

# Memorandum

## Florida Department of Environmental Protection

TO: Howard L. Rhodes

THROUGH: Dotty Diltz *[Signature]*

FROM: M. D. Harley *[Signature]*

DATE: February 24, 1997

SUBJECT: Approval of Alternate Sampling Procedure for Georgia-Pacific Corporation,  
No. 4 Recovery Furnace, Palatka, Florida, Order No. 92-P-01

RECEIVED

MAR 26 2004

STATE OF FLORIDA  
DEPT. OF ENV. PROTECTION

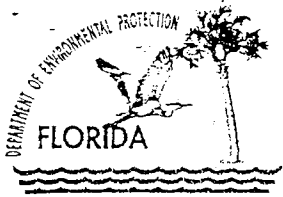
Attached for your approval and signature is an Order prepared by the Bureau of Air Monitoring and Mobile Sources that authorizes Georgia-Pacific to use a modified version of EPA Method 8, which incorporates the EPA Method 8 train and a heated quartz filter, to measure sulfuric acid mist emissions from the No. 4 Recovery Furnace at their Palatka facility. The EPA headquarters and Region 4 Office concur with the action proposed by the recommended Order.

The request for approval of an alternate sampling procedure is based on the NCASI Air Quality Improvement Technical Bulletin No. 106, entitled, "A Study of SO<sub>x</sub> Measurement Procedures and Their Use at Kraft Recovery Furnaces" and results of comparative testing between EPA Method 8 and NCASI Method 106 on the No. 4 Recovery Furnace. These findings indicate that the positive bias in EPA Method 8 measurements, which results from the presence of sulfate particulate, is minimized through the use of NCASI Method 106.

I recommend your approval and signature.

MDH/mb

Attachments



ORIGINAL

# Department of Environmental Protection

Lawton Chiles  
Governor

Twin Towers Office Building  
2600 Blair Stone Road  
Tallahassee, Florida 32399-2400

Virginia B. Wetherell  
Secretary

March 4, 1996

Certified Mail - Return Receipt Requested

Myra Carpenter  
Superintendent of  
Environmental Affairs  
Georgia-Pacific Corporation  
Post Office Box 919  
Palatka, Florida 32178-0919

Dear Ms. Carpenter:

Enclosed is a copy of an administrative order concerning the request for approval to use NCASI Method 106 in lieu of EPA Reference Method 8 for the measurement of sulfuric acid mist emissions from your No. 4 Recovery Furnace.

If you have any questions concerning the above, please call Matthew Benson at 904/488-6140, or write to me.

Sincerely,

M. D. Harley, P.E., DEE  
P.E. Administrator  
Emissions Monitoring Section  
Bureau of Air Monitoring and  
Mobile Sources

MDH:mdb

Enclosure

cc: Scott H. Osborne, FPC  
Pat Comer, FDEP  
Bill Thomas, Southwest District  
Peter A. Hessling, PCDEM

*"Protect, Conserve and Manage Florida's Environment and Natural Resources"*

*Printed on recycled paper.*

STATE OF FLORIDA  
DEPARTMENT OF ENVIRONMENTAL PROTECTION

In the matter of:	)	
	)	
Georgia-Pacific Corporation,	)	ASP No. 92-P-01
	)	
Petitioner.	)	

ORDER ON REQUEST  
FOR  
ALTERNATE PROCEDURES AND REQUIREMENTS

Pursuant to Rule 62-297.620, Florida Administrative Code (F.A.C.), Georgia-Pacific Corporation petitioned for approval to use the method arrived at in NCASI (National Council of the Paper Industry for Air and Stream Improvement, Inc.) Atmospheric Quality Improvement Technical Bulletin No. 106, entitled, "A Study of SO<sub>x</sub> Measurement Procedures and their use at Kraft Recovery Furnaces", in lieu of EPA Method 8 for the measurement of sulfuric acid mist from the No. 4 Recovery Furnace, permit number AC 54-266676, at Petitioner's facility in Palatka, Putnam County, Florida.

Having considered Petitioner's written request and all supporting documentation, the following Findings of Fact, Conclusions of Law, and Order are entered:

FINDINGS OF FACT

1. Petitioner requested approval to use a modified version of EPA Reference Method 8 which incorporates a heated quartz filter, as described by NCASI Atmospheric Quality Improvement Technical Bulletin No. 106, to measure sulfuric acid mist (SAM), in lieu of Method 8. [Exhibit 1]

2. As justification for use of the alternate sampling procedure, Petitioner stated, "According to Appendix A of Title 40 part 60, Code of Federal Regulations, this method is applicable for the determination of sulfuric acid mist (including sulfur trioxide) and sulfur dioxide emissions from stationary sources in the absence of particulate matter. Therefore, EPA Method 8 is not appropriate for measuring emissions on Kraft recovery furnaces." In addition, Petitioner stated, "NCASI recommends using a Method 8 train with a heated quartz filter in lieu of EPA Method 8 for determining compliance with SAM emission limitations because of the particulate matter present in Kraft recovery furnace flue gases. Most of the particulate is sodium sulfate, of which the sulfate fraction will be reported as SO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub>. This results in a significant positive bias." [Exhibit 1]

3. The previously issued construction permit for the No. 4 Recovery Boiler, permit number AC 54-192550, states, "Sulfuric acid mist emissions shall not exceed 3.24 lbs/hr (14.2 TPY; based on 0.81 ppm in the stack gases (NCASI Technical Bulletin No. 106) and 427,560 acfm)." [Exhibit 2]

4. As stated above, a sulfuric acid mist concentration of 0.81 ppm in the stack gases is based upon results in the NCASI Technical Bulletin No. 106. The results are as follows: "Field tests on five Kraft recovery furnaces showed  $\text{SO}_3/\text{H}_2\text{SO}_4$  concentrations on the order of 0 to 2.98 ppm, with an average of 0.81 ppm." These test results were obtained using a modified version of EPA Method 8, which incorporates an EPA Method 8 train with a heated quartz filter, as described in NCASI Technical Bulletin No. 106. [Exhibit 3]

5. Upon reviewing Petitioner's request, the Region 4 Office of the U.S. EPA conditionally recommended approval of the proposed method in NCASI Technical Bulletin No. 106 for the measurement of sulfuric acid mist from the No. 4 Recovery Boiler. [Exhibit 4]

6. Region 4 stated, "... the GP concerns are valid since sulfate particulate in the flue gas would be collected in the first impinger if the sample train is operated without a filter between the probe and first impinger. Any sulfate particulate captured in the first impinger could dissociate and form sulfate ions that would cause a high bias in acid mist/ $\text{SO}_3$  results when the contents of the first impinger are analyzed by barium-thorin titration". In addition, Region 4 also stated, "... it has been determined that including a heated filter between the probe and the first impinger in the Method 8 sample train used for sulfuric acid mist/ $\text{SO}_3$  testing on the No. 4 recovery furnace at GP will be acceptable if the filter and probe are heated to a temperature of at least 320°F during sampling." [Exhibit 4]

7. The test report for the EPA Method 8 and NCASI Method 106 emission tests conducted on the No. 4 Recovery Furnace indicates that the above recommendations of the Region 4 Office of the U.S. EPA were implemented. Also, Table 2.3. of the test report, entitled, " $\text{SO}_2$  AND  $\text{H}_2\text{SO}_4$  EMISSION DATA - NO. 4 RECOVERY FURNACE", presents a comparison between the sulfuric acid mist emission test results for EPA Method 8 and NCASI Method 106. The results for NCASI 106 are significantly lower than those obtained with EPA Method 8. The results are also similar in magnitude to the permit limit, which was based upon results obtained from the NCASI Method 106 testing of five Kraft recovery furnaces. [Exhibit 5]

8. Upon review of NCASI Technical Bulletin No. 106, the U.S. EPA stated to NCASI that, "We believe that your evaluation convincingly demonstrates that your candidate method can accurately measure sulfuric acid emission from Kraft recovery furnaces. We have concluded that this method, which you identified as Method 8A, should be used instead of Method 8 when measuring sulfuric acid from Kraft recovery furnaces." [Exhibit 6]

9. On December 20, 1996 the Department received a copy of the NCASI recovery furnace  $\text{SO}_3/\text{H}_2\text{SO}_4$  testing method, described in NCASI Technical Bulletin No. 106, in a format similar to an EPA reference method. [Exhibit 7].

### CONCLUSIONS OF LAW

1. The Department has jurisdiction to consider Petitioner's request pursuant to Section 403.061, Florida Statutes (F.S.), and Rule 62-297.620, F.A.C.
2. Pursuant to Rule 62-297.310(7), F.A.C., the Department may require Petitioner to conduct compliance tests that identify the nature and quantity of pollutant emissions, if, after investigation, it is believed that any applicable emission standard or condition of the applicable permits is being violated.
3. Petitioner has provided reasonable justification that the use of the method described in NCASI Atmospheric Quality Improvement Technical Bulletin No. 106, for the measurement of sulfuric acid mist, will be adequate to verify compliance with the applicable standard.

### ORDER

Having considered Petitioner's written request and supporting documentation, it is hereby ordered that:

1. Petitioner shall use a modified version of EPA Reference Method 8 incorporating a Method 8 train with a heated quartz filter, as described by NCASI Atmospheric Quality Improvement Technical Bulletin No. 106, to measure sulfuric acid mist from the No. 4 Recovery Boiler; and,
2. Pursuant to Rule 62-297.310(8), F.A.C., Petitioner shall submit the compliance test report to the District Director of the Department's Northeast District Office within 45 days of completion of the test.

### PETITION FOR ADMINISTRATIVE REVIEW

The Department will take the action described in this Order unless a timely petition for an administrative hearing is filed pursuant to sections 120.569 and 120.57 of the Florida Statutes, or a party requests mediation as an alternative remedy under section 120.573 before the deadline for filing a petition. Choosing mediation will not adversely affect the right to a hearing if mediation does not result in a settlement. The procedures for petitioning for a hearing are set forth below, followed by the procedures for requesting mediation.

A person whose substantial interests are affected by the Department's proposed decision may petition for an administrative hearing in accordance with sections 120.569 and 120.57 of the Florida Statutes. The petition must contain the information set forth below and must be filed (received) in the Office of General Counsel of the Department at 3900 Commonwealth Boulevard,

Mail Station 35, Tallahassee, Florida 32399-3000. Petitions must be filed within 21 days of receipt of this Order. A petitioner must mail a copy of the petition to the applicant at the address indicated above, at the time of filing. The failure of any person to file a petition (or a request for mediation, as discussed below) within the appropriate time period shall constitute a waiver of that person's right to request an administrative determination (hearing) under sections 120.569 and 120.57 of the Florida Statutes, or to intervene in this proceeding and participate as a party to it. Any subsequent intervention will be only at the approval of the presiding officer upon the filing of a motion in compliance with Rule 28-5.207 of the Florida Administrative Code.

A petition must contain the following information:

- (a) The name, address, and telephone number of each petitioner, the applicant's name and address, the Department File Number, and the county in which the project is proposed;
- (b) A statement of how and when each petitioner received notice of the Department's action or proposed action;
- (c) A statement of how each petitioner's substantial interests are affected by the Department's action or proposed action;
- (d) A statement of the material facts disputed by each petitioner, if any;
- (e) A statement of facts that the petitioner contends warrant reversal or modification of the Department's action or proposed action;
- (f) A statement identifying the rules or statutes each petitioner contends require reversal or modification of the Department's action or proposed action; and,
- (g) A statement of the relief sought by each petitioner, stating precisely the action each petitioner wants the Department to take with respect to the Department's action or proposed action in the notice of intent.

Because the administrative hearing process is designed to formulate final agency action, the filing of a petition means that the Department's final action may be different from the position taken by it in this Order. Persons whose substantial interests will be affected by any such final decision of the Department on the application have the right to petition to become a party to the proceeding, in accordance with the requirements set forth above.

A person whose substantial interests are affected by the Department's proposed decision, may elect to pursue mediation by asking all parties to the proceeding to agree to such mediation and by filing with the Department a request for mediation and the written agreement of all such parties to mediate the dispute. The request and agreement must be filed in (received by) the Office of General Counsel of the Department at 3900 Commonwealth Boulevard, Mail Station 35, Tallahassee, Florida 32399-3000, by the same deadline as set forth above for the filing of a petition.

A request for mediation must contain the following information:

- (a) The name, address, and telephone number of the person requesting mediation and that person's representative, if any;
- (b) A statement of the preliminary agency action;
- (c) A statement of the relief sought; and
- (d) Either an explanation of how the requester's substantial interests will be affected by the action or proposed action addressed in this notice of intent or a statement clearly identifying the petition for hearing that the requester has already filed, and incorporating it by reference.

The agreement to mediate must include the following:

- (a) The names, addresses, and telephone numbers of any persons who may attend the mediation;
- (b) The name, address, and telephone number of the mediator selected by the parties, or a provision for selecting a mediator within a specified time;
- (c) The agreed allocation of the costs and fees associated with the mediation;
- (d) The agreement of the parties on the confidentiality of discussions and documents introduced during mediation;
- (e) The date, time, and place of the first mediation session, or a deadline for holding the first session, if no mediator has yet been chosen;
- (f) The name of each party's representative who shall have authority to settle or recommend settlement; and
- (g) The signatures of all parties or their authorized representatives.

As provided in section 120.573 of the Florida Statutes, the timely agreement of all parties to mediate will toll the time limitations imposed by sections 120.569 and 120.57 for requesting and holding an administrative hearing. Unless otherwise agreed by the parties, the mediation must be concluded within sixty days of the execution of the agreement. If mediation results in settlement of the administrative dispute, the Department must enter a final order incorporating the agreement of the parties. Persons whose substantial interests will be affected by such a modified final decision of the Department have a right to petition for a hearing only in accordance with the requirements for such petitions set forth above. If mediation terminates without settlement of the dispute, the Department shall notify all parties in writing that the administrative hearing processes under sections 120.569 and 120.57 remain available for disposition of the dispute, and the notice

will specify the deadlines that then will apply for challenging the agency action and electing remedies under those two statutes.

In addition to the above, a person subject to regulation has a right to apply for a variance from or waiver of the requirements of particular rules, on certain conditions, under section 120.542 of the Florida Statutes. The relief provided by this state statute applies only to state rules, not statutes, and not to any federal regulatory requirements. Applying for a variance or waiver does not substitute or extend the time for filing a petition for an administrative hearing or exercising any other right that a person may have in relation to the action proposed in this notice of intent.

The application for a variance or waiver is made by filing a petition with the Office of General Counsel of the Department, 3900 Commonwealth Boulevard, Mail Station 35, Tallahassee, Florida 32399-3000.

The petition must specify the following information:

- (a) The name, address, and telephone number of the petitioner;
- (b) The name, address, and telephone number of the attorney or qualified representative of the petitioner, if any;
- (c) Each rule or portion of a rule from which a variance or waiver is requested;
- (d) The citation to the statute underlying (implemented by) the rule identified in (c) above;
- (e) The type of action requested;
- (f) The specific facts that would justify a variance or waiver for the petitioner;
- (g) The reason why the variance or waiver would serve the purposes of the underlying statute (implemented by the rule); and
- (h) A statement whether the variance or waiver is permanent or temporary and, if temporary, a statement of the dates showing the duration of the variance or waiver requested.

The Department will grant a variance or waiver when the petition demonstrates both that the application of the rule would create a substantial hardship or violate principles of fairness, as each of those terms is defined in section 120.542(2) of the Florida Statutes, and that the purpose of the underlying statute will be or has been achieved by other means by the petitioner. Persons subject to regulation pursuant to any federally delegated or approved air program should be aware that Florida is specifically not authorized to issue variances or waivers from any requirements of any such federally delegated or approved program. The requirements of the program remain fully enforceable by the Administrator of the EPA and by any person under the Clean Air Act unless



and until the Administrator separately approves any variance or waiver in accordance with the procedures of the federal program.

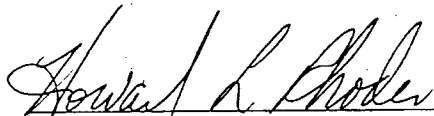
This Order constitutes final agency action unless a petition is filed in accordance with the above paragraphs. Upon timely filing of a petition, this Order will not be effective until further Order of the Department.

#### RIGHT TO APPEAL

Any party to this Order has the right to seek judicial review of the Order pursuant to Section 120.68, F.S., by the filing of a Notice of Appeal pursuant to Rule 9.110, Florida Rules of Appellate Procedure, with the Clerk of the Department in the Office of General Counsel, 3900 Commonwealth Boulevard, Mail Station 35, Tallahassee, Florida 32399-3000; and, by filing a copy of the Notice of Appeal accompanied by the applicable filing fees with the appropriate District Court of Appeal. The Notice of Appeal must be filed within 30 days from the date the Notice of Agency Action is filed with the Clerk of the Department.

DONE AND ORDERED this 17 day of Feb, 1997 in Tallahassee, Florida.

STATE OF FLORIDA DEPARTMENT  
OF ENVIRONMENTAL PROTECTION



HOWARD L. RHODES, Director  
Division of Air Resources Management  
Twin Towers Office Building  
2600 Blair Stone Road  
Tallahassee, Florida 32399-2400  
(904) 488-0114

**CERTIFICATE OF SERVICE**

The undersigned duly designated deputy clerk hereby certifies that a true copy of the foregoing was mailed to Myra Carpenter, Superintendent of Environmental Affairs, Georgia Pacific Corporation, Post Office Box 919, Palatka, Florida 32178-0919 on this 4<sup>th</sup> day of March 1997.

Clerk Stamp

**FILING AND ACKNOWLEDGMENT**

**FILED**, on this date, pursuant to §120.52(11), Florida Statutes, with the designated Department Clerk, receipt of which is hereby acknowledged.

Myra Janellise 3/4/97  
Clerk Date



Georgia-Pacific Corporation

Palatka Operations  
Southern Pulp & Paper  
P.O. Box 919  
Palatka, Florida 32178-0919  
Telephone (904) 325-2001

November 12, 1992

RECEIVED

NOV 17 1992

Division of Air  
Resources Management

Mr. Mike Harley, P.E.  
Administrator  
Division of Air Resource Management  
Emissions Monitoring Section  
Florida Department of Environmental Regulation  
Twin Towers Office Building  
2600 Blair Stone Road  
Tallahassee, Florida 32399-2400

RE: Georgia-Pacific Corporation, Palatka, Florida - Request for Exception and Approval of an Alternate Sampling Procedure (SAM)

Dear Mr. Harley:

The purpose of this letter is to provide the basis for requesting approval from the Florida Department of Environmental Regulation (FDER) of an alternate sampling procedure (ASP) when conducting sulfuric acid mist (SAM) emission testing on the No. 4 Recovery Furnace at the Georgia-Pacific Corporation (G-P) mill located in Palatka, Florida. This ASP request is in accordance with Chapter 17-2.700(3), F.A.C.

1. Source and Permit Number

No. 4 Recovery Furnace Number AO54-209650

2. Current Regulations and Requested Exception

Section 17-2.700, F.A.C., pertains to source emission test procedures to be used for emission compliance testing. The No. 4 Recovery Furnace is by rule and specific conditions of its permit, subject to the source sampling method of Section 17-2.700, F.A.C., i.e., EPA Reference Method 8 for the measurement of SAM emissions.

Exception is being sought to change the SAM emission test methodology as required in the permit from EPA Reference Method 8 to a modified



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EXHIBIT 1

MR. MIKE HARLEY, P.E.

Page Two

November 12, 1992

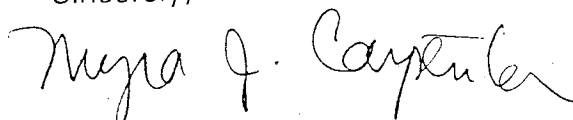
version of the EPA Reference Method 8 incorporating a Method 8 train with a heated quartz filter, as described by NCASI Air Technical Bulletin No. 106.

3. Basis for Exception

- A. EPA Method 8 was developed for sulfuric acid plants which do not emit any sulfate salts. Consequently, the method does not include a particulate filter. According to Appendix A of Title 40 Part 60, Code of Federal Regulations, this method is applicable for the determination of sulfuric acid mist (including sulfur trioxide) and sulfur dioxide emissions from stationary sources in the absence of other particulate matter. Therefore, EPA Method 8 is not appropriate for measuring emissions on kraft recovery furnaces.
- B. NCASI recommends using a Method 8 train with a heated quartz filter in lieu of EPA Method 8 for determining compliance with SAM emission limitations because of the particulate matter present in kraft recovery furnace flue gasses. Most of the particulate is sodium sulfate, of which the sulfate fraction will be reported as  $\text{SO}_3/\text{H}_2\text{SO}_4$ . This results in a significant positive bias (see attachment).

We appreciate the Department's consideration of our request for an alternate sampling procedure. If you have any questions, please call me or Vernon Adams at 904-325-2001.

Sincerely,



Myra J. Carpenter  
Senior Environmental Engineer

kb

Attachment

MR. MIKE HARLEY, P.E.

Page Three

November 12, 1992

cc: V. L. Adams  
W. L. Baxter  
J. L. Mullis  
W. R. Wilson  
L. C. Yarbrough  
C. S. Cooley, GA030, G-48

## NATIONAL COUNCIL OF THE PAPER INDUSTRY FOR AIR AND STREAM IMPROVEMENT, INC.

October 20, 1992

Ms. Myra J. Carpenter  
Georgia-Pacific Corporation  
Post Office Box 919  
Palatka, Florida 32077

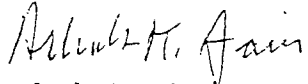
Dear Myra:

This is to follow-up on our discussion relative to the measurement of  $\text{SO}_3/\text{H}_2\text{SO}_4$  in kraft recovery furnace stack gases. As I indicated to you, EPA Method 8 was developed for testing  $\text{SO}_3/\text{H}_2\text{SO}_4$  emissions from sulfuric acid plants which do not emit any sulfate salts and, consequently, the method does not include a particulate filter. The flue gases from kraft recovery furnaces, however, contain a significant amount of particulate, most of which is sodium sulfate. If Method 8 is used for  $\text{SO}_3/\text{H}_2\text{SO}_4$  testing on kraft recovery furnaces, the sulfate fraction of the sodium sulfate contained in the particulate matter will be reported as  $\text{SO}_3/\text{H}_2\text{SO}_4$ , resulting in a significant positive bias. For example, kraft recovery furnace flue gases containing 0.044 gr/SDCF of particulate, 80 percent of which is sodium sulfate, would show 14 ppm  $\text{H}_2\text{SO}_4$  according to Method 8. (In the EPA-funded NCASI study of kraft recovery furnace sulfuric acid emissions reported in NCASI Atmospheric Quality Improvement Technical Bulletin No. 106, April, 1980, the results of tests at five recovery furnaces showed a range of from not detected to 3.0 ppm sulfuric acid, with a mean of 0.81 ppm.)

In our tests of kraft recovery furnaces, in order to correct the problem of  $\text{Na}_2\text{SO}_4$  interference, we used a heated quartz filter. The design of the filter and our experience with its use are described in Air Technical Bulletin No. 106. The sampling train described in TB 106 included a controlled condensation apparatus, which is not essential. If NCASI were involved today in a study aimed at measuring  $\text{SO}_3/\text{H}_2\text{SO}_4$  emissions from a kraft recovery furnace we would use the Method 8 train with a heated quartz filter, as per Air Technical Bulletin No. 106.

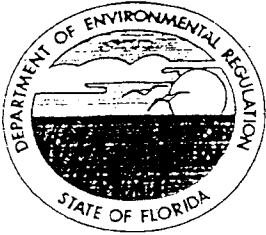
I hope that the above discussion is adequate for your current information needs. Should you need additional information, please call.

Sincerely,

A handwritten signature in cursive script, appearing to read "Ashok K. Jain".

Ashok K. Jain  
Regional Manager

AKJ:tls



## Florida Department of Environmental Regulation

Twin Towers Office Bldg. • 2600 Blair Stone Road • Tallahassee, Florida 32399-2400

Lawton Chiles, Governor

Carol M. Browner, Secretary

### PERMITTEE:

Georgia-Pacific Corporation  
P. O. Box 919  
Palatka, Florida 32078-0919

Permit Numbers: AC 54-192550

PSD-FL-171

Expiration Date: May 31, 1992

County: Putnam

Latitude/Longitude: 29°41'00"N  
81°40'45"W

Project: No. 4 Recovery Boiler

This permit is issued under the provisions of Chapter 403, Florida Statutes, Florida Administrative Code (F.A.C.) Chapters 17-2 and 17-4, and 40 CFR (July 1, 1990 version). The above named permittee is hereby authorized to perform the work or operate the facility shown on the application and approved drawing(s), plans, and other documents attached hereto or on file with the Department and made a part hereof and specifically described as follows:

For the modification of the No. 4 Recovery Boiler to allow an increase in the total process input rate of black liquor solids (BLS) and the potential pollutant emissions. The maximum total process input rate is 323,077 black liquor @ 65% solids. An electrostatic precipitator (ESP) is used to control PM/PM<sub>10</sub> emissions and visible emissions and has a minimum design efficiency of 99% for the control of particulate matter of submicron size. The project will occur at the permittee's existing facility/mill located north of S.R. 216 and west of U.S. 17. The UTM coordinates are Zone 17, 434.0 km East and 3283.4 km North.

The Standard Industrial Codes are: Industry No. 2611-Pulp Mills

The Standard Classification Codes are: Pulp & Paper Industry

Major Group 26: Sulfate (Kraft) Pulping

o Recovery Furnace/Direct 3-07-001-04 tons ADUP (air dried  
Contact Evaporator unbleached pulp)

The source shall be constructed in accordance with the permit application, plans, documents, amendments, drawings, and supplementary information, except as otherwise noted in the General and Specific Conditions.

Attachments are listed below:

1. Application to Modify Air Pollution Sources, DER Form 17-1.202(1), received February 13, 1991.
2. Mr. Vernon L. Adam's letter with attachments received March 8, 1991.
3. Ms. Jewell A. Harper's letter received March 12, 1991, via FAX.
4. Mr. Andrew Kutyna's Interoffice Memorandum received March 13, 1991, via FAX.
5. Mr. C. H. Fancy's letter dated March 15, 1991.
6. Mr. Vernon L. Adam's letter with attachments received March 18, 1991.



PERMITTEE:

Permit Number: AC 54-192550

PSD-FL-171

Georgia-Pacific Corporation

Expiration Date: May 31, 1992

SPECIFIC CONDITIONS:

5. Sulfur dioxide ( $\text{SO}_2$ ) emissions shall not exceed 109.9 lbs/hr (481.4 TPY).
6. Sulfuric acid mist emissions shall not exceed 3.24 lbs/hr (14.2 TPY; based on 0.81 ppm in the stack gases (NCASI Technical Bulletin No. 106) and 427,560 acfm).
7. Objectionable odors shall not be allowed off plant property in accordance with F.A.C. Rule 17-2.620(2).
8.
  - a. The initial and annual compliance tests for  $\text{PM}/\text{PM}_{10}$  shall be conducted using EPA Method 5, Determination of Particulate Emissions from Stationary Sources, which includes EPA Methods 1-4, in accordance with F.A.C. Rule 17-2.700 and 40 CFR 60, Appendix A;
  - b. The initial and annual compliance tests for TRS shall be conducted using EPA Method 16 or 16A, Determination of TRS Emissions from Stationary Sources, in accordance with F.A.C. Rule 17-2.700 and 40 CFR 60, Appendix A;
  - c. The initial and annual compliance tests for  $\text{SO}_2$  shall be conducted using EPA Method 8, Determination of Sulfuric Acid Mist and Sulfur Dioxide Emissions from Stationary Sources, in accordance with F.A.C. Rule 17-2.700 and 40 CFR 60, Appendix A;
  - d. The initial and annual compliance tests for  $\text{NO}_x$  shall be conducted using EPA Method 7E, Determination of Nitrogen Oxide Emissions from Stationary Sources, in accordance with F.A.C. Rule 17-2.700 and 40 CFR 60, Appendix A;
  - e. The initial and annual compliance tests for CO shall be conducted using EPA Method 10, Determination of Carbon Monoxide Emissions from Stationary Sources, in accordance with F.A.C. Rule 17-2.700 and 40 CFR 60, Appendix A;
  - f. The initial and annual compliance tests for VOC shall be conducted using EPA Method 25, Determination of Total Gaseous Non-Methane Organic Emissions from Stationary Sources, in accordance with F.A.C. Rule 17-2.700 and 40 CFR 60, Appendix A; and,
  - g. The initial and annual compliance tests for VE shall be conducted using EPA Method 9, Visual Determination of the Opacity Emissions from Stationary Sources, in accordance with F.A.C. Rule 17-2.700 and 40 CFR 60, Appendix A.

# ncasi

# technical bulletin

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

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## A STUDY OF SO<sub>x</sub> MEASUREMENT PROCEDURES AND THEIR USE AT KRAFT RECOVERY FURNACES

ATMOSPHERIC QUALITY IMPROVEMENT  
TECHNICAL BULLETIN No. 106

APRIL 1980

EXHIBIT 3

Best results were obtained with Ace Glass Type C frit and a 200-cm coil when the temperature was maintained at 75 to 85°C (167 to 195°F).

(3) The flow rate and concentration of  $H_2SO_4$  did not significantly affect the efficiency of  $H_2SO_4$  capture in the condenser over the flow and concentration conditions studied.

(4) The quartz filter assembly did not cause any loss of  $H_2SO_4$  when it was maintained above 260°C (500°F).

(5) In the presence of particulate,  $H_2SO_4$  losses across the filter holder varied for different particulate samples.

(6) Field tests on five kraft recovery furnaces showed  $SO_3/H_2SO_4$  concentrations on the order of 0 to 2.98 ppm, with an average of 0.81 ppm. The  $SO_2$  concentrations during these tests varied from 14 to 416 ppm.

(7) An analysis of the emission data showed a poor correlation between  $SO_3/H_2SO_4$  and  $SO_2$  concentrations.

(8) The  $H_2SO_4$  concentrations in kraft recovery furnace flue gases are generally less than 10 percent of the  $H_2SO_4$  concentrations measured in oil- and coal-fired boiler stack gases.

## IX LITERATURE REFERENCES

- (1) Hillenbrand, L. J., R. B. Engdahl, and R. E. Barrett. Chemical Composition of Particulate Air Pollutants from Fossil-Fuel Combustion Sources. Battelle Columbus Laboratories, II-2 (March 1, 1973).
- (2) Yost, D. M. and H. Russell, Jr. Systematic Inorganic Chemistry. Prentice-Hall, Inc., N. Y., (1946), 336 pp.
- (3) Lundgren, D. A. and T. C. Gunderson. Filtration Characteristics of Glass Fiber Filter Media at Elevated Temperatures. EPA/2-76-192, U. S. Environmental Protection Agency, July 1976.
- (4) Thomas, J. S., and W. F. Barker. The Partial Pressure of Water Vapor and of Sulfuric Acid Over Concentrated Solutions of Sulfuric Acid at High Temperatures. J. Chem. Soc., London, 127 pp., (1925).
- (5) Abel, E. The Vapor Phase Above the System Sulfuric Acid-Water. J. Phys. Chem., 50, 260 (1946).



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

REGION IV

345 COURTLAND STREET, N.E.  
ATLANTA, GEORGIA 30365

APR 08 1993

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4APT-AEB

Mr. Michael D. Harley, P.E., DEE  
Administrator  
Emissions Monitoring Section  
Air Resources Management Division  
Florida Department of Environmental  
Regulation  
2600 Blair Stone Road  
Tallahassee, Florida 323989-2400

APR 14 1993

Division of Air  
Resources Management

RE: Alternative Sulfuric Acid Mist Testing Method Proposed by  
the Georgia-Pacific Corporation, Palatka, Florida

Dear Mr. Harley:

This letter is in response to your February 8, 1993, request that we review the referenced alternative test method proposed by the Georgia-Pacific Corporation (GP). After reviewing the proposal, it has been determined that including a heated filter between the probe and the first impinger in the Method 8 sample train used for sulfuric acid mist/SO<sub>3</sub> testing on the No. 4 recovery furnace at GP will be acceptable if the filter and probe are heated to a temperature of at least 320°F during sampling.

GP requested that they be allowed to include a heated filter between the probe and first impinger because of concerns that sulfate particulate in the boiler flue gas may cause a high bias in acid mist results. It has been determined that the GP concerns are valid since sulfate particulate in the flue gas would be collected in the first impinger if the sample train is operated without a filter between the probe and first impinger. Any sulfate particulate captured in the first impinger could dissociate and form sulfate ions that would cause a high bias in acid mist/SO<sub>3</sub> results when the contents of the first impinger are analyzed by barium-thorin titration.

The most practical approach to avoiding the potential high bias in acid mist/SO<sub>3</sub> results caused by sulfate particulate would be to include a heated filter between the probe and the first impinger in the Method 8 sample train. If this approach is used, however, the probe and filter should be heated to a temperature of at least 320°F in order to avoid a potential low bias in acid mist results caused by acid mist condensation on the filter. The recommended probe and filter temperature correspond to those specified in EPA Method 5B, which is the method that EPA has developed for avoiding positive biases in particulate results when sampling in gas streams where sulfuric acid mist may be present.

EXHIBIT 4

- 2 -

If you have any questions about the determination provided in this letter, please contact Mr. David McNeal of my staff at 404/347-5014.

Sincerely yours,

*for* *Jewell A. Harper*  
Jewell A. Harper, Chief  
Air Enforcement Branch  
Air, Pesticides, and Toxics  
Management Division



Georgia-Pacific Corporation

Palatka Operation  
South Pulp & Paper Manufacturing  
P.O. Box 919  
Palatka, Florida 32178-0919  
Telephone (904) 325-2001

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FEB 18 1994

Bureau of  
Air Regulation

February 16, 1994

Michael D. Harley  
Florida Department of Environmental Protection  
Administrator  
Emissions Monitoring Section  
Twin Towers Office Building  
2600 Blair Stone Road  
Tallahassee, Florida 32399-2400

Re: Georgia-Pacific Corporation (DEP #548515762) - Request for  
Exception and Approval of an Alternate Sampling Procedure for  
the Measurement of Sulfuric Acid Mist Fraction from No. 4  
Recovery Furnace

Dear Mr. Harley:

Georgia-Pacific wishes to proceed with the above referenced request for approval of an alternate test method. Attached are copies of sulfuric acid mist emission test reports for both EPA Method 8 and NCASI Method 106 emission tests conducted on the No. 4 Recovery Furnace on 17 February 1993. Although it was necessary to retest because the boiler was temporarily out of service until just a few hours before the February testing, the information can still be used to illustrate the inappropriateness of using Method 8 for measuring emissions on kraft recovery furnaces. We are attempting to resolve the issue of the crystalline form of the sodium sulfate particulate found in the furnace emissions and its solubility in alcohol with WESTON.

If you have any further questions please call me or Vernon Adams at (904) 325-2001.

Sincerely,

*Myra Carpenter*  
Myra Carpenter  
Sr. Environmental  
Engineer

cc: Vernon Adams (w/o attachments)  
Bill Baxter (w/o attachments)  
James Norwood (w/o attachments)  
Joe Oven - WESTON (w/o attachments)

EXHIBIT 5

Sulfuric acid mist was measured on the No. 4 Recovery Furnace using EPA Reference Method 8 and National Council of the Paper Industry for Air and Stream Improvement, Inc. (NCASI) Method 106. EPA Reference Method 8 results were approximately three times higher than NCASI Method 106 results. EPA Reference Method 8 is an inappropriate method for use on this source due to the presence of sulfate particulate matter which interferes with the analysis. EPA Reference Method 8 was promulgated for use with sulfuric acid plants with no particulate present. The results as measured by NCASI Method 106 are representative of the source.

The following subsections present the results obtained from each of the sources. Tables of data are presented and further discussion of the validity of the methods used is not included. One should realize that the sulfuric acid mist data presented by the use of EPA Reference Method 8 are not valid data.

TABLE 2.3. SO<sub>2</sub> AND H<sub>2</sub>SO<sub>4</sub> EMISSION DATA -  
NO. 4 RECOVERY FURNACE

	RUN 2 <sup>a</sup>	RUN 3	RUN 4	MEAN
Date	02/17/93	02/17/93	02/17/93	---
Time Began	1135	1336	1552	---
Time Ended	1246	1448	1701	---
Stack Gas				
Temperature, °F	405	403	405	404
Velocity, ft/sec	51.6	50.7	50.2	50.8
Moisture, %	28.2	28.8	27.9	28.3
CO <sub>2</sub> Concentration, %	14.0	14.0	14.2	14.1
O <sub>2</sub> Concentration, %	4.6	4.6	4.6	4.6
Volumetric Flow Rate				
At Stack Conditions, x 10 <sup>5</sup> ft <sup>3</sup> /min	4.22	4.14	4.10	4.15
At Standard Conditions <sup>b</sup> , x 10 <sup>5</sup> ft <sup>3</sup> /min	1.86	1.81	1.81	1.83
Sulfur Dioxide				
Isokinetic Sampling Rate, %	101	101	102	101
Concentration, ppmvd	203	175	118	165
Emission Rate, lb/hr	375	315	214	301
Permit Limit, lb/hr	---	---	---	109.9
Sulfuric Acid Mist				
Concentration, mg/dscm				
EPA 8	14.1	18.7	15.7	16.2
NCASI 106	5.85	6.51	6.47	6.28
Emission Rate, lb/hr				
EPA 8	9.77	12.7	10.7	11.0
NCASI 106	4.07	4.41	4.38	4.29
Permit Limit, lb/hr	---	---	---	3.24 <sup>c</sup>

<sup>a</sup>Run 1 was voided due to broken glassware.

<sup>b</sup>68°F, 29.92 in. Hg.

<sup>c</sup>Based on 0.81 ppm in gas (NCASI 106) and 427,560 acfm.



The probe and nozzle were washed with deionized water or acetone after each run to remove adhering particulate matter. The filter was removed from the holder and stored in aluminum foil until analyzed. The filter holder was then rinsed with the appropriate solvent. This rinse was added to the probe rinse. Liquid levels were marked, and the container was sealed and labeled for transport to the laboratory.

The mass of particulate matter on the filters was measured in the WESTON laboratory. The mass of particulate matter collected in the wash was analyzed in the laboratory by evaporating the solvent in a tared beaker and then measuring the residue. The filter tare mass and solvent blank corrections were subtracted from the final mass to give the mass of the particulate matter collected. The total mass was used to calculate the particulate concentration. Mass measurements were made on the same Mettler balance (accurate to 0.1 mg).

The mean temperatures of the stack gas and the dry gas meter were used in calculating the final data. The mean isokinetic sampling rate, the stack gas velocity, and the volumetric flow rate were calculated from the mean of the square roots of the velocity pressure measured at each traverse point.

#### Sulfur Dioxide, Sulfuric Acid Mist (EPA 8)

For the No. 4 Lime Kiln, sulfur dioxide testing was conducted in accordance with EPA Reference Method 8 in conjunction with EPA Reference Method 5. The first impinger contained 100 mL of 80 percent isopropanol. An empty impinger was placed between the first and third impingers to prevent sulfuric acid mist carry over. The third and fourth impingers each contained 100 mL of three percent hydrogen peroxide. The total impinger contents were measured and recorded, the first and second impinger contents were discarded, and the third and fourth impinger contents were retained for analysis. The analysis was performed by titrating the sample with barium chloride using thorin as an indicator.

For the No. 4 Recovery Furnace, sulfur dioxide and sulfuric acid mist testing were conducted in accordance with EPA Reference Method 8. A sampling train similar to Figures 3.1 and 3.2 was used, except for the filter location. A glass probe was used. The first impinger contained 100 mL of 80 percent isopropanol. A filter and empty impinger were placed between the first and third impingers to prevent sulfuric acid mist carry over. The third and fourth impingers each contained 100 mL of three percent hydrogen peroxide. The nozzle and probe were rinsed with deionized water, and this rinse and the filter were added to the first impinger. The analysis was performed by titrating the samples with barium chloride using thorin as an indicator.

#### Sulfuric Acid Mist (NCASI 106)

Sulfuric acid mist testing was performed using the most recent National Council of the Paper Industry for Air and Stream Improvement, Inc. (NCASI) procedure for measurement of sulfuric acid mist in a gas stream from a kraft process. A sketch of the sample train is presented in Figure 3.3.

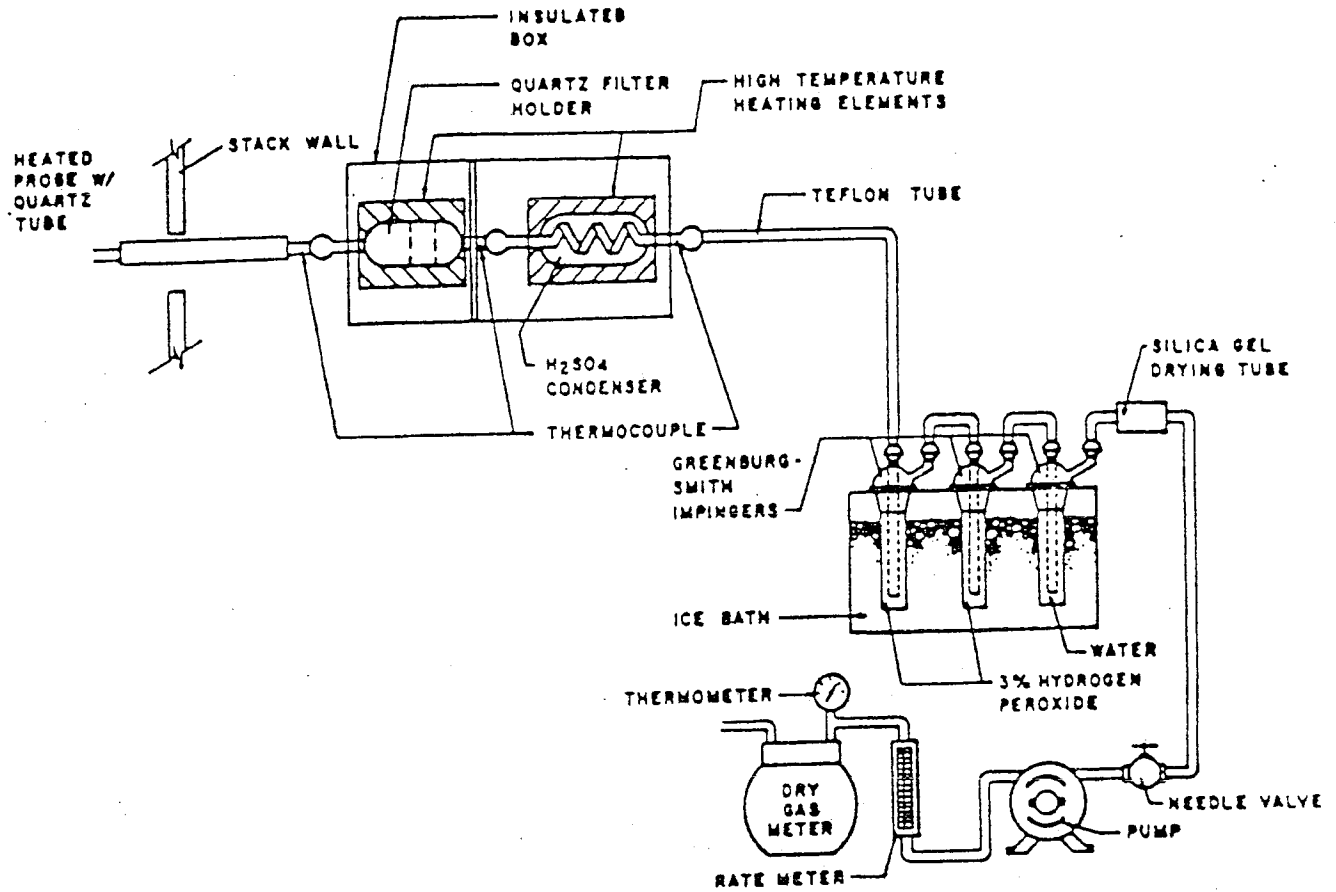


FIGURE 3.3. NCASI 106 SULFURIC ACID MIST SAMPLING TRAIN

The gas extracted from the stack was maintained at a temperature of 500°F through the probe and filter assembly to ensure no  $H_2SO_4$  loss on the filter. The gas then passed through the graham condenser which contained a 170°F water bath for the purpose of trapping the  $H_2SO_4$  on the frit located at the back of the condenser. At the conclusion of the test, the condenser was removed, rinsed with deionized water into a clean sample bottle, and analyzed by WESTON lab personnel. The analysis was performed by titrating the sample with barium chloride using thorin as an indicator.

### Nitrogen Oxides

Nitrogen oxides testing was conducted in accordance with EPA Reference Method 7E using a Teco Model 10 Analyzer. A heated sample line was used to sample stack gas at a rate of 1-4 L/min. A sample conditioner was used to remove moisture from the gas stream. Samples of gas were transported to a  $NO_x$ -to-NO converter to produce NO molecules. A chemiluminescent reaction of NO and ozone was then used to produce  $NO_2$ ,  $O_2$ , and ultraviolet light. This ultraviolet light was measured using a highly sensitive optical filter/photomultiplier whose output is linearly proportional to the NO concentration.

### Carbon Monoxide

Carbon monoxide testing was conducted in accordance with EPA Reference Method 10 using a Teco Model 48 CO Non-Dispersive Infrared (NDIR) Analyzer. A heated sample line was used to sample stack gas at a rate of 1-4 L/min. A sample conditioner was used to remove moisture from the gas stream. The analyzer used gas filter correlation spectroscopy to measure the amount of CO present in the sample. Infrared radiation was chopped and passed through an alternating CO and  $N_2$  correlation filter wheel and the sample stream. Carbon monoxide in the stream absorbed the infrared radiation, leaving the remaining radiation to be measured by a detector producing a linear output signal.

### Total Reduced Sulfur

The total reduced sulfur testing was performed using the techniques and procedures described in EPA Reference Method 16. Appendix H provides a detailed description of the methodology, equipment, and instrumentation normally used by WESTON to conduct TRS testing. That appendix also includes a discussion of calculation procedures and a demonstration of interference-free analysis of TRS in the presence of carbon dioxide. The following paragraphs summarize the methodology used during this project.

A Teflon-lined, stainless steel probe of sufficient length to monitor the gas stream without wall effects was used to extract a gas sample from the emission source. The probe tip was directed away from stack gas flow to minimize particulate and moisture entrainment. The probe was plumbed directly to the recovery gas line and sample conditioning system. EPA Reference Method 16 assumes uniform mixture of the stack gas; therefore, the stack was not traversed during testing.



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RESEARCH TRIANGLE PARK, NC 27711

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Bureau of Air Monitoring  
& Mobile Sources

Mr. Ashok Jain  
NCASI  
Southern Regional Center  
P.O. Box 141020  
Gainesville, Florida 32604

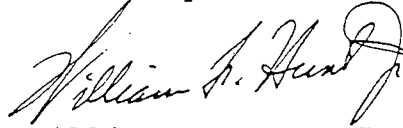
Dear Mr. Jain:

We have reviewed your Technical Bulletin 106 describing your study of sulfur oxide measurement procedures from Kraft recovery furnaces. Although you performed your evaluation before Method 301 existed, we believe that it demonstrates that your proposed test method for sulfuric acid from Kraft recovery furnaces is acceptable. If Method 301 had existed when you were evaluating candidate procedures, it would have required that you compare your candidate procedure to Method 8. However, as your evaluation shows, Method 8 has a potentially significant positive bias when used to measure sulfuric acid emissions from Kraft recovery furnaces. Thus, you could not compare your candidate method directly to Method 8. The alternative that you chose was to investigate as thoroughly as possible whether your candidate method could recover known amounts of sulfuric acid in the presence of the interferences typically found in a stack sample. We believe that your evaluation convincingly demonstrates that your candidate method can accurately measure sulfuric acid emissions from Kraft recovery furnaces. We have concluded that this method, which you identified as Method 8A, should be used instead of Method 8 when measuring sulfuric acid from Kraft recovery furnaces.

EXHIBIT 6

We are currently trying to file electronically as many of our documents as possible. Could you please send us an electronic file of Method 8A? The preferred format would be Word Perfect, Version 5.1 or 6.1, but any format would be acceptable.

Sincerely,

A handwritten signature in cursive script, appearing to read "William F. Hunt, Jr.", written in dark ink.

William F. Hunt, Jr.  
Emissions, Monitoring, and  
Analysis Division

cc: Joe Taylor, Georgia Pacific  
Mike Harley, Florida Department of  
Environmental Protection



SOUTHERN REGIONAL CENTER

P.O. Box 141020

Gainesville, FL 32614-1020

(352) 377-4708

FAX (352) 371-6557

NATIONAL COUNCIL OF THE PAPER INDUSTRY FOR AIR AND STREAM IMPROVEMENT, INC.

December 18, 1996

Mr. Mike Harley  
Florida Department of  
Environmental Protection  
2600 Blair Stone Road  
Twin Towers Office Bldg.  
Tallahassee, Florida 32301

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Bureau of Air Monitoring  
& Mobile Sources

Dear Mike:

Enclosed is a write-up of the NCASI recovery furnace  $\text{SO}_3/\text{H}_2\text{SO}_4$  testing method as we submitted it to Gary McAlister of EPA on September 23rd.

If you need any further information, please give us a call.

Sincerely,

A handwritten signature in dark ink, appearing to read "Ashok K. Jain", is written over a horizontal line.

Ashok K. Jain  
Regional Manager

AKJ/sck

Enclosure

EXHIBIT 7

METHOD 8A DETERMINATION OF SULFURIC  
ACID VAPOR OR MIST AND SULFUR DIOXIDE  
EMISSIONS FROM KRAFT RECOVERY FURNACES

1. Principle and Applicability

1.1 Principle. A gas sample is extracted from the sampling point in the recovery furnace stack. The sulfuric acid vapor or mist (including sulfur trioxide) and the sulfur dioxide are separated, and both fractions are measured separately by the barium-thorin titration method.

1.2 Applicability. This method is applicable for the determination of sulfuric acid vapor or mist (including sulfur trioxide, and in the presence of other particulate matter) and sulfur dioxide emissions from kraft recovery furnaces. Tests have shown the minimum detectable limits of the method are 0.50 milligrams/cubic meter ( $3.1 \times 10^{-8}$  lb/ft<sup>3</sup>) for sulfur trioxide. No upper limits have been established. Based on theoretical calculations, for 200 milliliters of 3 percent hydrogen peroxide solution, the upper concentration limit for sulfur dioxide in a 1.0 m<sup>3</sup> (35.3 ft<sup>3</sup>) gas sample is about 12,500 mg/in<sup>3</sup> ( $7.7 \times 10^{-4}$  lb/ft<sup>3</sup>). The upper limit can be extended by increasing the quantity of peroxide solution in the impingers.

Possible interfering agents of this method are fluorides, free ammonia, dimethyl aniline and recovery furnace salt cake.

2. Apparatus

2.1 Sampling. A schematic of the sampling train used in this method is shown in Figure 1. Component parts are discussed below. The schematic is similar to the Method 6 train except that the impingers are not the midjet type but larger as in the Method 8 train. Also, the impingers are preceded by a heated sampling probe, a heated quartz filter holder and a heated H<sub>2</sub>SO<sub>4</sub> condenser.

2.1.1 Probe. Quartz, straight tube approximately 12-mm inside diameter, with a heating element and a stainless steel jacket. A thermocouple taped on the quartz tube and insulated with glass wool allows for measurement of the probe temperature.

2.1.2 Sulfuric Acid Sampling Box. Insulated box with heating elements for Filter Holder and H<sub>2</sub>SO<sub>4</sub> Condenser.

2.1.2.1 Filter Holder. Quartz, as described in Figure 2. Filter medium is Tissuequartz filter paper with a 37-mm diameter (Pallflex Corporation). Filter holder is always maintained at temperatures >260°C (500°F) by a cylindrical heating

mantle.

2.1.2.2 H<sub>2</sub>SO<sub>4</sub> Condenser. Modified Graham Condenser, with Type C glass frit and 200 cm of 5-mm ID glass tubing for condenser coil, as shown in Figure 3. Condenser filled with water and temperature maintained between 75 and 85°C (167 to 185°F) with a cylindrical heating mantle.

2.1.3 Thermocouples. Copper-constantan thermocouples to measure temperatures at the probe end, after the filter holder and after the H<sub>2</sub>SO<sub>4</sub> condenser (see Figure 1).

2.1.4 Impingers. Three, as shown in Figure 1 (similar to the 2nd, 3rd and 4th impingers in the Method 8 train, Figure 8-1). The first and third impinger shall be of the Greenburg-Smith design with standard tips. The second shall be of the Greenburg-Smith design, modified by replacing the insert with an approximately 13 mm (0.5 in.) ID glass tube, having an unstricted tip located 13 mm (0.5 in.) from the bottom of the flask.

2.1.5 Metering System. Same as Method 6, Sections 2.1.5 to 2.1.10, except rotameter should be capable of measuring flow rate to within 2 percent of the selected flow rate of about 10,000 cc/min (and not 1,000 cc/min).

2.1.6 Barometer. Same as Method 6, Section 2.1.11.

2.1.7 Vacuum Gauge and Rotameter. Same as Method 6, Section 2.1.12.

2.2 Sample Recovery. Same as Method 8, Section 2.2.

2.3 Analysis. Same as Method 8, Section 2.3.

3. Reagents

3.1 Sampling.

3.1.1 Filters. Tissuequartz filter papers with a 37-mm diameter (Pallflex Corporation).

3.1.2 Silica Gel, Water, Hydrogen Peroxide, Crushed Ice. Same as described in Method 8.

3.2 Sample Recovery.

Water. Same as for Method 8.

3.3 Analysis.

3.3.1 Water, Thorin Indicator, Barium Perchlorate and Sulfuric Acid Standard. Same as for Method 8.

4. Procedure

4.1 Sampling.

4.1.1 Preparation of collection train. Measure 100 ml of 3 percent hydrogen peroxide into each of the first two impingers. Pour 100 ml of distilled deionized water into the third impinger. Retain a portion of each

reagent used as a blank solution. Assemble the train as shown in Figure 1. Adjust probe heater to maintain probe temperature above 177°C (350°F) to prevent condensation of H<sub>2</sub>SO<sub>4</sub> in the gas passing through the probe. Adjust heaters to the quartz filter and sulfuric acid condenser to the desired temperatures given in Sections 2.1.2.1 and 2.1.2.2. Place crushed ice around the impingers.

4.1.2 Leak-check procedure. Follow the procedure laid out in Method 8, section 4.1.4.

4.1.3 Sample Collection. Record the initial dry gas meter reading and barometric pressure (See data sheet, Figure 4). To begin sampling, position the tip of the probe at the sampling point at right angles to direction of gas flow, connect the probe, filter and condenser assembly to the first impinger, and start the pump. Adjust the sample flow to a constant rate of about 10.0 liter/min as indicated by the rotameter. Maintain this constant rate ( $\pm 10$  percent) during the entire sampling run. Sample for a minimum of 30 minutes and take readings (dry gas meter, temperatures at dry gas meter, probe, filter and condenser) at least every five minutes (Figure 4). Add more ice during the run if needed. At the conclusion of each run, turn off the pump, remove probe from the stack, and record the final readings. Conduct a leak check as described in Section 4.1.2 (This leak check is mandatory). If the post-leakage rate exceeds the specified acceptable rate (see Section 4.1.4 of Method 8), the tester shall either correct the sample volume, as specified in Section 6.3 of Method 5, or shall void the run.

Drain the ice bath and, with the probe disconnected, purge the remaining part of the train by drawing clean ambient air through the system for 15 minutes at the average flow rate used for sampling (see Section 4.1.5 of Method 8 for details).

4.2 Sample Recovery. Disconnect the impingers after purging. Rinse separately the probe, quartz filter holder and the H<sub>2</sub>SO<sub>4</sub> condenser with deionized water using multiple rinses for good washing. Collect the condenser wash solution in Container No. 1, and the No. 1 and No. 2 impinger solutions in Container No. 2. Note levels of liquids in each container.

4.3 Sample Analysis. Note the level of liquid in containers 1 and 2, and confirm whether or not any sample was lost during shipment; note this on the analytical data sheet. If a noticeable amount of leakage has occurred, either void the sample or use

methods, subject to the approval of the administrator, to correct the final results.

4.3.1 Container No. 1. Transfer the entire contents of Container No. 1 into a 250 ml Erlenmeyer flask, add enough isopropyl alcohol to give a 80 percent isopropyl alcohol solution. Pipette a 100-ml aliquot of this solution into a 250-ml Erlenmeyer flask, add 2 to 4 drops of thorin indicator, and titrate to a pink end point using 0.0100 N barium perchlorate. Repeat the titration with a second aliquot of sample and average the titration values. Replicate titrations must agree within 1 percent or 0.2 ml, whichever is greater. Caution: The  $H_2SO_4$  concentrations in kraft recovery furnace stacks are typically so low that at times almost the entire sample in Container No. 1 may have to be used during the titration.

4.3.3 Container No. 2. If concurrent  $SO_2$  concentrations in the stack are desired carry out the following. Thoroughly mix the solution in Container No. 2 which holds the contents of the 1st and 2nd impingers. Pipette a 10-ml aliquot of this solution into a 250-ml Erlenmeyer flask. Add 40 ml isopropanol, 2 to 4 drops of thorin indicator, and titrate to a pink end point using 0.0100 N barium perchlorate. Repeat the titration with a second aliquot of sample and average the titration values. Replicate titrations must agree within 1 percent or 0.2 ml, whichever is greater.

4.3.4 Blanks. Prepare blanks by adding 2 to 4 drops of thorin indicator to 100 ml of 80 percent isopropanol. Titrate the blanks in the same manner as the samples.

5. *Calibration* - Same as section 5 of Method 8.

6. *Calculations* - Same as section 6 of Method 8, except that equation 8-1 should be replaced by equation 6-1 of Method 6 and references to isokinetic sampling in this section should be omitted. Recovery furnace stack gas temperatures are expected to be higher than the estimated dewpoint of  $H_2SO_4$  in the stack gas, and  $H_2SO_4$  is expected to be present in vapor phase only. Consequently, neither isokinetic sampling nor a stack traverse is required.

## 7. *Bibliography*

1. A Study of  $SO_x$  Measurement Procedures and Their Use at Kraft Recovery Furnaces. NCASI Atmospheric Quality Improvement

Technical Bulletin No. 106, National Council of the Paper Industry for Air & Stream Improvement, Research Triangle Park, NC. April 1980.



Figure 1.  $\text{SO}_2$  Sampling Train

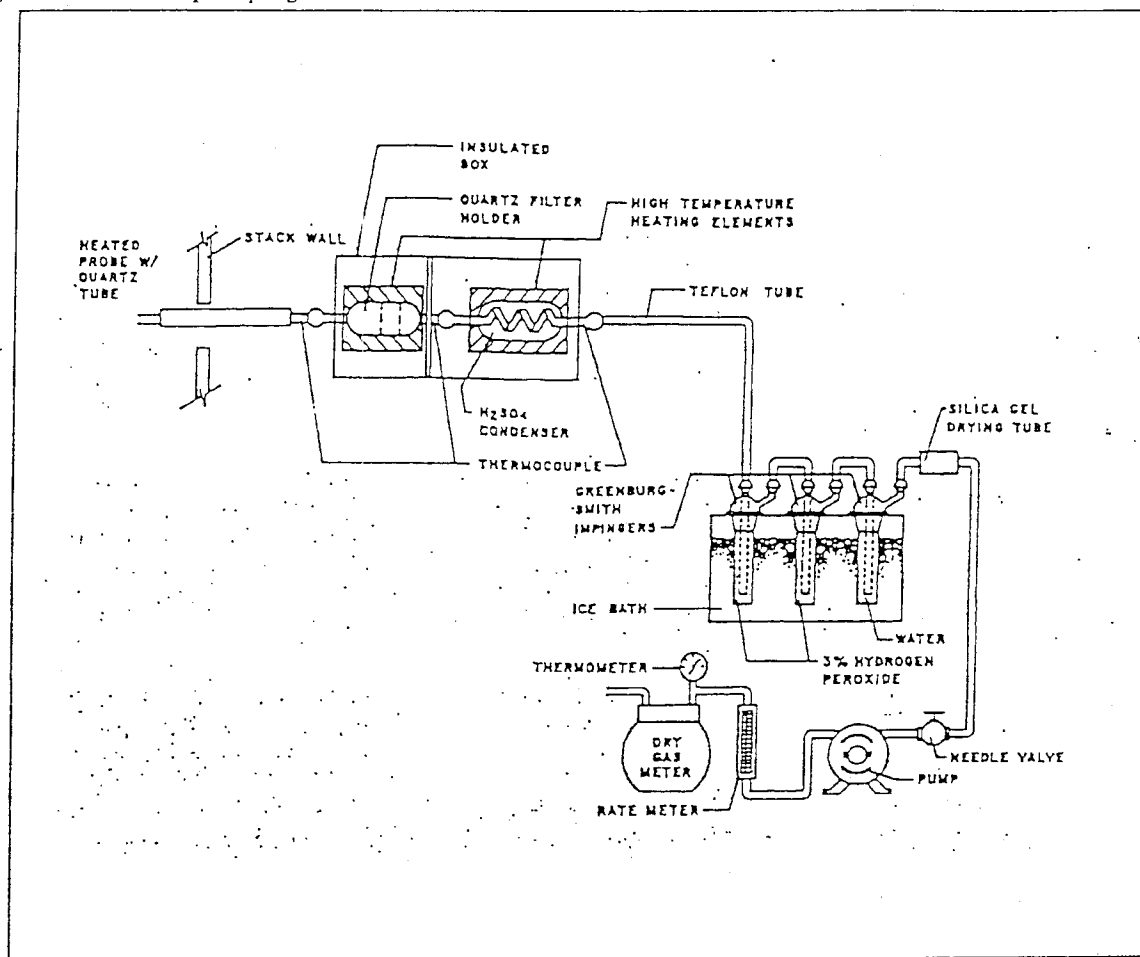


Figure 2. Quartz Filter Holder

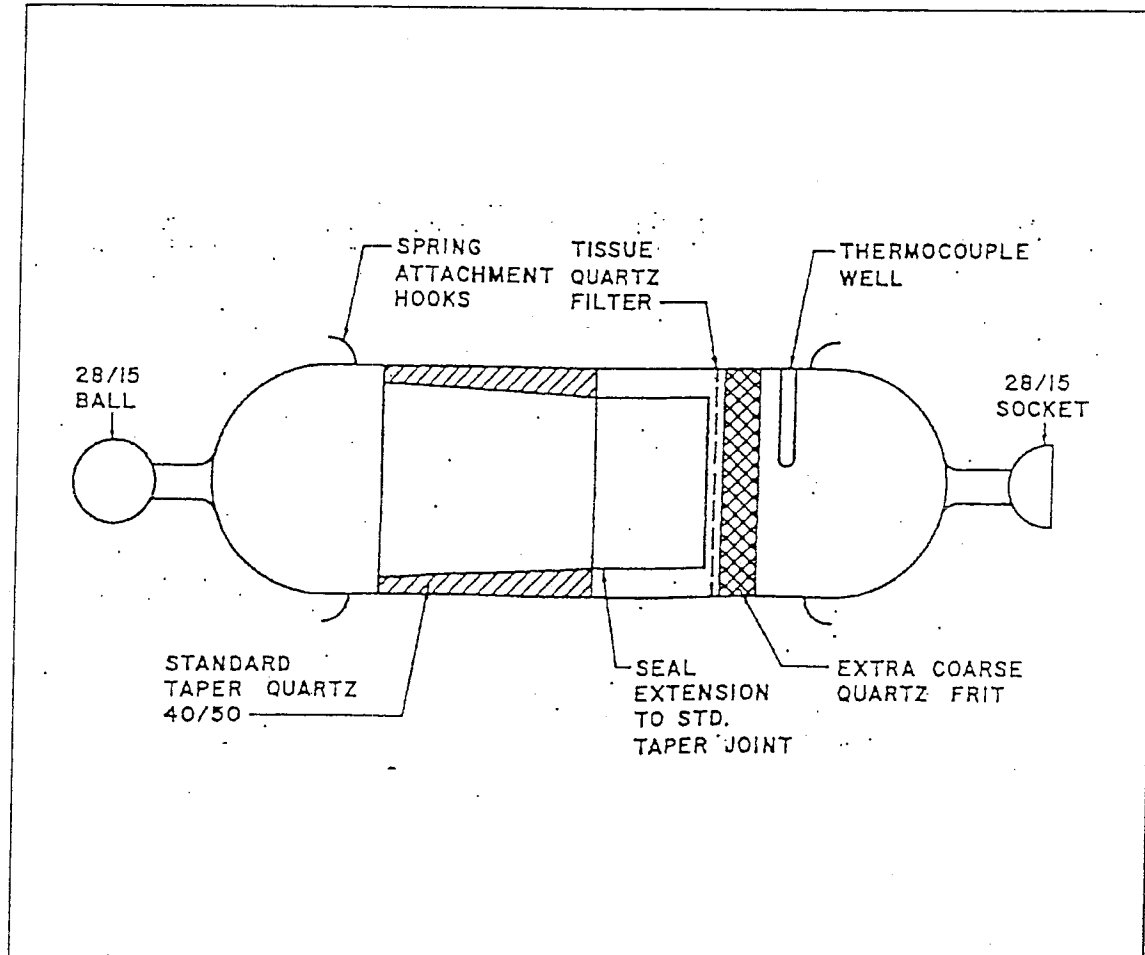


Figure 3.  $\text{H}_2\text{SO}_4$  Condenser

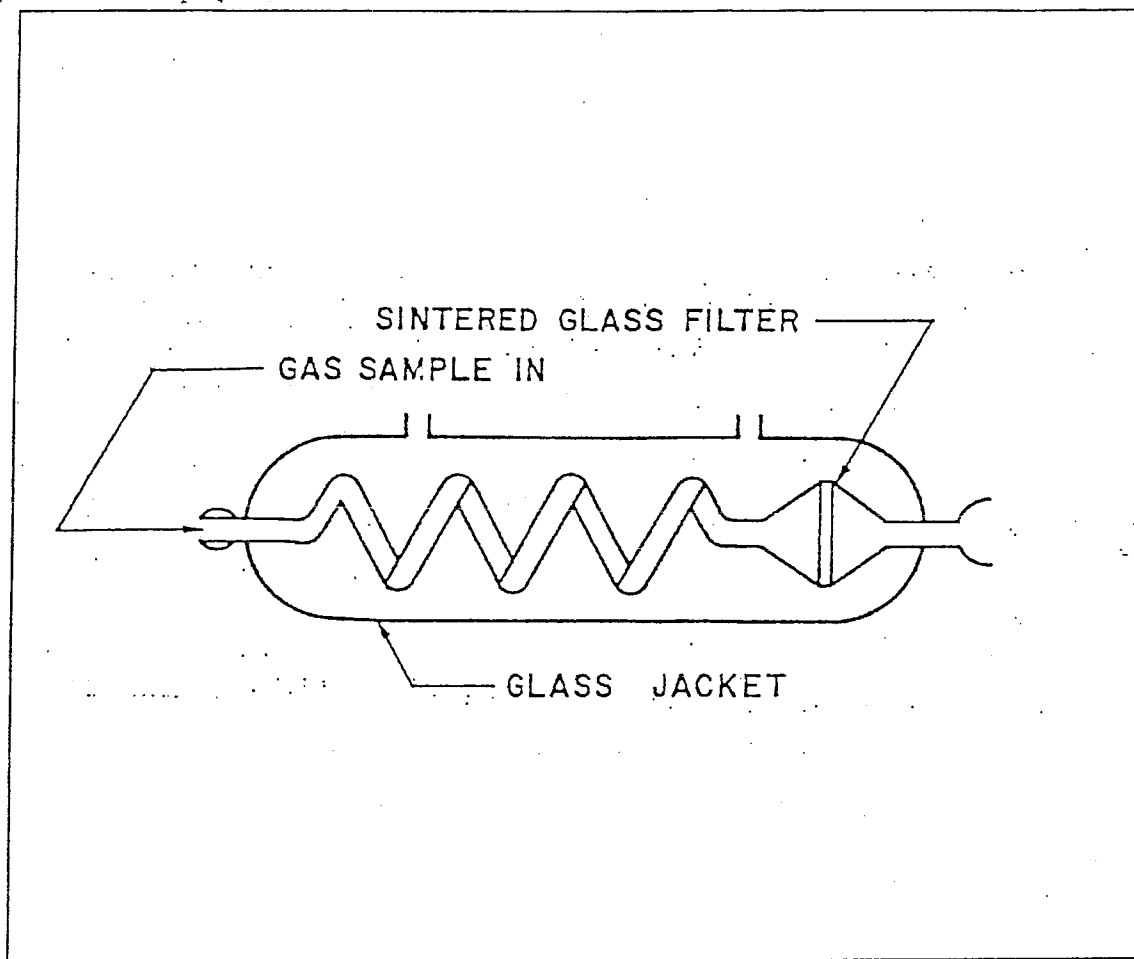


Figure 4. SO<sub>2</sub> Measurement Field Data Sheet

Source \_\_\_\_\_

Date \_\_\_\_\_

Run No. \_\_\_\_\_

Furnace Load \_\_\_\_\_

Stack Gas Temp. \_\_\_\_\_

Atmospheric Pressure \_\_\_\_\_

Final Dry Gas Meter Reading \_\_\_\_\_

Initial Dry Gas Meter Reading \_\_\_\_\_

Volume Sampled \_\_\_\_\_

Time (Min)	Temperature, °F				
				Dry Gas Meter	
	Probe	Filter	Condenser	In	Out
0					
5					
10					
15					
20					
25					
30					