	88	15.8	4.5	13.3	56	32	0	12	0
3	194	--	5.2	15.2	--	--	0	11	0
7171	67	13.7	2.7	13.3	31	36	0	5	0
2	75	13.8	3.0	13.8	33	42	0	7	0
3	95	14.2	2.6	12.0	35	61	0	5	0
4	74	14.6	2.8	14.0	32	42	0	4	0
7241	25	12.7	2.8	12.1	33	-8	0	15	0
2	59	13.0	2.8	14.4	28	31	0	11	0
3	16	14.5	3.2	12.3	41	-25	0	17	0
4	102	15.0	3.2	12.6	41	61	0	17	0

Reference 7

T/S

ncasi technical bulletin

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

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

TECHNICAL BULLETIN NO. 416

JANUARY 1984

NATIONAL COUNCIL OF THE PAPER INDUSTRY FOR AIR AND STREAM IMPROVEMENT, INC.
260 MADISON AVE. NEW YORK, N.Y. 10016 (212) 532-9000

Russell O. Blosser
Technical Director
(212) 532 9001

January 3, 1984

TECHNICAL BULLETIN NO. 416

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

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

ROB:gs
Attach.

TABLE OF CONTENTS

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

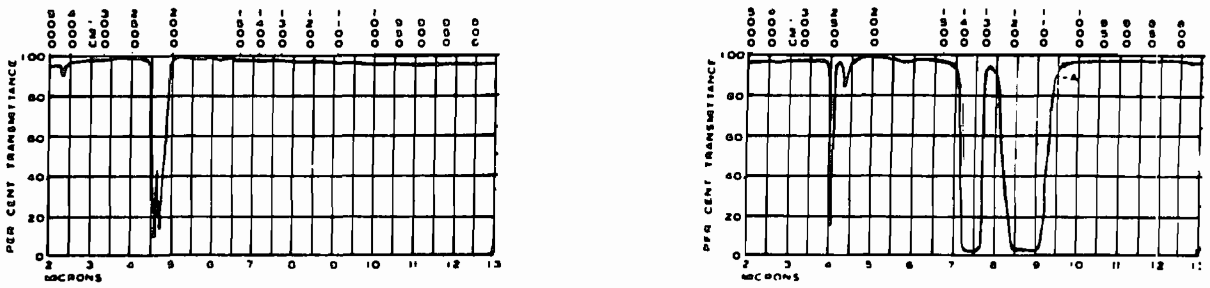
A. Principle of Operation

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)

SO$_2$ (Sulphur Dioxide)



714(mmHg)

CO$_2$ (Carbon Dioxide)

NO (Nitrogen Oxide)

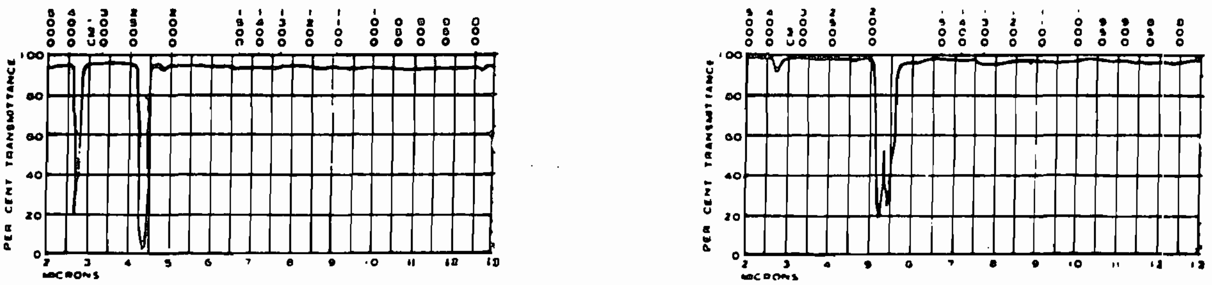


FIGURE 1

INFRARED 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.

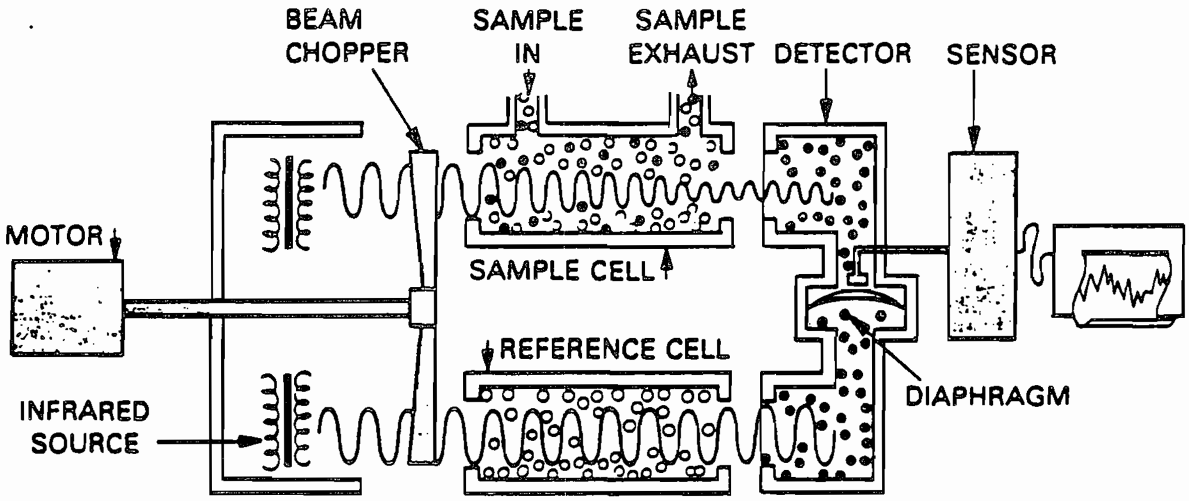


FIGURE 2

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.

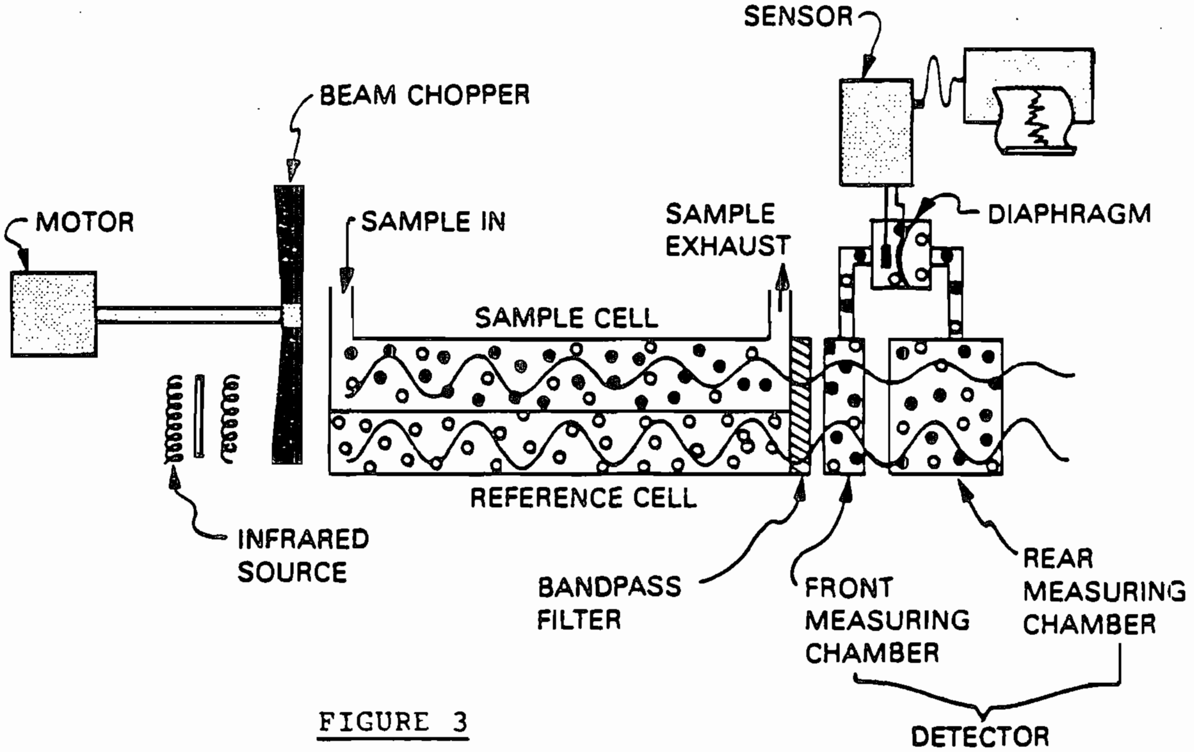


FIGURE 3

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.

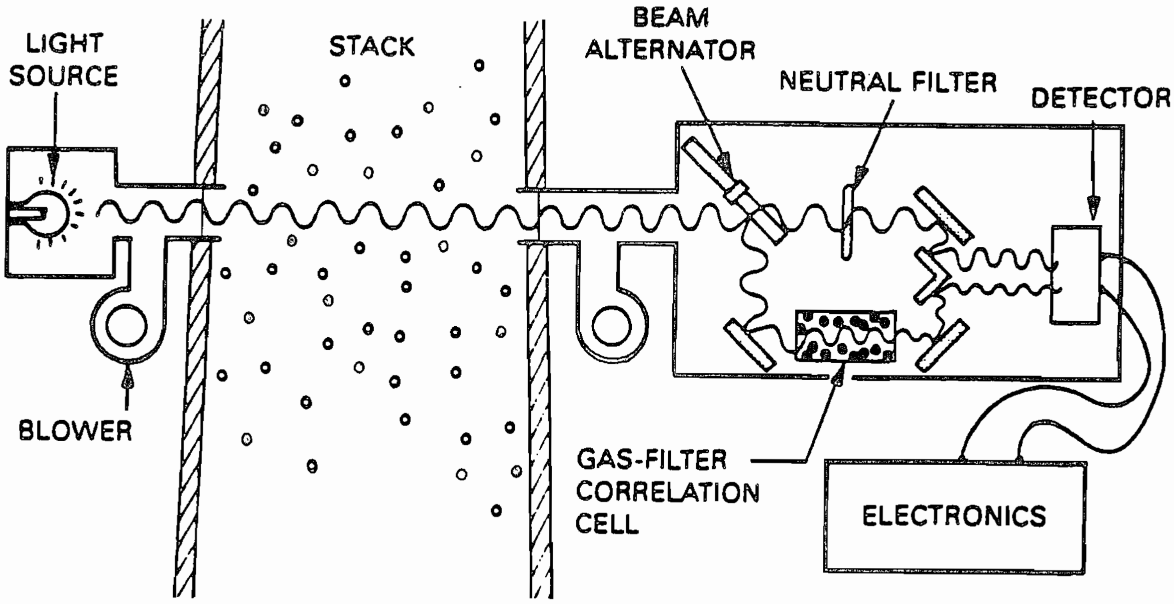


FIGURE 4

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.

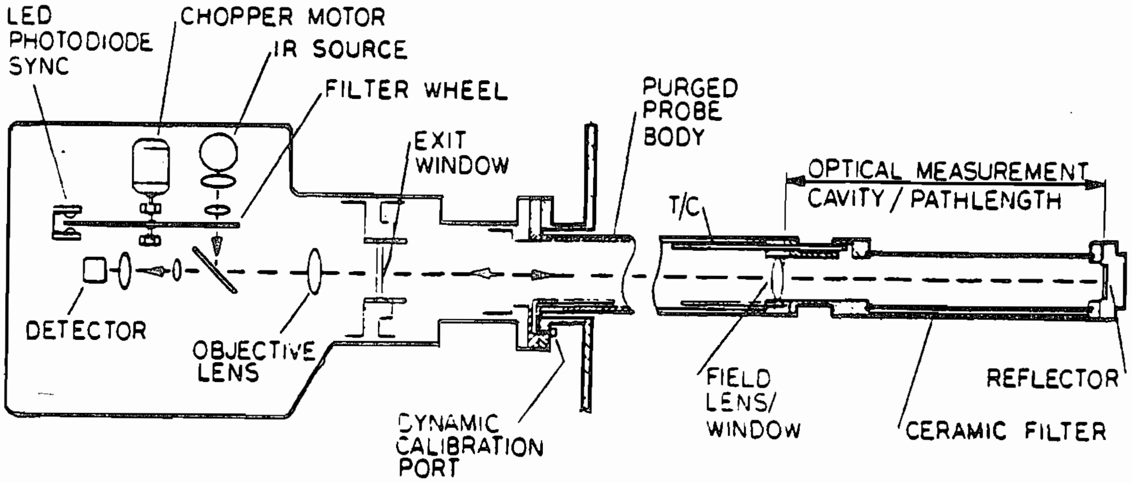


FIGURE 5

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

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) Boiler C - 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.

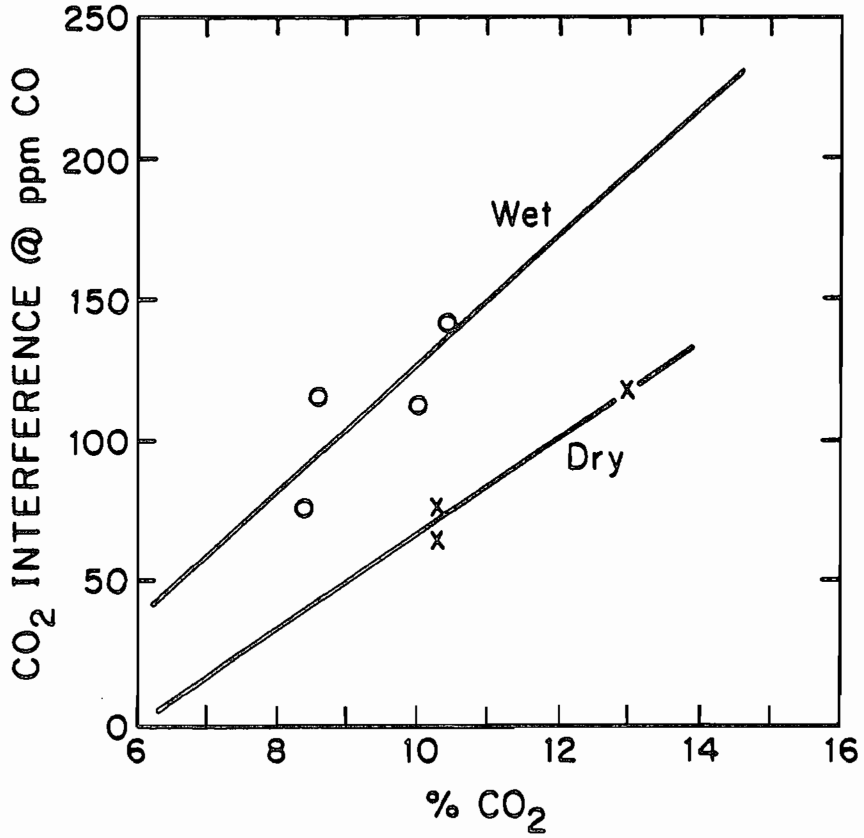


FIGURE 6

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) Recovery Furnace D - 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) Recovery Furnace E - 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) Lime Kiln A - 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 = $(2.59 \times 10^{-9}$ 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:

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

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

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

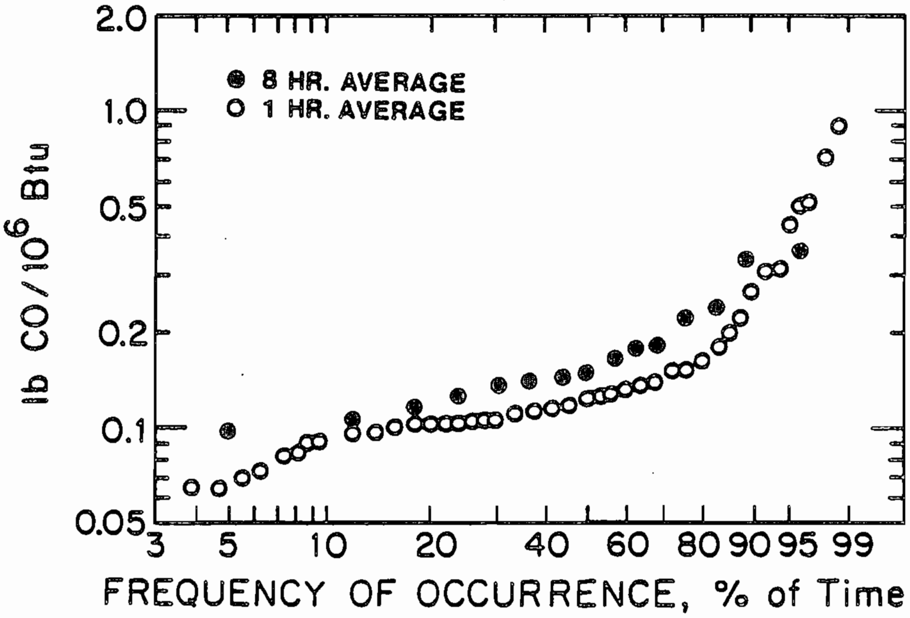


FIGURE 7

FREQUENCY OF OCCURRENCE OF CO EMISSIONS MEASURED AT BOILER A

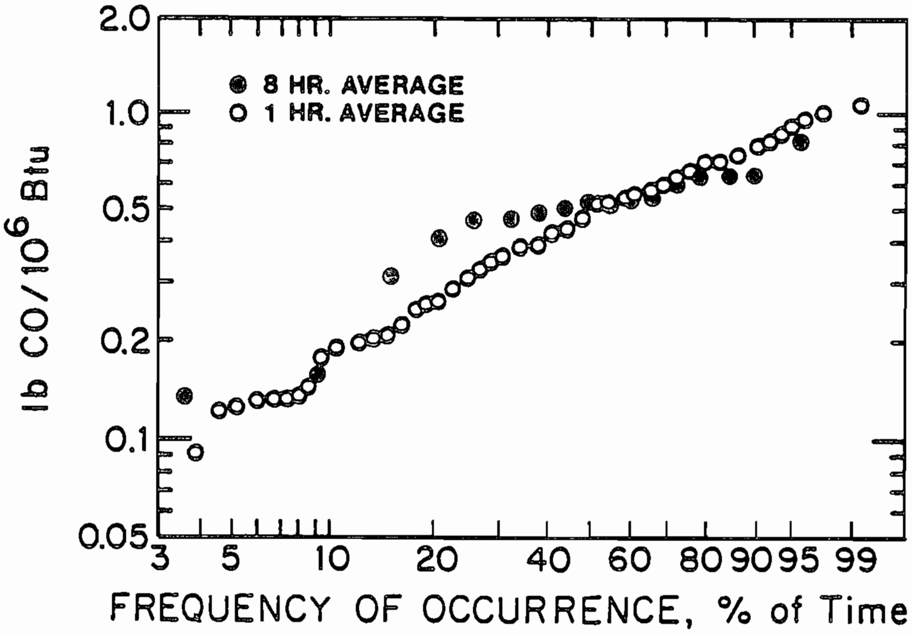


FIGURE 8

FREQUENCY OF OCCURRENCE OF CO EMISSIONS MEASURED AT BOILER B

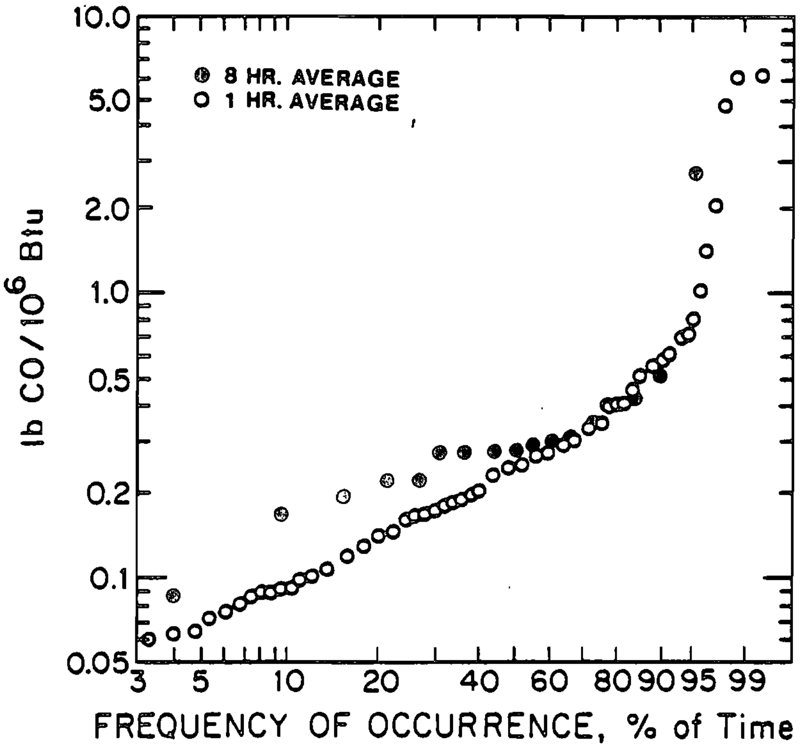


FIGURE 9

FREQUENCY OF OCCURRENCE OF CO EMISSIONS MEASURED AT BOILER C

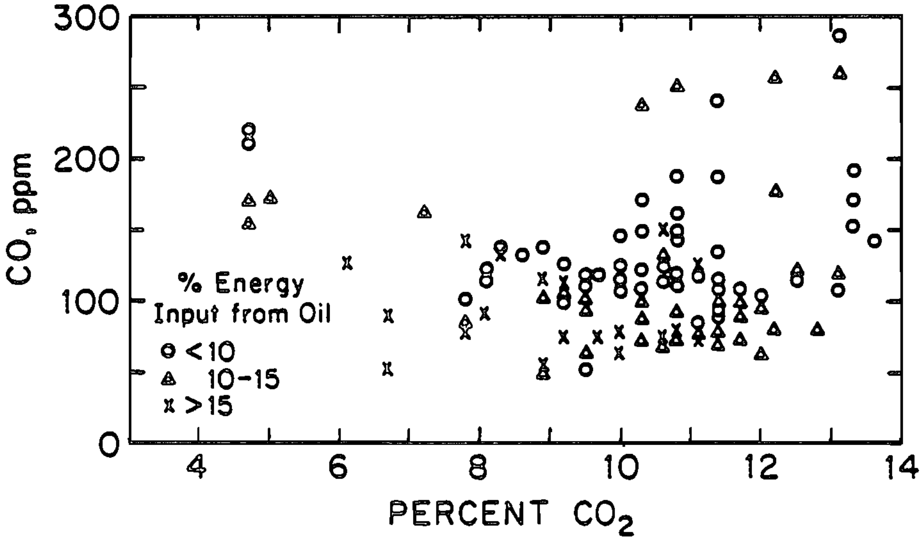


FIGURE 10

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

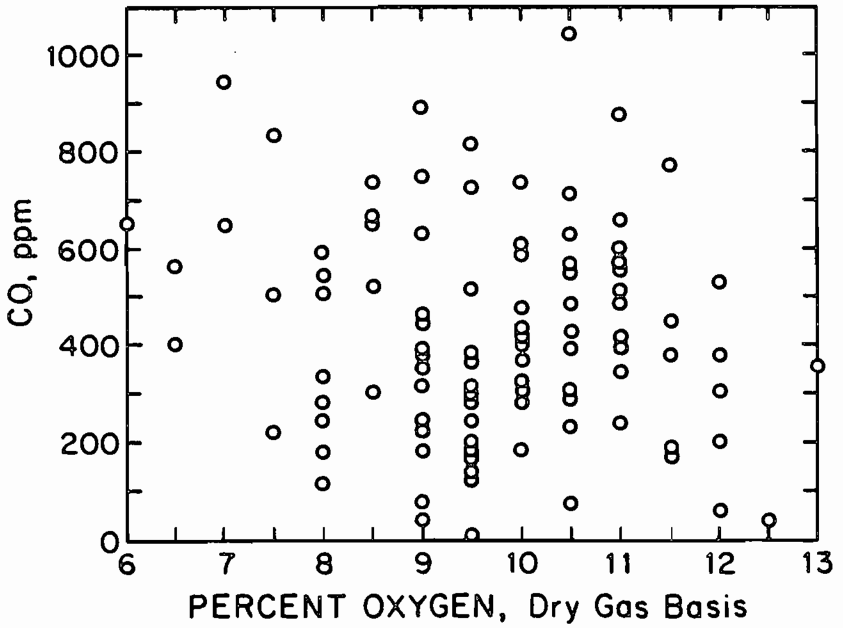


FIGURE 11

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

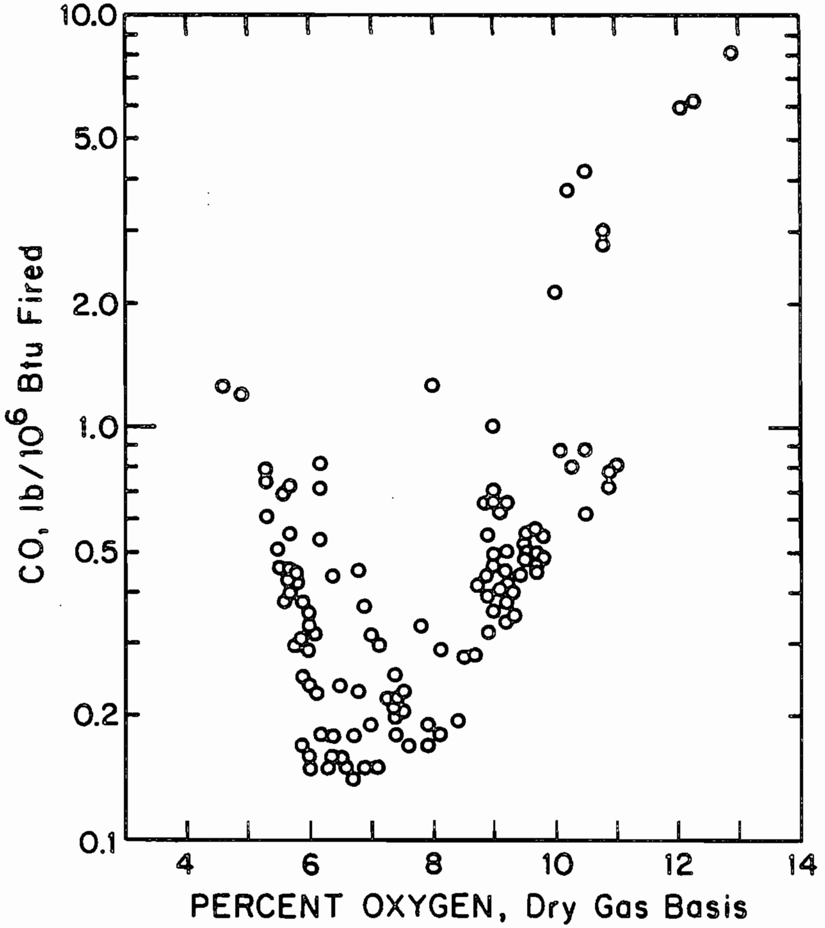


FIGURE 12

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 CE NDCE	88	0.14	0.43	0.06	0.08	3.8
B DCE	120	0.60	1.8	0.33	0.48	3.3
C NDCE	136	0.64	3.1	0.56	0.60 1.37.	3.2
D DCE	168	1.87	5.9	0.95	0.96	3.1
E DCE	152	13.3	42	12.2	12.5	2.8

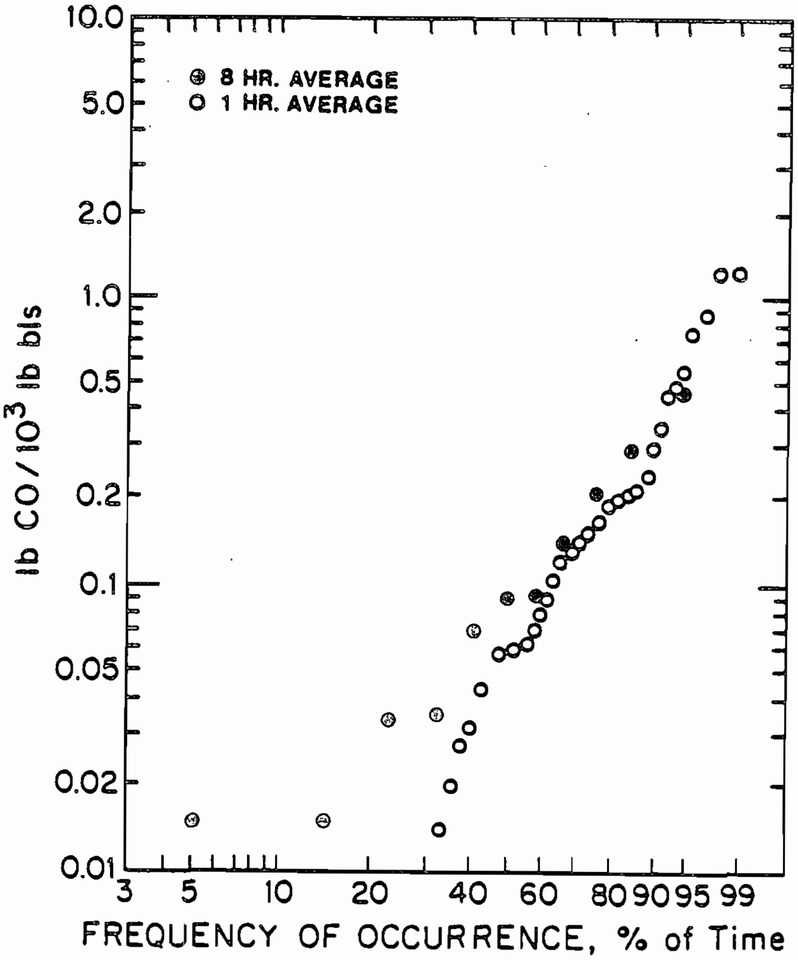


FIGURE 13

FREQUENCY OF CARBON MONOXIDE EMISSIONS FROM KRAFT RECOVERY FURNACE A

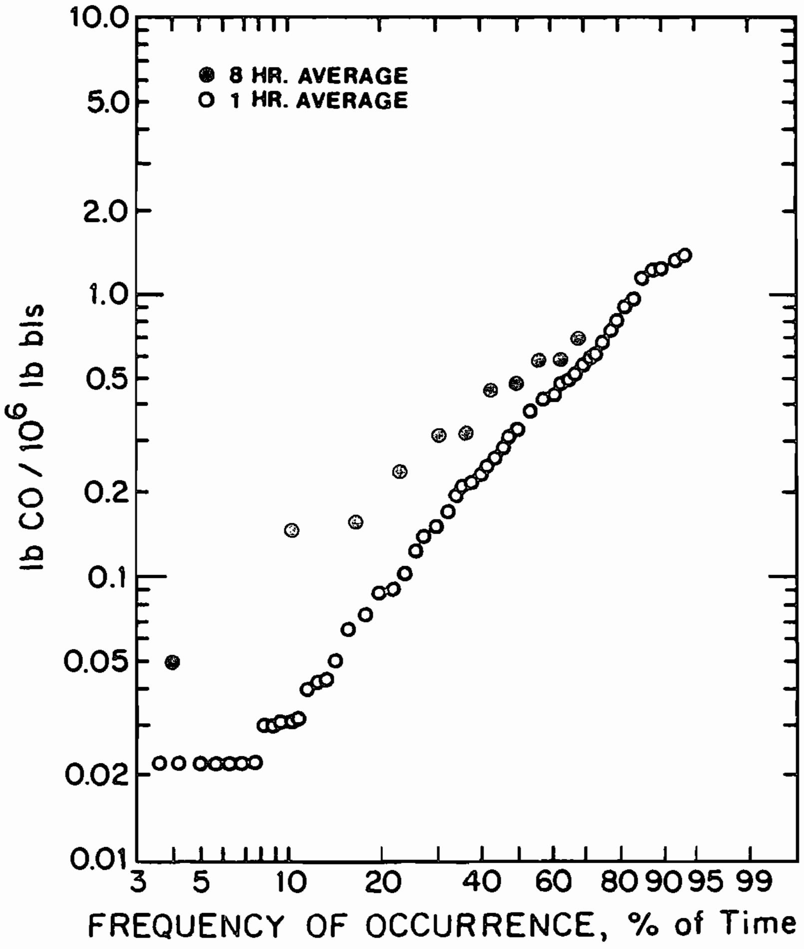


FIGURE 14

FREQUENCY OF CARBON
MONOXIDE EMISSIONS
FROM KRAFT RECOVERY FURNACE B

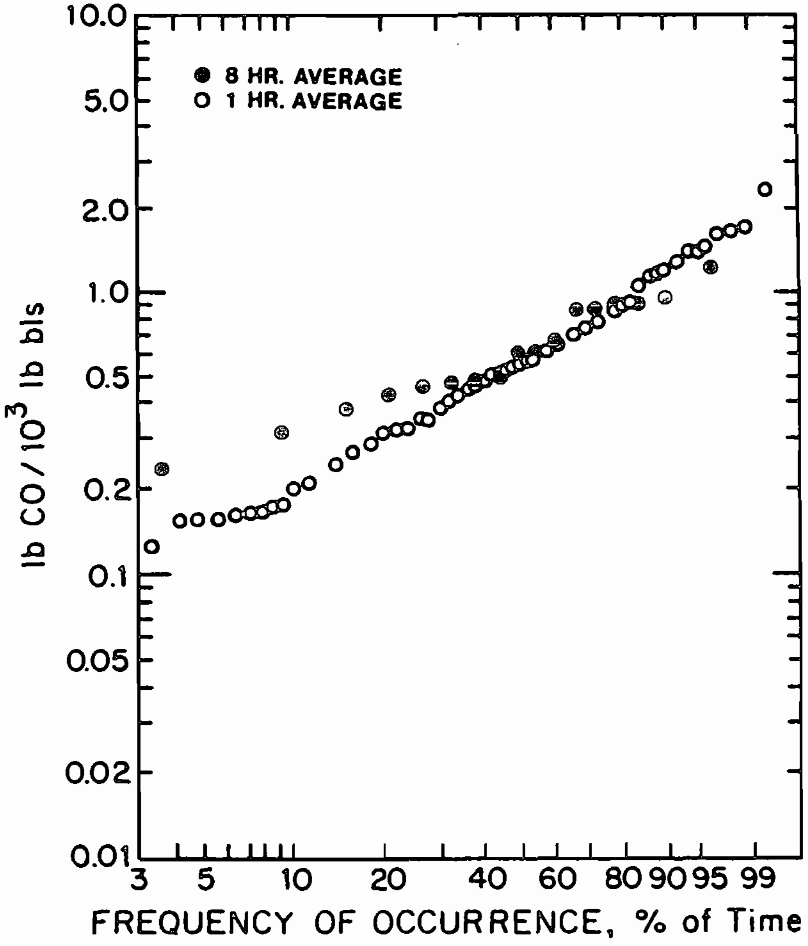


FIGURE 15

FREQUENCY OF CARBON
MONOXIDE EMISSIONS
FROM KRAFT RECOVERY FURNACE C

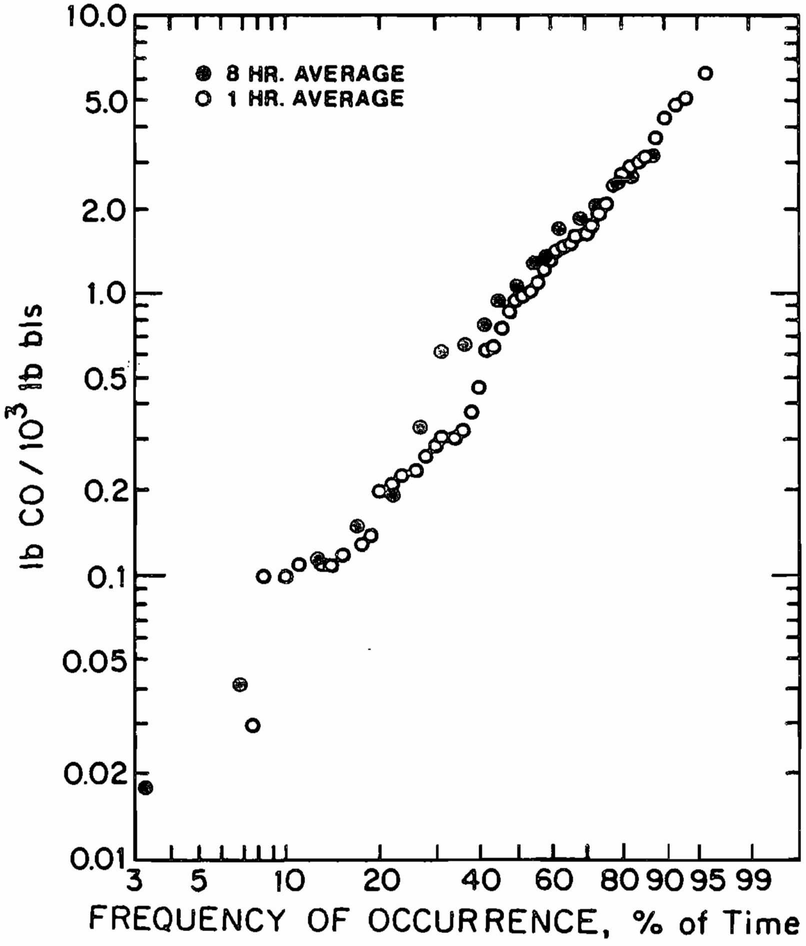


FIGURE 16

FREQUENCY OF CARBON
MONOIXDE EMISSIONS
FROM KRAFT RECOVERY FURNACE D

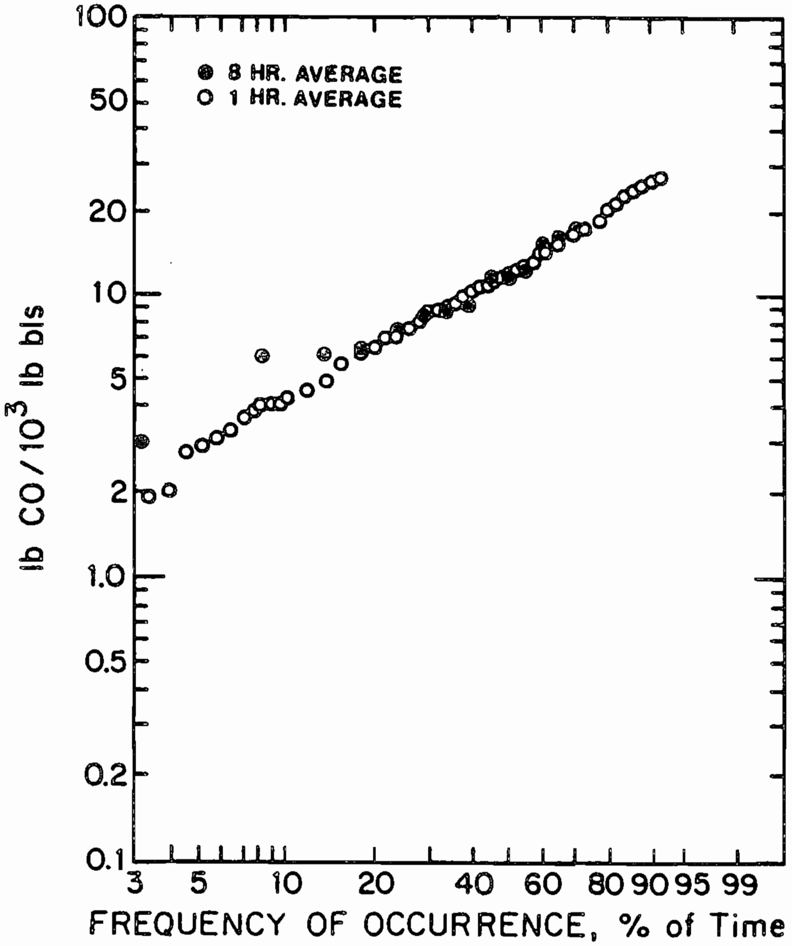


FIGURE 17

FREQUENCY OF CARBON
MONOXIDE EMISSIONS
FROM KRAFT RECOVERY FURNACE E

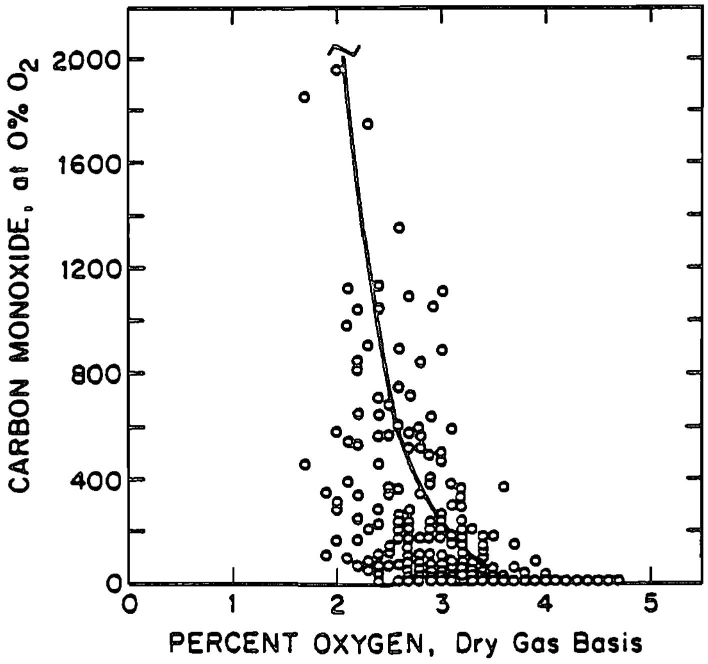


FIGURE 18

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

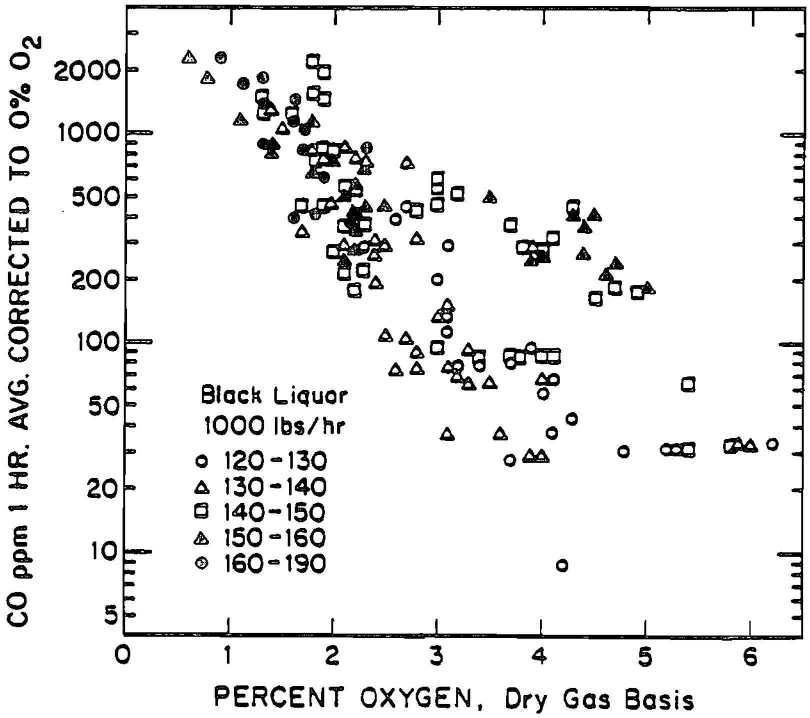


FIGURE 19

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

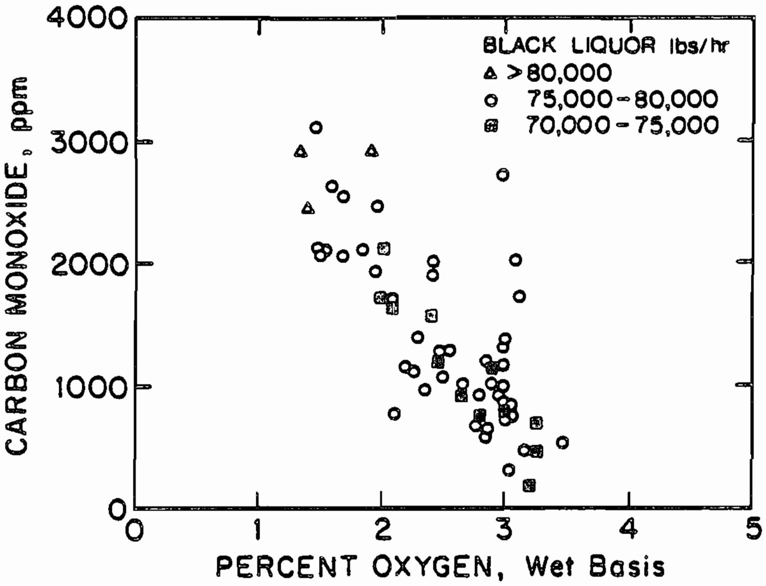


FIGURE 20

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

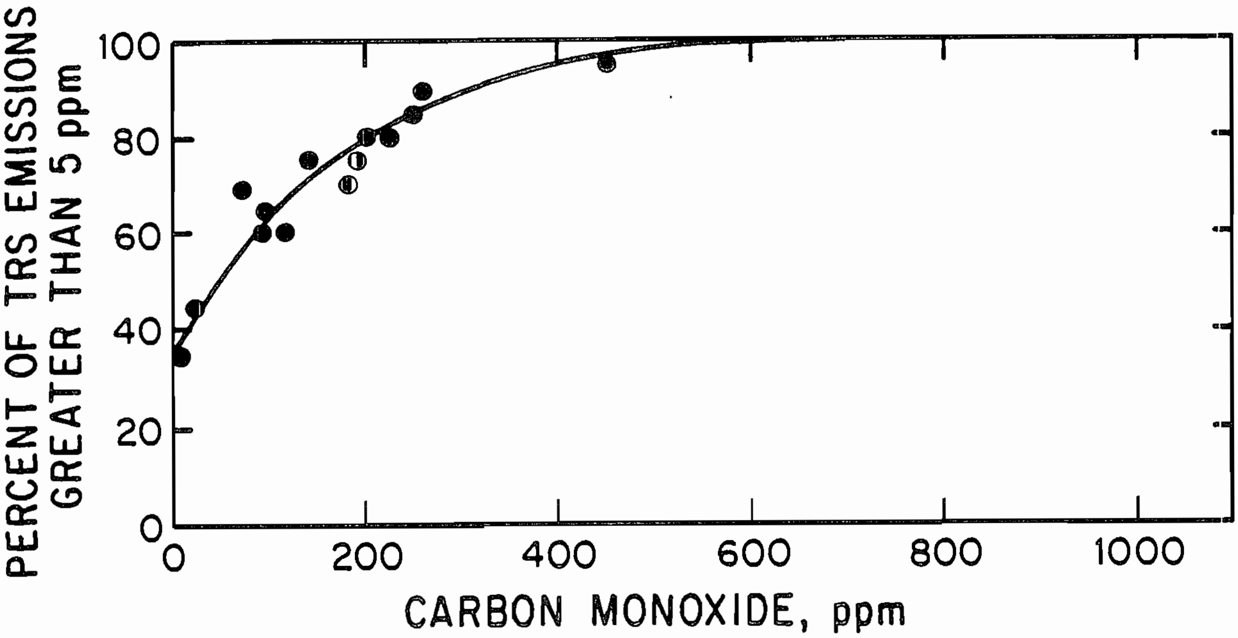


FIGURE 21

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

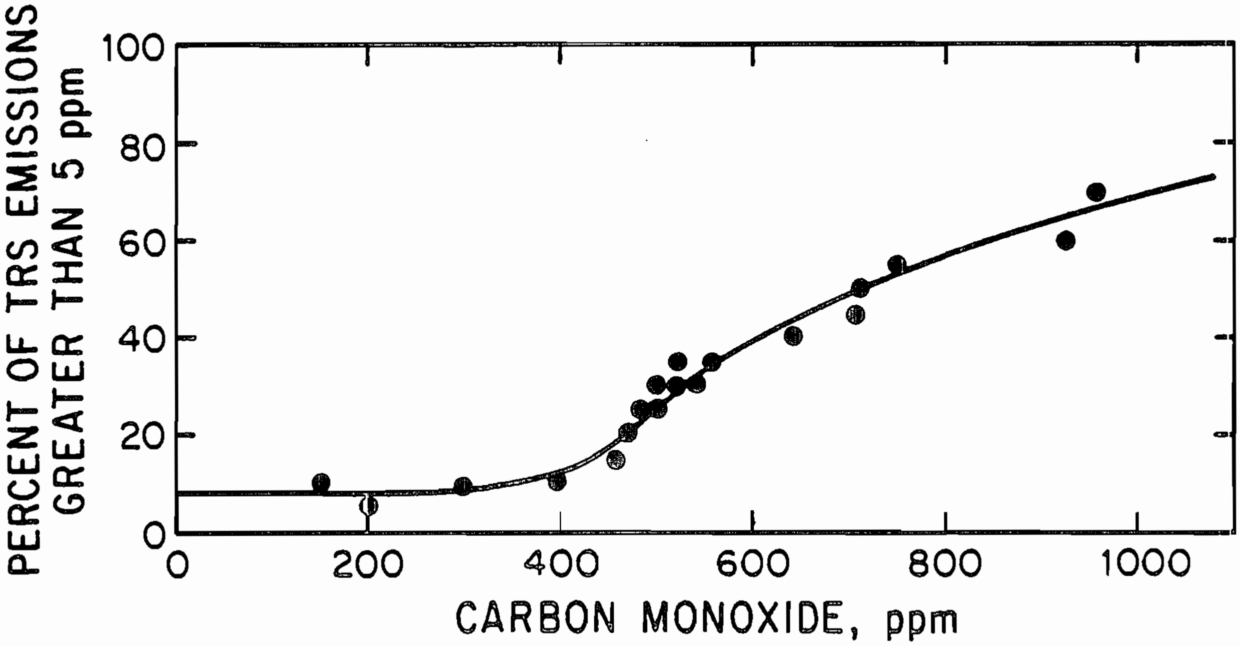


FIGURE 22

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.

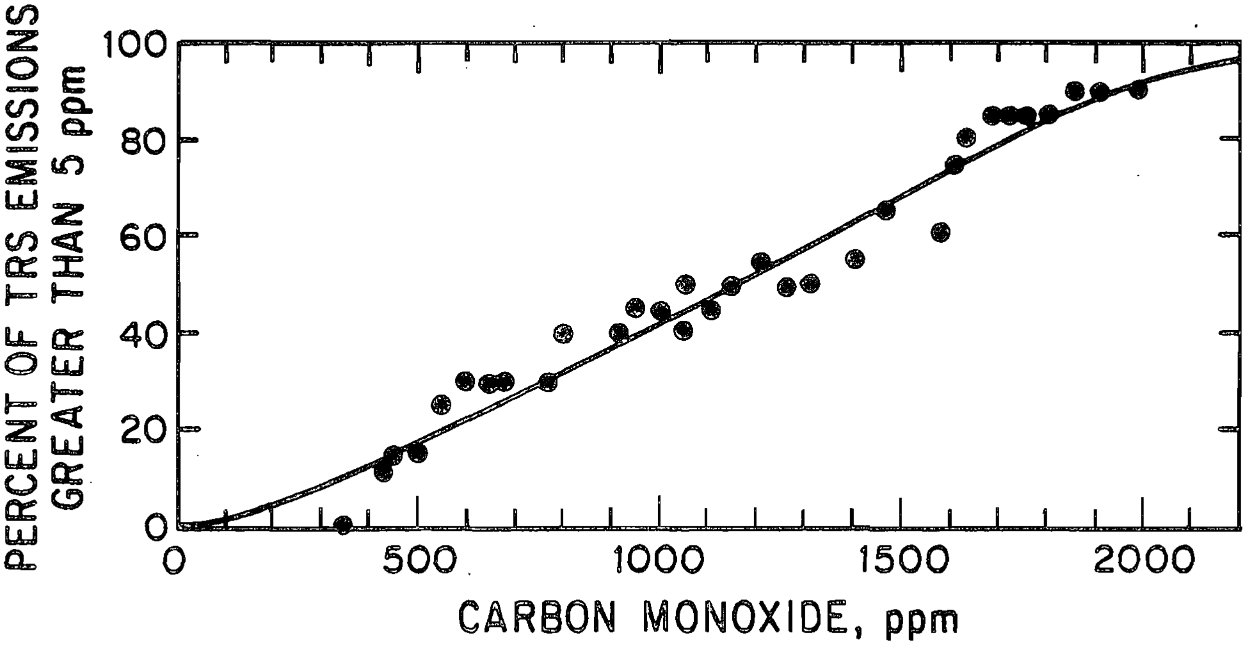


FIGURE 23

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

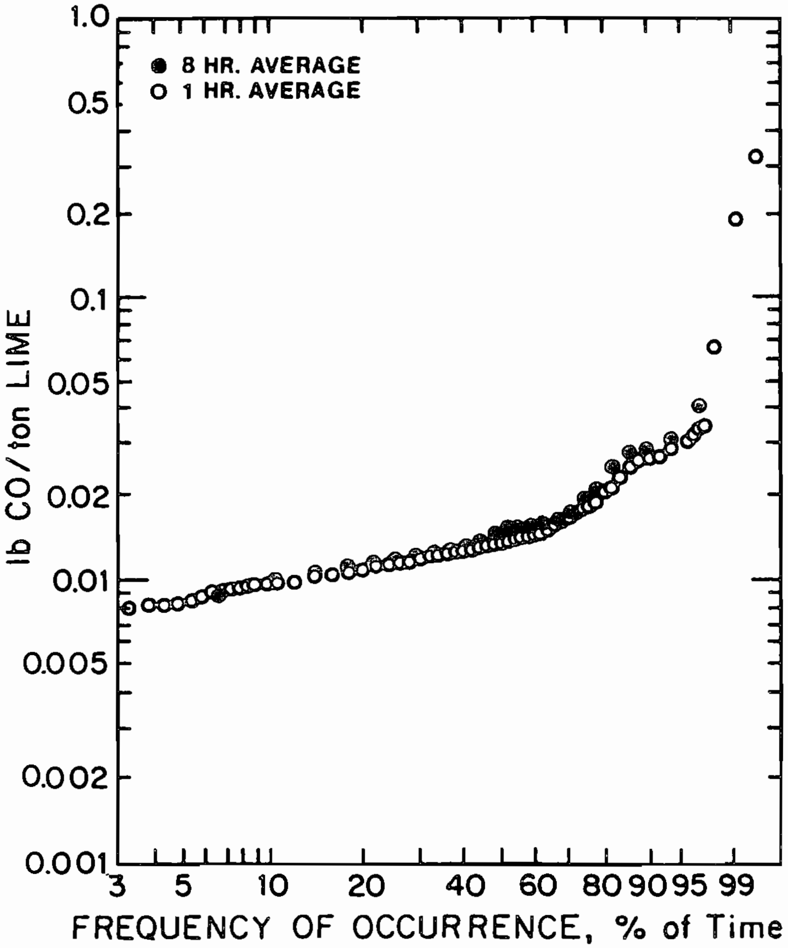


FIGURE 24

FREQUENCY OF OCCURRENCE OF CO EMISSIONS MEASURED AT LIME KILN A

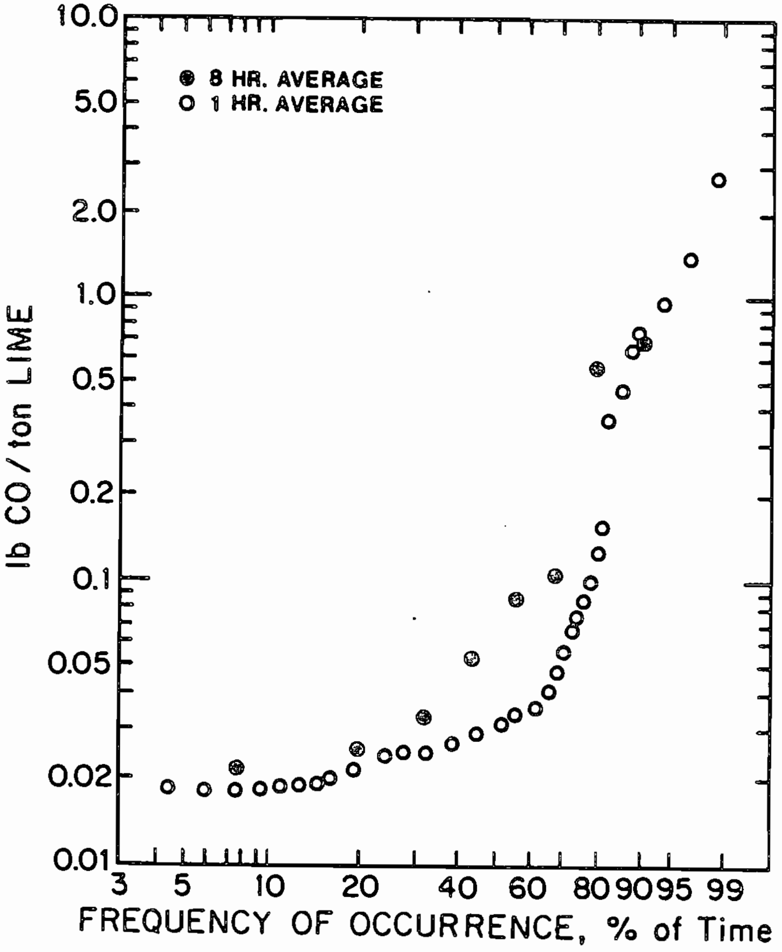


FIGURE 25

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.

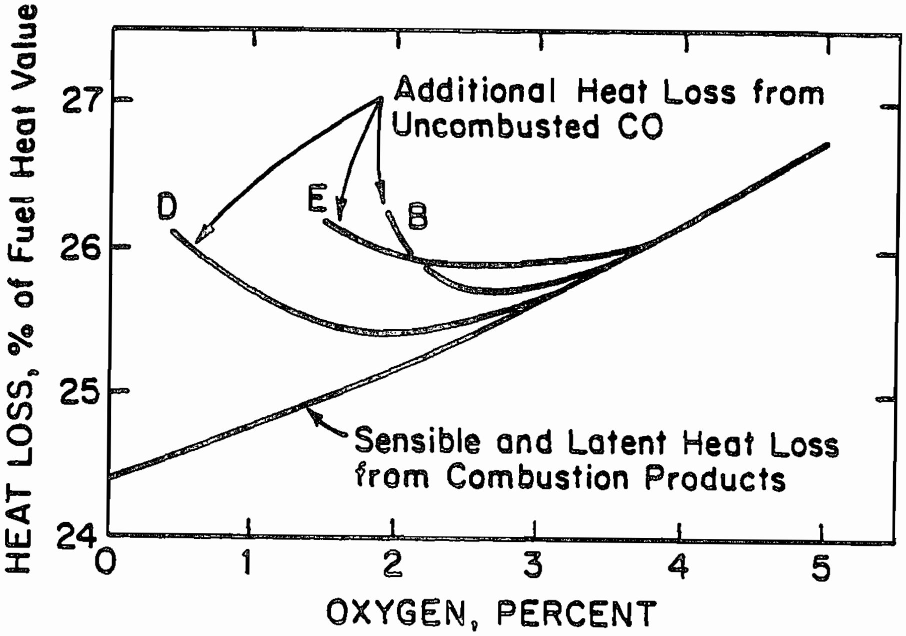


FIGURE 26

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

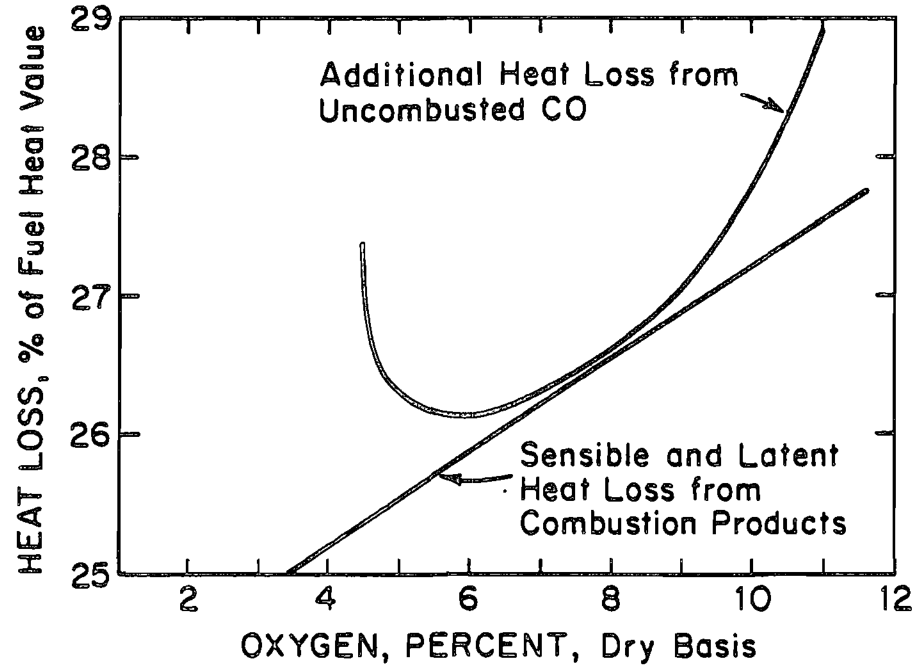


FIGURE 27

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 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 ft^3). 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.

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

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.

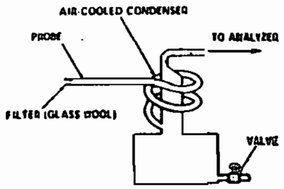

Figure 10-1. Continuous sampling train.

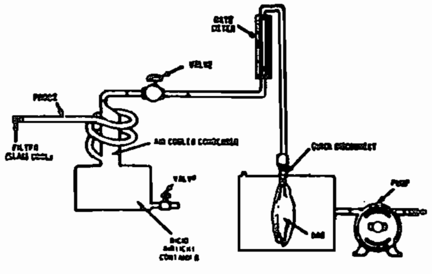

Figure 10-2. Integrated gas sampling train.

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.

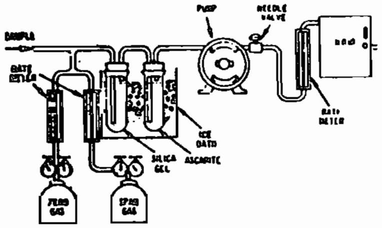

Figure 10-3. Analytical equipment.

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 computing 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.

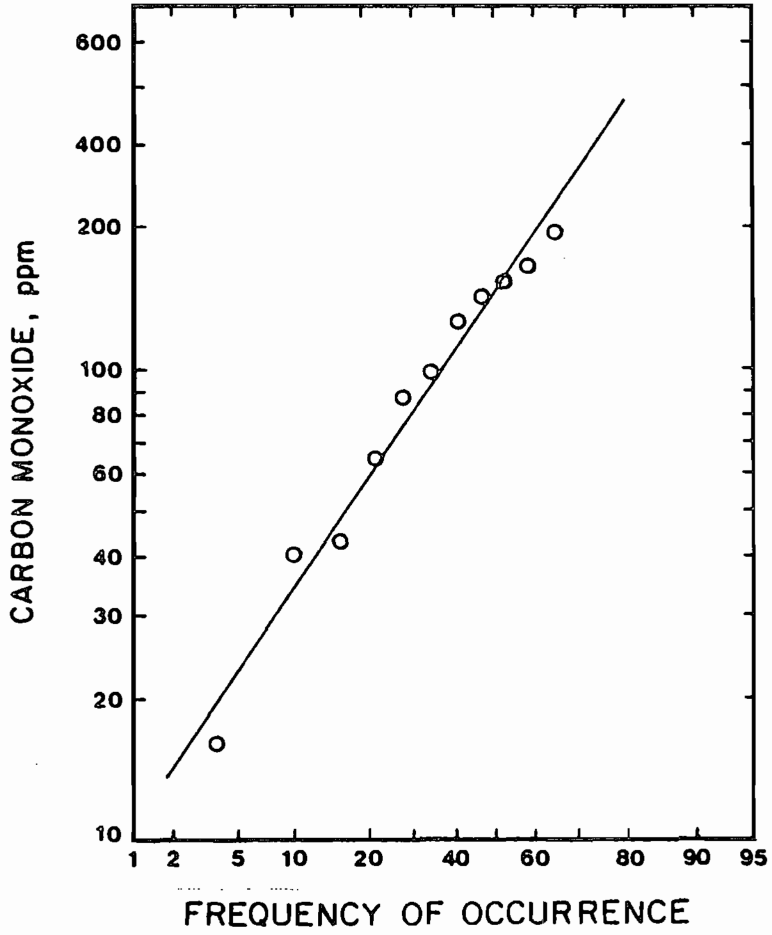

FIGURE B-1

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

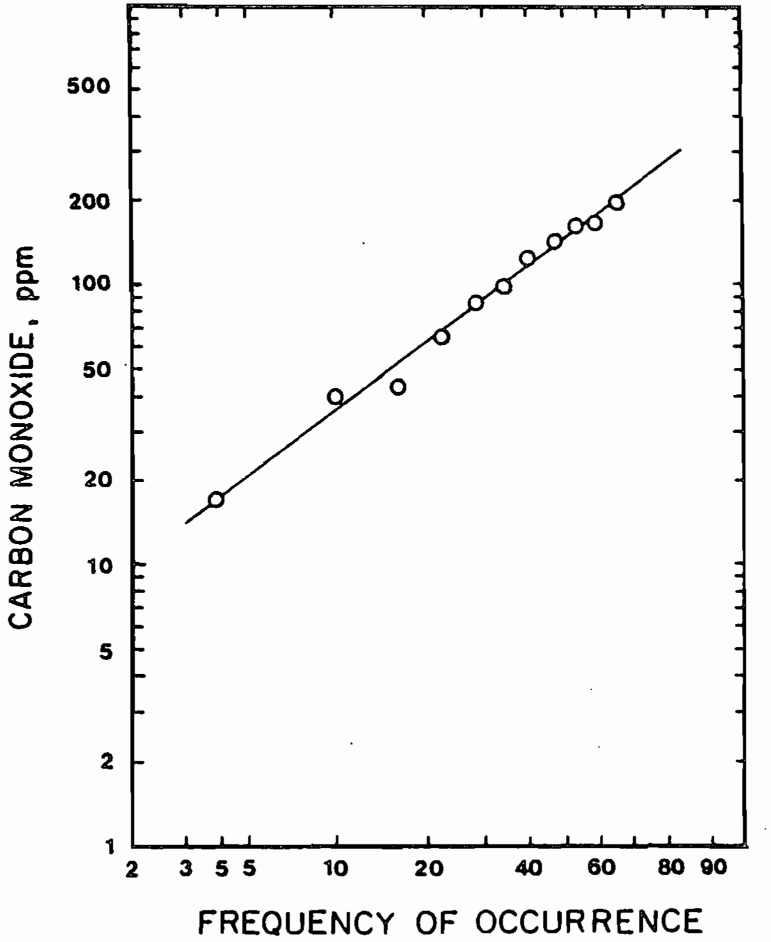

FIGURE B-2

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.

Reference 8

EPA-450/3-77-010

TECHNICAL GUIDANCE FOR CONTROL OF INDUSTRIAL PROCESS FUGITIVE PARTICULATE EMISSIONS

by

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Contract No. 68-02-1375
Task No. 33
Project No. 3155-GG

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Prepared for

ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Waste Management
Office of Air Quality Planning and Standards
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2.9 LIME MANUFACTURING

2.9.1 Process Description

The manufacture of lime involves the calcining of limestone ($CaCO_3$ or $CaCO_3 \cdot MgCO_3$) to release carbon dioxide and form quicklime (CaO or $CaO \cdot MgO$). There are three types of limestone used to produce lime. The limestone is classified as "high calcium" or "calcite" if the magnesium carbonate content is less than five percent, and "dolomitic limestone" or "dolomite" if the magnesium carbonate content is 30 to 40 percent. Magnesium limestone contains more magnesium carbonate than high calcium stone, but less than dolomite.

Most lime facilities are located at or in close proximity to a limestone quarry. Transfer of the quarried limestone to the crushing/screening site is most often accomplished by huge off-highway trucks. Section 2.6 describes in detail the processing operations at a limestone quarry.

Limestone and/or dolomite is crushed and size-classified by screening to obtain the desired feed size for the calcining kilns. In the United States, limestone is calcined in either vertical or rotary kilns. The limestone feed material size for vertical kilns is 15-20 cm (6-8 inches); consequently, only primary crushing is required. However, some vertical kilns do require 8-13 cm (3-5 inch) material feed size. Horizontal kilns require the smaller size feed provided by secondary crushing.

All vertical kilns operate similarly and have four distinct zones from top to bottom: stone storage zone, preheating zone, calcining zone, and cooling and discharge zone. The flow of stone in the kiln is countercurrent to the flow of cooling air and combustion gases. The stone is charged at the top and preheated by the hot exhaust gases from the calcining zone. Air blown into the bottom of the kiln cools the lime before it is discharged. This air is heated sufficiently by the time it reaches the calcining zone to be used as secondary combustion air. The lime is discharged to cars on tracks or to conveyor belts, and either shipped or further processed by hydrating.

The rotary kiln, which is supported by rollers, is a long inclined horizontal steel cylinder lined with refractory brick. Most rotary kilns rotate at a speed of about one rpm. The limestone flows countercurrent to the heat, the pebble size limestone entering at one end and the hot air entering at the other. Rotary kilns are composed of three fairly distinct zones: the feed or drying zone, the central or preheating zone, and the calcining zone. Though kilns are usually well controlled, an imperfect hood fit around the rotating kiln at the feed end can ~~be a source of~~ fugitive emissions.

Regardless of kiln type, the temperature in the feed end of the kiln is kept below 540°C (1000°F) while the operating temperatures in the preheating and calcining zones are generally in the 1,090 to 1,320°C (2,000 to 2,400°F) range, with higher temperatures being found in shorter kilns.

The calcined lime (quicklime - CaO) is then screened, milled, and shipped as is and/or futher processed to produce hydrated lime. Fines from calcination can be briquetted, fed to a hydrator, or ground or pulverized for market demands.

The hydration process involves adding water to crushed or ground quicklime in a mixing chamber (hydrator). The product, called slaked lime, is dried primarily by the heat of hydration. The slaked lime is conveyed to an air separator in preparation for final shipment. Dolomitic pressure hydrated lime involves an additional milling step prior to shipment.

Shipment of the quicklime and hydrated lime products is accomplished by packaging in bags, and by bulk handling in truck, rail, and ship/barge.

A process flow diagram for lime manufacturing is shown in Figure 2-19. Each potential process fugitive emission point is identified and explained in Table 2-53. Dust sources common to all lime producing facilities, but not specifically included in the Figure or Table, are plant roads which are discussed in Section 2.1.

2.9.2 IPFPE Emission Rates

Table 2-53 presents a summary of uncontrolled emission factors for a lime facility IPFPE sources. Since these are potential uncontrolled emission rates, the site-specific level of control must be considered for application to a specific plant. Also included are reliability factors for each estimate, as defined previously.

The largest potential IPFPE sources are secondary crushing/screening and the combined transfer and associated conveying sources (source 3 in Figure 2-19). Uncontrolled fugitive dust emissions from unpaved roads at lime plants and associated quarries are often larger overall IPFPE sources.

2.9.3 Example Plant Inventory

The example plant inventory for lime manufacturing as shown in Table 2-53 presents potential fugitive particulate emission quantities from the various uncontrolled sources within the process. The inventory represents a plant which processes 100,000 Mg (110,000 tons) of limestone ore per year. Because of the wide variability throughout the

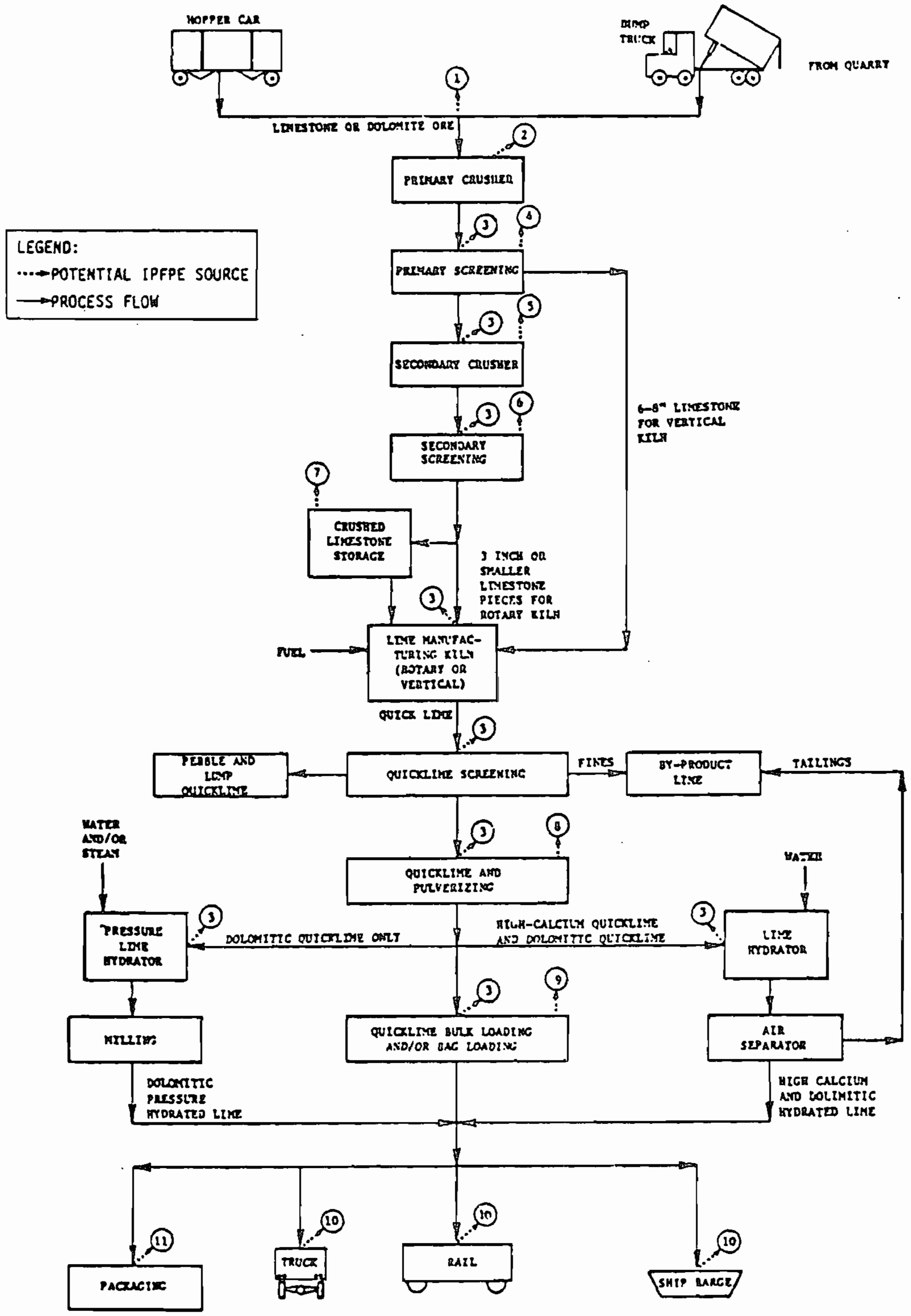

Figure 2-19. Process flow diagram for lime manufacturing showing potential industrial process fugitive particulate emission points.

Table 2-53. IDENTIFICATION AND QUANTIFICATION OF POTENTIAL FUGITIVE PARTICULATE EMISSION POINTS FOR LIME PRODUCTION

			Model plant fugitive emission inventory	
Source of IPFPE	Uncontrolled fugitive emission factor	Emission factor reliability rating	Operating parameter Mg/yr (tons/year)	Uncontrolled emissions Mg/yr (tons/yr)
1. Limestone/dolomite charging to primary crusher	0.00015-0.02 kg/Mg of rock charged[a] (0.00030-0.04 lb/ton)	D	Limestone/dolomite processed 100,000 (110,000)	1 (1)
2. Primary crushing	0.25 kg/Mg of limestone crushed[b] (0.5 lb/ton)	C	Limestone/dolomite processed 100,000 (110,000)	25 (28)
3. Transfer points and associated conveying	0.4 kg/Mg of quicklime produced[c] (0.8 lb/ton)	E	Quicklime produced 50,000 (55,000)	20 (22)
4. Primary screening	d			d
5. Secondary crushing	0.75 kg/Mg of limestone crushed[b] (1.5 lb/ton)	C	Limestone/dolomite processed 90,000 (99,000)	68 (74)
6. Secondary screening	e			e

Table 2-53 (continued). IDENTIFICATION AND QUANTIFICATION OF POTENTIAL FUGITIVE PARTICULATE EMISSION POINTS FOR LIME PRODUCTION

Source of IPFPE	Uncontrolled fugitive emission factor	Emission factor reliability rating	Model plant fugitive emission inventory: Operating parameter, Mg/yr (tons/year)	Model plant fugitive emission inventory: Uncontrolled emissions Mg/yr (tons/yr)
7. Crushed limestone storage				
Loading onto pile	$\frac{(0.02)\ (K_1)\ (S/1.5)}{(PE/100)^2}$ kg/Mg material loaded onto pile[f] $\left(\frac{(0.04)\ (K_1)\ (S/1.5)}{(PE/100)^2}\ \text{lb/ton}\right)$	D	Crushed limestone loaded 40,000 (44,000)	1 (1)
Vehicular traffic	$\frac{(0.065)\ (K_2)\ (S/1.5)}{(PE/100)^2}$ kg/Mg material stored[f] $\left(\frac{(0.13)\ (K_2)\ (S/1.5)}{(PE/100)^2}\ \text{lb/ton}\right)$	D	Crushed limestone stored 40,000 (44,000)	3 (3)
Loading out	$\frac{(0.025)\ (K_3)\ (S/1.5)}{(PE/100)^2}$ kg/Mg material loaded out[f] $\left(\frac{(0.055)\ (K_3)\ (S/1.5)}{(PE/100)^2}\ \text{lb/ton}\right)$	D	Crushed limestone loaded out 40,000 (44,000)	1 (1)
Wind erosion	$\frac{(0.055)\ (S/1.5)}{(PE/100)^2}\ (\frac{D}{90})$ kg/Mg material stored[f] $\left(\frac{(0.11)\ S/1.5)}{(PE/100)^2}\ (\frac{D}{90})\ \text{lb/ton}\right)$	D	Crushed limestone stored 40,000 (44,000)	2 (2)
8. Quicklime screening	[g]			[g]

Table 2-53 (continued). IDENTIFICATION AND QUANTIFICATION OF POTENTIAL FUGITIVE PARTICULATE EMISSION POINTS FOR LIME PRODUCTION

Source of IPFPE	Uncontrolled fugitive emission factor	Emission factor reliability rating	Model plant fugitive emission inventory	
			Operating parameter Mg/yr. (tons/year)	Uncontrolled emissions Mg/yr. (tons/yr)
9. Quicklime and hydrated lime crushing and pulverizing with leaks from mill and from feed/discharge exhaust systems.	0.05 kg/Mg of quicklime and hydrated lime produced[h] (0.1 lb/ton)	E	Quicklime and hydrated lime crushed and pulverized 50,000 (55,000)	2 (3)
10. Lime product silo vents	i			i
11. Truck, rail, ship/barge loading of quicklime and hydrated lime	0.118 kg/Mg of lime products loaded[j] (0.236 lb/ton	E	Lime products loaded 50,000 (55,000)	6 (6)
12. Packaging quicklime and hydrated lime	Negligible - 0.005 kg/Mg of lime products packaged[k] (0.01 lb/ton)	E	Lime products packaged 10,000 (11,000)	Negligible

[a] Reference 1.

[b] Reference 2 - AP-42. 80% and 60% of which falls out on plant property for points 2 and 5, respectively.

[c] Engineering judgment, assumed approximately same as emission factor for dry phosphate rock as reported in Reference 3.

[d] Emission from primary screening (point 4) included in emission factor for primary crushing (point 2).

[e] Emissions from secondary screening (point 6) included in emission factor for secondary crushing (point 5).

[f] For complete development of this factor, refer to Section 2.1.4. For this example, it was assumed that S = 1.5, D = 90, PE = 100, and K_1, K_2, and K_3 = 1. Reference 4.

[g] Emission from quicklime screening (point 8) included in emission factor for quicklime crushing and pulverizing (point 9).

[h] Engineering judgment based on controlled cement milling emissions reported by a cement manufacturing company.

[i] Emissions from lime product silo vents (point 10) included in emission factor for lime loading (point 11).

[j] Engineering judgment, assumed same as for loading of hydraulic cement obtained from Reference 5.

[k] Engineering judgment based on observations and emission tests of controlled similar sources.

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Supplement 15

SUPPLEMENT NO. 15

FOR

COMPILATION OF AIR POLLUTANT EMISSION FACTORS, THIRD EDITION (INCLUDING SUPPLEMENTS 1-7)

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TABLE 1.3-1. UNCONTROLLED EMISSION FACTORS FOR FUEL OIL COMBUSTION

EMISSION FACTOR RATING: A

Boiler Type[a]	Particulate Matter[b]		Sulfur Dioxide[c]		Sulfur Trioxide		Carbon Monoxide[d]		Nitrogen Oxide[e]		Volatile Organics[f]			
											Nonmethane		Methane	
	kg/10³l	lb/10³gal	kg/10³l	lb/10³gal	kg/10³l	lb/10³gal	kg/10³l	lb/10³gal	kg/10³l	lb/10³gal	kg/10³l	lb/10³gal	kg/10³l	lb/10³gal
Utility Boilers														
Residual Oil	g	g	19S	157S	0.34S[h]	2.9S[h]	0.6	5	8.0 (12.6)(5)[i]	67 (105)(42)[i]	0.09	0.76	0.03	0.28
Industrial Boilers														
Residual Oil	g	g	19S	157S	0.24S	2S	0.6	5	6.6[j]	55[j]	0.034	0.28	0.12	1.0
Distillate Oil	0.24	2	17S	142S	0.24S	2S	0.6	5	2.4	20	0.024	0.2	0.006	0.052
Commercial Boilers														
Residual Oil	g	g	19S	157S	0.24S	2S	0.6	5	6.6	55	0.14	1.13	0.057	0.475
Distillate Oil	0.24	2	17S	142S	0.24S	2S	0.6	5	2.4	20	0.04	0.34	0.026	0.216
Residential Furnaces														
Distillate Oil	0.3	2.5	17S	142S	0.24S	2S	0.6	5	2.2	18	0.085	0.713	0.214	1.78

[a] Boilers can be approximately classified according to their gross (higher) heat rate as shown below:
Utility (power plant) boilers: >106 x 10^9 J/hr (>100 x 10^6 Btu/hr)
Industrial boilers: 10.6 x 10^9 to 106 x 10^9 J/hr (10 x 10^6 to 100 x 10^6 Btu/hr)
Commercial boilers: 0.5 x 10^9 to 10.6 x 10^9 J/hr (0.5 x 10^6 to 10 x 10^6 Btu/hr)
Residential furnaces: <0.5 x 10^9 J/hr (<0.5 x 10^6 Btu/hr)

[b] References 3-7 and 24-25. Particulate matter is defined in this section as that material collected by EPA Method 5 (front half catch).

[c] References 1-5. S indicates that the weight % of sulfur in the oil should be multiplied by the value given.

[d] References 3-5 and 8-10. Carbon monoxide emissions may increase by factors of 10 to 100 if the unit is improperly operated or not well maintained.

[e] Expressed as NO_2. References 1-5, 8-11, 17 and 26. Test results indicate that at least 95% by weight of NO_x is NO for all boiler types except residential furnaces, where about 75% is NO.

[f] References 18-21. Volatile organic compound emissions are generally negligible unless boiler is improperly operated or not well maintained, in which case emissions may increase by several orders of magnitude.

[g] Particulate emission factors for residual oil combustion are, on average, a function of fuel oil grade and sulfur content:
Grade 6 oil: 1.25(S) + 0.38 kg/10^3 liter [10(S) + 3 lb/10^3 gal] where S is the weight % of sulfur in the oil. This relationship is based on 81 individual tests and has a correlation coefficient of 0.65.
Grade 5 oil: 1.25 kg/10^3 liter (10 lb/10^3 gal)
Grade 4 oil: 0.88 kg/10^3 liter (7 lb/10^3 gal)

[h] Reference 25.

[i] Use 5 kg/10^3 liters (42 lb/10^3 gal) for tangentially fired boilers, 12.6 kg/10^3 liters (105 lb/10^3gal) for vertical fired boilers, and 8.0 kg/10^3 liters (67 lb/10^3 gal) for all others, at full load and normal (>15%) excess air. Several combustion modifications can be employed for NO_x reduction: (1) limited excess air can reduce NO_x emissions 5-20%, (2) staged combustion 20-40%, (3) using low NO_x burners 20-50%, and (4) ammonia injection can reduce NO_x emissions 40-70% but may increase emissions of ammonia. Combinations of these modifications have been employed for further reductions in certain boilers. See Reference 23 for a discussion of these and other NO_x reducing techniques and their operational and environmental impacts.

[j] Nitrogen oxides emissions from residual oil combustion in industrial and commercial boilers are strongly related to fuel nitrogen content, estimated more accurately by the empirical relationship:
kg NO_2/10^3 liters = 2.75 + $50(N)^2$ [lb NO_2/10^3gal = 22 + $400(N)^2$] where N is the weight % of nitrogen in the oil. For residual oils having high (>0.5 weight %) nitrogen content, use 15 kg NO_2/10^3 liter (120 lb NO_2/10^3gal) as an emission factor.

TABLE 1.6-1. EMISSION FACTORS FOR WOOD AND BARK COMBUSTION IN BOILERS

Pollutant/Fuel Type	kg/Mg	lb/ton	Emission Factor Rating
Particulate[a,b]			
Bark[c]			
Multiclone, with flyash reinjection[d]	7	14	B
Multiclone, without flyash reinjection[d]	4.5	9	B
Uncontrolled	24	47	B
Wood/bark mixture[e]			
Multiclone, with flyash reinjection[d,f]	3	6	C
Multiclone, without flyash reinjection[d,f]	2.7	5.3	C
Uncontrolled[g]	3.6	7.2	C
Wood[h]			
Uncontrolled	4.4	8.8	C
Sulfur Dioxide[i]	0.075 (0.01 - 0.2)	0.15 (0.02 - 0.4)	B
Nitrogen Oxides (as NO_2)[j]			
50,000 - 400,000 lb steam/hr	1.4	2.8	B
<50,000 lb steam/hr	0.34	0.68	B
Carbon Monoxide[k]	2-24	4-47	C
VOC			
Nonmethane[l]	0.7	1.4	D
Methane[m]	0.15	0.3	E

[a] References 2,4,9,17-18. For boilers burning gas or oil as an auxiliary fuel, all particulates are assumed to result from only wood waste fuel.

[b] May include condensible hydrocarbons consisting of pitches and tars, mostly from back half catch of EPA Method 5. Tests reported in Reference 20 indicate that condensible hydrocarbons account for 4% of total particulate weight.

[c] Based on fuel moisture content of about 50%.

[d] After control equipment, assuming an average collection efficiency of 80%. Data from References 4, 7 and 8 indicate that 50% flyash reinjection increases the dust load at the cyclone inlet 1.2 to 1.5 times, while 100% flyash reinjection increases the load 1.5 to 2 times the load without reinjection.

[e] Based on fuel moisture content of 33%.

[f] Based on large dutch ovens and spreader stokers (averaging 23,430 kg steam/hr) with steam pressures from 20 - 75 kpa (140 - 530 PSI).

[g] Based on small dutch ovens and spreader stokers (usually operating <9075 kg steam/hr), with pressures from 5 - 30 kpa (35 - 230 PSI). Careful air adjustments and improved fuel separation and firing were used on some units, but the effects cannot be isolated.

[h] References 12-13, 19, 27. Wood waste includes cuttings, shavings, sawdust and chips, but not bark. Moisture content ranges from 3 - 50% by weight. Based on small units (<3000 kg steam/hr) in New York and North Carolina.

[i] Reference 23. Based on tests of fuel sulfur content and sulfur dioxide emissions at four mills burning bark. The lower limit of the range (in parentheses) should be used for wood, and higher values for bark. A heating value of 5000 kcal/kg (9000 BTU/lb) is assumed. The factors are based on the dry weight of fuel.

[j] References 7, 24-26. Several factors can influence emission rates, including combustion zone, temperatures, excess air, boiler operating conditions, fuel moisture and fuel nitrogen content.

[k] Reference 30.

[l] References 20, 30. Nonmethane VOC reportedly consists of compounds with a high vapor pressure such as alpha pinene.

[m] Reference 30. Based on an approximation of methane/nonmethane ratio, which is very variable. Methane, expressed as a percent of total volatile organic compounds, varied from 0 - 74 weight %.

In the United States, the major use of lime is in chemical and metallurgical applications. Two of the largest uses in these areas are as steel flux and in alkali production. Other lesser uses include construction, refractory, and agricultural applications.

8.15.2 Emissions and Controls[3-5]

Potential air pollutant emitting points in lime manufacturing plants are shown in Figure 8.15-1. Particulate is the only pollutant of concern from most of the operations; however, gaseous pollutants are also emitted from kilns.

The largest source or particulate is the kiln. Of the various kiln types in use, fluidized-bed kilns have the highest uncontrolled particulate emissions. This is due primarily to the very small feed size combined with the high air flow through these kilns. Fluidized-bed kilns are well controlled for maximum product recovery. The rotary kiln is second to the fluidized-bed kiln in uncontrolled particulate emissions. This is attributed to the small feed size and relatively high air velocities and dust entrainment caused by the rotating chamber. The rotary hearth, or "calcimatic" kiln ranks third in dust production, primarily because of the larger feed size combined with the fact that the limestone remains in a stationary position relative to the hearth during calcination. The vertical kiln has the lowest uncontrolled dust emissions due to the large lump-size feed and the relatively slow air velocities and slow movement of material through the kiln.

Some sort of particulate control is generally employed on most kilns. Rudimentary fallout chambers and cyclone separators are commonly used for control of the larger particles; fabric and gravel bed filters, wet (commonly venturi) scubbers, and electrostatic precipitators are employed for secondary control. Table 8.15-1 yields approximate efficiencies of each type of control on the various types of kilns.

Nitrogen oxides, carbon monoxide, and sulfur oxides are all produced in kilns, although the latter are the only gaseous pollutant emitted in significant quantities. Not all of the sulfur in the kiln fuel is emitted as sulfur oxides because some fraction reacts with the materials in the kiln. Some sulfur oxide reduction is also effected by the various equipment used for secondary particulate control. Estimates of the quantities of sulfur oxides emitted from kilns, both before and after controls, are presented in Table 8.15-1.

Hydrator emissions are low because water sprays or wet scrubbers are usually installed for economic reasons to prevent product loss in the exhaust gases. Emissions from pressure hydrators may be higher than from the more common atmospheric hydrators because the exhaust gases are released intermittently over short time intervals, making control more difficult.

Product coolers are emission sources only when some of their exhaust gases are not recycled through the kiln for use as combustion air. The trend is away from the venting of product cooler exhaust, however, to maximize fuel use efficiencies. Cyclones, baghouses, and wet scrubbers have been employed on coolers for particulate control.

Other particulate sources in lime plants include primary and secondary crushers, mills, screens, mechanical and pneumatic transfer operations, storage piles, and unpaved roads. If quarrying is a part of the lime plant operation, particulate may also result from drilling and blasting. Emission factors for some of these operations are presented in Sections 8.20 and 11.2.

Emission factors for lime manufacturing are presented in Table 8.15-1.

Table 8.15-1. EMISSION FACTORS FOR LIME MANUFACTURING
EMISSION FACTOR RATING: B

Source	Emissions[a]							
	Particulate		Sulfur dioxide		Nitrogen oxides		Carbon monoxide	
	lb/ton	kg/MT	lb/ton	kg/MT	lb/t	kg/MT	lb/ton	kg/MT
Crushers, screens, conveyors, storage piles, unpaved roads	b	b	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.
Rotary kilns								
Uncontrolled[c]	340	170	d	d	3	1.5	2	1
After settling chamber or large diameter cyclone	200	100	d	d	3	1.5	2	1
After multiple cyclones	85[e]	43[e]	d	d	3	1.5	2	1
After secondary dust collection[f]	1	0.5	g	g	3	1.5	2	1
Vertical kilns								
Uncontrolled	8	4	NA[h]	NA[h]	NA	NA	NA	NA
Calcimatic kilns[i]								
Uncontrolled	50	25	NA	NA	0.2	0.1	NA	NA
After multiple cyclones	6	3	NA	NA	0.2	0.1	NA	NA
After secondary dust collection[j]	NA	NA	NA	NA	0.2	0.1	NA	NA
Fluidized-bed kilns	NA[k]	NA[k]	NA	NA	NA	NA	NA	NA
Product coolers								
Uncontrolled	40[l]	20[l]	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.
Hydrators	0.1[m]	0.05[m]	Neg.	Neg.	Neg.	Neg.	Neg.	Neg.

[a] All emission factors for kilns and coolers are per unit of lime produced. Divide by two to obtain factors per unit of limestone feed to the kiln. Factors for hydrators are per unit of hydrated lime produced. Multiply by 1.25 to obtain factors per unit of lime feed to the hydrator. All emissions data are based on References 4 through 6.

[b] Emission factors for these operations are presented in Sections 8.20 and 11.2.

[c] No particulate control except for settling that may occur in the stack breeching and chimney base.

[d] When low-sulfur (less than 1 percent, by weight) fuels are used, only about 10 percent of the fuel sulfur is emitted as SO_2. When high-sulfur fuels are used, approximately 50 percent of the fuel sulfur is emitted as SO_2.

[e] This factor should be used when coal is fired in the kiln. Limited data suggest that when only natural gas or oil is fired, particulate emissions after multiple cyclones may be as low as 20 to 30 lb/ton (10 to 15 kg/MT).

[f] Fabric or gravel bed filters, electrostatic precipitators, or wet (most commonly venturi) scrubbers. Particulate concentrations as low as 0.2 lb/ton (0.1 kg/MT) have been achieved using these devices.

[g] When scrubbers are used, less than 5 percent of the fuel sulfur will be emitted as SO_2, even with high-sulfur coal. When other secondary collection devices are used, about 20 percent of the fuel sulfur will be emitted as SO_2 with high-sulfur fuels and less than 10 percent with low-sulfur fuels.

[h] Not available.

[i] Calcimatic kilns generally employ stone preheaters. All factors represent emissions after the kiln exhaust passes through a preheater.

[j] Fabric filters and venturi scrubbers have been employed on calcimatic kilns. No data are available on particulate emissions after secondary control.

[k] Fluidized-bed kilns must employ sophisticated dust collection equipment for process economics; hence, particulate emissions will depend on the efficiency of the control equipment installed.

[l] Some or all of the cooler exhaust is typically used in the kiln as combustion air. Emissions will result only from that fraction that is not recycled to the kiln.

[m] This is a typical particulate loading for atmospheric hydrators following water sprays or wet scrubbers. Limited data suggest particulate emissions from pressure hydrators may be approximately 2 lb/ton (1 kg/MT) of hydrate produced, after wet collectors.

Table 10.1.2-1. EMISSION FACTORS FOR SULFATE PULPING[a]
(unit weights of air-dried unbleached pulp)
EMISSION FACTOR RATING: A

Source	Type control	Particulates[b]		Sulfur dioxide (SO_2)[c]		Carbon monoxide[d]		Hydrogen sulfide($S^=$)[e]		RSH, RSR, RSSR($S^=$)[e,f]	
		lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT	lb/ton	kg/MT
Digester relief and blow tank	Untreated[g]	–	–	–	–	–	–	0.1	0.05	1.5	0.75
Brown stock washers	Untreated	–	–	0.01	0.005	–	–	0.02	0.01	0.2	0.1
Multiple effect evaporators	Untreated[g]	–	–	0.01	0.005	–	–	0.1	0.05	0.4	0.2
Recovery boiler and direct contact evaporator	Untreated[h]	150	75	5	2.5	2 - 60	1 - 30	12[i]	6[i]	1[i]	0.5[i]
	Venturi scrubber[j]	47	23.5	5	2.5	2 - 60	1 - 30	12[i]	6[i]	1[i]	0.5[i]
	Electrostatic precipitator	8	4	5	2.5	2 - 60	1 - 30	12[j]	6[i]	1[i]	0.5[i]
	Auxiliary scrubber	3 - 15[k]	1.5-7.5[k]	3	1.5	2 - 60	1 - 30	12[j]	6[i]	1[i]	0.5[i]
Smelt dissolving tank	Untreated	5	2.5	0.1	0.05	–	–	0.04	0.02	0.4	0.2
	Mesh pad	1	0.5	0.1	0.05	–	–	0.04	0.02	0.4	0.2
Lime kilns	Untreated	45	22.5	0.3	0.15	10	5	0.5	0.25	0.25	0.125
	Scrubber	3	1.5	0.2	0.1	10	5	0.5	0.25	0.25	0.125
Turpentine condenser	Untreated	–	–	–	–	–	–	0.01	0.005	0.5	0.25
Miscellaneous sources[l]	Untreated	–	–	–	–	–	–	–	–	0.5	0.25

[a] For more detailed data on specific types of mills, consult Reference 1.

[b] References 1, 7, 8.

[c] References 1, 7, 9, 10.

[d] References 6, 11. Use higher value for overloaded furnaces.

[e] References 1, 4, 7-10, 12, 13. These reduced sulfur compounds are usually expressed as sulfur.

[f] RSH-methyl mercaptan; RSR-dimethyl sulfide; RSSR-dimethyl disulfide.

[g] If the noncondensible gases from these sources are vented to the lime kiln, recovery furnace, or equivalent, the reduced sulfur compounds are destroyed..

[h] These factors apply when either a cyclonic scrubber or cascade evaporator is used for direct contact evaporation with no further controls.

[i] These reduced sulfur compounds (TRS) are typically reduced by 50 percent when black liquor oxidation is employed but can be cut by 90 to 99 percent when oxidation is complete and the recovery furnace is operated optimally.

[j] These factors apply when a venturi scrubber is used for direct contact evaporation with no further controls.

[k] Use 15(7.5) when the auxiliary scrubber follows a venturi scrubber and 3(1.5) when employed after an electrostatic precipitator.

[l] Includes knotter vents, brownstock seal tanks, etc., When black liquor oxidation is included, a factor of 0.6(0.3) should be used.