ENVIRONMENTAL PROTECTION AGENCY

40 CFR Part 63

[IL–64–2–5807; FRL–5978–2]

RIN 2060–AE78

National Emission Standards for Hazardous Air Pollutants; Proposed Standards for Hazardous Air Pollutants Emissions for the Portland Cement Manufacturing Industry

AGENCY: Environmental Protection Agency (EPA).

ACTION: Proposed rule and notice of public hearing.

SUMMARY: This action proposes national emission standards for hazardous air pollutants (NESHAP) for new and existing sources in portland cement manufacturing plants. Exposure to the hazardous air pollutants (HAPs) in these emissions may be associated with a wide variety of effects, including carcinogenic, respiratory, nervous system, dermal, developmental, and/or reproductive health effects. Implementation of the proposed requirements would reduce emissions of several HAPs.

The standards are proposed under the authority of section 112(d) of the Clean Air Act as amended (the Act) and are based on the Administrator's determination that portland cement manufacturing plants may reasonably be anticipated to emit several of the HAPs listed in section 112(b) of the Act from the various process operations found within the industry. The proposed NESHAP would provide protection to the public by requiring all portland cement plants which are major sources to meet emission standards reflecting the application of the maximum achievable control technology (MACT).

DATES: *Comments.* The EPA will accept comments on the proposed rule until May 26, 1998.

Public Hearing. If anyone contacts the Agency requesting to speak at a public hearing, the hearing will be held at the Agency's Office of Administration Auditorium, Research Triangle Park, North Carolina on April 23, 1998 beginning at 10:00 a.m. Persons wishing to present oral testimony must contact the Agency by April 14, 1998.

ADDRESSES: *Comments.* Comments should be submitted (in duplicate) to: Air and Radiation Docket and Information Center (6102), Attention: Docket No. A–92–53, U.S. Environmental Protection Agency, 401 M Street SW., Washington, DC 20460. The Agency requests that a separate copy also be sent to the contact person listed below (Mr. Joseph Wood). Comments and data may also be submitted electronically by following the instructions provided in the **SUPPLEMENTARY INFORMATION** section. No confidential business information (CBI) should be submitted through electronic mail.

Public Hearing. Persons wishing to present oral testimony or to inquire as to whether or not a hearing is to be held should notify Ms. Cathy Coats, Minerals and Inorganic Chemicals Group (MD–13), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711, telephone number (919) 541–5422. Additional information regarding the public hearing is given in the **SUPPLEMENTARY INFORMATION** section.

Docket. The official record for this rulemaking, as well as the public version, has been established under Docket No. A–92–53 (including comments and data submitted electronically as described below). A public version of this record, including printed, paper versions of electronic comments and data, which does not include any information claimed as CBI, is available for inspection from 8 a.m. to 4 p.m., Monday through Friday, excluding legal holidays. The official rulemaking docket is located at the address in the **ADDRESSES** section above. Alternatively, a docket index, as well as individual items contained within the docket, may be obtained by calling (202) 260–7548. A reasonable fee may be charged for copying.

FOR FURTHER INFORMATION CONTACT: For information about this proposed rule, contact Mr. Joseph Wood, P.E., Minerals and Inorganic Chemicals Group, Emission Standards Division (MD–13), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711, telephone number (919) 541–5446; electronic mail address wood.joe@epamail.epa.gov. For information about the proposed test methods contact Ms. Rima Dishakjian, Emission Measurement Center, Emissions, Monitoring and Analysis Division (MD–19), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711, telephone number (919) 541–0443.

SUPPLEMENTARY INFORMATION: *Electronic filing.* Electronic comments can be sent directly to the EPA at a-and-r-docket@epamail.epa.gov. Electronic comments and data must be submitted as an ASCII file avoiding the use of special characters and any form of encryption. Comments and data will also be accepted on disks in Wordperfect 5.1 or 6.1 file format or ASCII file format. All comments and data in electronic form must be identified by the docket number A–92–53. Electronic comments may be filed online at many Federal Depository Libraries.

Implementation of the proposed requirements would achieve an emission reduction from existing and projected new sources estimated at 82 megagrams per year (Mg/yr) (90 tons per year [tpy]) of HAPs and 4,900 Mg/yr (5,400 tpy) of other pollutants (volatile organic compounds [VOC] and particulate matter [PM]). The EPA is also proposing to require portland cement plants that are area sources to meet emission standards for dioxins and furans reflecting the application of MACT.

The EPA is also proposing Methods 320, 321, and 322 with the standards for addition to 40 CFR part 63, appendix A. These methods may be used to assist in determining the applicability of the proposed emission limitations.

Public Hearing. If a public hearing is requested and held, EPA will ask clarifying questions during the oral presentation but will not respond to the presentations or comments. Written statements and supporting information will be considered with equivalent weight as any oral statement and supporting information subsequently presented at a public hearing, if held.

Confidential Business Information. Commenters wishing to submit proprietary information for consideration should clearly distinguish such information from other comments and clearly label it "Confidential Business Information." Submissions containing such proprietary information should be sent directly to the following address, and not to the public docket, to ensure that proprietary information is not inadvertently placed in the docket: Attention: Mr. Joseph Wood, c/o Ms. Melva Toomer, U.S. EPA Confidential Business Information Manager, OAQPS (MD–13); Research Triangle Park, NC 27711. Information covered by such claim of confidentiality will be disclosed by the EPA only to the extent allowed and by the procedures set forth in 40 CFR part 2. If no claim of confidentiality accompanies a submission when it is received by the EPA, the submission may be made available to the public without further notice to the commenter.

Regulated entities. Entities potentially regulated by this action are those who have the potential to emit HAPs listed in section 112(b) of the Act in the regulated categories and entities shown in Table 1.

This table is not intended to be exhaustive, but rather provides a guide for readers regarding entities likely to be regulated by this action. This table lists the types of entities that the EPA is now aware could potentially be regulated by this action. Other types of entities not listed in this table could also be regulated. To determine whether your facility is regulated by this action, you should carefully examine the applicability criteria in § 63.1340 of the proposed rule. If you have questions regarding the applicability of this action to a particular entity, consult the person listed in the preceding **FOR FURTHER INFORMATION CONTACT** section of this preamble.

TABLE 1.—REGULATED ENTITIES

Category	Examples of regulated entities
Industry	Owners or operators of portland cement manufacturing plants.
State	Owners or operators of portland cement manufacturing plants.
Tribal associations	Owners or operators of portland cement manufacturing plants.
Federal agencies	None.

Technology Transfer Network. The proposed regulatory text is also available on the Technology Transfer Network (TTN), one of EPA's electronic bulletin boards. The TTN provides information and technology exchange in various areas of air pollution control. The service is free, except for the cost of a phone call. Dial (919) 541–5742 for up to a 14,400 BPS modem. The TTN is also accessible through the Internet (world wide web) at http://www.epa.gov/ttn/. If more information on the TTN is needed, call the HELP line at (919) 541–5384. The help desk is staffed from 11 a.m. to 5 p.m.; a voice menu is available at other times.

Outline. The information in this preamble is organized as shown below.

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I. Statutory Authority

The statutory authority for this proposal is provided by sections 101, 112, 114, 116, 183(f) and 301 of the Clean Air Act, as amended (42 U.S.C. 7401, 7411, 7414, 7416, 7511(f) and 7601).

II. Introduction

A. Background

Nationwide baseline HAP emissions from portland cement manufacturing plants are estimated to be 260 Mg/yr (290 tpy) at the current level of control. The HAPs released from kiln systems include acetaldehyde, arsenic, benzene, cadmium, chromium, chlorobenzene, dibenzofurans, formaldehyde, hexane, hydrogen chloride, lead, manganese, mercury, naphthalene, nickel, phenol, polycyclic organic matter, selenium, styrene, 2,3,7,8-tetrachlorodibenzo-p-dioxin, toluene, and xylenes. The HAPs released from raw material dryers should be similar to those from the kiln. The HAPs released from clinker coolers, raw mills, finish mills, storage bins, conveying system transfer points, bagging systems and bulk loading and unloading systems include arsenic, cadmium, chromium, lead, manganese, mercury, nickel, and selenium. Implementing MACT-level controls is expected to decrease emissions of these HAPs from existing and projected new sources by approximately 82 Mg/yr (90 tpy). Plants can achieve this reduction by upgrading or installing fabric filters (FF), also known as baghouses, and electrostatic precipitators (ESP) to decrease HAP metals; limiting temperatures at the particulate matter control device (PMCD) inlet to decrease dioxin and furan (D/F) emissions; and selecting suitable feed materials to decrease organic HAP emissions.

The overall effect of these standards would be to improve the control performance of the industry to the level achieved by the best performing plants. In addition to the health and environmental benefits associated with HAP emission reductions, benefits of this action include a decrease in site-specific emission levels of PM and VOC and lowered occupational exposure levels for employees.

The nationwide capital and annualized costs of the proposed NESHAP, including emission controls and associated monitoring equipment, are estimated at $88 million and $27 million/yr, respectively. The economic impacts are predicted to increase prices of portland cement by an average of 1.1 percent.

To minimize adverse impacts, the Agency has proposed controls at the MACT-floor level, tailored the requirements to allow less-costly testing and monitoring by using surrogates for HAP emissions and provided choice in methods of control. The proposed rule

is ''user friendly,'' with language that is easy to understand by all of the regulated community. The EPA also proposes to allow existing facilities up to 3 years to comply. And, as allowed under section 112(i)(3)(B) of the Act, the Administrator or delegated regulatory authority also may grant 1 additional year if necessary for the installation of controls.

B. NESHAP for Source Categories

Section 112 of the Act as amended specifically directs the EPA to develop a list of all categories of major sources and such area sources as appropriate that emit one or more of the HAPs listed in the Act. The EPA is further directed to develop NESHAP to control emissions of HAPs from both existing and new major sources, where a major source is defined as a source that emits or has the potential to emit 9.1 Mg/yr (10 tpy) or more of any one HAP or 22.7 Mg/yr (25 tpy) of any combination of HAPs. The statute requires the standards to reflect the maximum degree of reduction in HAP emissions that is achievable, taking into consideration the cost of achieving the emission reduction, any nonair quality health and environmental impacts, and energy requirements. This level of control is commonly referred to as MACT.

The control of HAPs is achieved through the promulgation of technology-based emission standards under sections 112(d) and 112(f) and work practice standards under 112(h) for categories of sources that emit HAPs. Emission reductions may be accomplished through the application of measures, processes, methods, systems, or techniques including, but not limited to: (1) Reducing the volume of, or eliminating emissions of, such pollutants through process changes, substitution of materials, or other modifications; (2) enclosing systems or processes to eliminate emissions; (3) collecting, capturing, or treating such pollutants when released from a process, stack, storage or fugitive emissions point; (4) design, equipment, work practice, or operational standards (including requirements for operator training or certification) as provided in subsection (h); or (5) a combination of the above. [See section 112(d)(2) of the Act.] The EPA may promulgate more stringent regulations to address residual risk that remains after the imposition of controls at a later date.

C. Health Effects of Pollutants

The Clean Air Act was created in part to protect and enhance the quality of the Nation's air resources so as to promote the public health and welfare and the productive capacity of its population. [See section 101(b)(1).] In the 1990 Amendments to the Clean Air Act, Congress specified that each standard for major sources must require the maximum reduction in emissions of HAPs that EPA determines is achievable considering cost, health and environmental impacts, and energy requirements. Title III of the Act establishes a control technology-based program to reduce stationary source emissions of HAPs. The goal of section 112(d) (in Title III) is to apply such control technology to reduce emissions and thereby reduce the hazard of HAPs emitted from stationary sources.

Section 112(b) of the Act lists HAPs believed to cause adverse health or environmental effects. The EPA recognizes that the degree of adverse effects to health can range from mild to severe. The extent and degree to which the health effects may be experienced is dependent upon: (1) The ambient concentrations observed in the area (e.g., as influenced by emission rates, meteorological conditions, and terrain); (2) the frequency of and duration of exposures; (3) characteristics of exposed individuals (e.g., genetics, age, pre-existing health conditions, and lifestyle) which vary significantly with the population; and (4) pollutant-specific characteristics (e.g., toxicity, half-life in the environment, bioaccumulation, and persistence). In essence, these MACT standards would ensure that all major sources of air toxic emissions achieve the level of control already being achieved by the better controlled and lower emitting sources in each category. This approach provides assurance to citizens that each major source of toxic air pollution will be required to effectively control its emissions. At the same time, this approach provides a level economic playing field, ensuring that facilities that employ cleaner processes and good emissions controls are not disadvantaged relative to competitors with poorer controls.

Available emission data, collected in conjunction with the development of this NESHAP, show that non-volatile HAP metals, mercury, organic HAPs and hydrogen chloride are the predominant HAPs emitted from portland cement manufacturing plants. These pollutants (except mercury and hydrogen chloride) have the potential to be reduced by implementation of the proposed emission limits. In addition to the HAPs, the portland cement manufacturing NESHAP would also control some of the pollutants whose emissions are controlled under the National Ambient Air Quality Standards (NAAQS). These pollutants include PM, VOC, and lead. The following is a summary of the potential health effects associated with exposures, at some level, to pollutants that would be reduced by the standard.

Almost all metals appearing on the section 112(b) list are emitted from portland cement manufacturing affected sources. There is a wide range of targets of toxicity for these metals. Effects include skin irritation, mucous membrane irritation (e.g., lung irritation), gastrointestinal effects, nervous system effects (including cognitive effects, tremor, and numbness), increased blood pressure, and reproductive and developmental effects. Additionally, several of the metals accumulate in the environment and in the human body. Cadmium, for example, is a cumulative pollutant which causes kidney effects after the cessation of exposure. Similarly, the onset of effects from beryllium exposure may be delayed by months to years. Many of the metal compounds are also known (arsenic, chromium (VI)) or probable (cadmium, nickel carbonyl, lead, and beryllium) human carcinogens.

Organic compounds which will potentially be decreased by the proposed standard include but are not limited to acetaldehyde, benzene, chlorobenzene, formaldehyde, D/F, hexane, naphthalene, phenol, polycyclic organic matter, styrene, toluene, and xylenes. Each of these organic compounds has a range of potential health effects associated with exposure at some level. Some of the effects associated with short-term inhalation exposure to these pollutants are similar and include irritation of the eyes, skin, and respiratory tract in humans; central nervous system effects (e.g., drowsiness, dizziness, headaches, depression, nausea, irregular heartbeat); reproductive and developmental effects; and, neurological effects. Exposure to benzene at extremely high concentrations may even lead to respiratory paralysis, coma, or death.

Health effects associated with long-term inhalation exposure in humans to the organic compounds which will potentially be decreased by the proposed standard may include mild symptoms such as nausea, headache, weakness, insomnia, intestinal pain, and burning eyes; effects on the central nervous system; disorders of the blood; toxicity to the immune system; reproductive disorders in women (e.g., increased risk of spontaneous abortion); developmental effects; gastrointestinal irritation; liver injury; and muscular effects.

In addition to the non-cancer effects described above, some of the organic HAPs that would be controlled under this proposed standard are either known (benzene) or probable (formaldehyde and D/F) human carcinogens.

Hydrogen chloride (HCl) is highly corrosive to the eyes, skin, and mucous membranes. Short-term inhalation of HCl by humans may cause coughing, hoarseness, inflammation and ulceration of the respiratory tract, as well as chest pain and pulmonary edema. Long-term occupational exposure of humans to HCl has been reported to cause inflammation of the stomach, skin, and lungs, and photosensitization.

The health effects of PM, lead, and VOC that would be reduced by this standard are described in EPA's Criteria Documents, which support the NAAQS. Briefly, PM emissions have been associated with aggravation of existing respiratory and cardiovascular disease and increased risk of premature death. Depending on the degree of exposure, lead can cause subtle effects on behavior and cognition, increased blood pressure, reproductive effects, seizures, and even death.

Volatile organic compounds are precursors to the formation of ozone in the ambient air. At ambient levels, ozone has been shown in human laboratory and community studies to be responsible for the reduction of lung function, respiratory symptoms (e.g., cough, chest pain, throat and nose irritation), increased hospital admissions for respiratory causes, and increased lung inflammation. Animal studies have shown increased susceptibility to respiratory infection and lung structure changes. Exposure to ozone has also been linked to harmful effects on agricultural crops and forests.

D. Portland Cement Manufacturing Industry Profile

Portland cement is a fine powder, usually gray in color, that consists of a mixture of the minerals dicalcium silicate, tricalcium silicate, tricalcium aluminate, and tetracalcium aluminoferrite, to which one or more forms of calcium sulfate have been added (docket item II–I–43, p. 746). The primary end use of portland cement is as the key ingredient in portland cement concrete, which is used in almost all construction applications.

In 1993, 44 companies operated 118 portland cement plants located in 37 states. The manufacture of portland cement is covered by SIC code 3241 for hydraulic cements. According to U.S. Small Business Administration size standards, companies owning portland

cement plants are categorized as small if the total number of employees at the company is less than 750. Otherwise the company is classified as large. A total of 7 companies are categorized as small, while the remaining 37 companies are in the large category (docket item II–D–200).

Few new plants are predicted to be constructed during the next 5 years. The EPA estimates that two to four existing plants will undergo reconstruction in the next 5 years.

All existing kilns and alkali bypasses have PM control devices. Some existing cement manufacturing plants are required to meet new source performance standards (NSPS) for PM (40 CFR part 60, subpart F). The affected facilities to which the NSPS apply are the kiln, kiln gas alkali bypass, clinker cooler, raw material dryer, and materials handling processes.

III. Summary of Proposed Standards

A. Applicability

The proposed standards apply to each existing, reconstructed, and newly constructed portland cement manufacturing plant at any facility which is a major source or an area source, with the following exception. Some portland cement plants fire hazardous wastes in the kiln to provide part or all of the fuel requirement for clinker production. Portland cement kilns and in-line kiln/raw mills subject to the NESHAP for hazardous waste combustors [1] (HWC) are not subject to this standard; however other affected sources at portland cement plants where hazardous waste is burned in the kiln are subject to this standard.

For portland cement plants with on-site non-metallic minerals processing facilities, the first affected source in the sequence of materials handling operations subject to this proposed NESHAP is the raw material storage, which is just prior to the raw mill. The primary and secondary crushers and any other equipment in the non-metallic minerals processing plant, which precede the raw material storage are not affected sources under the proposed NESHAP. Furthermore, the first conveyor system transfer point subject to the proposed NESHAP is the transfer point associated with the conveyor transferring material from the raw material storage to the raw mill. Conveyor system transfer points prior to this conveyor are not affected sources under this proposed NESHAP (docket item II–B–53).

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[1] The EPA proposed regulations for subpart EEE of 40 CFR part 63 on April 19, 1996 at 61 FR 17358.

This regulation does not apply to the emissions from cement kiln dust (CKD) storage facilities (i.e., CKD piles or landfills). A separate rulemaking will be forthcoming from EPA's Office of Solid Waste (OSW) that will apply to air emissions associated with CKD management and disposal facilities.

Except for hazardous waste burning (HW) cement kilns and HW in-line kiln/raw mills, EPA is proposing to apply these standards to all cement kilns and in-line kiln/raw mills regardless of the material being combusted in the kiln. This proposal, however, does not preclude EPA from determining that cement kilns combusting solid waste materials should be regulated under section 129 of the Clean Air Act, 42 U.S.C. 7429, and to revise the applicability section of these regulations accordingly at the time section 129 regulations applicable to cement kilns are promulgated.

The EPA believes that applying this regulation to all non-hazardous waste burning (NHW) cement kilns regardless of the material combusted in the kiln is necessary at this time due to the Court of Appeals for the District of Columbia's recent decision in *Davis County Solid Waste Management District* v. *Environmental Protection Agency*, 101 F.3d 1395 (D.C. Cir. 1996) (petition to review municipal waste combustor ("MWC") regulations promulgated on December 19, 1995 pursuant to section 129 of the Act, 60 FR 65387). In the applicability section of the MWC regulations, EPA applied the standards to all solid waste incineration units combusting more than 30-percent municipal solid waste. Two owners and operators of MWC units with capacity less than 250 tons/day filed petitions for review on the grounds that EPA improperly had included their units in the large category. The Cement Kiln Recycling Coalition ("CKRC") also filed a petition for review on the grounds that the standards should not apply to cement kilns. In its opinion dated December 6, 1996, the Court indicated its intent to vacate the standards in their entirety on the grounds raised by the two petitioners who own and operate MWC units; as a result, the Court did not reach the issue raised by CKRC. Accordingly, EPA believes that it is appropriate to apply these regulations as a gap-filling measure to control emissions from NHW cement kilns and in-line kiln/raw mills regardless of the material combusted in the kiln (except for hazardous waste) until EPA determines whether regulations applicable to cement kilns combusting solid waste materials should be re-promulgated under section 129. To

decide otherwise would have the potential effect of allowing cement kiln owners and operators to avoid regulation by adding some solid waste material to the cement kiln.

As background, section 129(a)(1)(A) requires the Administrator to establish performance standards and other requirements pursuant to section 111 and section 129 of the Act for each category of solid waste incineration units [42 U.S.C. 7429(a)(1)(A)]. Whereas section 112(c) of the Act requires EPA to determine major and area sources of the 188 hazardous air pollutants (HAPs) listed in section 112(b), Congress specifically listed in section 129 various categories of solid waste incineration units that EPA must regulate, including solid waste incineration units combusting municipal solid waste [sections 129(a)(1)(B) and (C)], solid waste incineration units combusting hospital waste, medical waste, and infectious waste [section 129(a)(1)(C)], solid waste incineration units combusting commercial or industrial waste [section 129(a)(1)(D)], and ''other categories of solid waste incineration units'' which are to be defined by EPA [42 U.S.C. 7429(a)(1)].

Section 129(g)(1) of the Act broadly defines a solid waste incineration unit (''SWIU'') as ''a distinct operating unit of *any* facility which combusts *any* solid waste material from commercial or industrial establishments or the general public * * *.'' 42 U.S.C. 7429(g)(1) (emphasis added). Section 129(g)(1) expressly states that ''incinerators or other units required to have a permit under section 3005 of the Solid Waste Disposal Act, 42 U.S.C. 6925'' shall not be considered a SWIU. That section also expressly excludes from the definition of SWIU the following units:

(A) materials recovery facilities (including primary or secondary smelters) which combust waste for the primary purpose of recovering metals, (B) qualifying small power production facilities, as defined in section 769(17)(C) of Title 16, or qualifying cogeneration facilities as defined in section 796(18)(B) of Title 16, which burn homogeneous waste (such as units which burn tires or used oil, but not including refuse-derived fuel) for the production of electric energy or in the case of qualifying cogeneration facilities which burn homogenous waste for the production of electric energy (such as heat) which are used for industrial, commercial, heating or cooling purposes, or (C) air curtain incinerators provided that such incinerators only burn wood wastes, yard wastes and clean lumber and that such air curtain incinerators comply with opacity limitations to be established by the Administrator by rule.

42 U.S.C. 7429(g)(1). Accordingly, with the exception of those solid waste

incineration units that are expressly excluded from regulation by section 129(g)(1), Congress intended EPA to establish regulations for all SWIU's under section 129. This includes cement kilns that combust solid waste materials, including refuse-derived fuel.

Section 129 is similar to section 112 of the Act in that both require EPA to establish performance standards that are based upon the performance of maximum achievable control technology (MACT). Section 112(b), however, lists 188 hazardous air pollutants (HAPs) for potential regulation, and section 112(c)(6) requires EPA to establish performance standards under section 112(d) for categories of sources emitting seven specific pollutants, including the following HAPs emitted by cement kilns: mercury and dioxins/dibenzofurans [42 U.S.C. 7412]. By comparison, section 129 expressly *requires* EPA to regulate emissions of the following criteria pollutants and HAPs—particulate matter, opacity (as appropriate), sulfur dioxide, hydrogen chloride, nitrogen oxides, carbon monoxide, lead, cadmium, mercury, and dioxins and dibenzofurans [42 U.S.C. 7429(a)(4)]. Section 129 also gives EPA the *discretion* to promulgate emission limitations or provide for the monitoring of postcombustion concentrations of surrogate substances or any other pollutant not expressly listed for regulation in section 129(a)(4). [See 42 U.S.C. 7429(a)(4).] In addition, section 129 contains other requirements not contained in section 112, such as operator training requirements. [See 42 U.S.C. 7429(d).]

As stated previously, the regulations being proposed today are pursuant to section 112 of the Act and apply to all cement kilns except portland cement kilns and in-line kiln/raw mills that would be subject to the NESHAP for hazardous waste combustors. In today's notice, the EPA is proposing to establish emission limitations for particulate matter (as a surrogate for metals, except mercury), dioxins/furans, and total hydrocarbons (as a surrogate for organic HAPs) regardless of the material being combusted in the cement kiln. If EPA determines that additional regulations are required under section 129 for cement kilns that combust solid waste materials (*e.g.,* cement kilns combusting materials containing more than 30-percent municipal solid waste or cement kilns combusting medical waste), then such regulations will be promulgated under section 129 and EPA will state clearly in the applicability section of those regulations when those standards apply and revise the

applicability section of these regulations accordingly.

At no time, will a cement kiln be expected to comply simultaneously with regulations promulgated pursuant to section 112 and regulations promulgated pursuant to section 129. Section 129(h)(1) expressly states that no solid waste incineration unit subject to performance standards under section 129 and section 111 shall be subject to standards under section 112(d) of the Act [42 U.S.C. 7429(h)(1)]. The EPA reads this provision to mean that for emissions potentially subject to section 129, the Agency must elect whether to cover such emissions under that section, or under section 112. If EPA elects to cover emissions under section 129, those emissions must be excluded from regulation under section 112. For example, if a cement kiln combusts only fossil fuels, it would have to comply with the regulations being proposed today. If the kiln combusts a mixture of 50% coal and 50% non-hazardous solid waste, it would continue to comply with the regulations being proposed today until EPA promulgates regulations applicable to such kilns under section 129 of the Act. At that time, if the kiln is burning the 50% coal and 50% solid waste mixture, it would have to comply with the section 129 regulations as long as it continued to combust solid waste material. Thus, in the same way that installation of a particular type of combustion device determines which regulation is applicable, combustion of certain materials in that combustion device would determine whether the section 112 regulation or section 129 regulation is applicable.

The EPA does not believe that this approach will subject cement kiln owners to duplicative regulations. As noted earlier, regulations under section 112 and section 129 are based on MACT. If EPA determines that additional regulations under section 129 are appropriate because cement kilns are combusting solid waste material, EPA would be required to promulgate *additional* MACT standards for the following pollutants pursuant to section 129(a)(4): opacity, sulfur dioxide, hydrogen chloride, nitrogen oxides, carbon monoxide, lead, cadmium, and mercury. The EPA also would determine whether the standards for particulate matter, total hydrocarbon, and dioxins/furans should be revised for kilns combusting solid waste materials [42 U.S.C. 7429(a)(4)].

B. Emission Limits and Requirements

The proposed NESHAP for portland cement manufacturing would apply to both major and area sources of HAPs.

The affected sources for which emission limits are proposed include the kiln, in-line kiln/raw mill, clinker cooler, raw material dryer, and materials handling processes that include the raw mill, finish mill, raw material storage, clinker storage, finished product storage, conveyor transfer points, bagging and bulk loading and unloading systems (hereafter referred to as materials handling processes).

The proposed NESHAP would limit emissions of HAPs from non-hazardous waste (NHW) portland cement kilns, NHW in-line kiln/raw mills, and NHW kiln alkali bypasses. Kiln emission limits would not apply to kilns or in-line kiln/raw mills that will be subject to the NESHAP for various hazardous waste combustor (HWC) types, including cement kilns which burn hazardous waste.[2]

The kiln emission limits would apply to the kiln and in-line kiln/raw mill gases and to kiln alkali bypass gases (which may or may not be discharged through a separate stack).

The proposed rule would limit emissions of HAPs from raw material dryers, clinker coolers and materials handling processes, regardless of the type of fuel burned in the kiln. The proposed rule would limit PM (surrogate for non-volatile HAP metals) emissions from new and existing NHW kilns, NHW in-line kiln/raw mills, and clinker coolers at portland cement plants which are major sources. Particulate matter emitted from portland cement manufacturing contains quantities of metal HAPs such as compounds of arsenic, cadmium, chromium, lead, manganese, mercury, nickel, and selenium. Controlling PM emissions would also control emissions of HAP metals. A surrogate approach is used for particulate metal HAPs in the proposed NESHAP to allow easier and less expensive measurement, analysis, and monitoring requirements, and because the control techniques for non-volatile metal HAPs are the same as the control techniques for PM. Although trace amounts of mercury may be found in the particulate matter, it is generally considered a volatile metal, and appreciable reductions of mercury

emissions are not expected through the use of PM controls. Opacity limits would also apply to NHW kilns, NHW in-line kiln/raw mills, clinker coolers, raw material dryers, and materials handling processes.

The proposed rule also would limit D/F emissions from new and existing NHW kilns and NHW in-line kiln/raw mills located at portland cement plants which are major or area sources of HAPs. In addition, the rule would limit total hydrocarbon (THC) as a surrogate for organic HAP emissions from new NHW kilns, new NHW in-line kiln/raw mills, and new raw material dryers at portland cement plants which are major sources. Kiln, in-line kiln/raw mill, and raw material dryer organic emissions contain various organic HAPs including, but not limited to, acetaldehyde, benzene, formaldehyde, hexane, naphthalene, styrene, toluene, and xylenes. Tables 2 and 3 present a summary of the proposed emission limits for new and existing portland cement affected sources.

TABLE 2.—SUMMARY OF PROPOSED EMISSION LIMITS[a] FOR AFFECTED SOURCES AT PORTLAND CEMENT PLANTS

[Metric units]

Affected source and pollutant	Emission limit for existing sources	Emission limit for new sources
NHW kiln and NHW in-line kiln/raw mill [b] PM ...	0.15 kg/Mg dry feed[d] and opacity level[b] no greater than 20 percent.	0.15 kg/Mg dry feed[d] and opacity level[b] no greater than 20 percent.
NHW kiln and NHW in-line kiln/raw mill D/F [b, c]	0.2 ng TEQ/dscm or 0.4 ng TEQ/dscm with PM control device operated at ≤204°C.	0.2 ng TEQ/dscm or 0.4 ng TEQ/dscm with PM control device operated at ≤204°C.
NHW kiln and NHW in-line kiln/raw mill THC ...	None	50 ppmvd (as propane).
Clinker cooler PM ...	0.05 kg/Mg dry feed and opacity level no greater than 10 percent.	0.05 kg/Mg dry feed and opacity level no greater than 10 percent.
Raw material dryer and materials handling processes (raw mill system, finish mill system, raw material storage, clinker storage, finished product storage, conveyor transfer points, bagging, and bulk loading and unloading systems) PM.	10 percent opacity	10 percent opacity.
Raw material dryer THC ...	None	50 ppmvd (as propane).

[a] All concentration limits at 7 percent oxygen.
[b] Includes main and alkali bypass stacks.
[c] Applies to both major and area source portland cement plants.
[d] If there is an alkali bypass stack associated with the kiln or in-line kiln/raw mill, the combined PM emission from the kiln or in-line kiln/raw mill and the alkali bypass must be less than 0.15 kg/Mg dry feed.

TABLE 3.—SUMMARY OF PROPOSED EMISSION LIMITS[a] FOR AFFECTED SOURCES AT PORTLAND CEMENT PLANTS

[English Units]

Affected source and pollutant	Emission limit for existing sources	Emission limit for new sources
NHW kiln and NHW in-line kiln/raw mill [b] PM ...	0.30 lb/ton dry feed[d] and opacity level[b] no greater than 20 percent.	0.30 lb/ton dry feed[d] and opacity level[b] no greater than 20 percent.
NHW kiln and NHW in-line kiln/raw mill D/F [b, c]	8.7×10^{-11} gr TEQ/dscf or 1.7×10^{-10} gr TEQ/dscf with PM control device operated at ≤400 °F.	8.7×10^{-11} gr TEQ/dscf or 1.7×10^{-10} gr TEQ/dscf with PM control device operated at ≤400 °F.
NHW kiln and NHW in-line kiln/raw mill THC ...	None	50 ppmvd (as propane).
Clinker cooler PM ...	0.10 lb/ton dry feed and opacity level no greater than 10 percent.	0.10 lb/ton dry feed and opacity level no greater than 10 percent.

[2] The EPA proposed regulations for subpart EEE of 40 CFR part 63 on April 19, 1996 at 61 FR 17358.

TABLE 3.—SUMMARY OF PROPOSED EMISSION LIMITS [a] FOR AFFECTED SOURCES AT PORTLAND CEMENT PLANTS— Continued

[English Units]

Affected source and pollutant	Emission limit for existing sources	Emission limit for new sources
Raw material dryer and materials handling processes (raw mill system, finish mill system, raw material storage, clinker storage, finished product storage, conveyor transfer points, bagging, and bulk loading and unloading systems) PM.	10 percent opacity	10 percent opacity.
Raw material dryer THC	None	50 ppmvd (as propane).

[a] All concentration limits at 7 percent oxygen.
[b] Includes main and alkali bypass stacks.
[c] Applies to both major and area source portland cement plants.
[d] If there is an alkali bypass stack associated with the kiln or in-line kiln/raw mill, the combined PM emission from the kiln or in-line kiln/raw mill and the alkali bypass must be less than 0.30 lb/ton dry feed.

C. Performance Test and Compliance Provisions

A performance test would be required to demonstrate initial compliance with each applicable numerical limit. Under the proposed standard, the owner or operator would use EPA Method 5, "Determination of Particulate Emissions from Stationary Sources" to measure PM emissions from kilns, in-line kiln/raw mills and clinker coolers. These tests would be repeated every 5 years. Kilns and in-line kiln/raw mills equipped with alkali bypasses would be required to meet the particulate standard based on combined emissions from the kiln exhaust and the alkali bypass. Owners or operators of in-line kiln/raw mills would be required to conduct a Method 5 performance test while the raw mill is operating and a separate Method 5 performance test while the raw mill is not operating. In conducting the Method 5 tests, a determination of the particulate matter collected in the impingers ("back half") of the particulate sampling train would not be required.

The opacity exhibited during the period of the initial Method 5 performance test would be determined, if feasible, through the use of a continuous opacity monitor (COM). Where the control device exhausts through a monovent or where the use of a COM in accordance with the installation specifications of EPA

Performance Specification (PS)–1 of appendix B to 40 CFR part 60, is not feasible, EPA Method 9, "Visual Determination of the Opacity of Emissions from Stationary Sources" would be used. Where the control device discharges through a FF with multiple stacks or an ESP with multiple stacks, the owner or operator would have the option of conducting an opacity test in accordance with Method 9, in lieu of installing a COM.

Under the proposed standard, the owner or operator would use EPA Method 23, "Determination of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans from Stationary Sources" to measure D/F emissions from kilns and in-line kiln/raw mills. These tests would be repeated every 5 years. The temperature at the inlet to the PMCD during the period of the Method 23 performance test would be continuously recorded. If carbon injection is used for D/F control the carbon injection rate during the period of the Method 23 performance test would be monitored. Owners or operators of in-line kiln/raw mills would be required to conduct a Method 23 performance test, and monitor the temperature at the inlet to the PMCD while the raw mill is operating, and a separate Method 23 performance test and inlet temperature monitoring while the raw mill is not operating. If applicable, the carbon injection rate

would be monitored during both performance tests. Where applicable, the exhausts from both the kiln or in-line kiln/raw mill and the alkali bypass would be required to meet the D/F standard.

Under the proposed standard, the owner or operator would use a THC continuous emission monitor (CEM) to continuously measure THC emissions from new or reconstructed kilns, new or reconstructed in-line kiln/raw mills, and new raw material dryers. Owners or operators of new or reconstructed in-line kiln/raw mills would be required to demonstrate initial compliance by measuring THC emissions while the raw mill is operating and while the raw mill is not operating. The proposed standard for THC does not apply to the exhaust from the alkali bypass of kilns or in-line kiln/raw mills. Each THC CEM would be required to be designed, installed, and operated in accordance with EPA Performance Specification (PS)–8A of 40 CFR part 60, appendix B. [3]

Under the proposed standard, the owner or operator would use EPA Method 9, "Visual Determination of the Opacity of Emissions from Stationary Sources" to measure the opacity of gases discharged from raw mills, finish mills, raw material dryers and materials handling processes. These tests would be repeated every five years. A summary of proposed compliance and monitoring options is given in Table 4.

TABLE 4.—SUMMARY OF PROPOSED COMPLIANCE DEMONSTRATION AND MONITORING REQUIREMENTS

Affected source and pollutant	Compliance demonstration	Monitoring requirement
New and existing NHW kiln and NHW in-line kiln/raw mill [b, c] PM.	EPA Method 5 [a]	COM if feasible [d, e] or daily EPA Method 9 visual opacity readings.
New and existing NHW kiln and NHW in-line kiln/raw mill [b, c, h, i] D/F.	EPA Method 23 [a]	Monitor temperature at inlet to PM control device [f] and minimum carbon injection rate if activated carbon injection is used.

[3] The EPA proposed amendments to appendix B of 40 CFR part 60 on April 19, 1996 at 61 FR 17358.

TABLE 4.—SUMMARY OF PROPOSED COMPLIANCE DEMONSTRATION AND MONITORING REQUIREMENTS—Continued

Affected source and pollutant	Compliance demonstration	Monitoring requirement
New NHW kiln and NHW in-line kiln/raw mill THC.	THC CEM (EPA PS–8A)[j]	THC CEM (EPA PS–8A)[j]
New and existing clinker cooler PM	EPA Method 5[a]	COM[d, g] or daily EPA Method 9 visual opacity readings.
New and existing raw and finish mill PM	EPA Method 9[a, g]	Daily EPA Method 22 visual opacity readings or operation of bag break detectors.
New and existing raw material dryer and materials handling processes (raw mill system, finish mill system, raw material storage, clinker storage, finished product storage, conveyor transfer points, bagging, and bulk loading and unloading systems) PM.	EPA Method 9[a, g]	None.
New raw material dryer THC	THC CEM (EPA PS–8A)[j]	THC CEM (EPA PS–8A)[j]

[a] Required initially and every 5 years thereafter.
[b] Includes main exhaust and alkali bypass.
[c] In-line kiln/raw mill to be tested with and without raw mill in operation.
[d] Must meet COM performance specification criteria. If the fabric filter or electrostatic precipitator has multiple stacks, daily EPA Method 9 visual opacity readings may be taken instead of using a COM.
[e] Opacity limit is 20 percent. Corrective action trigger is 15 percent.
[f] Site-specific temperature limit at APCD inlet is established during successful D/F emissions testing.
[g] Opacity limit is 10 percent.
[h] Alkali bypass is tested with the raw mill on.
[i] Temperature parameters determined separately with and without the raw mill operating.
[j] EPA Performance Specification (PS)-8A. Proposed on April 19, 1996 at 61 FR 17358.

D. Monitoring Requirements

The proposed rule requires owners or operators to monitor the opacity of gases discharged from kilns, in-line kiln/raw mills, alkali bypasses and clinker coolers using a COM, if a COM can be feasibly installed in accordance with PS–1 of appendix B to 40 CFR part 60. Where it is not feasible to install a COM, e.g., where the control device discharges through a monovent, the owner or operator would be required to monitor emissions by conducting daily Method 9 tests. Where the control device discharges through an FF with multiple stacks or an ESP with multiple stacks, the owner or operator would have the option of conducting daily tests in accordance with Method 9, in lieu of installing a COM. The duration of the Method 9 tests would be 30 minutes. Owners or operators would also be required to determine kiln or in-line kiln/raw mill feed rate.

The opacity limit for kilns and in-line kiln/raw mills would be 20 percent. Any 30-minute average opacity reading greater than 20 percent determined by the COM or daily Method 9 test would be a violation of the standard. Any ten consecutive 30-minute average COM readings exceeding 15 percent, or any single 30-minute average Method 9 reading exceeding 15 percent would trigger a site-specific operating and maintenance plan, incorporated within the owner or operator's part 70 permit. The owner or operator would be required to initiate the site-specific operating and maintenance plan within one hour. If the opacity exceeds 15

percent for five percent of the operating time as determined by 30-minute average COM readings, or if the 30-minute average readings exceed 15 percent during five percent of the daily Method 9 tests, during any 180 day reporting period, the owner or operator would be required to develop and implement a quality improvement plan (QIP) consistent with subpart D of the draft approach to compliance assurance monitoring.[4] The owner or operator would be required to implement the QIP as expeditiously as possible but in no case would the period for completing the implementation of the plan exceed 180 days. If the owner or operator determined that more than 180 days was required to complete the appropriate improvements, the owner or operator would be required to notify the permitting authority and obtain a site-specific resolution subject to the approval of the permitting authority.

The opacity limit for clinker coolers would be 10 percent, based on any 30-minute average COM or Method 9 reading.

The proposed rule requires the owner or operator to monitor D/F emissions from kilns and in-line kiln/raw mill systems and to maintain the temperature at the inlet to the PMCD at a level no greater than either: (1) the higher of 400 °F or the level established during the successful Method 23 performance test plus five percent (not to exceed 25 °F) of the temperature

[4] The EPA announced its intention to propose subpart D of 40 CFR part 64 on August 13, 1996 at 61 FR 41991.

measured in °F during the successful compliance test, if D/F emissions were determined to be no greater than 0.15 ng toxic equivalent (TEQ)/dscm (6.5×10^{-11} gr/dscf); (2) the higher of 400 °F or the level established during the successful Method 23 performance test, if D/F emissions were determined to be greater than 0.15 ng TEQ/dscm (6.5×10^{-11} gr/dscf) but less than 0.2 ng TEQ/dscm (8.7×10^{-11} gr/dscf); or (3) 400 °F if D/F emissions were greater than 0.2 ng TEQ/dscm (8.7×10^{-11} gr/dscf) but less than or equal to 0.4 ng TEQ/dscm (1.7×10^{-10} gr/dscf).

Owners or operators of in-line kiln/raw mills would be required to establish separate PMCD inlet temperatures applicable to periods when the raw mill is operating and periods when the raw mill is not operating. The appropriate "raw mill operating status dependent" PMCD inlet temperature could not be exceeded. Owners or operators of kilns or in-line kiln/raw mills equipped with alkali bypasses would be required to establish separate temperatures for the inlet to the kiln or in-line kiln raw mill exhaust PMCD and the kiln or in-line kiln alkali bypass PMCD.

If carbon injection is used for D/F control, the carbon injection rate would be monitored, and maintained at a level equaling or exceeding the rate which existed during the successful Method 23 performance test.

The proposed rule requires the owner or operator to monitor THC emissions from the main exhaust of new and reconstructed kilns; the main exhaust of new and reconstructed in-line kiln/raw mills; and new and reconstructed raw

material dryers using a CEM installed in accordance with PS–8A in 40 CFR part 60, appendix B.[5]

The proposed rule requires the owner or operator to monitor the opacity from raw mills and finish mills either by conducting a daily six-minute test in accordance with Method 22, ''Visual Determination of Fugitive Emissions from Material Sources and Smoke Emissions from Flares'', or by installing, calibrating, operating and maintaining a bag break detection system. In the event that fugitive emissions are observed during the Method 22 test, the owner or operator would be required to conduct a 30-minute Method 9 test commencing within 24 hours of the end of the Method 22 test. In addition, the owner or operator would be required to initiate, within one hour, a site-specific operating and maintenance plan developed as part of the application for a part 70 permit.

In the event that the bag break detection system alarm were triggered, the owner or operator would be required to initiate, within one hour, a site-specific operating and maintenance plan developed as part of the application for a part 70 permit.

As required by the NESHAP general provisions (40 CFR part 63, subpart A), the owner or operator also must develop and implement a startup, shutdown, and malfunction plan.

E. Notification, Recordkeeping, and Reporting Requirements

All notification, recordkeeping, and reporting requirements in the general provisions (40 CFR part 63, subpart A) would apply to portland cement manufacturing plants. These include: (1) Initial notification(s) of applicability, notification of performance test, and notification of compliance status; (2) a report of performance test results; (3) a startup, shutdown, and malfunction plan with semiannual reports of

reportable events (if they occur); and (4) semiannual reports of excess emissions. If excess emissions are reported, the owner or operator would report quarterly until a request to return the reporting frequency to semiannual is approved.

Owners and operators would also be required to prepare an operation and maintenance plan for kiln, in-line kiln/raw mill, raw mill and finish mill APCDs consistent with subpart D of the draft approach to compliance assurance monitoring (CAM).[6] The operation and maintenance plan would become part of their operating permit required by 40 CFR part 70.

Under circumstances described in section III. D. of this preamble, kiln and in-line kiln/raw mill monitoring may trigger a requirement to prepare and implement a site-specific Quality Improvement Program (QIP), that will also be consistent with the draft CAM rule.[7] Owners or operators would be required to report if a QIP were required, and to notify the permitting authority if a required QIP would take more than 180 days to implement.

The NESHAP general provisions (40 CFR part 63, subpart A) require that records be maintained for at least 5 years from the date of each record. The owner or operator must retain the records onsite for at least 2 years but may retain the records offsite the remaining 3 years. The files may be retained on microfilm, microfiche, on a computer disk, or on magnetic tape. Reports may be made on paper or on a labeled computer disk using commonly available and compatible computer software.

IV. Impacts of Proposed Standards

A. Applicability

The EPA estimates that there are currently 118 portland cement plants in the United States. All portland cement plants would be subject to the proposed

standards. The following sources would be affected when located at a portland cement plant that is a major source:

(1) New, reconstructed, and existing NHW kilns and NHW in-line kiln/raw mills including alkali bypasses that are not subject to the HWC NESHAP [8] would be subject to emission limits for PM, D/F, and opacity;

(2) New and reconstructed NHW kiln main exhausts and new and reconstructed NHW in-line kiln/raw mills main exhausts, that are not subject to the HWC NESHAP,[9] would be subject to an emission limit for THC;

(3) New and reconstructed raw material dryers would be subject to an emission limit for THC;

(4) New, reconstructed, and existing clinker coolers would be subject to emission limits for PM and opacity; and

(5) New, reconstructed, and existing raw material dryers, raw and finish mills, and material handling processes would be subject to an opacity limit.

The following sources would be affected when located at a portland cement plant that is an area source: new, reconstructed, and existing NHW kilns and NHW in-line kiln/raw mills, including alkali bypasses, that are not subject to the HWC NESHAP,[10] would be subject to emission limits for D/F.

B. Air Quality Impacts

Nationwide baseline HAP emissions from portland cement manufacturing plants are estimated to be 260 Mg/yr (290 tpy) at the current level of control. The proposed standards would reduce emissions of HAPs by 82 Mg/yr (90 tpy) from baseline levels. Estimates of annual emissions of HAPs and expected reductions from implementation of the proposed standards are given in metric and English units in Tables 5 and 6 (docket item II–B–76, docket item II–B–77). The following text reviews the information provided in Tables 5 and 6.

TABLE 5.—NATIONWIDE ANNUAL EMISSIONS OF HAPS AND OTHER POLLUTANTS FROM PORTLAND CEMENT MANUFACTURING PLANTS

[Metric units]

Source	Pollutant	Baseline emissions (Mg/yr)	Emission reduction (Mg/yr)
Kilns, in-line kiln/raw mills, and alkali bypasses	HAP Metals [a]	150	35.
	PM [a]	14,000	3,400.
	D/F (TEQ) [b]	44 g/yr	16 g/yr.
	Organic HAPs [c]	120	47.
	THC [c]	530	200.

[5] The EPA proposed amendments to appendix B of 40 CFR part 60 on April 19, 1996 at 61 FR 17358.

[6] The EPA announced its intention to propose subpart D of 40 CFR part 64 on August 13, 1996 at 61 FR 41991.

[7] The EPA announced its intention to propose subpart D of 40 CFR part 64 on August 13, 1996 at 61 FR 41991.

[8] The EPA proposed regulations for subpart EEE of 40 CFR part 63 on April 19, 1996 at 61 FR 17358.

[9] The EPA proposed regulations for subpart EEE of 40 CFR part 63 on April 19, 1996 at 61 FR 17358.

[10] The EPA proposed regulations for subpart EEE of 40 CFR part 63 on April 19, 1996 at 61 FR 17358.

TABLE 5.—NATIONWIDE ANNUAL EMISSIONS OF HAPS AND OTHER POLLUTANTS FROM PORTLAND CEMENT MANUFACTURING PLANTS—Continued

[Metric units]

Source	Pollutant	Baseline emissions (Mg/yr)	Emission re-duction (Mg/yr)
Clinker coolers	HAP Metals[a]	1.1	0.18.
	PM[a]	8,100	1,300.

[a] These numbers pertain to existing sources only.
[b] These numbers pertain to both new and existing NHW kilns.
[c] These numbers pertain to new NHW kilns only.

TABLE 6.—NATIONWIDE ANNUAL EMISSIONS OF HAPS AND OTHER POLLUTANTS FROM PORTLAND CEMENT MANUFACTURING PLANTS

[English units]

Source	Pollutant	Baseline emissions (tpy)	Emission re-duction (tpy)
Kilns, in-line kiln/raw mills, and alkali bypasses	HAP Metals[a]	160	38.
	PM[a]	16,000	3,800.
	D/F (TEQ)[b]	0.096 lbs/yr ..	0.035 lbs/yr.
	Organic HAPs[c]	130	52.
	THC[c]	580	220.
Clinker coolers	HAP Metals[a]	1.2	0.2.
	PM[a]	8,800	1,400.

[a] These numbers pertain to existing sources only.
[b] These numbers pertain to both new and existing NHW kilns.
[c] These numbers pertain to new NHW kilns only.

The proposed MACT standards would reduce PM emissions from the existing NHW cement kilns and in-line kiln/raw mills by 3,400 Mg/yr (3,800 tpy) from the baseline level, a reduction of 24 percent. Emissions of HAP metals from the affected existing NHW cement kilns and in-line kiln/raw mills would be reduced by 35 Mg/yr (38 tpy), a reduction of 24 percent from the baseline level. Emissions of D/F TEQ would be reduced by 15 grams (g)/yr (0.033 lb/yr), a reduction of 36 percent from the baseline level, at existing NHW cement kiln and in-line kiln/raw mills.

For new NHW cement kilns and in-line kiln/raw mills, the MACT standards are projected to reduce emissions of D/F TEQ by an average of 0.6 g/yr (0.001 lb/yr) over the next 5 years (from major and area sources), a 36 percent reduction from projected baseline emissions. For new kilns, the proposed standards would also reduce projected emissions of THC by an average of 200 Mg/yr (220 tpy) and organic HAPs by an average of 47 Mg/yr (52 tpy) over the next 5 years, an emissions reduction for each of 39 percent from corresponding estimated nationwide baseline emissions (docket item II–B–76).

The proposed MACT standards would reduce PM emissions from 35 percent of the existing clinker coolers by 1,300 Mg/yr (1,400 tpy) from the baseline level, a reduction of 16 percent. Emissions of HAP metals from the affected existing clinker coolers would be decreased by 0.18 Mg/yr (0.2 tpy), a reduction of 16 percent from the baseline level.

Additional reductions of THC and organic HAPs will result from the MACT standards for new raw material dryers. However, information on THC emission rates from raw material dryers and the number of such affected sources is not currently available, so nationwide reductions cannot be estimated.

The MACT standards would also reduce PM emissions from raw material dryers, and other material handling processes. However, no impacts were estimated for these affected sources because there is no available information on typical PM emissions from the affected sources that do not meet the NSPS, and no information on the number of sources potentially affected by this MACT standard.

C. Water Impacts

Control of D/F emissions using water injection for temperature reduction would result in an estimated increased water consumption (evaporated into the kiln exhaust gas for cooling) of 190 million gallons per year for existing NHW kilns and NHW in-line kiln/raw mills of 8 million gallons per year for new NHW kilns and NHW in-line kiln/raw mills (docket item II–B–77).

D. Solid Waste Impacts

The amount of solid waste from existing NHW kilns, in-line kiln/raw mills, and clinker coolers (located at major sources) would increase by an estimated 4,700 Mg/yr (5,200 tpy) due to the proposed standard for PM control (docket item II–B–77).

E. Energy Impacts

For existing NHW kilns and NHW in-line kiln/raw mills the proposed MACT standards for PM and D/F would increase energy consumption by an estimated 11 million kilowatt hours (KWh)/yr [38 billion British thermal units (Btu)/yr]. For new NHW kilns and NHW in-line kiln/raw mills the proposed MACT standards for D/F would increase energy consumption by an estimated (docket item II–B–77) 10,600 KWh/yr (36 million Btu/yr).

F. Nonair Health and Environmental Impacts

The reduction in HAP emissions would have a beneficial effect on nonair health and environment impacts. D/F and HAP metals have been found in the Great Lakes and have been listed as pollutants of concern due to their persistence in the environment, potential to bioaccumulate, and toxicity to humans and the environment (docket item II–A–31, pp. 18 to 21). Implementation of the proposed

NESHAP would aid in reducing aerial deposition of these emissions.

Occupational exposure limits under 29 CFR part 1910 are in place for some of the regulated HAPs (and surrogates) except D/F. The National Institute for Occupational Safety and Health recommends an exposure level for D/F at the lowest feasible concentration (docket item II–I–45, p. 124). The proposed NESHAP would reduce emissions, and consequently, occupational exposure levels for plant employees.

G. Cost Impacts

For existing NHW kilns, NHW in-line kilns/raw mills, clinker coolers, raw and finish mills, and materials handling facilities, the projected total capital costs (including estimated monitoring costs) of the proposed standard for controlling emissions of PM and D/F are $87 million. The projected annual costs (including monitoring costs) for these controls are $27 million. For new NHW kilns and NHW in-line kiln/raw mills, the projected total capital and annual costs of the MACT standard for D/F are $390,000 and $89,000, respectively. No capital and annual costs are projected for new and reconstructed NHW kilns, NHW in-line kilns/raw mills, and clinker coolers as a result of the proposed standard for PM because these sources will be required to comply with the existing NSPS for portland cement plants (40 CFR part 60, subpart F). The proposed THC emissions limit for new NHW kilns and NHW in-line kiln/raw mills can be met by processing materials with typical levels of organic content, without installing and operating add-on pollution control systems that would be relatively costly. Feed materials that have sufficiently low levels of organic matter are widespread across the U.S., and the siting of new kilns is not expected to be significantly limited by the proposed emission limit. Information is not available to quantify the costs of excluding deposits of feed materials with the highest levels of organic constituents as the primary feed for new kilns. Owners/operators of the few existing cement plants that process feed materials containing relatively high levels of organic material, and who desire to expand production through the addition of a new kiln, would need to blend their existing feed materials with lower THC materials from offsite, or selectively process lower organic portions of the feed materials from the onsite mine or quarry in the new kiln. Regarding the costs of monitoring, for new NHW kilns and in-line kiln/raw mills, the projected fifth-year national capital and annual costs of monitoring

THC with a continuous emission monitor at an estimated four new kilns are $576,000 and $340,000, respectively (docket item II–B–77).

H. Economic Impacts

An economic analysis of the proposed NESHAP was conducted. The EPA estimates that regional market price increases would be between 0.6 and 2.0 percent. The national average price increase is estimated to be 1.1 percent. The related decreases in quantity demanded are estimated to range from 0.5 to 1.8 percent, with a national average of 0.9 percent. Domestic production is estimated to decrease more than consumption (1.7 percent compared to 0.9 percent nationally because imports are estimated to increase by 6.3 percent). The decreases in domestic production may lead to the loss of approximately 230 jobs. No plants are expected to close; two kilns are expected to cease operating (docket item II–A–46).

V. Selection of Proposed Standards

A. Selection of Source Category

Section 112(c) of the Act directs the Agency to list each category of major and area sources, as appropriate, that emits one or more of the HAPs listed in section 112(b) of the Act. The EPA published an initial list of source categories on July 16, 1992 (57 FR 31576), and revised the list on June 4, 1996 (61 FR 28197). "Portland Cement Manufacturing" is one of the 174 categories of sources on the initial list. As defined in the EPA report, "Documentation for Developing the Initial Source Category List" (docket item II–A–18), the Portland Cement Manufacturing source category includes any facility engaged in manufacturing portland cement by either the wet or dry process. The category as described for the listing includes but is not limited to the following process facilities: kiln, clinker cooler, raw mill system, finish mill system, raw material dryer, raw material storage, clinker storage, finished product storage, conveyor transfer points, bagging, and bulk loading and unloading systems.

The term "major source" is defined under section 112(a)(1) of the Act and in the EPA general provisions (40 CFR 63.2) as:

* * * any stationary source or group of stationary sources located within a contiguous area under common control that emits or has the potential to emit considering controls, in the aggregate, 10 tons per year or more of any hazardous air pollutant or 25 tons per year or more of any combination of hazardous air pollutants * * *

This definition of major source has been upheld in a recent decision, *National Mining Ass'n* v. *EPA,* 59 F.3d 1351 (D.C. Cir. 1995). In this case, the Court also concluded that "EPA may require the inclusion of fugitive emissions in a site's aggregate emissions without conducting any special rule making" for the purpose of determining whether a source is major.

The listing of the portland cement major source category was based on the Administrator's determination that some portland cement plants would be major sources of particulate HAPs, including but not limited to compounds of arsenic, cadmium, chromium, lead, manganese, mercury, nickel, and selenium. Information and data have been compiled by the EPA characterizing the portland cement manufacturing process and its associated emission sources. There are three main steps to manufacturing portland cement: (1) kiln feed preparation (i.e., crushing and grinding), (2) firing the raw mix in a rotary kiln to produce clinker (including fuel handling), and (3) clinker grinding to produce cement. The responses received from the information collection request (ICR) that was sent to every company in the industry indicated that HAP emissions have been identified from all steps in the manufacturing process. The kiln feed preparation and clinker grinding operations all produce particulate emissions, a fraction of which are metal HAPs. The responses also showed that HAPs are emitted from the clinker production step; the kiln exhaust gases contain metal HAPs, organic HAPs, and HCl.

All kiln exhaust gases are controlled at the existing plants by either FFs or ESPs to limit PM emissions. Based on currently available data, there are no plants that would be defined as major sources according to section 112(a) of the Act on the basis of the mass of metal HAPs emitted from kilns. That is, the reported emissions, considering controls, did not exceed 9.1 Mg/yr (10 tpy) of a single metal HAP or greater than 22.7 Mg/yr (25 tpy) of a combination of metal HAPs from a cement kiln. However, operators of portland cement plants must include HAP emissions from fugitive sources in determining whether their facility is a major source of HAP emissions. Fugitive sources may emit enough HAP metals to make a plant a major source (when fugitive emissions are combined with all other HAP emissions at the site).

ICR responses for individual plants did show quantities of hydrogen chloride (HCl) and chlorine each being emitted in excess of 9.1 Mg/yr (10 tpy).

Most HCl emissions (reported in the ICR responses) were measured by EPA Method 26, a method that may underestimate HCl emissions by a factor of 2 to 25 (docket item II–I–121). Results of Fourier Transform Infrared (FTIR) spectroscopy emissions tests suggest that most plants may be major sources of HCl. Hydrochloric acid concentrations of two wet process portland cement kiln exhaust gases (docket item II–A–20, docket item II–A–40) determined by FTIR spectroscopy ranged from 11 parts per million by volume (ppmv) to 110 ppmv (dry basis corrected to 7 percent oxygen). Assuming an average HCl emission of 50 ppmv (dry basis, corrected to 7 percent oxygen), a wet kiln producing 600,000 tpy of clinker would emit approximately 150 tpy of HCl.

Some plants reported formaldehyde, benzene, and toluene emissions each to be in excess of 9.1 Mg/yr (10 tpy). One plant injects activated carbon into the kiln exhaust to reduce the plume opacity thought to be caused by hydrocarbons in the feed (docket item II–B–35). Various organic HAPs were detected in its kiln exhaust using FTIR spectroscopy (docket item II–A–41). Based on the kiln operating 330 d/yr, 24 hr/d, kiln emissions were estimated at 331 Mg/yr (365 tpy) of hexane, 29 Mg/yr (32 tpy) of benzene, 27 Mg/yr (30 tpy) of toluene, 15 Mg/yr (16 tpy) of naphthalene, and 12 Mg/yr (13 tpy) chlorobenzene (docket item II–A–41, docket item II–B–76).

Based on ICR responses, acetaldehyde, acrylonitrile, arsenic compounds, lead compounds, manganese compounds, mercury compounds, naphthalene, phosphorus, styrene, and xylenes were emitted at rates of one tpy or greater from at least one portland cement kiln (docket item II–B–69). The analysis of HAP emissions data from portland cement manufacturing plants summarized above indicates that most if not all cement plants are major sources of HAP emissions.

Consideration of subcategories or classes. Section 112(d)(1) of the Act provides that the Administrator may distinguish among classes, types and sizes of sources within a category or subcategory in establishing standards. The EPA reviewed the listed source category to determine if different classes were warranted. All portland cement is manufactured in direct-fired, rotating kilns. In 1993, 210 kilns at 118 plants were in operation throughout the nation and Puerto Rico (docket item II–I–101).

There are two main portland cement manufacturing processes differentiated on the basis of feed preparation: wet process and dry process. Approximately one-third of the kilns in operation use a wet process; the other two-thirds use a dry process. The trend in the industry for new kilns is toward the dry process because it is more energy efficient than the wet process. Within the dry process there are three variations: long kiln dry process, preheater process, and preheater/precalciner process. The wet process kilns and all variations of the dry process kilns use the same raw materials and use the same types of pollution controls for PM emissions (docket item II–C–94, attachment chapters 2 and 3). Based on ICR responses and test data the use of these pollution controls to meet the NSPS for PM is feasible for wet kilns and all types of dry kilns. Likewise test data show that lowering kiln exhaust gas temperature to 400° F at the APCD inlet, MACT for reducing D/F concentrations, is feasible for wet and all types of dry kilns. In any event, if classes were defined based on process type, the MACT floor technology would be identical (docket item II–B–73). For this reason, the EPA does not propose classes based on process type.

The EPA OSW has recently proposed NESHAPs for various HWC types, including cement kilns which burn hazardous waste.[11] The proposal is consistent with the terms of the 1993 settlement agreement between the Agency and a number of groups that challenged EPA's final RCRA rule entitled ''Burning of Hazardous Waste in Boilers and Industrial Furnaces'' (56 FR 7134, February 21, 1991) and with the Agency's Hazardous Waste Minimization and Combustion Strategy that was first announced in May 1993. Hazardous waste burning cement kilns are included in the portland cement manufacturing source category, but are subject to different regulations than the NHW kilns. This proposed NESHAP for portland cement manufacturing covers only NHW kilns and NHW in-line kiln/raw mills. However, this proposed NESHAP does cover the other affected sources (including clinker coolers, raw material dryers, and materials handling processes) located at manufacturing plants regardless of whether the plant has hazardous waste-burning cement kilns.

Decision to regulate portland cement area sources. Section 112(c)(6) of the Act states that by November 15, 2000, EPA must list and promulgate section 112(d)(2) or (d)(4) standards (i.e., standards reflecting MACT) for categories (and subcategories) of sources

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[11] The EPA proposed regulations for subpart EEE of 40 CFR part 63 on April 19, 1996 at 61 FR 17358.

emitting seven specific pollutants, including the following HAPs emitted by cement kilns: mercury, 2,3,7–8 tetrachlorodibenzofuran, and 2,3,7–8 tetrachlorodibenzo-p-dioxin. (Although other 112(c)(6) HAPs have been found in cement kiln exhaust, the majority of the emissions data and concern for NHW cement kiln 112(c)(6) HAPs is for mercury and dioxin/furans.) The EPA must assure that source categories accounting for not less than 90 percent of the aggregated emissions of each enumerated pollutant are subject to MACT standards. Congress (docket item II–I–13, p. 155 to 156) singled out the HAPs enumerated in section 112(c)(6) as being of ''specific concern'' not just because of their toxicity but because of their propensity to cause substantial harm to human health and the environment via indirect exposure pathways (i.e., from the air through other media, such as water, soil, food uptake, etc.). Furthermore, these pollutants have exhibited special potential to bioaccumulate, causing pervasive environmental harm in biota (and, ultimately, human health risks).

The EPA estimates that approximately five tons of mercury are emitted annually in aggregate from NHW cement kilns at portland cement plants in the U.S. (docket item II–B–65). Also, it is estimated that NHW kilns emit in aggregate approximately 22 lb of D/F (or about 0.10 lb TEQ per year (docket item II–B–57, docket item II–B–76). To assure that these pollutants are subject to MACT, EPA is proposing to add the portland cement manufacturing area source category to the list of source categories and subcategories listed pursuant to section 112(c)(6). [See 62 FR 33625, 33637–38; June 20, 1997.] The EPA is doing so because area and major source cement kilns emit these HAPs in roughly equal quantities, because the dioxins and furans emitted by area sources are equally toxic as those emitted by major sources (i.e., the distribution of dioxin and furan isomers is the same for both area and major sources), and because these are particularly toxic HAPs. In addition, EPA is already counting on control of these pollutants from cement kiln area sources through the MACT process in assuring that sources accounting for at least 90 percent of the emissions of these HAPs are subject to standards under section 112(c)(6). [See 62 FR at 33635, 33636; June 20, 1997.]

The EPA notes, however, as it did in the June 20th notice, that although the section 112(c)(6) listing process makes sources subject to standards under subsection (d)(2) or (d)(4), the language of section 112(c)(6) does not specify

either a particular degree of emissions control or a reduction in these specific pollutants emissions to be achieved by such regulations. Rather, the specific control requirements will result from determining the appropriate level of control under MACT [section 112(d)(2), or section 112(d)(4)], and this interpretation will be made during the section 112(d) rulemakings affecting the particular source category, not as part of the section 112(c)(6) listing process. [See 62 FR at 33631; June 20, 1997.]

As noted above, EPA is interpreting section 112(c)(6) to require the Agency to establish standards under section 112(d)(2) or 112(d)(4) for all sources listed pursuant to section 112(c)(6), whether such sources are major or area sources. This interpretation reflects the express language of section 112(c)(6) that sources * * * of each such pollutant are subject to standards under subsection (d)(2) or (d)(4) and is in accord with the function of section 112(c)(6):

To assure that sources emitting significant amounts of the most dangerous HAPs are subject to the rigorous MACT standard-setting process.

[See S. Rep. No. 228, 101st Cong. 1st Sess., pp. 155, 166.]

The EPA has in fact already adopted this interpretation in the proposed rule for hazardous waste combustion sources.

[See 61 FR at 17365; April 19, 1996.]

Under an alternative interpretation of section 112(c)(6), the Agency might also establish standards pursuant to section 112(d)(5)—based on generally available control technology (GACT)—for area sources listed under section 112(c)(6). Section 112(d)(5) states that for categories and subcategories of area sources listed pursuant to subsection 112(c), the Administrator may establish standards pursuant to GACT rather than MACT. Although the reference to listing area sources may have been intended to refer to the area source listing process in section 112(c)(3), it arguably extends to listing under section 112(c)(6) as well. The Agency requests comment on the use of this alternative approach to standard-setting for area sources listed under section 112(c)(6).

In addition, the EPA is interpreting section 112(c)(6) to require that, for sources listed under section 112(c)(6), MACT [or section 112(d)(4)] controls apply only to the section 112(c)(6) HAPs emitted by the source. Thus, in this proposed rule, only mercury, D/F, and POM (using THC as a surrogate) emitted by cement kiln area sources would be subject to the MACT standards. The EPA is aware that it proposed a different

interpretation in the hazardous waste combustion NESHAP (see 61 FR at 17365–66), but now believes that section 112(c)(6) is better read to apply only to particular HAPs rather than to the entire source. (Since the language of section 112(c)(6) is ambiguous as to whether the entire source must comply with MACT, or just for the HAPs enumerated in section 112(c)(6), [see 61 FR at 17365 n. 12], either interpretation is legally permissible.) Applying the provision to the entire source could result in applying MACT to all HAPs emitted by area sources under circumstances where control would not otherwise be warranted.

B. Selection of Emission Sources

The portland cement manufacturing process consists of the following unit operations:

(1) Grinding the carefully proportioned raw materials to a high degree of fineness;

(2) firing the raw mix in a rotary kiln to produce clinker;

(3) grinding the resulting clinker to a fine powder and mixing with gypsum to produce cement; and

(4) raw and finished materials handling.

The following sections include descriptions of the affected sources in the portland cement manufacturing source category, the origin of emissions from these affected sources, and factors affecting the emissions. The affected sources for which MACT standards are being proposed include the kiln, in-line kiln/raw mills, clinker cooler, raw and finish mills, raw material dryer, and materials handling processes.

1. Feed Preparation Processes (Grinding, Conveying)

Oxides of calcium, silicon, aluminum, and iron comprise the basic ingredients of cement. The calcareous raw materials include limestone, chalk, marl, sea shells, aragonite, and an impure limestone known in the industry as natural cement rock. The requisite silica and alumina may be derived from clay or shale from a limestone quarry. Such materials usually contain some of the required iron oxide, but many plants need to supplement the iron with mill scale, pyrite cinders, or iron ore. Silica is supplemented, if necessary by adding sand to the raw mix; alumina may be supplemented by adding bauxite or alumina-rich flint clays to the raw mix (docket item II–I–5, p. 180).

Industrial by-products and wastes are becoming more widely used as feed materials for cement production, e.g., slags contain carbonate-free lime, as well as substantial levels of silica and

alumina. Fly ash from coal-fired boilers can often be a suitable feed component, since it is already finely dispersed and provides silica and alumina (docket item II–I–5, p. 180).

Ball mills are used to grind the feed material to the required fineness for both the wet and dry processes. In the wet-kiln process, the raw materials are ground with water to produce a well-homogenized slurry. In the dry-kiln process, raw materials are ground in closed-circuit ball mills with air separators.

Emissions from the grinding and conveying operations are essentially particulate emissions (e.g., dust from limestone, clay, bauxite ore) which contain HAP metals. Particulate matter control devices (FFs and ESPs) serve as HAP control devices. The quantity of emissions of HAP metals from raw materials handling processes are site specific and depend on dust control practices and weather conditions.

2. Feed Preparation Processes (Drying, Blending, Storage)

Drying of kiln feed materials can be carried out in separate units that are gas- or coal-fired. However, to improve the process energy efficiency, waste heat can be utilized directly in the mill by routing the kiln gases through the raw mill. The catch from the APCDs that follow the raw mill is returned to the process and therefore, the APCD is also part of the process (docket item II–I–109, chapter 11.6). Where kiln gases are routed through the raw mill, emissions from the combined in-line kiln/raw mills must be controlled for the same pollutants and to the same extent as kiln gases.

The more energy efficient preheater and preheater/ precalciner kilns usually route the exhaust gas from the preheater to a raw mill to dry the material in suspension in the mill. The gas stream exits the raw mill heavily laden with kiln raw material and is exhausted to an APCD to recover the raw material and any material entrained from the kiln preheater system. The raw material is collected and fed to a blending system to provide the kiln with a homogenous raw feed. Dry process blending is usually accomplished in a silo with compressed air (docket item II–I–5, p. 183).

If the raw material dryer uses heat from a separate combustion source (fuel-fired raw material dryer), exhaust gases may contain trace quantities of products of incomplete combustion (PICs), HCl, and metals from the fuel. In addition, if the feed materials contain organic matter, this material may volatilize in the raw material dryer (regardless of the

source of the heat) and the dryer exhaust may contain organic HAPs. Under the NSPS, emissions from the raw material dryer and the feed preparation materials handling processes (raw mill system, raw material storage, and conveyor transfer points) are currently subject to a limit of 10 percent opacity.

3. Kiln

The high temperature processing required to produce portland cement takes place in the rotary kiln. The rotary kiln consists of a refractory-brick-lined cylindrical steel shell that is rotated by an electrical drive. It is a countercurrent heating device slightly inclined so that material fed into the cooler, upper end travels slowly by gravity to be discharged onto the clinker cooler from the hotter, lower discharge end. The burners at the firing end, i.e., the lower or discharge end, produce a current of hot gases that heats the clinker and the calcined and raw materials in succession as the gases pass toward the feed end. As has been mentioned, a kiln can be classified as wet (in which the kiln feed is a slurry) or dry. Dry process kilns include the older-style, long dry process kiln with a single firing point; the preheater/kiln system; and the preheater/precalciner kiln system. In the preheater/precalciner system, a second burner is used to carry out calcination in a separate vessel interposed between the preheater and the kiln. The precalciner uses preheated combustion air drawn from the clinker cooler and the kiln exit gases and is equipped with an oil or coal burner that burns 50 to 60 percent of the total kiln fuel input. The precalciner system permits the use of smaller kilns since only the actual clinkering process is carried out in the rotary kiln.

The kiln exhaust contains a wide variety of HAPs and other air pollutants that originate from the fuel combustion and from the feed material. In 1991, about 87 percent of the total U.S. kiln capacity used coal, coke, or a combination of coal and coke as the primary fuel (docket item II–I–42, p. 20). Only 3.5 percent of the kiln capacity is fired with natural gas alone (not in combination with other fuels) and oil as a primary fuel represented an insignificant fraction of the total kiln capacity. Plants firing waste-derived fuels account for the balance of the total capacity. The most common waste fuels used in cement kilns are RCRA hazardous waste, tires and tire-derived fuel. To a lesser extent, MSW, medical waste, and used motor oil are fired.

Feed materials are a source of gaseous organic HAP emissions. Some feed

materials contain organic carbon such as petroleum or kerogens. The organic carbon can volatilize in the kiln and appear at the stack exit as a "blue haze" which may contain organic HAPs. During one EPA-sponsored test at a cement kiln using feed material with a high organic matter content, significant levels of benzene (32 tpy) were detected in the kiln exhaust (docket item II–A–41, docket item II–B–76). Organic HAP emissions were found to vary with THC emissions during this test.

Chlorine entering the kiln system (from raw materials and also from fuels) may react with the organic compounds present in the raw materials or with PICs, to form chlorinated hydrocarbons or D/F in the kiln stack exhaust. Approximately 20 percent of the HAPs listed in section 112 of the Act are chlorinated organic compounds.

In the wet process and in the long kiln dry process, the emission point for the kiln gases is typically the APCD discharge stack. In the more complex preheater and precalciner process designs, the kiln gases are routed through other pieces of process equipment, such as the raw mill. In-line kiln/raw mills vent kiln gases through the raw mill. In these systems the gases discharged from the APCD on the raw mill, are in fact kiln exhaust gases.

The kiln alkali bypass stack is an additional emission point for kiln gases which is sometimes found with preheater and precalciner processes. The alkali bypass gas streams are kiln gases that have not contacted the incoming feed material. The kiln gases that are drawn out of the kiln prior to contact with the precalciner and preheater sections pass through a separate APCD and may be discharged to the atmosphere through a separate stack. In other process arrangements, the treated alkali bypass gases are combined with the main kiln exhaust gases and are discharged through a common stack. It is expected that the same HAPs found in the main kiln stack are found in the alkali bypass stack.

Kiln PM/HAP metals. All HAP metals have been identified in kiln exhaust PM at various levels. Based on analysis of emissions test reports, the total average HAP metal content of kiln exhaust PM is approximately one weight percent (docket item II–B–36). Mass emission rates of metal HAPs from the kiln depend on the concentration of metals in the PM and the emission rates of PM. Analyses of emissions data (docket item II–B–62) have shown that ESP-controlled PM emissions for six NHW kilns ranged from 0.009 to 0.20 gr/dscf (corrected to seven percent oxygen), with an average of 0.045 gr/dscf for 14

data points. Fabric filter-controlled PM emissions for five NHW kilns ranged from 0.002 to 0.29 gr/dscf (corrected to seven percent oxygen), with an average of 0.014 gr/dscf for 10 data points. For a 600,000 ton of clinker/year kiln (this represents the capacity of a mid-sized kiln), the range of kiln PM emissions (0.002 gr/dscf to 0.29 gr/dscf) corresponds to 9 tpy to 1,360 tpy (docket item II–B–76). Based on an average kiln PM emission of 0.03 gr/dscf, and assuming HAP metal emissions are one percent by weight of PM emissions, HAP metal emissions are approximately 1.4 tpy for a 600,000 ton of clinker/year kiln (docket item II–B–76). Based on ICR responses, at least one plant reported kiln emissions of over one tpy for one or more of the following metal HAPs: chromium, lead, arsenic, mercury, antimony, and manganese. However, no plant reported kiln emissions of more than 10 tpy of any single metal HAP (docket item II–B–69).

Kiln mercury. Mercury may be emitted in the kiln exhaust as either a particulate or a gas. A summary was compiled of all currently available mercury emission data for HW and NHW kilns (docket item II–B–65). There are 8 data points for 7 NHW kilns, and 19 data points from 21 HW kilns (two sets of kilns shared a stack). The HW kiln data were adjusted to remove mercury in the HW fuel and any mercury spikes. By removing the portion of emissions attributed to test method spiking and HW fuel mercury inputs, corrected emission data that are comparable with data from NHW kilns were developed.

For a 600,000 ton of clinker/year kiln, the range of the mercury emissions data [0.6 to 83 micrograms (μg)/dscm at 7 percent oxygen] corresponds to 0.0012 tpy to 0.17 tpy (docket item II–B–76), while the average mercury emission (24 μg/dscm) corresponds to approximately 0.05 tpy (docket item II–B–76). One plant responding to the ICR reported mercury emissions of over one ton per year.

Kiln D/F. For the purposes of analysis of the data, concentrations of dioxin and furan congeners (specifically the tetra, hepta, hexa, and octa congeners) were converted to a concentration that was equivalent to the toxicity of 2,3,7,8-tetrachlorodibenzo-p-dioxin. Determination of TEQ concentrations was performed according to the international method (docket item II–A–8).

An analysis of all available D/F emission data from 15 NHW kilns showed that concentrations of D/F TEQ emitted in the kiln exhaust gas measured downstream of the PMCD

ranged from 0.001 ng TEQ/dscm to over 1.2 TEQ ng/dscm with an average of 0.20 ng TEQ/dscm (all concentrations at 7 percent oxygen)[D/F test data are shown in Table 8 in Section V.D.2]. For a 600,000 ton of clinker/year kiln, the range of the D/F TEQ concentrations (0.001 to 1.2 ng/dscm) corresponds to 0.0018 g/yr to 2.2 g/yr (docket item II–B–76), while the average concentration (0.20 ng TEQ/dscm) corresponds to an emission of 0.4 g TEQ/year (docket item II–B–76).

The predominant factor affecting D/F emissions is the temperature of gases at the inlet to the PMCD (docket item II–I–81, docket item II–I–82). Test data collected from both HW and NHW kilns show a trend of decreasing D/F gas stream concentrations with decreasing temperature at the inlet to the PMCD. In tests conducted on individual cement kilns where the gas stream temperature was varied in the range of 350 to 500°F, reductions in D/F TEQ concentrations by factors of 5 to 10 were observed when gas temperatures entering the PMCD were lowered from the upper to lower end of the temperature range (docket item II–I–81, docket item II–I–82).

Kiln THC/organic HAPs. The THC and organic HAP concentrations and emission levels from kilns vary widely, depending primarily on the feed materials (docket item II–I–66, docket item II–I–67, docket item II–I–68). Some feed materials contain organic carbon such as petroleum or kerogens. One kiln operator has conducted an extensive study of the source of high THC and carbon monoxide (CO) emissions from the kiln (docket item II–I–107). Higher than normal emissions from this kiln were attributed to the shale used in the raw materials. Replacing the shale with fire clay in the raw mix resulted in a dramatic reduction of THC and CO emissions.

Another NHW kiln operator has determined that the raw materials are the source of the majority of the observed benzene emissions (docket item II–D–112). Kiln stack gas and preheater gas stream analyses before and after switching fuel from a combination of coal and petroleum coke to 100 percent natural gas showed little effect on benzene emissions. These test data suggest that benzene emissions derived from the raw materials (docket item II–I–41).

Fourier transform infrared spectroscopy was used to determine organic HAP emissions at a NHW kiln. Estimated organic HAP emissions (based on average concentrations measured in the kiln exhaust and 7,920 hr/yr of operation) showed that the kiln

was a major source based on organic HAP emissions. Organic HAP emission rates were estimated at 331 Mg/yr (365 tpy) hexane, 27 Mg/yr (30 tpy) toluene, 29 Mg/yr (32 tpy) benzene, 14.5 Mg/yr (16 tpy) naphthalene, and 12 Mg/yr (13.2 tpy) chlorobenzene (docket item II–A–41, docket item II–B–76).

In the ICR responses, many organic HAPs were reported as being emitted in the kiln exhaust gas. Organic HAPs for which there was at least one report of emissions of at least 0.91 Mg/yr (1.0 tpy) include benzene, naphthalene, toluene, formaldehyde, xylenes, styrene, and acetaldehyde. One facility reported more than 9.1 Mg/yr (10 tpy) each of benzene and toluene emissions (docket item II–B–69).

Stack concentrations of THC were available for 16 NHW kilns (docket item II–B–75). The concentrations were expressed in ppmv as propane on a dry basis (ppmvd) at seven percent oxygen. For a 600,000 ton of clinker/year kiln, the range of kiln THC emissions (0.4 ppmvd to 224 ppmvd as propane) corresponds to 1.5 tpy to 840 tpy (docket item II–B–76), while the average kiln THC emissions (35 ppmvd as propane) corresponds to 131 tpy (docket item II–B–76). Organic HAP concentrations, as a percentage of THC for these data, ranged from 0 to 98 percent (docket item II–B–75). With an average of 23 percent of the THC emissions being organic HAPs a 600,000 ton of clinker/year kiln would emit from 0.3 tpy to 190 tpy of organic HAPs, based on the range of THC stack concentrations.

The emissions from kiln alkali bypasses are expected to be the result of incomplete combustion of fuel in the kiln, since this exhaust gas stream does not contact incoming kiln feed materials. Alkali bypass concentrations of THC were available for two kilns operating under NHW conditions. The concentrations were expressed as ppmvd (as propane) at seven percent oxygen, and averaged 3.4 ppmvd and 27 ppmvd, respectively (docket item II–B–75). For typical alkali bypass gas flow rates at a 600,000 ton of clinker/year kiln, this range corresponds to approximately 2.4 tpy to 19 tpy of THC, while the average kiln bypass THC concentration (15 ppmvd) corresponds to 10.5 tpy of THC (docket item II–B–76). Assuming that 5 percent of the THC emissions from alkali bypasses are organic HAPs (docket item II–B–75), a 600,000 ton of clinker/year kiln would emit from 0.3 tpy to 6 tpy of organic HAPs, based on the range of THC alkali bypass stack concentrations.

Kiln HCl. The currently available HCl emission data obtained from a total of

46 NHW and HW kilns range from 0.2 ppmvd to 157 ppmvd and the average is 27 ppmvd for 72 data points (docket item II–B–62). (All concentrations were corrected to seven percent oxygen.) For a 600,000 ton of clinker/year kiln, the range of kiln HCl emissions corresponds to 0.6 tpy to 490 tpy, while the average HCl emission (27 ppmvd) corresponds to 84 tpy (docket item II–B–76). Based on analyses of test reports and ICR responses, HCl emissions range from less than 0.91 Mg/yr (1 tpy) to over 272 Mg/yr (300 tpy). Ten plants responding to the ICR reported emissions of HCl greater than 9.1 Mg/yr (10 tpy) from each of 15 different kilns (docket item II–B–69).

The EPA notes that with the exception of three kilns that were measured by FTIR, all of the HCl emission measurements included in the analysis were obtained using EPA Method 26. A recently completed study that compared the results of a draft test protocol using the gas filter correlation infrared (GFCIR) instrumental method (proposed EPA Method 322) and EPA Method 26 found that HCl measured by GFCIR was typically much higher than that measured by Method 26 (docket item II–I–121). Concentrations of HCl measured by GFCIR ranged from 1.5 to 4.5 times the concentrations measured by Method 26 for wet kilns and up to 30 times the concentrations measured by Method 26 for a dry kiln. Subsequent laboratory recovery efficiency analyses suggested that Method 26 is biased significantly low due to a scrubbing effect in the front half of the sampling train. Therefore, it is likely that currently available HCl emission data are understated.

4. Clinker Cooler

It is desirable to cool the clinker rapidly as it leaves the burning zone of the kiln. Heat recovery, preheating of kiln combustion air, and fast clinker cooling are achieved by clinker coolers of the traveling-grate, planetary, rotary, or shaft type. Most commonly used are grate coolers where the clinker is conveyed along the grate and subjected to cooling by ambient air, which passes through the clinker bed in cross-current heat exchange.

A portion of the clinker cooler exhaust serves as secondary combustion air in the kiln. The remainder of the clinker cooler exhaust is discharged to the atmosphere separately from the kiln exhaust gas through a PM emission control device. Clinker cooler gases are also sometimes routed through other pieces of process equipment, such as the coal or raw mill, as a source of warm,

dry air prior to being reused as combustion air.

Since clinker coolers are not combustion devices, the only HAP expected to be emitted are the metal HAPs associated with the clinker cooler particulate, i.e., clinker dust. HAP metals that have been detected in clinker include chromium, lead, nickel, arsenic, beryllium, antimony, selenium, and mercury. In one study conducted by the Portland Cement Association (docket item II–I–44, p. 4), the average concentration of metal HAPs that has been detected in clinker is 555 parts per million by weight (ppmw). In an earlier study, cited by EPA OSW the average HAP metal content in clinker was found to be 138 ppmw (docket item II–A–24, pp. 3–62 to 3–65). Under the existing NSPS, emissions of PM from clinker cooler gases are limited to 0.05 kg/Mg feed (dry basis) (0.10 lb/ton). A plant producing 600,000 tpy of clinker, emitting PM from the clinker cooler at the NSPS limit, would emit 6 kg (14 lb) of HAP metals per year, assuming a 140 ppmw HAP metal content in the PM (docket item II–B–76).

5. Finish Grinding/Conversion of Clinker to Portland Cement

The cooled clinker is conveyed to clinker storage or mixed with gypsum and introduced directly into the finish mills. The finish mills are large, rotating steel cylinders containing a charge of steel balls. The clinker and gypsum are ground to a fine, homogeneous powder. Two different types of mill systems may be used. In open-circuit milling, the material passes directly through the mill without any separation of fine and coarse particles. In closed-circuit grinding, the mill product is carried to a cyclonic air separator in which the coarse particles are rejected from the product and returned to the mill for further grinding.

The finished portland cement is conveyed to bulk storage silos from which it is dispensed for shipping. Portland cement is often loaded in bulk into hopper trucks or rail cars. It may also be packaged in ''tote bins'' or in 80 lb or 94 lb kraft paper bags. The bags are loaded onto pallets for handling, warehousing, and shipping.

The only HAPs expected to be emitted from clinker/cement handling processes are the metal HAPs associated with clinker and cement dust. As was noted above, clinker dust is estimated to contain 555 ppmw of metal HAPs. The HAP metals that have been identified in portland cement include chromium, nickel, arsenic, lead, antimony, selenium, beryllium, cadmium, and mercury. In cement (as opposed to

clinker), the concentrations of individual HAP metals range from an average of 0.014 ppmw mercury to an average of 76 ppmw chromium. The total average concentration of metal HAPs in portland cement is 143 ppmw (docket item II–I–44).

Total nationwide emissions of HAPs, PM, and VOCs from the above emission sources in portland cement plants are estimated at 23,300 Mg/yr (25,700 tpy). Over 260 Mg/yr (290 tpy) of these emissions are HAPs. Emissions of PM and VOCs are estimated at 23,000 Mg/ yr (25,400 tpy).

Given that these processes release significant quantities of HAPs and the availability of emission control systems, the Agency selected to develop and propose NESHAP for the following emission sources: NHW kilns and NHW in-line kiln/raw mills; NHW kiln alkali bypasses; clinker coolers; raw material dryers; feed preparation and materials handling processes including raw mills, finish mills, storage bins (raw material, clinker, finished product), conveying system transfer points, bagging system, and bulk loading and unloading systems. Additional information on the operations in portland cement plants selected for regulation, and other operations, is included in the docket.

C. Selection of Pollutants

The proposed standards would limit emissions of metal HAPs [almost all metals appearing in section 112(b) have been detected in portland cement plant emissions] and organic HAPs (including D/F) from portland cement manufacturing facilities. (Pollutant health effects were discussed in section II.C.) These HAPs are emitted in significant quantities from portland cement plant sources. The standards being proposed to address metal and organic HAP emissions establish limits for surrogate pollutants rather than for individual HAP compounds (a separate emission limit is established for D/F). The reasons for using surrogate pollutants are discussed below.

Controlling PM emissions will control the emissions of non-volatile metal HAPs (and also the condensed organic HAPs including D/F which are adsorbed on particulates). The available technologies used in the cement manufacturing industry for the control of non-volatile HAP metals are the same technologies (FFs and ESPs) as the proposed MACT floor technologies for control of PM. Metal HAPs are estimated to constitute about 1 percent by weight of kiln PM emissions from portland cement manufacturing and about 0.06 percent by weight of clinker cooler PM emissions. In addition, the

use of PM as a surrogate for non-volatile metal HAP emissions reduces the costs associated with compliance testing and monitoring.

The proposed standards establish an emission limit for THC as a surrogate for organic HAPs from new or reconstructed NHW kilns for the following reasons. Methods used in the cement manufacturing industry for the control of organic HAP emissions would be the same methods used to control THC emissions. These emission control methods include using feed materials with relatively low levels of organic matter and achieving good combustion (docket item II–B–47, docket item II–B– 48). Standards limiting emissions of THC will also result in decreases in organic HAP emissions (with the additional benefit of decreasing VOC emissions).

Establishing emission limits for specific organic HAPs (with the exception of D/F) would be impractical and costly. Total hydrocarbon, which is less expensive to test for and monitor, can be used as a surrogate for organic HAPs. Based on available data, organic HAPs range from 0 to 98 percent of THC and are estimated to account for approximately 23 percent on average of THC emissions from portland cement manufacturing (docket item II–B–75). The Agency recognizes that the level and distribution of organic HAPs associated with THC emissions from cement kilns will vary from kiln to kiln. Limiting THC as a surrogate for organic HAPs will eliminate costs associated with speciating numerous compounds.

The proposed standards establish separate emission limits for D/F because of the high toxicity associated with even low masses of these compounds. In addition, data available to EPA establish the existence of a separate MACT floor technology for D/F control.

The proposed regulation does not establish a limit for HCl emissions from cement kilns because no MACT floor technology has been identified. An HCl emission limit based on a beyond-the-floor control option was determined not to be justified as discussed in section V.D.2 of this document.

The proposed regulation does not establish limits for mercury emissions from cement kilns because no MACT floor control technology has been identified. A mercury emission limit based on a beyond-the-floor control option was determined not to be justified as discussed in section V.D.2.

D. Selection of Proposed Standards for Existing and New Sources

1. Background

After the EPA has identified the specific source categories or subcategories of sources to regulate under section 112, it must develop MACT standards for each category or subcategory. Section 112 establishes a minimum baseline or ''floor'' for standards. For new sources, the standards for a source category or subcategory cannot be less stringent than the emission control that is achieved in practice by the best-controlled similar source. [See section 112(d)(3)]. The standards for existing sources may be less stringent than standards for new sources, but they cannot be less stringent than the average emission limitation achieved by the best-performing 12 percent of existing sources for categories and subcategories with 30 or more sources, or the average of the best-performing 5 sources for categories or subcategories with fewer than 30 sources.

After the floor has been determined for a new or existing source in a source category or subcategory, the Administrator must set MACT standards that are technically achievable and no less stringent than the floor. Such standards must then be met by all sources within the category or subcategory. The regulatory alternatives selected for new and existing sources may be different because of different MACT floors, and separate emission limits may be established for new and existing sources.

The EPA also may consider an alternative ''beyond the floor.'' Here, EPA considers the achievable reductions in emissions of HAPs (and possibly other pollutants that are co-controlled), cost and economic impacts, energy impacts, and other nonair environmental impacts. The objective is to achieve the maximum degree of emission reduction without unreasonable economic, energy or secondary environmental impacts.

2. MACT Floor Technology, Emission Limits, and Format

The EPA conducted separate MACT determinations for PM (the surrogate for HAP metals), D/F, mercury, THC (the surrogate for organic HAPs), and HCl emissions from kilns and inline kiln/raw mills; for PM emissions from clinker coolers; for PM and THC emissions from raw material dryers; and for PM emissions from materials handling facilities. For each combination of pollutant and affected source, MACT floor technologies and beyond-the-floor control options were evaluated.

Several formats are available for establishing the emission limits based on MACT. These include mass concentration (mass per unit volume), volume concentration (volume per unit volume), mass emission rate (mass per unit time), process emission rate (mass per unit of production or other process parameter), and percent reduction.

For the portland cement manufacturing source category, EPA is proposing numerical emission standards expressed as a process emission rate and opacity limits for PM emissions from kilns; as mass per volume of exhaust gas for D/F emissions from kilns; as volume per volume of exhaust gas for THC emissions from kilns and raw material dryers; as a process emission rate and opacity limit for clinker cooler PM emissions; and as an opacity limit for materials handling facilities PM emissions.

The following sections present a discussion of the rationale for selecting the MACT technologies, emission limits, and format of the standard for each affected source and associated pollutant.

Kiln and in-line kiln/raw mill PM HAP emissions. Well-designed and properly operated FFs or ESPs are the PM control technologies presently in use by the best performing 12 percent of existing kilns and in-line kiln/raw mills. In the portland cement manufacturing industry, it is estimated that at least 30 percent (docket item II–A–4) of existing kilns are subject to the requirements of the NSPS for cement plants (40 CFR part 60, subpart F).

Table 7 lists the type of control device used with, and available PM emissions data from, kilns and in-line kiln/raw mills subject to the NSPS. The emission levels shown in Table 7 all meet the NSPS emission limit and were all achieved with FFs and ESPs designed to meet the NSPS. This represents the MACT floor technology for control of PM from kilns and in-line kiln/raw mills.

TABLE 7.—PARTICULATE EMISSIONS FROM NSPS KILNS

[Docket Item II–A–4, Docket Item II–A–43, Docket Item II–B–62]

Kiln type	APCD type	PM (kg/Mg dry feed)	Location
PH	FF	0.0011	Southdown—Kosmosdale, KY.
PC	FF	a 0.0039	Boxcrow Cement—Midlothian, TX.
PH	ESP	b 0.0075	Ash Grove—Durkee, OR.
DRY	FF	a 0.0090	Southdown #1—Fairborn, OH.
PC	ESP	c 0.015	RMC Lone Star—Davenport, CA.
PC	FF	0.015	Kaiser Cement—Cupertino, CA.
PH	ESP	0.015	Roanoke Cement—Cloverdale, VA.
PC	FF	0.020	Moore McCormack—Knoxville, TN.
PH	FF	0.029	Moore McCormack—Brooksville, FL.
PC	FF	0.033	Kaiser Cement—Lucerne Valley, CA.
PC	FF	0.035	Calif Portland—Mojave, CA.
PC	FF	0.04	Martin Marietta—Leamington, UT.
PC	ESP	0.044	Kaiser—San Antonio, TX.
PC	FF	0.048	Martin Marietta—Lyons, CO.
PH/PC	ESP	b 0.051	Lone Star—Cape Girardeau, MO.
WET	ESP	0.056	Monolith Portland—Laramie, WY.
DRY	FF	0.056	Lone Star—Pryor, OK.
DRY	ESP	d 0.058	Ash Grove #2—Louisville, NE.
PC	ESP	0.065	General Portland—New Braunfels, TX.
PC	FF	0.068	Davenport Industries—Buffalo, IA.
PH	FF	0.070	Ideal Basic—La Porte, CO.
PH	FF	0.074	Southwestern Portland—Odessa, TX.
DRY	ESP	0.11	Ash Grove #1—Louisville, NE.

TABLE 7.—PARTICULATE EMISSIONS FROM NSPS KILNS—Continued

[Docket Item II–A–4, Docket Item II–A–43, Docket Item II–B–62]

Kiln type	APCD type	PM (kg/Mg dry feed)	Location
PC	ESP	0.12	Texas Industries—Hunter, TX.
PC	ESP	0.13	Lehigh—Mason City, IA.
WET	ESP	0.15	Genstar—San Andreas, CA.
WET	FF	0.15	Lone Star—Salt Lake City, UT.

PC = precalciner.
PH = preheater.
a = average of four tests.
b = average of three tests.
c = average of two tests.
d = average of five tests.

The data in Table 7 were obtained from EPA Method 5 compliance tests on new kilns subject to the NSPS [0.15 kg/ Mg dry feed (0.30 lb/ton dry feed)]. These tests measure the performance of PM APCDs associated with new kilns over a relatively short period (typically three 1-hour test runs). These data show that PM emissions from ESPs and FFs designed to meet the NSPS and operated and maintained to demonstrate initial compliance with the NSPS under Method 5 test conditions varied within a range of 0.0011 kg/Mg dry feed (0.0022 lb/ton dry feed) to 0.15 kg/Mg dry feed (0.3 lb/ton dry feed). The data in Table 7 show equivalent performance can be expected from FFs and ESPs, and that neither technology offers a clear advantage. Due to the fact that the best performing kilns and in-line kiln/raw mills use FFs and ESPs designed to meet the NSPS and because of the variability in performance of well-designed, well-maintained and properly operated FFs and ESPs, the emission limit represented by the MACT floor technology is equivalent to the NSPS of 0.15 kg/Mg dry feed (0.30 lb/ton dry feed).

No technologies were identified for existing or new kilns or in-line kilns/ raw mills that would consistently achieve lower emission levels of PM than the NSPS limit. Consequently, there is no beyond-the-floor technology that has been shown to consistently achieve lower emissions. Therefore the PM emission limit proposed for new and existing kilns and in-line kiln/raw mills is 0.15 kg/Mg dry feed (0.30 lb/ton dry feed), which is equivalent to the NSPS limit.

The NSPS establishes an opacity limit, and an opacity limit is also being proposed under this standard. The maximum 6-minute average opacity level may not exceed 20 percent opacity, as is the case for the NSPS.

The production-based emission limit format was chosen for kiln and in-line kiln/raw mill PM emissions. The units for this emission standard are kg of PM per Mg of dry feed (lb PM per ton of dry feed). This format (mass per unit of production) and associated opacity limit are consistent with the format of the portland cement plant NSPS (40 CFR part 60, subpart F). At least 30 percent of the kilns in the industry are subject to the NSPS (docket item II–A–4) and these plants are already monitoring the production-based emission rate and the opacity.

A concentration format (*e.g.,* g/dscm [gr/dscf]) was considered for the kiln and in-line kiln/raw mill PM emission limit. One reason that this format was not chosen was that it would be inconsistent with the NSPS PM emission limit format. However, there are other considerations. A concentration format would penalize more energy efficient kilns, which burn less fuel and produce less kiln exhaust gas per megagram of dry feed. This is because with a concentration based standard the more energy-efficient kilns would be restricted to a lower level of PM emitted per unit of production.

Kiln and in-line kiln/raw mill D/F emissions. The EPA has identified two technologies for control of D/F emissions. One technology achieves low D/F emissions by a combination of proper kiln operation, proper combustion, proper control device operation, and a reduction in the kiln gas temperature at the inlet to the PMCD. The other technology is activated carbon injected into the kiln exhaust gas.

The discussion in this section refers to D/F emissions in units of TEQ. Toxic equivalent refers to the international method of expressing toxicity equivalents for dioxins and furans as defined in EPA report, ''Interim Procedures for Estimating Risks Associated with Exposures to Mixtures of Chlorinated Dibenzo-p-dioxins and -dibenzofurans (CDDs and CDFs) and 1989 Update'' (docket item II–A–8).

Dioxin/furan emissions data were obtained from testing that was conducted at NHW kilns, with NHW fuels at kilns that normally burn HW, and under worst-case conditions at kilns that burn HW (as part of Certificate of Compliance [COC] testing). Based on the test results for both NHW and HW kilns, the predominant factor affecting D/F emissions is the temperature of gases at the inlet to the PMCD (docket item II–A–42; docket item II–B–78; docket item II–I–81, pp. 127 to 133; docket item II–I–82, pp. 135 to 175). The highest D/F emissions (near 40 ng TEQ/dscm) occurred at the highest gas temperatures (between 500 °F and 700 °F) while the lowest emissions (near 0.02 ng TEQ/ dscm) occurred at the lowest temperature (at approximately 210 °F). [The emission 0.02 ng TEQ/dscm is the average of the four NHW D/F test results that were measured at gas temperatures less than 230 °F, as shown in Table 8.]

Dioxin/furan TEQ emissions data and stack temperatures from kilns firing NHW fuels are listed in Table 8. The data are listed in order of ascending stack temperature. Fourteen NHW data points were obtained during normal kiln operation, three points were obtained as NHW baseline runs prior to HW COC testing, one data point (at the 518 °F stack temperature) was obtained at maximum combustion temperature, and one point was obtained under unknown test conditions. Stack temperatures are presented, since inlet PMCD temperature data are not typically recorded during stack emissions testing. It is acknowledged that stack temperatures will be lower than inlet PMCD temperatures.

TABLE 8.—AVERAGE DIOXIN/FURAN TOXIC EQUIVALENT EMISSIONS (AT 7 PERCENT OXYGEN) AND AVERAGE STACK GAS TEMPERATURES FOR NHW CEMENT KILNS AND KILNS TESTED UNDER NHW CONDITIONS

[Docket Item II–B–78]

Kiln type	APCD type	Kiln fuel	Avg Gas T (°F)	Avg TEQ ng/ dscm	Kiln location
PH/PC	FF	Natural gas; main stack tested	183	0.011	Capital Aggregates—San Antonio TX.
PC	FF	Coal, tires, pulp/paper mill sludge	220 →	0.0063	Calaveras Cement—Redding CA.
PH/PC	FF	Natural gas; raw mill on	221	0.042	Ash Grove—Seattle WA (kiln/in-line mill).
PH/PC	ESP	Not reported	226	0.00087	RMC Lonestar—Davenport CA.
PC	FF	Coal & tires	233 →	0.21	Calaveras Cement—Redding, CA.
PH/PC	FF	Natural gas; bypass stack tested	299	0.054	Capital Aggregates—San Antonio TX.
WET	ESP	Coal	305	0.0024	Holnam—Florence CO.
WET	ESP	Coal & natural gas	315	0.072	Ash Grove—Montana City MT.
WET	ESP	Coal	346 ⇨	0.37	Lehigh—Union Bridge MD.
WET	ESP	coal & tires	358 ⇨	1.2	Lehigh—Union Bridge MD.
WET	ESP	Coal/coke	366	0.032	Holnam kiln #1—Holly Hill SC.
DRY	FF	Coal, gas, tire derived fuel	396	0.0035	Riverside—Oro Grande CA.
WET	ESP	Natural gas	397	0.020	Capital Aggregates—San Antonio TX.
DRY	FF	Coal & natural gas	403	0.0084	Riverside—Oro Grande CA.
WET	ESP	Coal	417	0.12	Lone Star—Greencastle IN.
WET	ESP	Coal/coke	418	0.04	Holnam kiln #2—Holly Hill SC.
DRY	ESP	Coal, coke, & tires	450	0.074	Lone Star—Oglesby IL.
WET	ESP	Coal	482	0.55	Continental Cement—Hannibal MO.
WET	ESP	Coal	518	1.0	Holnam—Clarksville MO.

Abbreviations:
PH/PC = preheater/precalciner.
ESP = electrostatic precipitator.
PC = precalciner.
FF = fabric filter.
Note: Entries flagged with → and ⇨ are listed in Table 9 and discussed in the text.

The data in Table 8 show that all NHW D/F emissions were less than 0.2 ng TEQ/dscm at stack temperatures below 340 °F, except for one data point which is discussed below. The stack temperature of 340 °F corresponds to an estimated inlet PMCD temperature of approximately 400 °F after accounting for cooling in the ductwork. The EPA estimates that approximately 50 percent of existing PMCDs used at both wet-and dry-type NHW kilns operate with a maximum inlet PMCD temperature of approximately 400 °F (docket item II–B–73). Since the MACT floor is based on the technology in use by the best performing 12 percent of the affected sources, the MACT floor for existing kilns corresponds to reduction of kiln exhaust gas stream temperature at the PMCD inlet to 400 °F.

One demonstrated method of temperature reduction is injection of water to provide rapid cooling of kiln exhaust gases upstream of the inlet to the PMCD. Rapid cooling reduces D/F formation that occurs within the temperature window 232 °C (450 °F) to 343 °C (650 °F).

As shown in Table 8, D/F emissions from 3 of the 13 tests conducted at stack temperatures below 400 °F exceeded 0.2 ng TEQ/dscm. For discussion purposes,

the three data points are listed in Table 9 with the corresponding stack temperature. The Calaveras kiln that emitted 0.21 ng TEQ/dscm when tested at a stack temperature of 233 °F emitted 97 percent less D/F at a slightly lower stack temperature and with a different mixture of fuels, demonstrating that the kiln could achieve 0.2 ng/dscm through proper kiln combustion.

TABLE 9.—DATA FROM KILNS AT WHICH DIOXIN/FURAN TEQ EMISSIONS EXCEEDED 0.2 NG/DSCM

Average stack gas temperature (°F)	Average D/F TEQ (ng/ dscm at 7% O$_2$)	Kiln location
233	0.21	Calaveras—Redding CA.
346	0.37	Lehigh—Union Bridge MD.
358	1.2	Lehigh—Union Bridge MD.

The Lehigh kiln emitted 0.37 ng TEQ/dscm at a stack temperature of 346 °F during coal combustion and 1.2 ng TEQ/dscm at a stack temperature of 358 °F during coal and tire combustion. The EPA concluded that the high emission

(of 1.2 ng TEQ/dscm) resulted from poorly controlled tire combustion/kiln operation, since (as shown in Table 8) three other NHW kilns emitted less than 0.2 ng TEQ/dscm when tested while burning tires. In the absence of detailed information on kiln and APCD operating conditions, fuel firing and combustion control, the Lehigh emission level of 0.37 ng TEQ/dscm at a stack temperature of 346 °F cannot be explained.

Temperature reduction to 400 °F, in conjunction with proper control of kiln and PMCD operation and efficient combustion will limit D/F emissions to 0.2 ng TEQ/dscm in most (if not all) cases, and the proposed D/F standard for existing kilns is set at this level. The EPA recognizes that the available emissions data show that one kiln (as illustrated by the Lehigh data in Table 9) cannot achieve 0.2 ng TEQ/dscm at an inlet temperature to the PMCD below 400 °F, and that parameters consistent with proper equipment operation have not been precisely specified. The proposed standards therefore provide that kilns that cannot meet the 0.2 ng TEQ/dscm limit would be required to maintain the temperature at the inlet to the PMCD at no more than 400 °F and to limit the D/F emissions to 0.4 ng

TEQ/dscm. This limit of 0.4 ng TEQ/dscm is consistent with the emissions from the Lehigh kiln during coal combustion with an estimated PMCD inlet gas temperature of 400 °F.

The Agency has considered whether and how to account for emissions variability in establishing the alternative TEQ limit of 0.4 ng/dscm in conjunction with the 400 °F temperature limit at the PMCD. As discussed in this section, available emissions data indicate that most kilns will be able to achieve an emission level of 0.2 ng TEQ/dscm or lower when operating the PMCD at or below 400 °F. Even though the Lehigh kiln's emissions were 0.37 ng TEQ/dscm at 346 °F (when not burning tires), we believe that a TEQ limit of 0.4 ng/dscm is appropriate given the preponderance of emissions data at or below 0.2 ng TEQ/dscm. These data (given the strong indications that all units will meet the 0.4 ng TEQ/dscm limit at temperatures of 400 °F or below) suggest that using a more specific approach for variability is not needed for this proposed standard. The Agency invites comments on other approaches for accommodating variability in D/F emissions for NHW cement kilns.

Thus, the proposed standard requires that the temperature at the inlet to the PMCD be maintained at a level no greater than either: (1) the higher of 400 °F or the temperature established during the successful Method 23 performance test plus five percent (not to exceed 25 °F) of the temperature measured in °F during the successful compliance test, if D/F emissions were determined to be no greater than 0.15 ng toxic equivalent (TEQ)/dscm (6.5×10^{-11} gr/dscf); (2) the higher of 400 °F or the temperature established during the successful Method 23 performance test, if D/F emissions were determined to be greater than 0.15 ng toxic equivalent (TEQ)/dscm (6.5×10^{-11} gr/dscf) but less than 0.2 ng toxic equivalent (TEQ)/dscm (8.7×10^{-11} gr/dscf);, or (3) 400 °F if D/F emissions were greater than 0.2 ng TEQ/dscm (8.7×10^{-11} gr/dscf) but less than or equal to 0.4 ng TEQ/dscm (1.7×10^{-10} gr/dscf).

Activated carbon injection (ACI) was investigated as a potential beyond-the-MACT-floor option for existing cement kilns. Activated carbon injection is used at one cement plant on two NHW kilns for the purpose of reducing plume opacity. The total capital cost of an ACI system is estimated to range from $680,000 to $4.9 million per kiln. The total annual costs of an ACI system are estimated to range from $426,000 to $3.3 million per kiln. These costs include the carbon injection system and an additional baghouse to collect the

carbon separately from the existing primary particulate collector (docket item II–B–67). Based on these costs, and considering the level of D/F emissions achievable at the floor level of control, the Administrator has determined that this beyond-the-floor (BTF) option for D/F MACT for existing kilns may not be justified. Therefore the Agency is not proposing a BTF standard. Notwithstanding these costs and the limited emissions reductions that a BTF standard would achieve, the Agency solicits comment on whether a BTF standard would be appropriate given the Agency's and the Congress' special concern about D/F. D/F are some of the most toxic compounds known due to their bioaccumulation potential and wide range of health effects at exceedingly low doses, including carcinogenesis. Exposure via indirect pathways was in fact a chief reason that Congress singled out D/F for priority MACT control in section 112(c)(6) of the Act [see S. Rep. No. 128, 101st Cong. 1st Sess. at 154–155 (1989)]. Thus costs to reduce dioxin emissions are frequently justified by the benefits of removing this very toxic HAP. [See 61 FR at 17382, 17392, and 17403 (April 19, 1996) (The EPA proposes BTF standards for D/F emissions from hazardous waste combustion sources).] The EPA is influenced here by the fact that most sources appear to be able to achieve the 0.2 ng TEQ/dscm BTF option through the use of the floor technology alone, i.e. solely through the use of temperature control. Thus, the floor standard (which facially allows the option of 0.4 ng TEQ/dscm) in reality may be virtually equivalent to the BTF level.

Activated carbon injection was also considered as a candidate MACT for new cement kilns. Since no D/F performance data are available on the existing cement kiln ACI system installed to reduce opacity, EPA considered the performance of ACI on other potentially similar sources. Experience with ACI on municipal waste combustors (MWCs) and medical waste incinerators (MWIs) has led EPA to develop emission limits for D/F for these sources in the range of 0.26 to 2.5 ng TEQ/dscm (docket item II–J–3, docket item II–J–7). Assuming the performance level of ACI on MWIs or MWCs to be similar to that of a cement kiln, the D/F emissions levels achieved with ACI are expected to be about the same level that can be achieved with temperature reduction. Therefore, considering the level of D/F emissions achievable by PMCD inlet temperature reduction alone, the Administrator has determined that the temperature

reduction plus ACI option for D/F MACT for new kilns may not be justified, and the Agency is not proposing a standard based on ACI. Notwithstanding the limited emissions reduction that such a standard would achieve, the Agency solicits comment on whether or not such a standard would be appropriate, given the Agency's and the Congress' special concern about D/F. The EPA is influenced here, similarly to the situation for existing kilns, by the fact that most new sources appear to be able to achieve a 0.2 ng TEQ/dscm emission level solely through the use of temperature control. Thus the proposed standards (which facially allow a 0.4 ng TEQ/dscm emission level where the implementation of temperature reduction may not achieve a 0.2 ng TEQ/dscm emission level) in reality may be virtually equivalent to a 0.2 ng TEQ/dscm emission level.

For the kiln and in-line kiln/raw mill D/F emission standard, a mass per volume concentration emission limit format was chosen. The specific units of the emission limit are ng of D/F TEQ/dscm, referenced to seven percent oxygen. This emission limit format has historically been used by EPA for many air emission standards. This format is consistent with the format of the OSW MACT standard for HW cement kilns.[12] The concentration is corrected to seven percent oxygen to put concentrations measured in stacks with different oxygen concentrations on a common basis. Also, the typical range of oxygen concentrations in cement kiln stack gas is from five to 10 percent oxygen; therefore, seven percent is representative.

A mass per volume concentration emission limit based on total D/F congeners rather than TEQ was also considered. However, the TEQ format was chosen in order to maintain consistency with the rule for cement kilns which burn hazardous waste.

Kiln and in-line kiln/raw mill mercury emissions. Activated carbon injection (ACI) was considered a potential control technology for mercury MACT for cement kilns, since a form of this technology has been demonstrated on medical waste incinerators and municipal waste combustors (docket item II–A–36, pp. 98 to 99 and B–7 to B–8; docket item II–A–11; docket item II–A–19; docket item II–A–23), and is being used at one cement plant on two NHW kilns to reduce the opacity (docket item II–B–35). In these

[12] The EPA proposed regulations for subpart EEE of 40 CFR part 63 on April 19, 1996 at 61 FR 17358.

applications, the activated carbon (AC) is injected into the uncontrolled exhaust gas stream ahead of the kiln PMCD.

In cement kiln applications for mercury control, the AC would need to be injected downstream from the kiln PMCD and subsequently collected in a separate PMCD, e.g., a baghouse. This is because the PM collected from the kiln exhaust, i.e., cement kiln dust (CKD), is typically recycled from the kiln PMCD back to the kiln, and in some cases may constitute as much as 50 percent of the feed material input to the kiln. If the AC is not injected downstream of the kiln PMCD, and then collected in a separate PMCD downstream of the kiln PMCD, the AC would also be recycled back to the kiln along with the adsorbed mercury. This recycling of mercury back to the cement kiln via the AC would result in the revaporization of the mercury in the kiln gas and ultimately the mercury would be emitted to the atmosphere. The two cement kiln ACI systems cannot be considered as controls for mercury for cement kilns because they do not include provisions for injecting the AC downstream of the kiln PMCD nor do they have the additional PMCD necessary to remove the injected carbon from the exhaust gas stream for disposal, but instead include the AC with the CKD that is recycled to the kiln. Therefore there is no mercury MACT floor for new or existing kilns.

Activated carbon injection (with an additional PMCD) was investigated as a potential beyond-the-MACT-floor option for mercury for new and existing cement kilns. The total capital cost of an ACI system is estimated to range from $680,000 to $4.9 million per kiln. The total annual costs of an ACI system are estimated to range from $430,000 to $3.3 million per kiln. These costs include the carbon injection system and an additional baghouse necessary to collect the carbon separately from the CKD (docket item II–B–67). The cost-effectiveness of ACI applied to cement kilns ranges from $20,000,000 to $50,000,000 per ton of mercury.

It is noted that the Agency has proposed a mercury emissions limit for hazardous waste burning (HW) cement kilns (61 FR 17358), based on the beyond-the-MACT-floor option of ACI. However, mercury levels in hazardous waste fuels per million BTU of heat input are generally higher than mercury levels in coal that is fired in non-hazardous waste burning (NHW) cement kilns. Thus, HW cement kilns generally have higher mercury emissions than NWH cement kilns. Further, the available data indicate that existing mercury emissions from essentially all individual NHW cement kilns are lower

than the beyond-the-MACT-floor emission limit that is now being considered by the Agency to be promulgated for HW cement kilns. Based on the relatively low levels of existing mercury emissions from individual NHW cement kilns, and the costs of reducing these emissions by ACI, the Administrator has determined that this beyond-the-MACT-floor option for reducing mercury from new and existing NHW kilns may not be justified. Thus, the Agency is not proposing a mercury standard for new and existing NHW cement kilns.

Notwithstanding the reasons for not proposing a mercury standard for NHW cement kilns, the Agency solicits comment on whether a BTF standard would be appropriate given the Agency's and Congress' special concern about mercury. Mercury is one of the more toxic metals known due to its bioaccumulation potential and the adverse neurological health effects at low concentrations especially to the most sensitive populations at risk (*i.e.* unborn children, infants and young children). In addition, as with D/F, Congress has singled out mercury in section 112(c)(6) of the Act for prioritized control. Furthermore, the amount of mercury emitted by these sources is not inconsequential, roughly 10,000 pounds annually (or about 60 pounds per kiln annually) making NHW cement kilns a significant source of mercury emissions that may warrant attention under section 112(c)(6) of the Act depending on what other opportunities for controlling mercury from other significant sources are available.

It is EPA's tentative conclusion, however, that concerns as to health risks from mercury emissions from these sources may be appropriately addressed pursuant to the timetable set out in the Act, namely through the residual risk determination process set out in section 112(f) of the Act. A more accelerated determination may be warranted, however, for other mercury-emitting sources, in particular hazardous waste combustion sources, where there are special considerations of immediately protective rules imposed by the Resource Conservation and Recovery Act. [See 61 FR at 17369–17370 (April 19, 1996).]

Kiln and in-line kiln/raw mill THC main exhaust emissions. Based on data from 31 tests conducted at 16 NHW kilns (docket item II–B–75), THC emissions varied between 0.4 ppmvd and 224 ppmvd (as propane, corrected to seven percent oxygen). With the exception of two kilns which employ a precalciner system with no preheater,

no add-on air pollution control technologies are presently in use that decrease emissions of THC (the surrogate for organic HAPs) from NHW cement kilns. On this basis the MACT floor for THC emissions from existing kilns and in-line kiln/raw mills is no control.

The precalciner/no preheater system was considered as a possible beyond-the-floor technology for existing kilns and as a possible MACT floor for new kilns (docket item II–B–47, docket item II–B–48). The precalciner/no preheater technology acts like an afterburner to combust organic material in the feed. However, it was found to increase fuel consumption 79 percent relative to the preheater/precalciner designs (docket item II–B–48, docket item II–D–199). The EPA estimates that precalciner/no preheater kilns would emit six times as much SO_2 (at 3.7 lb SO_2/ton clinker), two and one half times as much NO_X (at 9.8 lb NO_X/ton clinker), and 1.2 times as much CO_2 (at 2,086 lb CO_2/ton clinker) as a preheater/precalciner kiln of equivalent clinker capacity (docket item II–B–48). For a 600,000 ton clinker/year kiln, increased emissions for a flash precalciner relative to a preheater/precalciner are: 930 tpy SO_2, 1,740 tpy NO_X, and 109,000 tpy CO_2 (docket item II–B–76, docket item II–D–199).

One THC control method available is feed material selection. Total hydrocarbon emissions from kilns can be limited by avoiding feed materials which have excessive organic contents (docket item II–I–66, docket item II–I–67, docket item II–I–68). A few existing kilns have employed this method, but not enough to constitute a MACT floor for existing kilns. Also, this method is not available for existing kilns in that facilities are generally tied to existing raw materials sources in close proximity to the facility. Raw material proximity (transportation cost) is usually a major factor in plant site selection. Feed material selection can be employed in the siting process for new kilns, and to a limited extent at existing kilns.

The precalciner/no preheater technology was also considered as a MACT floor for new sources but, when NO_X, SO_2, and CO_2 emissions and energy penalties are considered, the Administrator has determined that it does not represent the MACT floor for new sources, since the kilns employing this technology cannot be considered to be the best controlled similar source. The combination of feed material selection, site location and feed material blending was determined to be MACT for new sources, in that this method has been used at some existing sources and that site selection based on availability

of acceptable raw material hydrocarbon content is feasible.

The numerical emission limit proposed for THC from the main exhaust of new kilns and new in-line kiln/raw mills is 50 ppmvd (as propane, corrected to seven percent oxygen). This represents a level which is consistently achievable, as shown by tests across a broad spectrum of feed material compositions, when feeds with high organic contents are avoided. Based on the available THC main exhaust concentration data for existing NHW kilns, approximately 62 percent of the tested NHW kilns could meet the 50 ppmvd limit (docket item II–B–75).

For the new kiln and in-line kiln/raw mill main exhaust THC emission standard, a volume per volume concentration emission limit format was chosen. The specific units of the emission limit are ppmvd (as propane, corrected to seven percent oxygen). This emission limit format has historically been used by EPA for many air emission standards. This format is consistent with the format of the OSW MACT standard for HW cement kilns.[13] The concentration is corrected to seven percent oxygen to put concentrations measured in stacks with different oxygen concentrations on a common basis, and because the typical range of oxygen concentrations in cement kiln stack gas is from five to 10 percent oxygen; therefore, seven percent is representative. The THC concentration can be monitored directly with the CEM required by this standard. The reference or calibration gas for the THC CEM is propane, and the data analyzed in the development of this standard were referenced to propane, therefore propane is the appropriate reference compound for concentration data.

Kiln and in-line kiln/raw mill HCl emissions. No technologies that control HCl emissions have been identified that are currently being used by more than six percent of the cement kilns in the U.S. For this reason, there is no MACT floor for existing kilns. One technology considered as potential MACT for new kilns was an alkaline scrubber, since two kilns in the U.S. operate scrubbers to control SO_2 emissions. However, these SO_2 scrubbers are operated only intermittently (docket item II–D–196) and thus cannot be considered best controlled similar source. For this reason there is no MACT floor for new kilns.

Alkaline scrubbers were considered as a beyond-the-floor option for HCl control. Based on engineering

assessment of HCl scrubbers used in MWC and MWI applications and transfer of similar technology to the cement industry and on vendor design information (docket item II–D–36), an alkaline scrubber could achieve 15 ppmv HCl outlet concentration at low inlet HCl loadings or at least 90 percent removal with an inlet HCl level of 100 ppmv or greater. Based on this estimated performance, annual emission reduction estimates range from 12 tpy of HCl and 27 tpy of SO_2 to 200 tpy of HCl and 600 tpy of SO_2 per kiln (docket item II–B–67). The total capital cost of installing an alkaline scrubber on an existing kiln is estimated to range from $980,000 to $4.6 million. The total annual cost is estimated to range from $300,000 to $1.5 million per kiln (docket item II–B–67).

Based on the costs of control and the emissions reductions that would be achieved, the Administrator has determined that beyond-the-floor controls are not warranted. Therefore, there is no proposed emission limit for HCl from new and existing NHW kilns and NHW in-line kiln/raw mills. Analyses indicate that the ambient concentrations of HCl produced by emissions from existing NHW kilns and in-line kiln/raw mills are below the health effects reference concentration for HCl (docket item II–B–71).

Clinker cooler PM HAP emissions. Particulate emissions from clinker coolers are typically controlled by FFs (docket item II–B–69). In the portland cement manufacturing industry, it is estimated that at least 54 existing clinker coolers (docket item II–A–4) are subject to the requirements of the NSPS for cement plants (40 CFR part 60, subpart F). This number represents about 25 percent of clinker coolers and, therefore, the NSPS represents the MACT floor. The NSPS level of control is being achieved through the use of well-designed and well-operated FFs. Typical design parameters for pulse jet cleaned fabric filters applied to clinker coolers are air-to-cloth ratios in the range of 0.02 cubic meters per second per square meter (m³/sec)/m² [4 actual cubic feet per minute per square foot (acfm/ft²)] to 0.046 (m³/sec)/m² (9 acfm/ft²).

Table 10 lists plants and the results of emission tests performed on FFs applied to clinker coolers from the May 1985 NSPS review report (docket item II–A–4).

TABLE 10.—FABRIC FILTER CONTROLLED CLINKER COOLER TEST RESULTS

[Docket Item II–A–4]

PM stack emissions (kg/Mg dry feed)	Plant and location
0.0041	Kaiser Cement—Cupertino, CA.
0.004	Moore McCormack—Knoxville, TN.
0.022	Moore McCormack—Brooksville, FL.
0.003 [a]	Kaiser Cement—Lucerne Valley, CA.
0.02	California Portland—Mojave, CA.
0.017	Martin Marietta—Leamington, UT
0.025	Kaiser—San Antonio, TX.
0.03 [b]	Lone Star—Cape Girardeau, MO.
0.002	Monolith Portland—Laramie, WY.
0.024	Ash Grove—Louisville, NE.
0.09552 [b]	Ideal Basic—La Porte, CO.
0.0117	Texas Industries—Hunter, TX
0.0245	Lone Star—Salt Lake City, UT.

[a] Includes alkali bypass emissions.
[b] Include raw mill emissions.

The data shown are short-term performance measurements at cement plants that became subject to the NSPS subsequent to the 1979 NSPS review. The data in Table 10 served as the basis for the decision on the 1985 NSPS review to keep the emission limit established by the original NSPS for clinker cooler PM emissions at 0.05 kg/Mg of dry feed (.1 lb/ton of dry feed). Because no other PM data on clinker coolers became available as a result of this rule development, the Agency is relying on these same data (and interpretation thereof) in establishing the MACT floor for clinker coolers. The results for FFs serving only clinker coolers ranged from 0.002 to 0.025 kg/Mg of dry feed, all of which were in compliance with the NSPS. These data represent the performance level achieved by FFs designed to meet the NSPS level of control. No technologies were identified for existing or new sources that would achieve significant additional reductions in PM or metal HAP emissions; consequently, there is no beyond-the-floor technology and the MACT for new clinker coolers is also the NSPS level. Therefore the PM emission limit proposed for new and existing clinker coolers is 0.05 kg/Mg dry feed (0.10 lb/ton dry feed), which is equivalent to the NSPS limit. An opacity limit of 10 percent (which is required under the NSPS) is also being proposed.

The production-based emission limit format was chosen for clinker cooler PM emissions. The units for this emission standard are kg of PM per Mg of dry feed (lb PM per ton of dry feed). This

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[13] The EPA proposed regulations for subpart EEE of 40 CFR Part 63 on April 19, 1996 at 61 FR 17358.

format (mass per unit of production) and associated opacity limit is consistent with the format of the portland cement plant NSPS (40 CFR part 60, subpart F).

Raw material dryer and materials handling processes opacity. Particulate matter emissions from raw material dryers and materials handling processes at portland cement plants are typically captured by enclosures (total or partial) and/or hooding of transfer points. In most cases, the exhaust gases are directed to FF systems. At least 31 portland cement plants (docket item II–A–4) have some affected sources that are subject to the requirements of the NSPS for portland cement plants (40 CFR part 60, subpart F). No technologies which are more efficient than FFs are in use for these affected sources. State agency personnel indicated that none of the facilities had problems meeting the NSPS opacity limit of 10 percent (docket item II–A–4, docket item II–B–71). The design characteristics of FFs applied to these emission sources include air-to-cloth ratios ranging from 0.02 (m^3/sec) /m^2 (4 acfm/ft^2) to 0.041 (m^3/ sec) /m^2 (8 acfm/ft2) at pulse-jet and pulsed-plenum cleaning systems in installations subject to the NSPS since the 1979 NSPS review (docket item II–A–4, II–I–43). Therefore, the MACT floor technology for control of PM emissions from portland cement materials handling processes and raw material dryers is a combination of total enclosures, partial enclosures, or hooding with FF systems. No beyond-the-floor technologies for control of PM from raw material dryers and materials handling processes were identified.

The emission limit established by the NSPS for raw material dryers and materials handling process PM emissions (surrogate for HAP metals) is an opacity limit of 10 percent. Given that no more effective technologies were identified, the emission limit corresponding to the MACT floor, which is the NSPS, is being proposed as MACT for PM emissions from new and existing portland cement materials handling processes and raw material dryers.

The proposed standard for PM emissions from new and existing materials handling systems and raw material dryers is an opacity limit of 10 percent. An opacity limit format was chosen for these affected sources because it is consistent with the NSPS format for these facilities.

Raw material dryer THC. Some plants may dry their raw materials in separate dryers prior to or during grinding (docket item II–I–43, p.750). This drying process can potentially lead to organic

HAP and THC emissions in a manner analogous to the release of organic HAPs and THC emissions from kilns when hot kiln gas contacts incoming feed materials. The method available for reducing THC emissions (and organic HAPs) is the same technology described for reducing THC emissions from kilns and in-line kiln/raw mills. Therefore, the combination of feed material selection, site location and feed material blending was determined to be MACT for new sources. The numerical emission limit proposed for THC from new raw material dryers is 50 ppmvd reported as propane, corrected to seven percent oxygen. This represents a level which is consistently achievable when feeds with high organic contents are avoided.

E. Selection of Testing and Monitoring Requirements

Testing requirements are being proposed for demonstrating compliance with all standards. Initial performance tests for all affected sources/pollutant combinations would demonstrate compliance with emission limits. These tests would be repeated every 5 years for PM from NHW kilns (including alkali bypasses), NHW in-line kiln/raw mills (including alkali bypasses), clinker coolers, raw material dryers and materials handling processes, and for D/F from kilns and in-line kiln/raw mills. Site-specific monitoring parameters would be established during the initial and subsequent performance tests for D/F from kilns and in-line kiln/raw mill systems. A PMCD inlet temperature parameter would be used to ensure continuous compliance with the D/F emission limit. The following paragraphs present the rationale for the selection of the proposed testing, test methods, and monitoring requirements for each affected source and associated pollutant.

1. Kiln and In-line Kiln Raw Mill PM Emissions

The proposed standards would require the owner or operator of an affected NHW kiln or NHW in-line kiln/raw mill to conduct initial and periodic (every 5 years) performance tests using appropriate existing EPA reference methods in 40 CFR part 60, appendix A. Method 5 would be used to demonstrate compliance with the NHW kiln and NHW in-line kiln/raw mill PM emission limits. (A determination of the particulate matter collected in the impingers [the ''back half''] of the Method 5 particulate sampling train would not be required.) Method 5 is the long-standing EPA method for making PM determinations from stationary

sources. Each performance test would consist of three runs conducted under representative operating conditions. Each run would have a minimum sampling volume of 0.85 dscm (30 dscf) and a minimum duration of 1 hour. The average of the three runs would be used to determine compliance. Method 5, as proposed, is currently required to demonstrate compliance with the NSPS.

If the kiln is equipped with a separate alkali bypass, PM emissions from the alkali bypass would be determined by a simultaneous Method 5 test and the combined emissions from the main exhaust and the alkali bypass would be subject to the PM emission limit.

Owners or operators of in-line kiln/raw mills would be required to conduct a compliance demonstration with the raw mill in operation and a separate compliance demonstration when the raw mill is not in operation, since emissions may vary depending on the operating status of the raw mill.

A COM would be required to ensure continuous compliance with the standard. During the initial Method 5 performance test, the owner or operator would use a COM to demonstrate compliance with the kiln and in-line kiln/raw mill opacity limit. If there is an alkali bypass, a COM would be required for the alkali bypass and compliance with the opacity limit would also be demonstrated for the alkali bypass during the initial Method 5 performance test.

If the PM control device exhausts through a monovent, or if the use of a COM in accordance with the installation specifications of PS–1 of 40 CFR part 60, appendix B were not feasible, a test in accordance with Method 9 of appendix A to 40 CFR part 60 would be conducted at the same time as the Method 5 performance test. If the control device exhausts through multiple stacks, the owner or operator would have the option of conducting a Method 9 test in lieu of installing COMs.

The opacity limit would be 20 percent and would apply to both main and alkali bypass stacks. Exceedance of the kiln or in-line kiln/raw mill opacity limit, or the alkali bypass opacity limit, for any 30-minute average would constitute a violation of the kiln or in-line kiln/raw mill PM emission limit. Owners or operators of in-line kiln/raw mills would demonstrate compliance with the opacity limits during initial performance tests to be conducted while the raw mill is operating and while the raw mill is not operating.

If the 30-minute average opacity exceeded 15 percent for any ten consecutive 30-minute periods as

percent oxygen) are greater than 0.2 ng/ dscm TEQ but less than 0.4 ng/dscm TEQ during the performance test, then the kiln specific temperature limit would be set at 400° F. (If D/F emissions exceed 0.4 ng/dscm, corrected to seven percent oxygen, the performance test would be unsuccessful and the kiln or in-line kiln/raw mill would not be in compliance with the standard.) The temperature would provide a direct indication of D/F emissions from the kiln or in-line kiln/raw mill and would be directly enforceable for compliance determinations.

Owners or operators of kilns and in-line kiln/raw mills equipped with alkali bypasses would establish a separate alkali bypass PMCD inlet temperature limit for the alkali bypass during the performance test. This limit would be based on the temperature at the inlet to the alkali bypass PMCD and would be established in the same manner as the kiln specific temperature limit. Owners or operators of in-line kiln/raw mills equipped with alkali bypasses would establish the temperature limit for the alkali bypass PMCD inlet during the performance test with the raw mill operating.

The proposed averaging period for inlet temperature to the PMCD is 9 hours, because the compliance test for D/F consists of 3-three hour manual tests which are averaged. Thus the inlet temperature limit is established as the average temperature level achieved over the three D/F runs in a performance test.

The Agency specifically requests comment on whether a 9-hour block average site-specific temperature limit is sufficient to ensure compliance with the D/F standard. Because EPA is concerned that D/F emissions emitted during high temperature episodes may not correspondingly be offset by low emissions during lower temperature episodes due to the non-linear relationship between dioxin formation and temperature, a 9-hour block average may not be adequate to ensure compliance with the D/F standard in some instances. The Agency addressed this concern in the proposal for HW combustion sources (cement kilns) [61 FR at 17424, (April 19, 1996)]. There, EPA proposed a site-specific ten-minute rolling average to control perturbations in temperature and a site-specific, one-hour rolling average to control average inlet PMCD temperatures. The ten-minute average was proposed to address the concern that short-term perturbations above the limit may result in D/F emissions that may not be offset by lower emissions at lower temperatures. The one-hour averaging period was proposed to limit average

temperatures. Thus, in today's proposal, the Agency requests comment on whether a shorter-term block or rolling average limit (i. e., less than 9 hours) is more appropriate than the one proposed, or whether a short-term limit in conjunction with the proposed 9-hour block average is needed to properly ensure compliance with the D/ F standard. The EPA further notes that it may also take these comments into account in considering what averaging time to adopt for hazardous waste combustion sources.

If carbon injection is used for D/F control, a kiln-specific (and where applicable, an alkali bypass-specific) carbon injection rate for each run would be established during the performance test. The average carbon injection rate for the three runs would be calculated. This carbon injection rate would serve as an additional monitoring limit and would be required to be maintained or exceeded for every 9-hour period of kiln operation. The carbon injection rate would provide a direct indication of D/ F emissions from the kiln and would be directly enforceable for compliance determinations.

3. Kiln and Raw Material Dryer THC Emissions

The proposed standards applicable to new NHW kiln main exhausts, new NHW in-line kiln/raw mill main exhausts and new raw material dryers would require the owner or operator to conduct an initial performance test of THC emissions from an affected source using a THC CEM and to demonstrate continuous compliance with the THC concentration limit of 50 ppmvd reported as propane (corrected to 7 percent oxygen), through operation of a THC CEM. The use of THC CEMs was selected as the monitoring method because these instruments are available, accurate and reliable, and when calibrated with propane provide an output which is consistent with the THC standard. Each THC CEM would be required to be designed, installed, and operated in accordance with PS–8A of 40 CFR part 60, appendix B [15]. The performance test would be of 3 hours duration. To determine compliance with the THC emission concentration limit, a 30-day block averaging period would be used. Any exceedance of the THC emission concentration limit over any 30-day block averaging period would constitute a violation of the new NHW kiln and in-line kiln/raw mill THC

standard, or the new raw material dryer THC standard.

The rationale for the 30-day block averaging time is that the organic content of the feed material may vary with quarry or mine location. Once raw material storage bins are filled with high organic content feed material and an excursion is experienced, it may take a considerable amount of time to consume these already stored feed materials and locate/obtain feed materials with lower organic content.

4. Clinker Cooler PM Emissions

As in the case with NHW kiln and NHW in-line kiln/raw mill PM emissions, the proposed standards would require the owner or operator of an affected clinker cooler to conduct initial and periodic (every 5 years) performance tests using EPA Method 5 of 40 CFR part 60, appendix A. Method 5 is the long-standing method for making PM determinations from stationary sources. (A determination of the particulate matter collected in the impingers [''back half''] of the Method 5 particulate sampling train would not be required.) Each performance test would consist of three runs conducted under representative operating conditions. Each run would have a minimum sampling volume of 0.85 dscm (30 dscf) and a minimum duration of 1-hour. The average of the three runs would be used to determine compliance with the PM limit. Method 5 is currently required to demonstrate compliance with the NSPS.

The opacity limit for clinker coolers is 10 percent. The proposed clinker cooler emissions monitoring requirements are the same as the proposed requirements for affected NHW kilns and NHW in-line kilns/raw mills. A COM would be required to ensure continuous compliance with the standard. During the initial Method 5 performance test, the owner or operator would use a COM to demonstrate initial compliance with the opacity limit.

If the control device exhausts through a monovent, or if the use of a COM in accordance with the installation specifications of PS–1 of 40 CFR part 60, appendix B were not feasible, a Method 9 test would be conducted at the same time as the Method 5 performance test. If the control device exhausts through multiple stacks, the owner or operator would have the option of conducting a Method 9 test in lieu of installing COMs. Exceedance of the clinker cooler opacity limit for any 30-minute average would constitute a violation of the clinker cooler PM emission standard.

Each COM would be required to be designed, installed, and operated in accordance with PS–1. The use of COMs

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[15] The EPA proposed amendments to appendix B of 40 CFR part 60 on April 19, 1996, at 61 FR 17358.

would provide a timely and direct indication of increased emissions. A COM gives an immediate indication of an exceedance, and provides for timely action that will minimize the duration and, therefore, the emissions of an upset. A COM can also signal the long-term gradual deterioration of performance of a control device. Failure of any 30-minute average reading to meet the clinker cooler opacity limit would constitute a violation of the clinker cooler PM emission standard.

Where the use of a COM is not feasible (or at the option of the owner or operator when the exhaust is discharged through multiple stacks), the proposed standards would require daily visual observations using Method 9. The duration of the Method 9 test would be 30 minutes. Method 9 is the established EPA method for visual determinations of opacity from stationary sources. Method 9 procedures for making visual observations and reducing the data would be followed. Failure of any daily reading to meet the 10 percent opacity limit would constitute a violation of the clinker cooler PM emission limit.

5. Raw and Finish Mill PM Emissions

The proposed standards would require the owner or operator of raw and finish mills to conduct initial and periodic (every five years) compliance tests using Method 9, and to either install, calibrate, maintain and operate a bag leak detection system or to conduct daily visual observations using Method 22 to ensure compliance with the opacity standard. The opacity limit for raw and finish mills is 10 percent. The duration of the Method 9 tests is 3-hours and the duration of the daily Method 22 tests is six minutes. The duration of the Method 9 test can be reduced to one hour if during the first hour of the test, there are no individual readings greater than 10 percent and there are no more than three individual readings of 10 percent.

If visible emissions are detected during any daily Method 22 test, the owner or operator must begin a 30-minute Method 9 test within 24 hours and initiate a site specific operating and maintenance plan within one hour. If the bag leak detection system alarm is triggered, the owner or operator must initiate a site specific operating and maintenance plan within one hour. Failure to conduct a Method 9 test as required, failure to initiate a site-specific operating and maintenance plan as required, or observation of any 30-minute average opacity in excess of 10 percent during the Method 9 test shall constitute a violation of the raw mill and finish mill opacity standard.

6. Raw Material Dryer and Materials Handling Processes PM Emissions

The proposed standards would require the owner or operator of raw material dryers and materials handling processes to conduct initial and periodic (every five years) performance tests of visual emissions. Particulate matter emissions from these sources are much lower than those from kilns, clinker coolers, and raw and finish mills, therefore, continuous opacity monitoring, and more frequent visual opacity measurements are not being proposed. Method 9 of 40 CFR part 60, appendix A is the proposed method for the visual opacity measurements. As previously noted, Method 9 is the established method for opacity determinations for stationary sources, and provides a directly enforceable opacity reading for compliance determinations.

Section 63.6(h)(5)(ii) of the NESHAP general provisions (40 CFR part 63, subpart A) requires 3 hours (30 6-minute averages) of Method 9 observations for determining compliance for fugitive emission sources. However, due to the potentially large number of affected materials handling sources at portland cement plants, the costs for observations from these sources are considered overly burdensome. Furthermore, data from similar facilities in non-metallic mineral processing plants (docket item II–J–10) show that the opacity readings for the first hour are typically the same as the readings for the second and third hours. Therefore EPA is proposing a reduction in Method 9 testing duration for these facilities to one hour (ten 6-minute averages), provided that no individual reading exceeds 10 percent and that no more than three individual readings of ten percent are observed during the first hour of the test. Exceedance of the 10-percent opacity limit for any 30-minute average reading would constitute a violation of the proposed opacity standard.

7. General Monitoring Requirements

The general provisions in 40 CFR part 63, subpart A require each owner or operator to develop and implement a startup, shutdown, and malfunction plan. The proposed NESHAP requires the owner or operator to include procedures to be followed in the event that a CEM, COM or temperature monitor indicates that emissions exceed the applicable standards. Block averages are proposed for opacity, D/F, and THC monitoring required by the standard.

Owners or operators are also required to develop site specific operating and

maintenance plans as part of the part 70 permit application process. Such plans are applicable to the operation and maintenance of kilns, in-line kiln/raw mills, raw mills and finish mills and the PM APCDs associated with these affected sources.

F. Selection of Notification, Recordkeeping, and Reporting Requirements

The proposed NESHAP would require portland cement manufacturing plants to comply with all applicable requirements in the NESHAP general provisions (40 CFR part 63, subpart A), including recordkeeping, notification, and reporting requirements. General recordkeeping requirements would include relevant records for each affected source of: (1) The occurrence and duration of each startup, shutdown, or malfunction of operation of process equipment, (2) the occurrence and duration of each malfunction of the air pollution control equipment, (3) all maintenance performed on the air pollution control equipment, (4) actions taken during startup, shutdown and malfunction that are different from the procedures specified in the source's startup, shutdown, and malfunction plan, (5) all information necessary to demonstrate conformance with the affected source's startup, shutdown, and malfunction plan when the plan procedures are followed, (6) each period during which a CMS is malfunctioning or inoperative (including out-of-control periods), (7) all required measurements needed to demonstrate compliance with the standards, (8) all results of performance tests, CMS performance evaluations, and opacity and visible emissions observations, (9) all measurements as may be necessary to determine the conditions of performance tests and performance evaluations, (10) all CMS calibration checks, (11) all adjustments and maintenance performed on CMS, (12) any information demonstrating whether a source is meeting the requirements for a waiver of record keeping or reporting requirements, (13) all emission levels relative to the criterion for obtaining permission to use an alternative to the relative accuracy test, (14) all records or any bag leak detection system alarm, and (15) all documentation supporting initial notifications and notifications of compliance status. Records would also be required of applicability determinations that the source is not subject to the requirements of the NESHAP and of CMS measurements, operation, and malfunctions.

General Provisions notification requirements would include: (1) initial

notifications, (2) notification of performance test, (3) notification of opacity and visible emission observations, (4) additional notifications required for sources with CMS and (5) notification of compliance status. Notifications of the requirement to develop and implement a QIP, and if applicable, notifications of the inability to implement a required QIP within 180 days would also be required by this subpart. Reporting requirements would include (1) a report of performance test results, (2) a report of results of opacity or visible emission observations done concurrently with performance test, (3) progress reports if required as a condition of receiving an extension of compliance, (4) periodic and immediate startup, shutdown, and malfunction reports, and (5) summary excess emissions and performance monitoring reports.

VI. Public Participation

The EPA seeks full public participation in arriving at its final decisions and encourages comments on all aspects of this proposal from all interested parties. Full supporting data and detailed analyses should be submitted with comments to allow EPA to make maximum use of the comments. All comments should be directed to the Air and Radiation Docket and Information Center, Docket No. A–92–53 (see **ADDRESSES**). Comments on this notice must be submitted on or before the date specified in **DATES**.

Commenters wishing to submit proprietary information for consideration should clearly distinguish such information from other comments and clearly label it ''Confidential Business Information'' (CBI). Submissions containing such proprietary information should be sent directly to the Emission Standards Division CBI Office, U.S. Environmental Protection Agency (MD–13), Research Triangle Park, North Carolina 27711, with a copy of the cover letter directed to the contact person listed above. Confidential business information should not be sent to the public docket. Information covered by such a claim of confidentiality will be disclosed by EPA only to the extent allowed and by the procedures set forth in 40 CFR part 2. If no claim of confidentiality accompanies the submission when it is received by EPA, it may be made available to the public without further notice to the commenter.

VII. Administrative Requirements

A. Docket

The docket is an organized and complete file of all the information considered by EPA in the development of this rulemaking. The docket is a dynamic file, because material is added throughout the rulemaking development. The docketing system is intended to allow members of the public and industries involved to readily identify and locate documents so that they can effectively participate in the rulemaking process. Along with the proposed and promulgated standards and their preambles, the contents of the docket will serve as the record in the case of judicial review. [See section 307(d)(7)(A) of the Act.]

B. Public Hearing

A public hearing will be held, if requested, to discuss the proposed standards in accordance with section 307(d)(5) of the Act. Persons wishing to make oral presentations on the proposed standards should contact EPA (see **ADDRESSES**). If a public hearing is requested and held, EPA will ask clarifying questions during the oral presentation but will not respond to the presentations or comments. To provide an opportunity for all who may wish to speak, oral presentations will be limited to 15 minutes each. Any member of the public may file a written statement on or before May 26, 1998. Written statements should be addressed to the Air and Radiation Docket and Information Center (see **ADDRESSES**), and refer to Docket No. A–92–53. Written statements and supporting information will be considered with equivalent weight as any oral statement and supporting information subsequently presented at a public hearing, if held. A verbatim transcript of the hearing and written statements will be placed in the docket and be available for public inspection and copying, or mailed upon request, at the Air and Radiation Docket and Information Center (see **ADDRESSES**).

C. Executive Order 12866

Under Executive Order 12866 (58 FR 51735, October 4, 1993), EPA must determine whether the regulatory action is ''significant'' and therefore subject to review by the Office of Management and Budget (OMB), and the requirements of the Executive Order. The Executive Order defines ''significant regulatory action'' as one that is likely to result in a rule that may:

(1) Have an annual effect on the economy of $100 million or more or adversely affect in a material way the economy, a sector of the economy, productivity, competition, jobs, the environment, public health or safety, or State, local, or tribal governments or communities;

(2) Create a serious inconsistency or otherwise interfere with an action taken or planned by another agency;

(3) Materially alter the budgetary impact of entitlements, grants, user fees, or loan programs, or the rights and obligation of recipients thereof; or

(4) Raise novel legal or policy issues arising out of legal mandates, the President's priorities, or the principles set forth in the Executive Order.

Because the projected annual costs (including monitoring) for this NESHAP are $27 million a regulatory impact analysis has not been prepared. However this action is considered a ''significant regulatory action'' within the meaning of Executive Order 12866, and the proposed regulation presented in this notice was submitted to the OMB for review. Any written comments are included in the docket listed at the beginning of today's notice under **ADDRESSES**. The docket is available for public inspection at the EPA's Air Docket Section, which is listed in the **ADDRESSES** section of this preamble.

D. Enhancing the Intergovernmental Partnership Under Executive Order 12875

In compliance with Executive Order 12875, EPA has involved State and local regulatory experts in the development of this proposed rule. One tribal government and one State government is believed to be affected by this proposed rule. Local governments, and State governments other than the one State which operates a portland cement plant are not directly impacted by the rule, i.e., they are not required to purchase control systems to meet the requirements of the rule. However, they will be required to implement the rule; e.g., incorporate the rule into permits and enforce the rule. They will collect permit fees that will be used to offset the burden of implementing the rule. Comments have been solicited from States and from local air pollution control agency representatives and these comments have been carefully considered in the rule development process. In addition, all States are encouraged to comment on this proposed rule during the public comment period, and the EPA intends to fully consider these comments in the development of the final rule.

E. Unfunded Mandates Reform Act

Section 202 of the Unfunded Mandates Reform Act of 1995 (UMRA), signed into law on March 22, 1995 (109

Stat. 48), requires that the Agency prepare a budgetary impact statement before promulgating a rule that includes a Federal mandate that may result in expenditure by State, local, and tribal governments, in aggregate, or by the private sector, of $100 million or more in any one year. Section 203 requires the Agency to establish a plan for obtaining input from and informing, educating, and advising any small governments that may be significantly or uniquely affected by the rule.

Under section 205 of the UMRA, the Agency must identify and consider a reasonable number of regulatory alternatives before promulgating a rule for which a budgetary impact statement must be prepared. The Agency must select from those alternatives the least costly, most cost-effective, or least burdensome alternative for State, local, and tribal governments and the private sector that achieves the objectives of the rule, unless the Agency explains why this alternative is not selected or unless the selection of this alternative is inconsistent with law.

Because this proposed rule, if promulgated, is estimated to result in the expenditure by State, local, and tribal governments or the private sector of less than $100 million in any one year, the Agency has not prepared a budgetary impact statement or specifically addressed the selection of the least costly, most cost-effective, or least burdensome alternative. Because small governments will not be significantly or uniquely affected by this rule, the Agency is not required to develop a plan with regard to small governments. Therefore, the requirements of the UMRA do not apply to this action.

F. Regulatory Flexibility Act

Under section 605 of the Regulatory Flexibility Act of 1980, 5 U.S.C. 601 *et seq.*, Federal agencies are required to assess the economic impact of Federal regulations on small entities. The Regulatory Flexibility Act specifies that Federal agencies must prepare an initial Regulatory Flexibility Analysis (RFA) if a proposed regulation will have a significant economic impact on a substantial number of small entities. For the purposes of the Agency's implementation of the Act, the EPA's guidelines define a "substantial number" as 100 or more firms.

The manufacture of portland cement is covered by SIC code 3241 for hydraulic cements. According to Small Business Administration size standards, firms owning portland cement plants are categorized as small if the total number of employees at the firm is less

than 750. Otherwise the firm is classified as large. A total of 7 firms are categorized as small, while the remaining 37 firms are large. Because a substantial number of small firms are not affected, and the EPA does not project a significant impact on small firms, the rule does not require an RFA.

I certify that the rule will not have a significant economic impact on a substantial number of small entities. This is because the rule has a control cost share of revenue of less than one percent for all of the seven cement plants which are considered small entities. [Refer to section IV.H. (Economic Impacts) for more details on the cost and estimated price increases.]

Although the rule will not have a significant impact on a substantial number of small entities, nevertheless the Agency has worked with portland cement small entities throughout the rulemaking process. Meetings were held on a regular basis with the Portland Cement Association (PCA) and industry representatives, including both small and large firms, to discuss the development of the rule, exchange information and data, solicit comments on draft rule requirements, and provide a list of the small firms. In addition, some cement industry representatives formed a group called the "Small Cement Company MACT Coalition", which was represented by counsel during meetings held with the PCA and industry representatives during the later stages of the proposal development process. Finally, the Small Cement Company MACT Coalition designated the PCA as its representative in future meetings with the EPA concerning the rulemaking for the portland cement industry.

To minimize adverse impacts on the small entities, the Agency has proposed controls at the MACT-floor level and tailored the requirements to permit less costly testing and monitoring by using surrogates for HAP emissions and provided choice in methods of demonstrating compliance. The Agency has also tried to make the rule "user friendly," with language that is easy to understand by all of the regulated community. To minimize capital availability problems EPA also proposes to allow affected firms up to 3 years from the effective date of the final rule to comply. An extra year may be granted by the Administrator or delegated regulatory authority if necessary to install controls.

G. Paperwork Reduction Act

The information collection requirements in this proposed rule have been submitted for approval to OMB

under the requirements of the Paperwork Reduction Act, 44 U.S.C. 3501 *et seq.* An Information Collection Request (ICR) document has been prepared by EPA (ICR No. 1801.01), and a copy may be obtained from Sandy Farmer, OPPE Regulatory Information Division, U.S. Environmental Protection Agency (2137), 401 M Street SW., Washington, DC 20460, or by calling (202) 260–2740.

The proposed information requirements include the notification, recordkeeping, and reporting requirements of the NESHAP general provisions (40 CFR part 63, subpart A), authorized under section 114 of the Act, which are mandatory for all owners or operators subject to national emission standards. All information submitted to EPA for which a claim of confidentiality is made is safeguarded according to Agency policies in 40 CFR part 2, subpart B. The proposed rule does not require any notifications or reports beyond those required by the general provisions. These information requirements are necessary to determine compliance with the standard.

The annual public reporting and recordkeeping burden for this collection is estimated at 77,000 labor hours per year at a total annual cost of $2,470,000 over the three-year period. This corresponds to an estimated burden of approximately 2000 hours per year for an estimated 39 respondents. This estimate includes performance tests and reports (with repeat tests where needed); one-time preparation of a startup, shutdown, and malfunction plan with semiannual reports of any event where the procedures in the plan were not followed; semiannual excess emissions reports; notifications; and recordkeeping. Total annualized capital costs associated with monitoring requirements over the three-year period of the ICR is estimated at $194,000; this estimate includes the capital and startup costs associated with installation of required continuous monitoring equipment for those affected subject to the standard. The total operation and maintenance cost is estimated at $191,000 per year.

Burden means the total time, effort, or financial resources expended by persons to generate, maintain, retain, or disclose or provide information to or for a Federal agency. This includes the time needed to review instructions; develop, acquire, install, and utilize technology and systems for the purpose of collecting, validating, and verifying information; processing and maintaining information, and disclosing and providing information; adjust the existing ways to comply with any

previously applicable instructions and requirements; train personnel to respond to a collection of information; search existing data sources; complete and review the collection of information; and transmit or otherwise disclose the information.

An Agency may not conduct or sponsor, and a person is not required to respond to a collection of information unless it displays a currently valid OMB control number. The OMB control numbers for EPA's regulations are listed in 40 CFR part 9 and 48 CFR chapter 15.

Send comments on the Agency's need for this information, the accuracy of the provided burden estimates, and any suggested methods for minimizing respondent burden, including through the use of automated collection techniques to the Director, OPPE Regulatory Information Division; U.S. Environmental Protection Agency (2137), 401 M Street SW., Washington, DC 20460; and to the Office of Information and Regulatory Affairs, Office of Management and Budget, 725 17th Street, NW, Washington, D.C. 20503, marked ''Attention: Desk Officer for EPA.'' Include the ICR number in any correspondence. Since OMB is required to make a decision concerning the ICR between 30 and 60 days after March 24, 1998, a comment to OMB is best assured of having its full effect if OMB receives it by April 23, 1998. The final rule will respond to any OMB or public comments on the information collection requirements contained in this proposal.

H. Clean Air Act

In accordance with section 117 of the Act, publication of this proposal was preceded by consultation with appropriate advisory committees, independent experts, and Federal departments and agencies. This regulation will be reviewed eight years from the date of promulgation. This review will include an assessment of such factors as evaluation of the residual health risks, any overlap with other programs, the existence of alternative methods, enforceability, improvements in emission control technology and health data, and the recordkeeping and reporting requirements.

List of Subjects in 40 CFR Part 63

Environmental protection, Air pollution control, Hazardous substances, Portland cement manufacturing, Reporting and recordkeeping requirements.

Dated: March 9, 1998.

Carol M. Browner,

Administrator.

For the reasons set out in the preamble, part 63 of title 40, chapter 1 of the Code of Federal Regulations is proposed to be amended as follows:

PART 63—NATIONAL EMISSION STANDARDS FOR HAZARDOUS AIR POLLUTANTS FOR SOURCE CATEGORIES

1. The authority citation for part 63 continues to read as follows:

Authority: Secs. 101, 112, 114, 116, 183(f) and 301 of the Clean Air Act as amended (42 U.S.C. *et seq*).

2. Part 63 is amended by adding a new subpart LLL consisting of §§ 63.1340 through 63.1359 to read as follows:

Subpart LLL—National Emission Standards for the Portland Cement Manufacturing Industry

Sec.
63.1340   Applicability and designation of affected sources.
63.1341   Definitions.
63.1342   Standards: General.
63.1343   Standards for kilns and in-line kiln/raw mills.
63.1344   Standards for clinker coolers.
63.1345   Standards for new and reconstructed raw material dryers.
63.1346   Standards for affected sources other than kilns, in-line kiln raw mills, clinker coolers, and new and reconstructed raw material dryers.
63.1347   Compliance dates.
63.1348   Initial compliance demonstration.
63.1349   Monitoring requirements.
63.1350   Additional test methods.
63.1351   Notification requirements.
63.1352   Reporting requirements.
63.1353   Recordkeeping requirements.
63.1354   Delegation of authority.
63.1355–63.1359   [Reserved]

Table 1 to Subpart LLL—Applicability of General Provisions

Subpart LLL—National Emission Standards for the Portland Cement Manufacturing Industry

§ 63.1340   Applicability and designation of affected sources.

(a) Except as specified in paragraphs (b) and (c) of this section, the provisions of this subpart apply to each new and existing portland cement plant which is a major source or an area source as defined in § 63.2 of this part.

(b) The affected sources subject to this subpart are:

(1) Each kiln and each in-line kiln/raw mill at any major or area source, including alkali bypasses, except for kilns and in-line kiln/raw mills that burn hazardous waste and are subject to

and regulated under subpart EEE of this part.[1]

(2) Each clinker cooler at any portland cement plant which is a major source;

(3) Each raw mill at any portland cement plant which is a major source;

(4) Each finish mill at any portland cement plant which is a major source;

(5) Each raw material dryer at any portland cement plant which is a major source;

(6) Each raw material, clinker, or finished product storage bin at any portland cement plant which is a major source;

(7) Each conveying system transfer point at any portland cement plant which is a major source;

(8) Each bagging system at any portland cement plant which is a major source; and

(9) Each bulk loading or unloading system at any portland cement plant which is a major source.

(c) For portland cement plants with on-site nonmetallic mineral processing facilities, the first affected source in the sequence of materials handling operations subject to this subpart is the raw material storage, which is just prior to the raw mill. The primary and secondary crushers and any other equipment of the on-site nonmetallic mineral processing plant which precedes the raw material storage are not subject to this subpart. Furthermore, the first conveyor transfer point subject to this subpart is the transfer point associated with the conveyor transferring material from the raw material storage to the raw mill.

(d) The owner or operator of any affected source subject to the provisions of this subpart is subject to title V permitting requirements.

§ 63.1341   Definitions.

All terms used in this subpart that are not defined below have the meaning given to them in the CAA and in subpart A of this part.

Alkali bypass means a duct between the feed end of the kiln and the preheater tower through which a portion of the kiln exit gas stream is withdrawn and quickly cooled by air or water to avoid excessive buildup of alkali and sulfur on the raw feed.

Bag leak detection system means a monitoring system for a fabric filter that identifies an increase in particulate emissions resulting from a broken filter bag or other malfunction and sounds an alarm.

Bagging system means the equipment which fills bags with portland cement.

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[1] The EPA proposed regulations for subpart EEE of 40 CFR part 63 on April 19, 1996 at 61 FR 17358.

Clinker cooler means equipment into which clinker product leaving the kiln is placed to be cooled by air supplied by a forced draft or natural draft supply system.

Conveying system means a device for transporting materials from one piece of equipment or location to another location within a facility. Conveying systems include but are not limited to the following: feeders, belt conveyors, bucket elevators and pneumatic systems.

Conveying system transfer point means a point where any material including but not limited to feed material, fuel, clinker or product, is transferred to or from a conveying system, or between separate parts of a conveying system.

Dioxins and furans (D/F) means tetra-, penta-, hexa-, hepta-, and octa-chlorinated dibenzo dioxins and furans.

Facility means all contiguous or adjoining property that is under common ownership or control, including properties that are separated only by a road or other public right-of-way.

Feed means the prepared and mixed materials, which include but are not limited to materials such as limestone, clay, shale, sand, iron ore, mill scale, and flyash, that are fed to the kiln and become part of the clinker product. Feed does not include the fuels used in the kiln to produce heat to form the clinker product.

Finish mill means a roll crusher, ball and tube mill or other size reduction equipment used to grind clinker to a fine powder. Gypsum and other materials may be added to and blended with clinker in a finish mill. The finish mill also includes the air separator associated with the finish mill.

Hazardous waste is defined in § 261.3 of this chapter.

In-line kiln/raw mill means a system in a portland cement production process where a dry kiln system is integrated with the raw mill so that all or a portion of the kiln exhaust gases are used to perform the drying operation of the raw mill, with no auxiliary heat source used. In this system the kiln is capable of operating without the raw mill operating, but the raw mill cannot operate without the kiln gases, and consequently, the raw mill does not generate a separate exhaust gas stream.

Kiln means a device, including any associated preheater or precalciner devices, that produces clinker by heating limestone and other materials for subsequent production of cement.

Monovent means an exhaust configuration of a building or emission control device (e. g. positive pressure fabric filter) that extends the length of the structure and has a width very small in relation to its length (i.e., length to width ratio is typically greater than 5:1). The exhaust may be an open vent with or without a roof, louvered vents, or a combination of such features.

Portland cement plant means any facility manufacturing portland cement.

Raw material dryer means an impact dryer, drum dryer, paddle-equipped rapid dryer, air separator, or other equipment used to reduce the moisture content of feed materials.

Raw mill means a ball and tube mill, vertical roller mill or other size reduction equipment, that is not part of an in-line kiln/raw mill, used to grind feed to the appropriate size. Moisture may be added or removed from the feed during the grinding operation. If the raw mill is used to remove moisture from feed materials, it is also, by definition, a raw material dryer. The raw mill also includes the air separator associated with the raw mill.

TEQ means the international method of expressing toxicity equivalents for dioxins and furans as defined in U.S. EPA, Interim Procedures for Estimating Risks Associated with Exposures to Mixtures of Chlorinated Dibenzo-p-dioxins and -dibenzofurans (CDDs and CDFs) and 1989 Update, March 1989.

§ 63.1342   Standards: General.

Table 1 to this subpart provides cross references to the 40 CFR part 63, subpart A, general provisions, indicating the applicability of the general provisions requirements to subpart LLL.

§ 63.1343   Standards for kilns and in-line kiln/raw mills.

(a) The provisions in this section apply to each kiln, each in-line kiln/raw mill, and any alkali bypass associated with that kiln or in-line kiln/raw mill.

(b) No owner or operator of an existing kiln or in-line kiln/raw mill at a facility that is a major source subject to the provisions of this subpart shall cause to be discharged into the atmosphere from these affected sources, any gases which:

(1) Contain particulate matter in excess of 0.15 kg per Mg (0.30 lb per ton) of feed (dry basis) to the kiln. When there is an alkali bypass associated with a kiln or in-line kiln/raw mill, the combined particulate matter emissions from the kiln or in-line kiln/raw mill and the alkali bypass are subject to this emission limit.

(2) Exhibit opacity greater than 20 percent.

(3) Contain D/F in excess of

(i) 0.20 ng per dscm (8.7×10^{-11} gr per dscf)(TEQ) corrected to seven percent oxygen; or

(ii) 0.40 ng per dscm (1.7×10^{-10} gr per dscf)(TEQ) corrected to seven percent oxygen, when the temperature at the inlet to the particulate matter air pollution control device is 204 °C (400°(F) or less.

(c) No owner or operator that commences construction of a new kiln or new inline kiln/raw mill, or commences reconstruction of a kiln or in-line kiln/raw mill at a facility which is a major source subject to the provisions of this subpart shall cause to be discharged into the atmosphere from these affected sources any gases which:

(1) Contain particulate matter in excess of 0.15 kg per Mg (0.30 lb per ton) of feed (dry basis) to the kiln. When there is an alkali bypass associated with a kiln or in-line kiln/raw mill, the combined particulate matter emissions from the kiln or in-line kiln/raw mill and the bypass stack are subject to this emission limit.

(2) Exhibit opacity greater than 20 percent.

(3) Contain D/F in excess of

(i) 0.20 ng per dscm (8.7×10^{-11} gr per dscf) (TEQ) corrected to seven percent oxygen; or

(ii) 0.40 ng per dscm (1.7×10^{-10} gr per dscf) (TEQ) corrected to seven percent oxygen, when the temperature at the inlet to the particulate matter air pollution control device is 204 °C (400 °F) or less.

(4) Contain total hydrocarbon (THC), from the main exhaust of the kiln or in-line kiln/raw mill, in excess of 50 ppmvd as propane, corrected to seven percent oxygen.

(d) No owner or operator of a new or existing kiln or in-line kiln/raw mill at a facility that is an area source subject to the provisions of this subpart shall cause to be discharged into the atmosphere from these affected sources any gases which contain D/F in excess of:

(1) 0.20 ng per dscm (8.7×10^{-11} gr per dscf) (TEQ) corrected to seven percent oxygen; or

(2) 0.40 ng per dscm (1.7×10^{-10} gr per dscf) (TEQ) corrected to seven percent oxygen, when the temperature at the inlet to the particulate matter air pollution control device is 204 °C (400 °F) or less.

§ 63.1344   Standards for clinker coolers.

(a) No owner or operator of a new or existing clinker cooler at a facility which is a major source subject to the provisions of this subpart shall cause to be discharged into the atmosphere from the clinker cooler any gases which:

(1) Contain particulate matter in excess of 0.050 kg per Mg (0.10 lb per ton) of feed (dry basis) to the kiln.

(2) Exhibit opacity greater than ten percent.

(b) [Reserved]

§ 63.1345 Standards for new and reconstructed raw material dryers.

(a) No owner or operator of a new or reconstructed raw material dryer at a facility which is a major source subject to this subpart shall cause to be discharged into the atmosphere from the new or reconstructed raw material dryer any gases which:

(1) Contain THC in excess of 50 ppmvd, reported as propane, corrected to seven percent oxygen.

(2) Exhibit opacity greater than ten percent.

(b) [Reserved]

§ 63.1346 Standards for affected sources other than kilns, in-line kiln/raw mills, clinker coolers, and new and reconstructed raw material dryers.

The owner or operator of each new or existing raw mill; finish mill; raw material, clinker, or finished product storage bin; conveying system transfer point; bagging system; and bulk loading or unloading system; and each existing raw material dryer, at a facility which is a major source subject to the provisions of this subpart shall not cause to be discharged any gases from these affected sources which exhibit opacity in excess of ten percent.

§ 63.1347 Compliance dates.

(a) The compliance date for an owner or operator of an existing affected source subject to the provisions of this subpart is no later than 36 months after publication of the final rule.

(b) The compliance date for an owner or operator of an affected source subject to the provisions of this subpart that commences new construction or reconstruction after March 24, 1998 is the date of publication of the final rule or immediately upon startup of operations, whichever is later.

§ 63.1348 Initial compliance demonstration.

(a) The owner or operator of an affected source subject to this subpart shall demonstrate initial compliance with the emission limits of §§ 63.1343–63.1346 using the test methods and procedures in paragraph (b) of this section and § 63.7. Performance test results shall be documented in complete test reports that contain the information required by paragraphs (a)(1) through (a)(10) of this section, as well as all other relevant information. The plan to be followed during testing shall be made available to the Administrator prior to testing, if requested.

(1) A brief description of the process and the air pollution control system;

(2) Sampling location description(s);

(3) A description of sampling and analytical procedures and any modifications to standard procedures;

(4) Test results;

(5) Quality assurance procedures and results;

(6) Records of operating conditions during the test, preparation of standards, and calibration procedures;

(7) Raw data sheets for field sampling and field and laboratory analyses;

(8) Documentation of calculations;

(9) All data recorded and used to establish parameters for compliance monitoring; and

(10) Any other information required by the test method.

(b) Performance tests to demonstrate initial compliance with this subpart shall be conducted as specified in paragraphs (b)(1) through (b)(5) of this section.

(1) The owner or operator of a kiln subject to limitations on particulate matter emissions shall demonstrate initial compliance by conducting a performance test as specified in paragraphs (b)(1)(i) through (b)(1)(iv) of this section. The owner or operator of an in-line kiln/raw mill shall demonstrate initial compliance by conducting separate performance tests as specified in paragraphs (b)(1)(i) through (b)(1)(iv) of this section while the raw mill of the in-line kiln/raw mill is under normal operating conditions and while the raw mill of the in-line kiln/raw mill is not operating. The owner or operator of a clinker cooler subject to limitations on particulate matter emissions shall demonstrate initial compliance by conducting a performance test as specified in paragraphs (b)(1)(i) through (b)(1)(iii) of this section. The opacity exhibited during the period of the Method 5 performance tests required by paragraph (b)(1)(i) of this section shall be determined as required in paragraphs (b)(1)(v) through (vi) of this section.

(i) EPA Method 5 of appendix A to part 60 of this chapter shall be used to determine PM emissions. Each performance test shall consist of three separate runs under the conditions that exist when the affected source is operating at the highest load or capacity level reasonably expected to occur. Each run shall be conducted for at least one hour, and the minimum sample volume shall be 0.85 dscm (30 dscf). The average of the three runs shall be used to determine compliance. A determination of the particulate matter collected in the impingers ("back half") of the Method 5 particulate sampling train is not required.

(ii) Suitable methods shall be used to determine the kiln or inline kiln/raw mill feed rate, except for fuels, for each run.

(iii) The emission rate, E, of PM shall be computed for each run using equation 1:

$$E = (c_s Q_{sd}) / P$$

Where:

E = emission rate of particulate matter, kg/Mg of kiln feed.

c_s = concentration of PM, kg/dscm.

Q_{sd} = volumetric flow rate of effluent gas, dscm/hr.

P = total kiln feed (dry basis), Mg/hr.

(iv) When there is an alkali bypass associated with a kiln or in-line kiln/raw mill, the main exhaust and alkali bypass of the kiln or in-line kiln/raw mill shall be tested simultaneously and the combined emission rate of particulate matter from the kiln or in-line kiln/raw mill and alkali bypass shall be computed for each run using equation 2,

$$E_c = (c_{sk}Q_{sdk} + c_{sb}Q_{sdb})/P$$

Where:

E_c = the combined emission rate of particulate matter from the kiln or in-line kiln/raw mill and bypass stack, kg/Mg of kiln feed,

c_{sk} = concentration of particulate matter in the kiln or in-line kiln/raw mill effluent, kg/dscm,

Q_{sdk} = volumetric flow rate of kiln or in-line kiln/raw mill effluent, dscm/hr,

c_{sb} = concentration of particulate matter in the alkali bypass gas, kg/dscm,

Q_{sdb} = volumetric flow rate of alkali bypass gas, dscm/hr, and P = total kiln feed (dry basis), Mg/hr.

(v) Except as provided in paragraph (b)(1)(vi) of this section the opacity exhibited during the period of the Method 5 performance tests required by paragraph (b)(1)(i) of this section shall be determined through the use of a continuous opacity monitor (COM). The maximum six-minute average opacity during the three Method 5 test runs shall be determined during each Method 5 test run, and used to demonstrate initial compliance with the applicable opacity limits of §§ 63.1343(b)(2), 63.1343(c)(2), or 63.1344(a)(2) of this subpart.

(vi) Each owner or operator of a kiln, in-line kiln/raw mill, or clinker cooler subject to the provisions of this subpart using a fabric filter with multiple stacks or an electrostatic precipitator with multiple stacks may, in lieu of installing the continuous opacity monitoring system required by paragraph (b)(1)(v) of this section, conduct an opacity test in accordance with Method 9 of appendix A to part 60 of this chapter

during each Method 5 performance test required by paragraph (b)(1)(i) of this section. If the control device exhausts through a monovent, or if the use of a COM in accordance with the installation specifications of Performance Specification 1 (PS–1) of appendix B to part 60 of this chapter is not feasible, a test shall be conducted in accordance with Method 9 of appendix A to part 60 of this chapter during each Method 5 performance test required by paragraph (b)(1)(i) of this section. The maximum six-minute average opacity shall be determined during the three Method 5 test runs, and used to demonstrate initial compliance with the applicable opacity limits of §§ 63.1343(b)(2), 63.1343(c)(2), or 63.1344(a)(2) of this subpart.

(2) The owner or operator of a raw mill or finish mill subject to limitations on opacity under this subpart shall demonstrate initial compliance with the raw mill and finish mill opacity limit by conducting a performance test in accordance with Method 9 of appendix A to part 60 of this chapter. The performance test shall be conducted under the conditions that exist when the affected source is operating at the highest load or capacity level reasonably expected to occur. The maximum six-minute average opacity exhibited during the performance test shall be used to determine whether the affected source is in initial compliance with the standard. The duration of the Method 9 performance test shall be 3-hours (30 6-minute averages), except that the duration of the Method 9 performance test may be reduced to 1-hour if the conditions of paragraphs (b)(2)(i) through (ii) of the section apply:

(i) There are no individual readings greater than 10 percent opacity;

(ii) There are no more than three readings of 10 percent for the first 1-hour period.

(3) The owner or operator of any affected source subject to limitations on opacity under this subpart that is not subject to § 63.1348(b)(1) through (2) shall demonstrate initial compliance with the affected source opacity limit by conducting a test in accordance with Method 9 of appendix A to part 60 of this chapter. The maximum six-minute average opacity exhibited during the test period shall be used to determine whether the affected source is in initial compliance with the standard. The duration of the Method 9 performance test shall be 3-hours (30 6-minute averages), except that the duration of the Method 9 performance test may be reduced to 1-hour if the conditions of paragraphs (b)(3)(i) through (ii) of the section apply:

(i) There are no individual readings greater than 10 percent opacity;

(ii) There are no more than three readings of 10 percent for the first 1-hour period.

(4) The owner or operator of an affected source subject to limitations on D/F emissions shall demonstrate initial compliance with the D/F emission limit by conducting a performance test using Method 23 of appendix A to part 60 of this chapter. The owner or operator of an in-line kiln/raw mill shall demonstrate initial compliance by conducting separate performance tests while the raw mill of the in-line kiln/raw mill is under normal operating conditions and while the raw mill of the in-line kiln/raw mill is not operating. The owner or operator of a kiln or in-line kiln/raw mill equipped with an alkali bypass shall conduct simultaneous performance tests of the kiln or in-line kiln/raw mill exhaust and the alkali bypass, however the owner or operator of an in-line kiln/raw mill is not required to conduct a performance test of the alkali bypass exhaust when the raw mill of the in-line kiln/raw mill is not operating.

(i) Each performance test shall consist of three separate runs; each run shall be conducted under the conditions that exist when the affected source is operating at the highest load or capacity level reasonably expected to occur. The duration of each run shall be at least three hours and the sample volume for each run shall be at least 2.5 dscm (90 dscf). The arithmetic average concentration measured during each of the three runs shall be used to determine compliance.

(ii) The temperature at the inlet to the kiln or in-line kiln/raw mill PM APCD, and where applicable, the temperature at the inlet to the alkali bypass PM APCD, must be continuously recorded during the period of the Method 23 test, and the continuous temperature record(s) must be included in the performance test report. The arithmetic average temperature must be determined for each run. The arithmetic average of the averages for the three runs must be calculated and included in the performance test report and will determine the applicable temperature limit in accordance with § 63.1349(d)(4) of this subpart.

(iii) If carbon injection is used for D/F control, the carbon injection rate must be measured during the period of each run. The average carbon injection rate measured for the three runs shall be determined and included in the test report, and shall be used for compliance purposes in accordance with § 63.1349(e) of this subpart.

(5) The owner or operator of an affected source subject to limitations on emissions of THC shall demonstrate initial compliance with the THC limit by operating a continuous emission monitor in accordance with Performance Specification 8A of appendix B to part 60 of this chapter.[2] The duration of the performance test shall be three hours, and the average THC concentration during the three hour performance test shall be calculated. The owner or operator of an in-line kiln/raw mill shall demonstrate initial compliance by conducting separate performance tests while the raw mill of the in-line kiln/raw mill is under normal operating conditions and while the raw mill of the in-line kiln/raw mill is not operating.

(c) Performance tests required under paragraphs (b)(1) through (4) of this section shall be repeated every five years, except that the owner or operator of a kiln, in-line kiln/raw mill or clinker cooler is not required to repeat the initial performance test of opacity.

§ 63.1349 **Monitoring requirements.**

(a) The owner or operator of a kiln or in-line kiln/raw mill shall demonstrate continuous compliance with the opacity standard at each point where emissions are vented from these affected sources including alkali bypasses in accordance with paragraphs (a)(1) through (a)(5) of this section.

(1) Except as provided in paragraph (a)(2) of this section, the owner or operator shall install, calibrate, maintain, and continuously operate a continuous opacity monitor (COM) located at the outlet of the PM control device to continuously monitor the opacity. The COM shall be installed, maintained, calibrated, and operated as required by subpart A, general provisions of this part, and according to PS–1 of appendix B to part 60 of this chapter.

(2) The owner or operator of a kiln or in-line kiln/raw mill subject to the provisions of this subpart using a fabric filter with multiple stacks or an electrostatic precipitator with multiple stacks may, in lieu of installing the continuous opacity monitoring system required by paragraph (a)(1) of this section, monitor opacity in accordance with paragraphs (a)(2)(i) through (ii) of this section. If the control device exhausts through a monovent, or if the use of a COM in accordance with the installation specifications of PS–1 of appendix B to part 60 of this chapter is not feasible, the owner or operator must

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[2] The EPA proposed amendments to appendix B to 40 CFR part 60 on April 19, 1996 at 61 FR 17358.

monitor opacity in accordance with paragraphs (a)(2)(i) through (ii) of this section.

(i) Perform daily visual opacity observations of each stack in accordance with the procedures of Method 9 of appendix A of part 60 of this chapter. The duration of the Method 9 test shall be at least 30 minutes each day.

(ii) Use the Method 9 procedures to monitor and record the average opacity for each six-minute period during the test.

(3) To remain in compliance, the opacity must be maintained such that the average of the 6-minute average opacities for any 30-minute period does not exceed 20 percent. If the average of the six-minute average opacities for any 30-minute period exceeds 20 percent, this shall constitute a violation of the standard.

(4) If the average opacity as determined in accordance with paragraph (a)(1) of this section exceeds 15 percent for any ten consecutive 30-minute periods, or if the average opacity as determined in accordance with paragraphs (a)(2)(i) through (ii) of this section exceeds 15 percent for any 30-minute period, the owner or operator shall initiate a site-specific operating and maintenance plan within one hour. The site-specific operating and maintenance plan shall be developed in accordance with paragraph (g) of this section. Failure to initiate the site-specific operating and maintenance plan within one hour shall constitute a violation of the standard.

(5) If the average 30-minute opacity as determined in accordance with paragraph (a)(1) of this section exceeds 15 percent for five percent or more of the kiln operating time in any six-month reporting period, or if the 30-minute average opacity reading as determined in accordance with paragraphs (a)(2)(i) through (ii) of this section exceeds 15 percent during five percent or more of the daily readings in any six-month reporting period, the owner or operator shall notify the permitting authority within 48 hours and shall develop and implement a quality improvement plan (QIP) within 180 days. The QIP shall be developed in accordance with paragraph (h) of this section. Failure to notify the permitting authority within 48 hours shall constitute a violation of the standard. Failure to develop and implement a QIP within 180 days shall constitute a violation of the standard.

(b) The owner or operator of a clinker cooler shall demonstrate continuous compliance with the opacity standard at each point where emissions are vented from the clinker cooler in accordance with paragraphs (b)(1) through (b)(3) of this section.

(1) Except as provided in paragraph (b)(2) of this section, the owner or operator shall install, calibrate, maintain, and continuously operate a COM located at the outlet of the clinker cooler PM control device to continuously monitor the opacity. The COM shall be installed, maintained, calibrated, and operated as required by subpart A, general provisions of this part, and according to PS–1 of appendix B to part 60 of this chapter.

(2) The owner or operator of a clinker cooler subject to the provisions of this subpart using a fabric filter with multiple stacks or an electrostatic precipitator with multiple stacks may, in lieu of installing the continuous opacity monitoring system required by paragraph (b)(1) of this section, monitor opacity in accordance with paragraphs (b)(2)(i) through (ii) of this section. If the control device exhausts through a monovent, or if the use of a COM in accordance with the installation specifications of PS–1 of appendix B to part 60 of this chapter is not feasible, the owner or operator must monitor opacity in accordance with paragraphs (b)(2)(i) through (ii) of this section.

(i) Perform daily visual opacity observations of each stack in accordance with the procedures of Method 9 of appendix A of part 60 of this chapter. The duration of the Method 9 test shall be at least 30 minutes each day.

(ii) Use the Method 9 procedures to monitor and record the average opacity for each six-minute period during the test.

(3) To remain in compliance, the opacity must be maintained such that the average of the 6-minute average opacities for any 30-minute period does not exceed 10 percent. If the average of the six-minute average opacities for any 30-minute period exceeds 10 percent, this shall constitute a violation of the standard.

(c) The owner or operator of a raw mill or finish mill shall demonstrate continuous compliance with the opacity standard either by conducting visual emissions observations in accordance with paragraph (c)(1) of this section or through the use of a bag leak detection system in accordance with paragraphs (c)(2)(i) through (vii) of this section.

(1) An owner or operator may demonstrate compliance by performing daily visual emissions observations in accordance with the procedures of Method 22 of appendix A of part 60 of this chapter. The duration of the Method 22 test shall be six-minutes. If no visual emissions are observed at any time within the six-minute test, the source is in compliance.

(2) An owner or operator may demonstrate compliance by installing, calibrating, maintaining, and continuously operating a bag leak detection system in accordance with paragraphs (c)(2)(i) through (vii) of this section.

(i) The bag leak detection system must be capable of detecting PM emissions at concentrations of 1.0 mg per actual cubic meter (0.00044 grains per actual cubic foot) and greater.

(ii) The bag leak detection system sensor must provide output of relative or absolute PM emissions.

(iii) The bag leak detection system must be equipped with an alarm system that will sound when an increase in PM emissions is detected.

(iv) For positive pressure baghouses, a bag leak detector must be installed in each baghouse compartment. If a negative pressure or induced air baghouse is used, the bag leak detector must be installed downstream of the baghouse. Where multiple detectors are required (for either type of baghouse), the system instrumentation and alarm may be shared among detectors.

(v) The bag leak detection system shall be installed, operated, calibrated, and maintained in a manner consistent with available guidance from the U. S. Environmental Protection Agency or, in the absence of such guidance, the manufacturer's written specifications and recommendations.

(vi) Calibration of the system shall, at minimum, consist of establishing the relative baseline output level by adjusting the sensitivity and averaging period of the device and establishing the alarm set points and the alarm delay time.

(vii) The owner or operator shall not adjust the sensitivity, averaging period, alarm set points, or alarm delay time after the initial performance test unless a subsequent performance test is performed.

(3) If, in accordance with paragraph (c)(1) of this section visual emissions are observed the owner or operator shall follow the procedures of paragraphs (c)(3)(i) through (ii) of this section. If, in accordance with paragraphs (c)(2)(i) through (vii) of this section, the bag leak detection system alarm is triggered, the owner or operator shall follow the procedure of paragraphs (c)(3)(i) of this section.

(i) Initiate, within one-hour, a site specific operating and maintenance plan developed in accordance with paragraph (g) of this section. If a site specific operating and maintenance plan is not initiated within one hour, this

shall constitute a violation of the standard.

(ii) Conduct a visual opacity observation of each stack from which visible emissions were observed in accordance with the procedures of Method 9 of appendix A of part 60 of this chapter. The owner or operator must begin the Method 9 test within 24 hours of the end of the Method 22 test in which visible emissions were observed. The duration of the Method 9 test shall be thirty-minutes. If the average of the six-minute average opacities recorded during the Method 9 test exceeds 10 percent, this shall constitute a violation of the standard. If the owner or operator fails to begin the Method 9 test within 24 hours of the end of the Method 22 test in which visible emissions were observed, this shall constitute a violation of the standard.

(d) The owner or operator of an affected source subject to a limitation on D/F emissions shall comply with the following monitoring requirements to demonstrate continuous compliance with the D/F emission standard:

(1) The owner or operator shall install, calibrate, maintain, and continuously operate a device to monitor and record the temperature of the exhaust gases from the kiln, in-line kiln/raw mill and alkali bypass, if applicable, at the inlet to the kiln, in-line kiln/raw mill and/or alkali bypass PM control devices consistent with the requirements for continuous monitoring systems in subpart A, general provisions. The device shall have an accuracy of ±2 degrees Fahrenheit or ±1 percent of the temperature measured in degrees Fahrenheit.

(2) The owner or operator shall monitor and continuously record the temperature of the exhaust gases from the kiln, in-line kiln/raw mill and alkali bypass, if applicable, at the inlet to the kiln, in-line kiln/raw mill and/or alkali bypass PM control device.

(3) To remain in compliance with the D/F emission limit, the owner or operator of a kiln must maintain the temperature of the gas at the inlet to the kiln PM control device and alkali bypass PM control device, if applicable, such that the applicable temperature limits specified in paragraph (d)(4) of this section are never exceeded for any nine-hour block averaging period. If any nine-hour average temperature exceeds these temperature limits, this shall constitute a violation of the standard. To remain in compliance with the D/F emission limit, the owner or operator of an in-line kiln/raw mill must maintain the temperature of the gas at the inlet to the in-line kiln/raw mill PM control

device and in-line kiln/raw mill alkali bypass PM control device, if applicable, such that,

(i) When the raw mill of the in-line kiln/raw mill is operating, the applicable temperature limit(s) specified in paragraph (d)(4) of this section and established during the performance test when the raw mill was operating is (are) never exceeded for any nine-hour average. If any nine-hour average temperature exceeds the applicable temperature limit, this shall constitute a violation of the standard, and

(ii) When the raw mill of the in-line kiln/raw mill is not operating, the applicable temperature limit for the main in-line kiln/raw mill exhaust, specified in paragraph (d)(4) of this section and established during the performance test when the raw mill was not operating, is never exceeded for any nine-hour block averaging period. If any nine-hour average temperature exceeds the applicable temperature limit, this shall constitute a violation of the standard, and

(iii) If the in-line kiln/raw mill is equipped with an alkali bypass, the applicable temperature limit for the alkali bypass, specified in paragraph (d)(4) of this section and established during the performance test when the raw mill was operating, is never exceeded for any nine-hour block averaging period. If any nine-hour average temperature exceeds the applicable temperature limit, this shall constitute a violation of the standard.

(4) The temperature limit for affected sources meeting the limits of §§ 63.1343(b)(3)(ii), 63.1343(c)(3)(ii) and 63.1343(d)(2) of this subpart is 204 degrees C (400 degrees F). The temperature limits(s) for affected sources meeting the limits of §§ 63.1343(b)(3)(i), 63.1343(c)(3)(i) and 63.1343(d)(1) is (are) determined according to paragraphs (d)(4)(i) through (iii) of this section.

(i) Except as provided in paragraph (d)(4)(iii) of this section, if the D/F emissions determined by the most recent performance test conducted in accordance with § 63.1348(b)(4) of this subpart do not exceed 0.15 ng TEQ/dscm (6.5×10^{-11} gr/dscf), the temperature limit(s) is (are) the average temperature(s) recorded during the performance test plus five percent of the temperature expressed in degrees Fahrenheit, or the average temperature(s) recorded during the performance test plus 25° F, whichever is lower.

(ii) Except as provided in paragraph (d)(4)(iii) of this section, if the D/F emissions determined by the most recent performance test conducted in

accordance with § 63.1348(b)(4) of this subpart is (are) between 0.15 ng TEQ/dscm (6.5×10^{-11} gr TEQ/dscf) and 0.20 ng TEQ/dscm (8.7×10^{-11} gr TEQ/dscf), the temperature limit(s) is (are) the average temperature(s) recorded during the performance test.

(iii) No temperature limit established under this section shall be less than 204 °C (400 °F).

(5) The calibration of all thermocouples and other temperature sensors shall be verified every three months.

(e) The owner or operator of an affected source subject to a limitation on D/F emissions that employs carbon injection as an emission control technique shall comply with the monitoring requirements of paragraphs (d)(1) through (d)(5) and (e)(1) through (e)(2) of this section to demonstrate continuous compliance with the D/F emission standard:

(1) Measure the mass of carbon injected for every nine-hour period.

(2) If the carbon injection rate averaged over any nine-hour period is less than the average of the carbon injection rates for the three runs of the performance test conducted in accordance with § 63.1348(b)(4) of this subpart, this shall constitute a violation of the standard.

(f) The owner or operator of an affected source subject to a limitation on THC emissions under this subpart shall comply with the monitoring requirements of paragraphs (f)(1) and (f)(2) of this section to demonstrate continuous compliance with the THC emission standard:

(1) The owner or operator shall install, operate and maintain a THC continuous emission monitoring system in accordance with Performance Specification 8A, of appendix B to part 60 of this chapter [3] and comply with all of the requirements for continuous monitoring systems found in subpart A, general provisions of this part.

(2) Any thirty-day block average THC concentration in any gas discharged from a new or reconstructed raw material dryer, a new or reconstructed kiln, or a new or reconstructed in-line kiln/raw mill, exceeding 50 ppmvd, reported as propane, corrected to seven percent oxygen, is a violation of the standard.

(g) The owner or operator of each portland cement plant shall prepare for each kiln, in-line kiln raw mill, raw mill and finish mill which is an affected source subject to the provisions of this subpart, a written operations and maintenance plan. The plan shall be

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[3] Ibid.

submitted to the Administrator for review and approval as part of the application for a part 70 permit and shall include the following information:

(1) Procedures for proper operation and maintenance of the affected source and APCDs in order to meet the emission limits of § 63.1343 of this subpart for kilns and in-line kiln raw mills and § 63.1346 of this subpart for raw mills and finish mills, and

(2) Corrective actions to be taken when required by paragraphs (a)(4) or (c)(3)(i) of this section.

(h) If required under paragraph (a)(5) of this section, an owner or operator shall implement a QIP in accordance with paragraphs (h)(1) through (h)(4) of this section.

(1) A QIP shall be a written plan.

(2) An initial QIP shall include procedures that are adequate for evaluating the control performance problems monitored under paragraph (a)(5) of this section.

(3) Based on the results of the evaluation procedures, the QIP shall be modified to include procedures for conducting one or more of the actions described in paragraphs (h)(3)(i) through (v) of this section:

(i) Improved preventive maintenance practices,

(ii) Process operation changes,

(iii) Appropriate improvements in control methods,

(iv) Other steps appropriate to correct control performance, and

(v) More frequent or improved monitoring in conjunction with one or more steps under paragraphs (h)(3)(i) through (iv) of this section.

(4) The owner or operator shall act to develop and implement a QIP as expeditiously as practicable but in no case shall the period for completing implementation of the QIP exceed 180 days from the date on which notice of the need to implement the QIP must be provided to the permitting authority under paragraph (a)(5) of this section. If the owner or operator determines that more than 180 days will be necessary to complete the appropriate improvements, the owner or operator shall notify the permitting authority and obtain a site-specific resolution subject to the approval of the permitting authority. Where appropriate, the QIP may rely on procedures and corrective actions specified in an existing plan developed to satisfy a separate applicable requirement (such as a startup, shutdown, and malfunction plan or an operations and maintenance plan).

63.1350 Additional test methods.

(a) Owners or operators conducting tests to determine the rates of emission

of hydrogen chloride (HCl) from kilns, in-line kiln/raw mills and associated bypass stacks at portland cement manufacturing facilities, for use in applicability determinations under § 63.1340 of this subpart are permitted to use Method 321 or Method 322 of appendix A to this part.

(b) Owners or operators conducting tests to determine the rates of emission of HCl from kilns, in-line kiln/raw mills and associated bypass stacks at portland cement manufacturing facilities, for use in applicability determinations under § 63.1340 of this subpart are permitted to use Method 26 of appendix A to part 60 of this chapter, provided that the conditions of paragraphs (b)(1) through (b)(3) of this section are met:

(1) Method 321 or Method 322 of appendix A to this part is used to validate Method 26 of appendix A to part 60 of this chapter in accordance with section 6.1 of Method 301 of appendix A to this part.

(2) If a dry kiln or in-line kiln/raw mill is tested by Method 26, the Method 301 validation is conducted on a dry kiln or in-line kiln/raw mill.

(3) If a wet kiln is tested by Method 26, the Method 301 validation is conducted on a wet kiln.

(c) Owners or operators conducting tests to determine the rates of emission of HCl from kilns, in-line kiln/raw mills and associated bypass stacks at portland cement manufacturing facilities, for use in applicability determinations under § 63.1340 of this subpart are permitted to use Method 26A of appendix A to part 60 of this chapter, provided that the conditions of paragraphs (c)(1) through (c)(3) of this section are met:

(1) Method 321 or Method 322 of appendix A to this part is used to validate Method 26A of appendix A to part 60 of this chapter in accordance with section 6.1 of Method 301 of appendix A to this part.

(2) If a dry kiln or in-line kiln/raw mill is tested by Method 26A, the Method 301 validation is conducted on a dry kiln or in-line kiln/raw mill.

(3) If a wet kiln is tested by Method 26A, the Method 301 validation is conducted on a wet kiln.

(d) Owners or operators conducting tests to determine the rates of emission of specific organic HAP from raw material dryers, kilns and in-line kiln/raw mills at portland cement manufacturing facilities, for use in applicability determinations under § 63.1340 of this subpart are permitted to use Method 320 of appendix A to this part, or Method 18 of appendix A to part 60 of this chapter.

§ 63.1351 Notification requirements.

(a) The notification provisions of 40 CFR part 63, subpart A that apply and those that do not apply to owners and operators of affected sources subject to this subpart are listed in Table 1 of this subpart. If any State requires a notice that contains all of the information required in a notification listed in this section, the owner or operator may send the Administrator a copy of the notice sent to the State to satisfy the requirements of this section for that notification.

(b) Each owner or operator subject to the requirements of this subpart shall comply with the notification requirements in § 63.9 of this part as follows:

(1) Initial notifications as required by § 63.9(b) through (d) of this part. For the purposes of this subpart, a Title V or part 70 permit application may be used in lieu of the initial notification required under § 63.9(b), provided the same information is contained in the permit application as required by § 63.9(b), and the State to which the permit application has been submitted has an approved operating permit program under part 70 of this chapter and has received delegation of authority from the EPA. Permit applications shall be submitted by the same due dates as those specified for the initial notification.

(2) Notification of performance tests, as required by §§ 63.7 and 63.9(e) of this part.

(3) Notification of opacity and visible emission observations required by § 63.1348(b)(1) through (3) in accordance with §§ 63.6(h)(5) and 63.9(f) of this part.

(4) Notification, as required by § 63.9(g) of this part, of the date that the continuous emission monitor performance evaluation required by § 63.8(e) of this part is scheduled to begin.

(5) Notification of compliance status, as required by § 63.9(h) of this part.

(c) Each owner or operator subject to the requirements of this subpart that is required to implement a QIP shall submit notifications as follows:

(1) Notification, as required by § 63.1349(a)(5) of this subpart, of the requirement to implement a QIP.

(2) Notification, as required by § 63.1349(h)(4) of this subpart, if applicable, that more than 180 days will be required to complete the appropriate improvements.

§ 63.1352 Reporting requirements.

(a) The reporting provisions of 40 CFR part 63, subpart A that apply and those that do not apply to owners or operators

of affected sources subject to this subpart are listed in Table 1 of this subpart. If any State requires a report that contains all of the information required in a report listed in this section, the owner or operator may send the Administrator a copy of the report sent to the State to satisfy the requirements of this section for that report.

(b) The owner or operator of an affected source shall comply with the reporting requirements specified in § 63.10 of the general provisions to part 63, subpart A as follows:

(1) As required by § 63.10(d)(2) of this part, the owner or operator shall report the results of performance tests as part of the notification of compliance status.

(2) As required by § 63.10(d)(3) of this part, the owner or operator of an affected source shall report the opacity or visible emission results from tests required by § 63.1348(b)(1)–(3) of this subpart along with the results of the performance test required under § 63.7 of this part.

(3) As required by § 63.10(d)(4) of this part, the owner or operator of an affected source who is required to submit progress reports as a condition of receiving an extension of compliance under § 63.6(i) of this part shall submit such reports by the dates specified in the written extension of compliance.

(4) As required by § 63.10(d)(5) of this part, if actions taken by an owner or operator during a startup, shutdown, or malfunction of an affected source (including actions taken to correct a malfunction) are consistent with the procedures specified in the source's startup, shutdown, and malfunction plan specified in § 63.6(e)(3) of this part, the owner or operator shall state such information in a semiannual report. Reports shall only be required if a startup, shutdown, or malfunction occurred during the reporting period. The startup, shutdown, and malfunction report may be submitted simultaneously with the excess emissions and continuous monitoring system performance reports; and

(5) Any time an action taken by an owner or operator during a startup, shutdown, or malfunction (including actions taken to correct a malfunction) is not consistent with the procedures in the startup, shutdown, and malfunction plan, the owner or operator shall make an immediate report of the actions taken for that event within 2 working days, by telephone call or facsimile (FAX) transmission. The immediate report shall be followed by a letter, certified by the owner or operator or other responsible official, explaining the circumstances of the event, the reasons for not following the startup, shutdown, and malfunction plan, and whether any excess emissions and/or parameter monitoring exceedances are believed to have occurred.

(6) As required by § 63.10(e)(2) of this part, the owner or operator shall submit a written report of the results of the performance evaluation for the continuous monitoring system required by § 63.8(e) of this part. The owner or operator shall submit the report simultaneously with the results of the performance test.

(7) As required by § 63.10(e)(2) of this part, the owner or operator of an affected source using a continuous opacity monitoring system to determine opacity compliance during any performance test required under § 63.7 of this part and described in § 63.6(d)(6) of this part shall report the results of the continuous opacity monitoring system performance evaluation conducted under § 63.8(e) of this part.

(8) As required by § 63.10(e)(3) of this part, the owner or operator of an affected source equipped with a continuous emission monitor shall submit an excess emissions and continuous monitoring system performance report for any event when the continuous monitoring system data indicate the source is not in compliance with the applicable emission limitation or operating parameter limit.

(9) The owner or operator shall submit a summary report semiannually which contains the information specified in § 63.10(e)(3)(vi) of this part. In addition, the summary report shall include:

(i) All exceedences of maximum control device inlet gas temperature limits determined under § 63.1349(d)(4) of this subpart,

(ii) All failures to calibrate thermocouples and other temperature sensors as required under § 63.1349(d)(5) of this subpart, and

(iii) All exceedences in carbon injection rate as required under § 63.1349(e)(2) of this subpart.

(10) If the total continuous monitoring system downtime for any CEM or any continuous monitoring system (CMS) for the reporting period is five percent or greater of the total operating time for the reporting period, the owner or operator shall submit an excess emissions and continuous monitoring system performance report along with the summary report.

§ 63.1353 Recordkeeping requirements.

(a) The owner or operator shall maintain files of all information (including all reports and notifications) required by this section recorded in a form suitable and readily available for inspection and review as required by § 63.10(b)(1). The files shall be retained for at least five years following the date of each occurrence, measurement, maintenance, corrective action, report, or record. At a minimum, the most recent two years of data shall be retained on site. The remaining three years of data may be retained off site. The files may be maintained on microfilm, on a computer, on floppy disks, on magnetic tape, or on microfiche.

(b) The owner or operator shall maintain records for each affected source as required by § 63.10(b)(2) and (b)(3) of this part, and

(1) All documentation supporting initial notifications and notifications of compliance status under § 63.9 of this part.

(2) All records of applicability determination, including supporting analyses, and

(3) If the owner or operator has been granted a waiver under § 63.8(f)(6) of this part, any information demonstrating whether a source is meeting the requirements for a waiver of recordkeeping or reporting requirements.

(c) In addition to the recordkeeping requirements in paragraph (b) of this section, the owner or operator of an affected source equipped with a continuous monitoring system shall maintain all records required by § 63.10(c) of this part.

(d) In addition to the recordkeeping requirements in paragraph (b) of this section, the owner or operator of an affected source equipped with a bag leak detection system shall maintain records of any bag leak detection system alarm, including the date and time of the alarm and the date and time that corrective action was initiated, with a brief explanation of the cause of the alarm and the corrective action taken.

§ 63.1354 Delegation of authority.

(a) In delegating implementation and enforcement authority to a State under subpart E of this part, the authorities contained in paragraph (b) of this section shall be retained by the Administrator and not transferred to a State.

(b) Authority which will not be delegated to States: § 63.1348(b), approval of alternate test methods for particulate matter determination; approval of alternate test methods for opacity; approval of alternate test methods for D/F; § 63.1350, approval of alternate test methods for Hcl.

§§ 63.1355–63.1359 [Reserved]

TABLE 1 TO SUBPART LLL.—APPLICABILITY OF GENERAL PROVISIONS

General provisions citation	Requirement	Applies to subpart LLL	Comment
63.1(a)(1)–(4)	Applicability	Yes	
63.1(a)(5)		No	[Reserved].
63.1(a)(6)–(a)(8)	Applicability	Yes	
63.1(a)(9)		No	[Reserved].
63.1(a)(10)–(14)	Applicability	Yes	
63.1(b)(1)	Initial Applicability Determination	No	§ 63.1340 specifies applicability.
63.1(b)(2)–(3)	Initial Applicability Determination	Yes	
63.1(c)(1)	Applicability After Standard Established.	Yes	
63.1(c)(2)	Permit Requirements	Yes	Area sources must obtain Title V permits.
63.1(c)(3)		No	[Reserved].
63.1(c)(4)–(5)	Extensions, Notifications	Yes	
63.1(d)		No	[Reserved].
63.1(e)	Applicability of Permit Program	Yes	
63.2	Definitions	Yes	Additional definitions in § 63.1341.
63.3(a)–(c)	Units and Abbreviations	Yes	
63.4(a)(1)–(a)(3)	Prohibited Activities	Yes	
63.4(a)(4)		No	[Reserved].
63.4(a)(5)	Compliance date	Yes	
63.4(b)–(c)	Circumvention, Severability	Yes	
63.5(a)(1)–(2)	Construction/Reconstruction	Yes	
63.5(b)(1)	Compliance Dates	Yes	
63.5(b)(2)		No	[Reserved].
63.5(b)(3)–(6)	Construction Approval, Applicability	Yes	
63.5(c)		No	[Reserved].
63.5(d)(1)–(4)	Approval of Construction/Reconstruction.	Yes	
63.5(e)	Approval of Construction/Reconstruction.	Yes	
63.5(f)(1)–(2)	Approval of Construction/Reconstruction.	Yes	
63.6(a)	Compliance for Standards and Maintenance.	Yes	
63.6(b)(1)–(5)	Compliance Dates	Yes	
63.6(b)(6)		No	[Reserved].
63.6(b)(7)	Compliance Dates	Yes	
63.6(c)(1)–(2)	Compliance Dates	Yes	
63.6(c)(3)–(c)(4)		No	[Reserved].
63.6(c)(5)	Compliance Dates	Yes	
63.6(d)		No	[Reserved].
63.6(e)(1)–(e)(2)	Operation & Maintenance	Yes	
63.6(e)(3)	Startup, Shutdown Malfunction Plan	Yes	
63.6(f)(1)–(3)	Compliance with Emission Standards.	Yes	
63.6(g)(1)–(g)(3)	Alternative Standard	Yes	
63.6(h)(1)–(2)	Opacity/VE Standards	Yes	
63.6(h)(3)		No	Reserved
63.6(h)(4)–(h)(5)(i)	Opacity/VE Standards	Yes	
63.6(h)(5)(ii)–(iv)	Opacity/VE Standards	No	Test duration specified in Subpart LLL
63.6(h)(6)	Opacity/VE Standards	Yes	
63.6(i)(1)–(i)(14)	Extension of Compliance	Yes	
63.6(i)(15)		No	[Reserved].
63.6(i)(16)	Extension of Compliance	Yes	
63.6(j)	Exemption from Compliance	Yes.	
63.7(a)(1)–(a)(3)	Performance Testing Requirements	Yes	§ 63.1348 has specific requirements.
63.7(b)	Notification	Yes	
63.7(c)	Quality Assurance/Test Plan	Yes	
63.7(d)	Testing Facilities	Yes	
63.7(e)(1)–(4)	Conduct of Tests	Yes	
63.7(f)	Alternative Test Method	Yes	
63.7(g)	Data Analysis	Yes	
63.7(h)	Waiver of Tests	Yes	
63.8(a)(1)	Monitoring Requirements	Yes	
63.8(a)(2)	Monitoring	No	§ 63.1349 includes CEM requirements.
63.8(a)(3)		No	[Reserved].
63.8(a)(4)	Monitoring	No	Flares not applicable.
63.8(b)(1)–(3)	Conduct of Monitoring	Yes	
63.8(c)(1)–(8)	CMS Operation/ Maintenance	Yes	
63.8(d)	Quality Control	Yes	

TABLE 1 TO SUBPART LLL.—APPLICABILITY OF GENERAL PROVISIONS—Continued

General provisions citation	Requirement	Applies to subpart LLL	Comment
63.8(e)	Performance Evaluation for CMS	Yes	
63.8(f)(1)–(f)(5)	Alternative Monitoring Method	Yes	
63.8(f)(6)	Alternative to RATA Test	Yes	
63.8(g)	Data Reduction	Yes	
63.9(a)	Notification Requirements	Yes	Additional notification requirements in §363.1351 (c).
63.9(b)(1)–(5)	Initial Notifications	Yes	
63.9(c)	Request for Compliance Extension ..	Yes	
63.9(d)	New Source Notification for Special Compliance Requirements.	Yes	
63.9(e)	Notification of Performance Test	Yes	
63.9(f)	Notification of VE/Opacity Test	Yes	Notification not required for VE/ opacity test under §63.1349.
63.9(g)	Additional CMS Notifications	Yes	
63.9(h)(1)–(h)(3)	Notification of Compliance Status	Yes	
63.9(h)(4)	....	No	[Reserved].
63.9(h)(5)–(h)(6)	Notification of Compliance Status	Yes	
63.9(i)	Adjustment of Deadlines	Yes	
63.9(j)	Change in Previous Information	Yes	
63.10(a)	Recordkeeping/Reporting	Yes	
63.10(b)	General Requirements	Yes	
63.10(c)(1)	Additional CMS Recordkeeping	Yes	
63.10(c)(2)–(c)(4)	....	No	[Reserved].
63.10(c)(5)–(c)(8)	Additional CMS Recordkeeping	Yes	
63.10(c)(9)	....	No	[Reserved].
63.10(c)(10)–(15)	Additional CMS Recordkeeping	Yes	
63.10(d)(1)	General Reporting Requirements	Yes	
63.10(d)(2)	Performance Test Results	Yes	
63.10(d)(3)	Opacity or VE Observations	Yes	
63.10(d)(4)	Progress Reports	Yes	
63.10(d)(5)	Startup, Shutdown, Malfunction Reports.	Yes	
63.10(e)(1)–(e)(2)	Additional CMS Reports	Yes	
63.10(e)(3)	Excess Emissions and CMS Performance Reports.	Yes	Exceedences are defined in §63.1349.
63.10(f)	Waiver for Recordkeeping/Reporting	Yes	
63.11(a)–(b)	Control Device Requirements	No	Flares not applicable.
63.12(a)–(c)	State Authority and Delegations	Yes	
63.13(a)–(c)	State/Regional Addresses	Yes	
63.14(a)–(b)	Incorporation by Reference	Yes	
63.15(a)–(b)	Availability of Information	Yes	

3. Appendix A of part 63 is amended by adding, in numerical order, Methods 320, 321, and 322 to read as follows:

Appendix A to Part 63-Test Methods

*   *   *   *   *

METHOD 320

Measurement of Vapor Phase Organic and Inorganic Emissions by Extractive Fourier Transform Infrared (FTIR) Spectroscopy

1.0 Introduction.

Persons unfamiliar with basic elements of FTIR spectroscopy should not attempt to use this method. This method describes sampling and analytical procedures for extractive emission measurements using Fourier transform infrared (FTIR) spectroscopy. Detailed analytical procedures for interpreting infrared spectra are described in the ''Protocol for the Use of Extractive Fourier Transform Infrared (FTIR) Spectrometry in Analyses of Gaseous Emissions from Stationary Sources,'' hereafter referred to as the ''Protocol.'' Definitions not given in this method are given in appendix A of the Protocol.

References to specific sections in the Protocol are made throughout this Method. For additional information refer to references 1 and 2, and other EPA reports, which describe the use of FTIR spectrometry in specific field measurement applications and validation tests. The sampling procedure described here is extractive. Flue gas is extracted through a heated gas transport and handling system. For some sources, sample conditioning systems may be applicable. Some examples are given in this method. (Note: sample conditioning systems may be used providing the method validation requirements in Sections 9.2 and 13.0 of this method are met.)

1.1   Scope and Applicability.

1.1.1   Analytes. Analytes include hazardous air pollutants (HAPs) for which EPA reference spectra have been developed. Other compounds can also be measured with this method if reference spectra are prepared according to section 4.6 of the protocol.

1.1.2   Applicability. This method applies to the analysis of vapor phase organic or inorganic compounds which absorb energy in the mid-infrared spectral region, about 400 to 4000 cm^{-1} (25 to 2.5 μm). This method is used to determine compound-specific

concentrations in a multi-component vapor phase sample, which is contained in a closed-path gas cell. Spectra of samples are collected using double beam infrared absorption spectroscopy. A computer program is used to analyze spectra and report compound concentrations.

1.2   Method Range and Sensitivity. Analytical range and sensitivity depend on the frequency-dependent analyte absorptivity, instrument configuration, data collection parameters, and gas stream composition. Instrument factors include: (a) spectral resolution, (b) interferometer signal averaging time, (c) detector sensitivity and response, and (d) absorption path length.

1.2.1   For any optical configuration the analytical range is between the absorbance values of about .01 (infrared transmittance relative to the background = 0.98) and 1.0 (T = 0.1). (For absorbance > 1.0 the relation between absorbance and concentration may not be linear.)

1.2.2   The concentrations associated with this absorbance range depend primarily on the cell path length and the sample temperature. An analyte absorbance greater than 1.0, can be lowered by decreasing the

optical path length. Analyte absorbance increases with a longer path length. Analyte detection also depends on the presence of other species exhibiting absorbance in the same analytical region. Additionally, the estimated lower absorbance (A) limit (A = 0.01) depends on the root mean square deviation (RMSD) noise in the analytical region.

1.2.3 The concentration range of this method is determined by the choice of optical configuration.

1.2.3.1 The absorbance for a given concentration can be decreased by decreasing the path length or by diluting the sample. There is no practical upper limit to the measurement range.

1.2.3.2 The analyte absorbance for a given concentration may be increased by increasing the cell path length or (to some extent) using a higher resolution. Both modifications also cause a corresponding increased absorbance for all compounds in the sample, and a decrease in the signal throughput. For this reason the practical lower detection range (quantitation limit) usually depends on sample characteristics such as moisture content of the gas, the presence of other interferants, and losses in the sampling system.

1.3 Sensitivity. The limit of sensitivity for an optical configuration and integration time is determined using appendix D of the Protocol: Minimum Analyte Uncertainty, (MAU). The MAU depends on the RMSD noise in an analytical region, and on the absorptivity of the analyte in the same region.

1.4 Data Quality. Data quality shall be determined by executing Protocol pre-test procedures in appendices B to H of the protocol and post-test procedures in appendices I and J of the protocol.

1.4.1 Measurement objectives shall be established by the choice of detection limit (DL_i) and analytical uncertainty (AU_i) for each analyte.

1.4.2 An instrumental configuration shall be selected. An estimate of gas composition shall be made based on previous test data, data from a similar source or information gathered in a pre-test site survey. Spectral interferants shall be identified using the selected DL_i and AU_i and band areas from reference spectra and interferant spectra. The baseline noise of the system shall be measured in each analytical region to determine the MAU of the instrument configuration for each analyte and interferant (MIU_i).

1.4.3 Data quality for the application shall be determined, in part, by measuring the RMS (root mean square) noise level in each analytical spectral region (appendix C of the Protocol). The RMS noise is defined as the RMSD of the absorbance values in an analytical region from the mean absorbance value in the region.

1.4.4 The MAU is the minimum analyte concentration for which the AU_i can be maintained; if the measured analyte concentration is less than MAU_i, then data quality are unacceptable.

2.0 Summary of Method.

2.1 Principle. References 4 through 7 provide background material on infrared spectroscopy and quantitative analysis. A summary is given in this section.

2.1.1 Infrared absorption spectroscopy is performed by directing an infrared beam through a sample to a detector. The frequency-dependent infrared absorbance of the sample is measured by comparing this detector signal (single beam spectrum) to a signal obtained without a sample in the beam path (background).

2.1.2 Most molecules absorb infrared radiation and the absorbance occurs in a characteristic and reproducible pattern. The infrared spectrum measures fundamental molecular properties and a compound can be identified from its infrared spectrum alone.

2.1.3 Within constraints, there is a linear relationship between infrared absorption and compound concentration. If this frequency dependent relationship (absorptivity) is known (measured), it can be used to determine compound concentration in a sample mixture.

2.1.4 Absorptivity is measured by preparing, in the laboratory, standard samples of compounds at known concentrations and measuring the FTIR ''reference spectra'' of these standard samples. These ''reference spectra'' are then used in sample analysis: (1) compounds are detected by matching sample absorbance bands with bands in reference spectra, and (2) concentrations are measured by comparing sample band intensities with reference band intensities.

2.1.5 This method is self-validating provided that the results meet the performance requirement of the QA spike in sections 9.0 and 8.6.2 of this method, and results from a previous method validation study support the use of this method in the application.

2.2 Sampling and Analysis. In extractive sampling a probe assembly and pump are used to extract gas from the exhaust of the affected source and transport the sample to the FTIR gas cell. Typically, the sampling apparatus is similar to that used for single-component continuous emission monitor (CEM) measurements.

2.2.1 The digitized infrared spectrum of the sample in the FTIR gas cell is measured and stored on a computer. Absorbance band intensities in the spectrum are related to sample concentrations by what is commonly referred to as Beer's Law.

$$A_i = a_i b c_i \qquad \text{(Eq. 320–1)}$$

Where:

A_i = absorbance at a given frequency of the ith sample component.

a_i = absorption coefficient (absorptivity) of the ith sample component.

b = path length of the cell.

c_i = concentration of the ith sample component.

2.2.2 Analyte spiking is used for quality assurance (QA). In this procedure (section 8.6.2 of this method) an analyte is spiked into the gas stream at the back end of the sample probe. Analyte concentrations in the spiked samples are compared to analyte concentrations in unspiked samples. Since the concentration of the spike is known, this procedure can be used to determine if the sampling system is removing the spiked analyte(s) from the sample stream.

2.3 Reference Spectra Availability. Reference spectra of over 100 HAPs are available in the EPA FTIR spectral library on the EMTIC (Emission Measurement Technical Information Center) computer bulletin board service and at internet address http://info.arnold.af.mil/epa/welcome.htm. Reference spectra for HAPs, or other analytes, may also be prepared according to section 4.6 of the Protocol.

2.4 Operator Requirements. The FTIR analyst shall be trained in setting up the instrumentation, verifying the instrument is functioning properly, and performing routine maintenance. The analyst must evaluate the initial sample spectra to determine if the sample matrix is consistent with pre-test assumptions and if the instrument configuration is suitable. The analyst must be able to modify the instrument configuration, if necessary.

2.4.1 The spectral analysis shall be supervised by someone familiar with EPA FTIR Protocol procedures.

2.4.2 A technician trained in CEM test methods is qualified to install and operate the sampling system. This includes installing the probe and heated line assembly, operating the analyte spike system, and performing moisture and flow measurements.

3.0 Definitions.

See appendix A of the Protocol for definitions relating to infrared spectroscopy. Additional definitions are given below.

3.1 Analyte. A compound that this method is used to measure. The term ''target analyte'' is also used. This method is multi-component and a number of analytes can be targeted for a test.

3.2 Reference Spectrum. Infrared spectrum of an analyte prepared under controlled, documented, and reproducible laboratory conditions according to procedures in section 4.6 of the Protocol. A library of reference spectra is used to measure analytes in gas samples.

3.3 Standard Spectrum. A spectrum that has been prepared from a reference spectrum through a (documented) mathematical operation. A common example is de-resolving of reference spectra to lower-resolution standard spectra (Protocol, appendix K). Standard spectra, prepared by approved, and documented, procedures can be used as reference spectra for analysis.

3.4 Concentration. In this method concentration is expressed as a molar concentration, in ppm-meters, or in (ppm-meters)/K, where K is the absolute temperature (Kelvin). The latter units allow the direct comparison of concentrations from systems using different optical configurations or sampling temperatures.

3.5 Interferant. A compound in the sample matrix whose infrared spectrum overlaps with part of an analyte spectrum. The most accurate analyte measurements are achieved when reference spectra of interferants are used in the quantitative analysis with the analyte reference spectra.

The presence of an interferant can increase the analytical uncertainty in the measured analyte concentration.

3.6 Gas Cell. A gas containment cell that can be evacuated. It is equipped with the

optical components to pass the infrared beam through the sample to the detector. Important cell features include: path length (or range if variable), temperature range, materials of construction, and total gas volume.

3.7 Sampling System. Equipment used to extract the sample from the test location and transport the sample gas to the FTIR analyzer. This includes sample conditioning systems.

3.8 Sample Analysis. The process of interpreting the infrared spectra to obtain sample analyte concentrations. This process is usually automated using a software routine employing a classical least squares (cls), partial least squares (pls), or K- or P- matrix method.

3.9 One hundred percent line. A double beam transmittance spectrum obtained by combining two background single beam spectra. Ideally, this line is equal to 100 percent transmittance (or zero absorbance) at every frequency in the spectrum. Practically, a zero absorbance line is used to measure the baseline noise in the spectrum.

3.10 Background Deviation. A deviation from 100 percent transmittance in any region of the 100 percent line. Deviations greater than ±5 percent in an analytical region are unacceptable (absorbance of 0.021 to −0.022). Such deviations indicate a change in the instrument throughput relative to the background single beam.

3.11 Batch Sampling. A procedure where spectra of discreet, static samples are collected. The gas cell is filled with sample and the cell is isolated. The spectrum is collected. Finally, the cell is evacuated to prepare for the next sample.

3.12 Continuous Sampling. A procedure where spectra are collected while sample gas is flowing through the cell at a measured rate.

3.13 Sampling resolution. The spectral resolution used to collect sample spectra.

3.14 Truncation. Limiting the number of interferogram data points by deleting points farthest from the center burst (zero path difference, ZPD).

3.15 Zero filling. The addition of points to the interferogram. The position of each added point is interpolated from neighboring real data points. Zero filling adds no information to the interferogram, but affects line shapes in the absorbance spectrum (and possibly analytical results).

3.16 Reference CTS. Calibration Transfer Standard spectra that were collected with reference spectra.

3.17 CTS Standard. CTS spectrum produced by applying a de-resolution procedure to a reference CTS.

3.18 Test CTS. CTS spectra collected at the sampling resolution using the same optical configuration as for sample spectra. Test spectra help verify the resolution, temperature and path length of the FTIR system.

3.19 RMSD. Root Mean Square Difference, defined in EPA FTIR Protocol, appendix A.

3.20 Sensitivity. The noise-limited compound-dependent detection limit for the FTIR system configuration. This is estimated by the MAU. It depends on the RMSD in an analytical region of a zero absorbance line.

3.21 Quantitation Limit. The lower limit of detection for the FTIR system

configuration in the sample spectra. This is estimated by mathematically subtracting scaled reference spectra of analytes and interferences from sample spectra, then measuring the RMSD in an analytical region of the subtracted spectrum. Since the noise in subtracted sample spectra may be much greater than in a zero absorbance spectrum, the quantitation limit is generally much higher than the sensitivity. Removing spectral interferences from the sample or improving the spectral subtraction can lower the quantitation limit toward (but not below) the sensitivity.

3.22 Independent Sample. A unique volume of sample gas; there is no mixing of gas between two consecutive independent samples. In continuous sampling two independent samples are separated by at least 5 cell volumes. The interval between independent measurements depends on the cell volume and the sample flow rate (through the cell).

3.23 Measurement. A single spectrum of flue gas contained in the FTIR cell.

3.24 Run. A run consists of a series of measurements. At a minimum a run includes 8 independent measurements spaced over 1 hour.

3.25 Validation. Validation of FTIR measurements is described in sections 13.0 through 13.4 of this method. Validation is used to verify the test procedures for measuring specific analytes at a source. Validation provides proof that the method works under certain test conditions.

3.26 Validation Run. A validation run consists of at least 24 measurements of independent samples. Half of the samples are spiked and half are not spiked. The length of the run is determined by the interval between independent samples.

3.27 Screening. Screening is used when there is little or no available information about a source. The purpose of screening is to determine what analytes are emitted and to obtain information about important sample characteristics such as moisture, temperature, and interferences. Screening results are semi-quantitative (estimated concentrations) or qualitative (identification only). Various optical and sampling configurations may be used. Sample conditioning systems may be evaluated for their effectiveness in removing interferences. It is unnecessary to perform a complete run under any set of sampling conditions. Spiking is not necessary, but spiking can be a useful screening tool for evaluating the sampling system, especially if a reactive or soluble analyte is used for the spike.

3.28 Emissions Test. An FTIR emissions test is performed according specific sampling and analytical procedures. These procedures, for the target analytes and the source, are based on previous screening and validation results. Emission results are quantitative. A QA spike (sections 8.6.2 and 9.2 of this method) is performed under each set of sampling conditions using a representative analyte. Flow, gas temperature and diluent data are recorded concurrently with the FTIR measurements to provide mass emission rates for detected compounds.

3.29 Surrogate. A surrogate is a compound that is used in a QA spike

procedure (section 8.6.2 of this method) to represent other compounds. The chemical and physical properties of a surrogate shall be similar to the compounds it is chosen to represent. Under given sampling conditions, usually a single sampling factor is of primary concern for measuring the target analytes: for example, the surrogate spike results can be representative for analytes that are more reactive, more soluble, have a lower absorptivity, or have a lower vapor pressure than the surrogate itself.

4.0 Interferences.

Interferences are divided into two classifications: analytical and sampling.

4.1 Analytical Interferences. An analytical interference is a spectral feature that complicates (in extreme cases may prevent) the analysis of an analyte. Analytical interferences are classified as background or spectral interference.

4.1.1 Background Interference. This results from a change in throughput relative to the single beam background. It is corrected by collecting a new background and proceeding with the test. In severe instances the cause must be identified and corrected. Potential causes include: (1) deposits on reflective surfaces or transmitting windows, (2) changes in detector sensitivity, (3) a change in the infrared source output, or (4) failure in the instrument electronics. In routine sampling throughput may degrade over several hours. Periodically a new background must be collected, but no other corrective action will be required.

4.1.2 Spectral Interference. This results from the presence of interfering compound(s) (interferant) in the sample. Interferant spectral features overlap analyte spectral features. Any compound with an infrared spectrum, including analytes, can potentially be an interferant. The Protocol measures absorbance band overlap in each analytical region to determine if potential interferants shall be classified as known interferants (FTIR Protocol, section 4.9 and appendix B). Water vapor and CO_2 are common spectral interferants. Both of these compounds have strong infrared spectra and are present in many sample matrices at high concentrations relative to analytes. The extent of interference depends on the (1) interferant concentration, (2) analyte concentration, and (3) the degree of band overlap. Choosing an alternate analytical region can minimize or avoid the spectral interference. For example, CO_2 interferes with the analysis of the 670 cm⁻¹ benzene band. However, benzene can also be measured near 3000 cm⁻¹ (with less sensitivity).

4.2 Sampling System Interferences. These prevent analytes from reaching the instrument. The analyte spike procedure is designed to measure sampling system interference, if any.

4.2.1 Temperature. A temperature that is too low causes condensation of analytes or water vapor. The materials of the sampling system and the FTIR gas cell usually set the upper limit of temperature.

4.2.2 Reactive Species. Anything that reacts with analytes. Some analytes, like formaldehyde, polymerize at lower temperatures.

4.2.3   Materials. Poor choice of material for probe, or sampling line may remove some analytes. For example, HF reacts with glass components.

4.2.4   Moisture. In addition to being a spectral interferant, condensed moisture removes soluble compounds.

5.0   Safety.

The hazards of performing this method are those associated with any stack sampling method and the same precautions shall be followed. Many HAPs are suspected carcinogens or present other serious health risks. Exposure to these compounds should be avoided in all circumstances. For instructions on the safe handling of any particular compound, refer to its material safety data sheet. When using analyte standards, always ensure that gases are properly vented and that the gas handling system is leak free. (Always perform a leak check with the system under maximum vacuum and, again, with the system at greater than ambient pressure.) Refer to section 8.2 of this method for leak check procedures. This method does not address all of the potential safety risks associated with its use. Anyone performing this method must follow safety and health practices consistent with applicable legal requirements and with prudent practice for each application.

6.0   Equipment and Supplies.

Note: Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

The equipment and supplies are based on the schematic of a sampling system shown in Figure 1. Either the batch or continuous sampling procedures may be used with this sampling system. Alternative sampling configurations may also be used, provided that the data quality objectives are met as determined in the post-analysis evaluation. Other equipment or supplies may be necessary, depending on the design of the sampling system or the specific target analytes.

6.1   Sampling Probe. Glass, stainless steel, or other appropriate material of sufficient length and physical integrity to sustain heating, prevent adsorption of analytes, and to transport analytes to the infrared gas cell. Special materials or configurations may be required in some applications. For instance, high stack sample temperatures may require special steel or cooling the probe. For very high moisture sources it may be desirable to use a dilution probe.

6.2   Particulate Filters. A glass wool plug (optional) inserted at the probe tip (for large particulate removal) and a filter (required) rated for 99 percent removal efficiency at 1-micron (e.g., Balston™) connected at the outlet of the heated probe.

6.3   Sampling Line/Heating System. Heated (sufficient to prevent condensation) stainless steel, polytetrafluoroethane, or other material inert to the analytes.

6.4   Gas Distribution Manifold. A heated manifold allowing the operator to control flows of gas standards and samples directly to the FTIR system or through sample conditioning systems. Usually includes heated flow meter, heated valve for selecting and sending sample to the analyzer, and a by-pass vent. This is typically constructed of stainless steel tubing and fittings, and high-temperature valves.

6.5   Stainless Steel Tubing. Type 316, appropriate diameter (e.g., 3/8 in.) and length for heated connections. Higher grade stainless may be desirable in some applications.

6.6   Calibration/Analyte Spike Assembly. A three way valve assembly (or equivalent) to introduce analyte or surrogate spikes into the sampling system at the outlet of the probe upstream of the out-of-stack particulate filter and the FTIR analytical system.

6.7   Mass Flow Meter (MFM). These are used for measuring analyte spike flow. The MFM shall be calibrated in the range of 0 to 5 L/min and be accurate to ±2 percent (or better) of the flow meter span.

6.8   Gas Regulators. Appropriate for individual gas standards.

6.9   Polytetrafluoroethane Tubing. Diameter (e.g., 3/8 in.) and length suitable to connect cylinder regulators to gas standard manifold.

6.10   Sample Pump. A leak-free pump (e.g., KNF™), with by-pass valve, capable of producing a sample flow rate of at least 10 L/min through 100 ft of sample line. If the pump is positioned upstream of the distribution manifold and FTIR system, use a heated pump that is constructed from materials non-reactive to the analytes. If the pump is located downstream of the FTIR system, the gas cell sample pressure will be lower than ambient pressure and it must be recorded at regular intervals.

6.11   Gas Sample Manifold. Secondary manifold to control sample flow at the inlet to the FTIR manifold. This is optional, but includes a by-pass vent and heated rotameter.

6.12   Rotameter. A 0 to 20 L/min rotameter. This meter need not be calibrated.

6.13   FTIR Analytical System. Spectrometer and detector, capable of measuring the analytes to the chosen detection limit. The system shall include a personal computer with compatible software allowing automated collection of spectra.

6.14   FTIR Cell Pump. Required for the batch sampling technique, capable of evacuating the FTIR cell volume within 2 minutes. The pumping speed shall allow the operator to obtain 8 sample spectra in 1 hour.

6.15   Absolute Pressure Gauge. Capable of measuring pressure from 0 to 1000 mmHg to within ± 2.5 mmHg (e.g., Baratron™).

6.16   Temperature Gauge. Capable of measuring the cell temperature to within ± 2°C.

6.17   Sample Conditioning. One option is a condenser system, which is used for moisture removal. This can be helpful in the measurement of some analytes. Other sample conditioning procedures may be devised for the removal of moisture or other interfering species.

6.17.1   The analyte spike procedure of section 9.2 of this method, the QA spike procedure of section 8.6.2 of this method, and the validation procedure of section 13 of this method demonstrate whether the sample conditioning affects analyte concentrations. Alternatively, measurements can be made with two parallel FTIR systems; one measuring conditioned sample, the other measuring unconditioned sample.

6.17.2   Another option is sample dilution. The dilution factor measurement must be documented and accounted for in the reported concentrations. An alternative to dilution is to lower the sensitivity of the FTIR system by decreasing the cell path length, or to use a short-path cell in conjunction with a long path cell to measure more than one concentration range.

7.0   Reagents and Standards.

7.1   Analyte(s) and Tracer Gas. Obtain a certified gas cylinder mixture containing all of the analyte(s) at concentrations within ±2 percent of the emission source levels (expressed in ppm-meter/K). If practical, the analyte standard cylinder shall also contain the tracer gas at a concentration which gives a measurable absorbance at a dilution factor of at least 10:1. Two ppm SF_6 is sufficient for a path length of 22 meters at 250 °F.

7.2   Calibration Transfer Standard(s). Select the calibration transfer standards (CTS) according to section 4.5 of the FTIR Protocol. Obtain a National Institute of Standards and Technology (NIST) traceable gravimetric standard of the CTS (±2 percent).

7.3   Reference Spectra. Obtain reference spectra for each analyte, interferant, surrogate, CTS, and tracer. If EPA reference spectra are not available, use reference spectra prepared according to procedures in section 4.6 of the EPA FTIR Protocol.

8.0   Sampling and Analysis Procedure.

Three types of testing can be performed: (1) screening, (2) emissions test, and (3) validation. Each is defined in section 3 of this method. Determine the purpose(s) of the FTIR test. Test requirements include: (a) AU_I, DL_I, overall fractional uncertainty, OFU_I, maximum expected concentration ($CMAX_I$), and t_{AN} for each, (b) potential interferants, (c) sampling system factors, e.g., minimum absolute cell pressure, (P_{MIN}), FTIR cell volume (V_{SS}), estimated sample absorption pathlength, L_S', estimated sample pressure, P_S', T_S', signal integration time (t_{SS}), minimum instrumental linewidth, MIL, fractional error, and (d) analytical regions, e.g., m = 1 to M, lower wavenumber position, FL_M, center wavenumber position, FC_M, and upper wavenumber position, FU_M, plus interferants, upper wavenumber position of the CTS absorption band, FFU_M, lower wavenumber position of the CTS absorption band, FFL_M, wavenumber range FNU to FNL. If necessary, sample and acquire an initial spectrum. From analysis of this preliminary spectrum determine a suitable operational path length. Set up the sampling train as shown in Figure 1 or use an appropriate alternative configuration. Sections 8.1 through 8.11 of this method provide guidance on pre-test calculations in the EPA protocol, sampling and analytical procedures, and post-test protocol calculations.

8.1   Pretest Preparations and Evaluations. Using the procedure in section 4.0 of the FTIR Protocol, determine the optimum sampling system configuration for measuring the target analytes. Use available information to make reasonable assumptions about moisture content and other interferences.

8.1.1 Analytes. Select the required detection limit (DL$_i$) and the maximum permissible analytical uncertainty (AU$_i$) for each analyte (labeled from 1 to i). Estimate, if possible, the maximum expected concentration for each analyte, CMAX$_i$. The expected measurement range is fixed by DL$_i$ and CMAX$_i$ for each analyte (i).

8.1.2 Potential Interferants. List the potential interferants. This usually includes water vapor and CO_2, but may also include some analytes and other compounds.

8.1.3 Optical Configuration. Choose an optical configuration that can measure all of the analytes within the absorbance range of .01 to 1.0 (this may require more than one path length). Use Protocol sections 4.3 to 4.8 for guidance in choosing a configuration and measuring CTS.

8.1.4 Fractional Reproducibility Uncertainty (FRU$_i$). The FRU is determined for each analyte by comparing CTS spectra taken before and after the reference spectra were measured. The EPA para-xylene reference spectra were collected on 10/31/91 and 11/01/91 with corresponding CTS spectra ''cts1031a,'' and ''cts1101b.'' The CTS spectra are used to estimate the reproducibility (FRU) in the system that was used to collect the references. The FRU must be < AU. Appendix E of the protocol is used to calculate the FRU from CTS spectra. Figure 2 plots results for 0.25 cm^{-1} CTS spectra in EPA reference library: S$_3$ (cts1101b—cts1031a), and S$_4$ [(cts1101b + cts1031a)/2]. The RMSD (SRMS) is calculated in the subtracted baseline, S$_3$, in the corresponding CTS region from 850 to 1065 cm^{-1}. The area (BAV) is calculated in the same region of the averaged CTS spectrum, S$_4$.

8.1.5 Known Interferants. Use appendix B of the EPA FTIR Protocol.

8.1.6 Calculate the Minimum Analyte Uncertainty, MAU (section 1.3 of this method discusses MAU and protocol appendix D gives the MAU procedure). The MAU for each analyte, i, and each analytical region, m, depends on the RMS noise.

8.1.7 Analytical Program. See FTIR Protocol, section 4.10. Prepare computer program based on the chosen analytical technique. Use as input reference spectra of all target analytes and expected interferants. Reference spectra of additional compounds shall also be included in the program if their presence (even if transient) in the samples is considered possible. The program output shall be in ppm (or ppb) and shall be corrected for differences between the reference path length, L$_R$, temperature, T$_R$, and pressure, P$_R$, and the conditions used for collecting the sample spectra. If sampling is performed at ambient pressure, then any pressure correction is usually small relative to corrections for path length and temperature, and may be neglected.

8.2 Leak-check.

8.2.1 Sampling System. A typical FTIR extractive sampling train is shown in Figure 1. Leak check from the probe tip to pump outlet as follows: Connect a 0- to 250-mL/min rate meter (rotameter or bubble meter) to the outlet of the pump. Close off the inlet to the probe, and record the leak rate. The leak rate shall be ≤ 200 mL/min.

8.2.2 Analytical System Leak check. Leak check the FTIR cell under vacuum and under pressure (greater than ambient). Leak check connecting tubing and inlet manifold under pressure.

8.2.2.1 For the evacuated sample technique, close the valve to the FTIR cell, and evacuate the absorption cell to the minimum absolute pressure P$_{min}$. Close the valve to the pump, and determine the change in pressure ΔP_v after 2 minutes.

8.2.2.2 For both the evacuated sample and purging techniques, pressurize the system to about 100 mmHg above atmospheric pressure. Isolate the pump and determine the change in pressure ΔP_p after 2 minutes.

8.2.2.3 Measure the barometric pressure, P$_b$ in mmHg.

8.2.2.4 Determine the percent leak volume %V$_L$ for the signal integration time t$_{SS}$ and for ΔP_{max}, i.e., the larger of ΔP_v or ΔP_p, as follows:

$$\% V_L = 50 t_{ss} \frac{\Delta P_{max}}{P_{ss}} \qquad \text{(Eq. 320-2)}$$

Where 50=100% divided by the leak-check time of 2 minutes.

8.2.2.5 Leak volumes in excess of 4 percent of the FTIR system volume V$_{SS}$ are unacceptable.

8.3 Detector Linearity. Once an optical configuration is chosen, use one of the procedures of sections 8.3.1 through 8.3.3 to verify that the detector response is linear. If the detector response is not linear, decrease the aperture, or attenuate the infrared beam. After a change in the instrument configuration perform a linearity check until it is demonstrated that the detector response is linear.

8.3.1 Vary the power incident on the detector by modifying the aperture setting. Measure the background and CTS at three instrument aperture settings: (1) at the aperture setting to be used in the testing, (2) at one half this aperture and (3) at twice the proposed testing aperture. Compare the three CTS spectra. CTS band areas shall agree to within the uncertainty of the cylinder standard and the RMSD noise in the system. If test aperture is the maximum aperture, collect CTS spectrum at maximum aperture, then close the aperture to reduce the IR throughput by half. Collect a second background and CTS at the smaller aperture setting and compare the spectra again.

8.3.2 Use neutral density filters to attenuate the infrared beam. Set up the FTIR system as it will be used in the test measurements. Collect a CTS spectrum. Use a neutral density filter to attenuate the infrared beam (either immediately after the source or the interferometer) to approximately ½ its original intensity. Collect a second CTS spectrum. Use another filter to attenuate the infrared beam to approximately ¼ its original intensity. Collect a third background and CTS spectrum. Compare the CTS spectra. CTS band areas shall agree to within the uncertainty of the cylinder standard and the RMSD noise in the system.

8.3.3 Observe the single beam instrument response in a frequency region where the detector response is known to be zero. Verify that the detector response is ''flat'' and equal to zero in these regions.

8.4 Data Storage Requirements. All field test spectra shall be stored on a computer disk and a second backup copy must stored on a separate disk. The stored information includes sample interferograms, processed absorbance spectra, background interferograms, CTS sample interferograms and CTS absorbance spectra. Additionally, documentation of all sample conditions, instrument settings, and test records must be recorded on hard copy or on computer medium. Table 1 to this method gives a sample presentation of documentation.

8.5 Background Spectrum. Evacuate the gas cell to ≤ 5 mmHg, and fill with dry nitrogen gas to ambient pressure (or purge the cell with 10 volumes of dry nitrogen). Verify that no significant amounts of absorbing species (for example water vapor and CO_2) are present. Collect a background spectrum, using a signal averaging period equal to or greater than the averaging period for the sample spectra. Assign a unique file name to the background spectrum. Store two copies of the background interferogram and processed single-beam spectrum on separate computer disks (one copy is the back-up).

8.5.1 Interference Spectra. If possible, collect spectra of known and suspected major interferences using the same optical system that will be used in the field measurements. This can be done on-site or earlier. A number of gases, e.g. CO_2, SO_2, CO, NH_3, are readily available from cylinder gas suppliers.

8.5.2 Water vapor spectra can be prepared by the following procedure. Fill a sample tube with distilled water. Evacuate above the sample and remove dissolved gasses by alternately freezing and thawing the water while evacuating. Allow water vapor into the FTIR cell, then dilute to atmospheric pressure with nitrogen or dry air. If quantitative water spectra are required, follow the reference spectrum procedure for neat samples (protocol, section 4.6). Often, interference spectra need not be quantitative, but for best results the absorbance must be comparable to the interference absorbance in the sample spectra.

8.6 Pre-Test Calibrations

8.6.1 Calibration Transfer Standard. Evacuate the gas cell to ≤ 5 mmHg absolute pressure, and fill the FTIR cell to atmospheric pressure with the CTS gas. Alternatively, purge the cell with 10 cell volumes of CTS gas. (If purge is used, verify that the CTS concentration in the cell is stable by collecting two spectra 2 minutes apart as the CTS gas continues to flow. If the absorbance in the second spectrum is no greater than in the first, within the uncertainty of the gas standard, then this can be used as the CTS spectrum.) Record the spectrum.

8.6.2 QA Spike. This procedure assumes that the method has been validated for at least some of the target analytes at the source. For emissions testing perform a QA spike. Use a certified standard, if possible, of an analyte, which has been validated at the source. One analyte standard can serve as a QA surrogate for other analytes which are less reactive or less soluble than the

standard. Perform the spike procedure of section 9.2 of this method. Record spectra of at least three independent (section 3.22 of this method) spiked samples. Calculate the spiked component of the analyte concentration. If the average spiked concentration is within 0.7 to 1.3 times the expected concentration, then proceed with the testing. If applicable, apply the correction factor from the Method 301 of this appendix validation test (not the result from the QA spike).

8.7 Sampling. If analyte concentrations vary rapidly with time, CEM sampling is preferable using the smallest cell volume, fastest sampling rate and fastest spectra collection rate possible. CEM sampling requires the least operator intervention even without an automated sampling system. For continuous monitoring at one location over long periods, CEM sampling is preferred. Batch sampling and continuous static sampling are used for screening and performing test runs of finite duration. Either technique is preferred for sampling several locations in a matter of days. Batch sampling gives reasonably good time resolution and ensures that each spectrum measures a discreet (and unique) sample volume. Continuous static (and CEM) sampling provide a very stable background over long periods. Like batch sampling, continuous static sampling also ensures that each spectrum measures a unique sample volume. It is essential that the leak check procedure under vacuum (section 8.2 of this method) is passed if the batch sampling procedure is used. It is essential that the leak check procedure under positive pressure is passed if the continuous static or CEM sampling procedures are used. The sampling techniques are described in sections 8.7.1 through 8.7.2 of this method.

8.7.1 Batch Sampling. Evacuate the absorbance cell to ≤ 5 mmHg absolute pressure. Fill the cell with exhaust gas to ambient pressure, isolate the cell, and record the spectrum. Before taking the next sample, evacuate the cell until no spectral evidence of sample absorption remains. Repeat this procedure to collect eight spectra of separate samples in 1 hour.

8.7.2 Continuous Static Sampling. Purge the FTIR cell with 10 cell volumes of sample gas. Isolate the cell, collect the spectrum of the static sample and record the pressure. Before measuring the next sample, purge the cell with 10 more cell volumes of sample gas.

8.8 Sampling QA and Reporting.

8.8.1 Sample integration times shall be sufficient to achieve the required signal-to-noise ratio. Obtain an absorbance spectrum by filling the cell with N_2. Measure the RMSD in each analytical region in this absorbance spectrum. Verify that the number of scans used is sufficient to achieve the target MAU.

8.8.2 Assign a unique file name to each spectrum.

8.8.3 Store two copies of sample interferograms and processed spectra on separate computer disks.

8.8.4 For each sample spectrum, document the sampling conditions, the sampling time (while the cell was being filled), the time the spectrum was recorded,

the instrumental conditions (path length, temperature, pressure, resolution, signal integration time), and the spectral file name. Keep a hard copy of these data sheets.

8.9 Signal Transmittance. While sampling, monitor the signal transmittance. If signal transmittance (relative to the background) changes by 5 percent or more (absorbance = −.02 to .02) in any analytical spectral region, obtain a new background spectrum.

8.10 Post-test CTS. After the sampling run, record another CTS spectrum.

8.11 Post-test QA.

8.11.1 Inspect the sample spectra immediately after the run to verify that the gas matrix composition was close to the expected (assumed) gas matrix.

8.11.2 Verify that the sampling and instrumental parameters were appropriate for the conditions encountered. For example, if the moisture is much greater than anticipated, it may be necessary to use a shorter path length or dilute the sample.

8.11.3 Compare the pre- and post-test CTS spectra. The peak absorbance in pre- and post-test CTS must be ± 5 percent of the mean value. See appendix E of the FTIR Protocol.

9.0 Quality Control.

Use analyte spiking (sections 8.6.2, 9.2 and 13.0 of this method) to verify that the sampling system can transport the analytes from the probe to the FTIR system.

9.1 Spike Materials. Use a certified standard (accurate to ± 2 percent) of the target analyte, if one can be obtained. If a certified standard cannot be obtained, follow the procedures in section 4.6.2.2 of the FTIR Protocol.

9.2 Spiking Procedure. QA spiking (section 8.6.2 of this method) is a calibration procedure used before testing. QA spiking involves following the spike procedure of sections 9.2.1 through 9.2.3 of this method to obtain at least three spiked samples. The analyte concentrations in the spiked samples shall be compared to the expected spike concentration to verify that the sampling system is working properly. Usually, when QA spiking is used, the method has already been validated at a similar source for the analyte in question. The QA spike demonstrates that the validated sampling conditions are being duplicated. If the QA spike fails then the sampling system shall be repaired before testing proceeds. The method validation procedure (section 13.0 of this method) involves a more extensive use of the analyte spike procedure of sections 9.2.1 through 9.2.3 of this method. Spectra of at least 12 independent spiked and 12 independent unspiked samples are recorded. The concentration results are analyzed statistically to determine if there is a systematic bias in the method for measuring a particular analyte. If there is a systematic bias, within the limits allowed by Method 301 of this appendix, then a correction factor shall be applied to the analytical results. If the systematic bias is greater than the allowed limits, this method is not valid and cannot be used.

9.2.1 Introduce the spike/tracer gas at a constant flow rate of ≤ 10 percent of the total sample flow. (*Note:* Use the rotameter at the

end of the sampling train to estimate the required spike/tracer gas flow rate.) Use a flow device, e.g., mass flow meter (± 2 percent), to monitor the spike flow rate. Record the spike flow rate every 10 minutes.

9.2.2 Determine the response time (RT) of the system by continuously collecting spectra of the spiked effluent until the spectrum of the spiked component is constant for 5 minutes. The RT is the interval from the first measurement until the spike becomes constant. Wait for twice the duration of the RT, then collect spectra of two independent spiked gas samples. Duplicate analyses of the spiked concentration shall be within 5 percent of the mean of the two measurements.

9.2.3 Calculate the dilution ratio using the tracer gas as follows:

$$DF = \frac{SF_{6(dir)}}{SF_{6(spk)}} \qquad (Eq.\ 320\text{-}3)$$

Where:

$$CS = \frac{Spike_{dir}}{DF} \qquad (Eq.\ 320\text{-}4)$$

DF = Dilution factor of the spike gas; this value shall be ≥10.

$SF_{6(dir)}$ = SF_6 (or tracer gas) concentration measured directly in undiluted spike gas.

$SF_{6(spk)}$ = Diluted SF_6 (or tracer gas) concentration measured in a spiked sample.

$Spike_{dir}$ = Concentration of the analyte in the spike standard measured by filling the FTIR cell directly.

CS = Expected concentration of the spiked samples.

10.0 Calibration and Standardization.

10.1 Signal-to-Noise Ratio (S/N). The RMSD in the noise must be less than one tenth of the minimum analyte peak absorbance in each analytical region. For example if the minimum peak absorbance is 0.01 at the required DL, then RMSD measured over the entire analytical region must be ≤ 0.001.

10.2 Absorbance Path length. Verify the absorbance path length by comparing reference CTS spectra to test CTS spectra. See appendix E of the FTIR Protocol.

10.3 Instrument Resolution. Measure the line width of appropriate test CTS band(s) to verify instrument resolution. Alternatively, compare CTS spectra to a reference CTS spectrum, if available, measured at the nominal resolution.

10.4 Apodization Function. In transforming the sample interferograms to absorbance spectra use the same apodization function that was used in transforming the reference spectra.

10.5 FTIR Cell Volume. Evacuate the cell to ≤ 5 mmHg. Measure the initial absolute temperature (T_i) and absolute pressure (P_i). Connect a wet test meter (or a calibrated dry gas meter), and slowly draw room air into the cell. Measure the meter volume (V_m), meter absolute temperature (T_m), and meter absolute pressure (P_m); and the cell final absolute temperature (T_f) and absolute

pressure (P_f). Calculate the FTIR cell volume V_{SS}, including that of the connecting tubing, as follows:

$$V_{ss} = \frac{V_m \frac{P_m}{T_m}}{\left[\frac{P_f}{T_f} - \frac{P_i}{T_i}\right]} \quad \text{(Eq. 320-5)}$$

11.0   Data Analysis and Calculations.

Analyte concentrations shall be measured using reference spectra from the EPA FTIR spectral library. When EPA library spectra are not available, the procedures in section 4.6 of the Protocol shall be followed to prepare reference spectra of all the target analytes. 11.1 Spectral De-resolution. Reference spectra can be converted to lower resolution standard spectra (section 3.3 of this method) by truncating the original reference sample and background interferograms. Appendix K of the FTIR Protocol gives specific deresolution procedures. Deresolved spectra shall be transformed using the same apodization function and level of zero filling as the sample spectra. Additionally, pre-test FTIR protocol calculations (e.g., FRU, MAU, FCU) shall be performed using the de-resolved standard spectra.

11.2   Data Analysis. Various analytical programs are available for relating sample absorbance to a concentration standard. Calculated concentrations shall be verified by analyzing residual baselines after mathematically subtracting scaled reference spectra from the sample spectra. A full description of the data analysis and calculations is contained in the FTIR Protocol (sections 4.0, 5.0, 6.0 and appendices). Correct the calculated concentrations in the sample spectra for differences in absorption path length and temperature between the reference and sample spectra using equation 6,

$$C_{corr} = \left(\frac{L_r}{L_s}\right)\left(\frac{T_s}{T_r}\right)C_{calc} \quad \text{(Eq. 320-6)}$$

Where:

C_{corr} = Concentration, corrected for path length.

C_{calc} = Concentration, initial calculation (output of the analytical program designed for the compound).

L_r = Reference spectra path length.

L_s = Sample spectra path length.

T_s = Absolute temperature of the sample gas, K.

T_r = Absolute gas temperature of reference spectra, K.

12.0   Method Performance.

12.1   Spectral Quality. Refer to the FTIR Protocol appendices for analytical requirements, evaluation of data quality, and analysis of uncertainty.

12.2   Sampling QA/QC. The analyte spike procedure of section 9 of this method, the QA spike of section 8.6.2 of this method, and the validation procedure of section 13 of this method are used to evaluate the performance of the sampling system and to quantify sampling system effects, if any, on the measured concentrations. This method is self-validating provided that the results meet the performance requirement of the QA spike in sections 9.0 and 8.6.2 of this method and results from a previous method validation study support the use of this method in the application. Several factors can contribute to uncertainty in the measurement of spiked samples. Factors which can be controlled to provide better accuracy in the spiking procedure are listed in sections 12.2.1 through 12.2.4 of this method.

12.2.1   Flow meter. An accurate mass flow meter is accurate to ± 1 percent of its span. If a flow of 1 L/min is monitored with such a MFM, which is calibrated in the range of 0–5 L/min, the flow measurement has an uncertainty of 5 percent. This may be improved by re-calibrating the meter at the specific flow rate to be used.

12.2.2   Calibration gas. Usually the calibration standard is certified to within ± 2 percent. With reactive analytes, such as HCl, the certified accuracy in a commercially available standard may be no better than ± 5 percent.

12.2.3   Temperature. Temperature measurements of the cell shall be quite accurate. If practical, it is preferable to measure sample temperature directly, by inserting a thermocouple into the cell chamber instead of monitoring the cell outer wall temperature.

12.2.4   Pressure. Accuracy depends on the accuracy of the barometer, but fluctuations in pressure throughout a day may be as much as 2.5 percent due to weather variations.

13.0   Method Validation Procedure.

This validation procedure, which is based on EPA Method 301 (40 CFR part 63, appendix A), may be used to validate this method for the analytes in a gas matrix. Validation at one source may also apply to another type of source, if it can be shown that the exhaust gas characteristics are similar at both sources.

13.1   Section 5.3 of Method 301 (40 CFR part 63, appendix A), the Analyte Spike procedure, is used with these modifications. The statistical analysis of the results follows section 6.3 of EPA Method 301. Section 3 of this method defines terms that are not defined in Method 301.

13.1.1   The analyte spike is performed dynamically. This means the spike flow is continuous and constant as spiked samples are measured.

13.1.2   The spike gas is introduced at the back of the sample probe.

13.1.3   Spiked effluent is carried through all sampling components downstream of the probe.

13.1.4   A single FTIR system (or more) may be used to collect and analyze spectra (not quadruplicate integrated sampling trains).

13.1.5   All of the validation measurements are performed sequentially in a single "run" (section 3.26 of this method).

13.1.6   The measurements analyzed statistically are each independent (section 3.22 of this method).

13.1.7   A validation data set can consist of more than 12 spiked and 12 unspiked measurements.

13.2   Batch Sampling. The procedure in sections 13.2.1 through 13.2.2 may be used for stable processes. If process emissions are highly variable, the procedure in section 13.2.3 shall be used.

13.2.1   With a single FTIR instrument and sampling system, begin by collecting spectra of two unspiked samples. Introduce the spike flow into the sampling system and allow 10 cell volumes to purge the sampling system and FTIR cell. Collect spectra of two spiked samples. Turn off the spike and allow 10 cell volumes of unspiked sample to purge the FTIR cell. Repeat this procedure until the 24 (or more) samples are collected.

13.2.2   In batch sampling, collect spectra of 24 distinct samples. (Each distinct sample consists of filling the cell to ambient pressure after the cell has been evacuated.)

13.2.3   Alternatively, a separate probe assembly, line, and sample pump can be used for spiked sample. Verify and document that sampling conditions are the same in both the spiked and the unspiked sampling systems. This can be done by wrapping both sample lines in the same heated bundle. Keep the same flow rate in both sample lines. Measure samples in sequence in pairs. After two spiked samples are measured, evacuate the FTIR cell, and turn the manifold valve so that spiked sample flows to the FTIR cell. Allow the connecting line from the manifold to the FTIR cell to purge thoroughly (the time depends on the line length and flow rate). Collect a pair of spiked samples. Repeat the procedure until at least 24 measurements are completed.

13.3   Simultaneous Measurements With Two FTIR Systems. If unspiked effluent concentrations of the target analyte(s) vary significantly with time, it may be desirable to perform synchronized measurements of spiked and unspiked sample. Use two FTIR systems, each with its own cell and sampling system to perform simultaneous spiked and unspiked measurements. The optical configurations shall be similar, if possible. The sampling configurations shall be the same. One sampling system and FTIR analyzer shall be used to measure spiked effluent. The other sampling system and FTIR analyzer shall be used to measure unspiked flue gas. Both systems shall use the same sampling procedure (i.e., batch or continuous).

13.3.1   If batch sampling is used, synchronize the cell evacuation, cell filling, and collection of spectra. Fill both cells at the same rate (in cell volumes per unit time).

13.3.2   If continuous sampling is used, adjust the sample flow through each gas cell so that the same number of cell volumes pass through each cell in a given time (i.e. $TC_1 = TC_2$).

13.4   Statistical Treatment. The statistical procedure of EPA Method 301 of this appendix, section 6.3 is used to evaluate the bias and precision. For FTIR testing a validation "run" is defined as spectra of 24 independent samples, 12 of which are spiked with the analyte(s) and 12 of which are not spiked.

13.4.1   Bias. Determine the bias (defined by EPA Method 301 of this appendix, section 6.3.2) using equation 7:

$B = S_m - M_m - CS$ (Eq. 320–7)

Where:

B = Bias at spike level.

S_m = Mean concentration of the analyte spiked samples.

M_m = Mean concentration of the unspiked samples.

CS = Expected concentration of the spiked samples.

13.4.2 Correction Factor. Use section 6.3.2.2 of Method 301 of this appendix to evaluate the statistical significance of the bias. If it is determined that the bias is significant, then use section 6.3.3 of Method 301 to calculate a correction factor (CF). Analytical results of the test method are multiplied by the correction factor, if $0.7 \leq CF \leq 1.3$. If it is determined that the bias is significant and CF > $\pm$ 30 percent, then the test method is considered to be "not valid."

13.4.3 If measurements do not pass validation, evaluate the sampling system, instrument configuration, and analytical system to determine if improper set-up or a malfunction was the cause. If so, repair the system and repeat the validation.

14.0 Pollution Prevention.

The extracted sample gas is vented outside the enclosure containing the FTIR system and gas manifold after the analysis. In typical method applications the vented sample volume is a small fraction of the source volumetric flow and its composition is identical to that emitted from the source. When analyte spiking is used, spiked pollutants are vented with the extracted sample gas. Approximately 1.6×10^{-4} to 3.2×10^{-4} lbs of a single HAP may be vented to the atmosphere in a typical validation run of 3 hours. (This assumes a molar mass of 50 to 100 g, spike rate of 1.0 L/min, and a standard concentration of 100 ppm). Minimize emissions by keeping the spike flow off when not in use.

15.0 Waste Management.

Small volumes of laboratory gas standards can be vented through a laboratory hood. Neat samples must be packed and disposed according to applicable regulations. Surplus materials may be returned to supplier for disposal.

16.0 References.

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3. "Method 301—Field Validation of Pollutant Measurement Methods from Various Waste Media," 40 CFR part 63, appendix A.

4. "Molecular Vibrations; The Theory of Infrared and Raman Vibrational Spectra," E. Bright Wilson, J.C. Decius, and P.C. Cross, Dover Publications, Inc., 1980. For a less intensive treatment of molecular rotational-vibrational spectra see, for example, "Physical Chemistry," G.M. Barrow, chapters 12, 13, and 14, McGraw Hill, Inc., 1979.

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6. "Computer-Assisted Quantitative Infrared Spectroscopy," Gregory L. McClure (ed.), ASTM Special Publication 934 (ASTM), 1987.

7. "Multivariate Least-Squares Methods Applied to the Quantitative Spectral Analysis of Multicomponent Mixtures," Applied Spectroscopy, 39(10), 73–84, 1985.

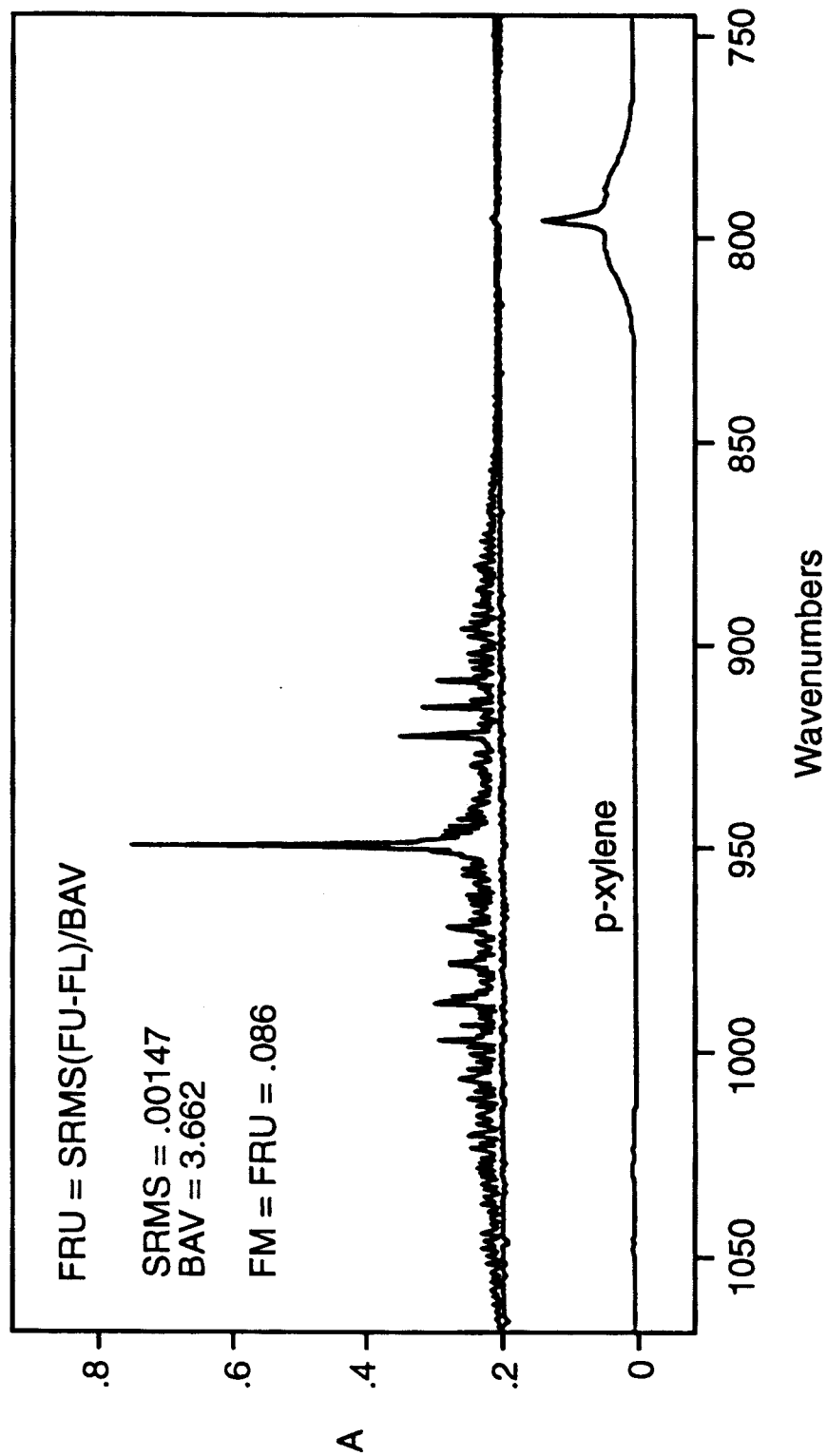TABLE 1.—EXAMPLE PRESENTATION OF SAMPLING DOCUMENTATION

Sample time	Spectrum file name	Background file name	Sample conditioning	Process condition

Sample time	Spectrum file	Interferogram	Resolution	Scans	Apodization	Gain	CTS spectrum

BILLING CODE 6560–50–P
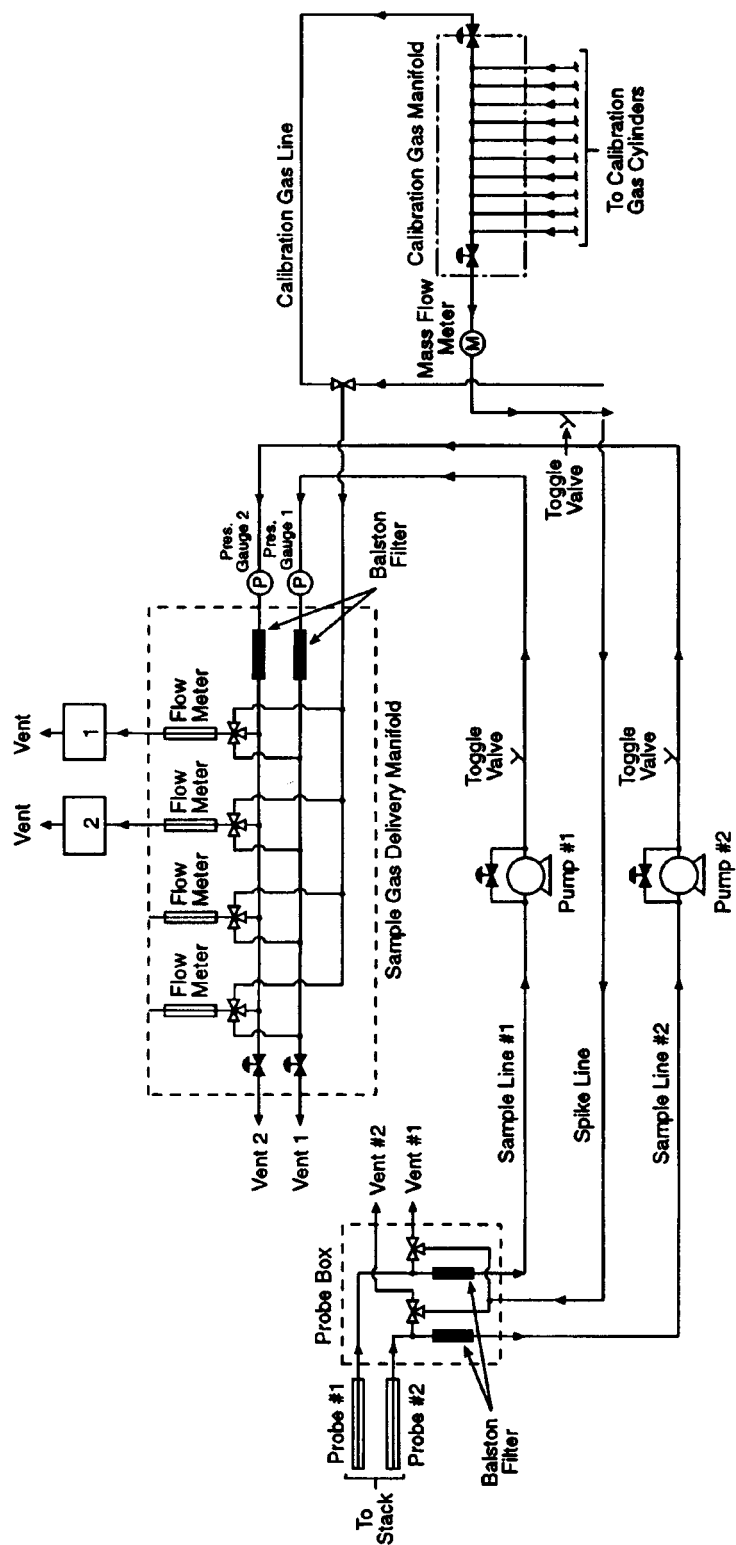
Figure 1. Extractive FTIR sampling system.

Figure 2. Fractional Reproducibility. Top: average of cts1031a and cts1101b. Bottom: Reference spectrum of p-xylene.

Addendum to Method 320—Protocol for the Use of Extractive Fourier Transform Infrared (FTIR) Spectrometry for the Analyses of Gaseous Emissions From Stationary Sources

1.0   Introduction

The purpose of this addendum is to set general guidelines for the use of modern FTIR spectroscopic methods for the analysis of gas samples extracted from the effluent of stationary emission sources. This addendum outlines techniques for developing and evaluating such methods and sets basic requirements for reporting and quality assurance procedures.

1.1   Nomenclature

1.1.1   Attachment A to this addendum lists definitions of the symbols and terms used in this Protocol, many of which have been taken directly from American Society for Testing and Materials (ASTM) publication E 131–90a, entitled ''Terminology Relating to Molecular Spectroscopy.''

1.1.2   Except in the case of background spectra or where otherwise noted, the term ''spectrum'' refers to a double-beam spectrum in units of absorbance vs. wavenumber (cm^{-1}).

1.1.3   The term ''Study'' in this addendum refers to a publication that has been subjected to EPA- or peer-review.

2.0   Applicability and Analytical Principle

2.1   Applicability. This Protocol applies to the determination of compound-specific concentrations in single- and multiple-component gas phase samples using double-beam absorption spectroscopy in the mid-infrared band. It does not specifically address other FTIR applications, such as single-beam spectroscopy, analysis of open-path (non-enclosed) samples, and continuous measurement techniques. If multiple spectrometers, absorption cells, or instrumental linewidths are used in such analyses, each distinct operational configuration of the system must be evaluated separately according to this Protocol.

2.2   Analytical Principle.

2.2.1   In the mid-infrared band, most molecules exhibit characteristic gas phase absorption spectra that may be recorded by FTIR systems. Such systems consist of a source of mid-infrared radiation, an interferometer, an enclosed sample cell of known absorption pathlength, an infrared detector, optical elements for the transfer of infrared radiation between components, and gas flow control and measurement components. Adjunct and integral computer systems are used for controlling the instrument, processing the signal, and for performing both Fourier transforms and quantitative analyses of spectral data.

2.2.2   The absorption spectra of pure gases and of mixtures of gases are described by a linear absorbance theory referred to as Beer's Law. Using this law, modern FTIR systems use computerized analytical programs to quantify compounds by comparing the absorption spectra of known (reference) gas samples to the absorption spectrum of the sample gas. Some standard mathematical techniques used for comparisons are classical least squares, inverse least squares, cross-correlation, factor analysis, and partial least squares. Reference A describes several of these techniques, as well as additional techniques, such as differentiation methods, linear baseline corrections, and non-linear absorbance corrections.

3.0   General Principles of Protocol Requirements

The characteristics that distinguish FTIR systems from gas analyzers used in instrumental gas analysis methods (e.g., Methods 6C and 7E of appendix A to part 60 of this chapter) are: (1) Computers are necessary to obtain and analyze data; (2) chemical concentrations can be quantified using previously recorded infrared reference spectra; and (3) analytical assumptions and results, including possible effects of interfering compounds, can be evaluated after the quantitative analysis. The following general principles and requirements of this Protocol are based on these characteristics.

3.1   Verifiability and Reproducibility of Results. Store all data and document data analysis techniques sufficient to allow an independent agent to reproduce the analytical results from the raw interferometric data.

3.2   Transfer of Reference Spectra. To determine whether reference spectra recorded under one set of conditions (e.g., optical bench, instrumental linewidth, absorption pathlength, detector performance, pressure, and temperature) can be used to analyze sample spectra taken under a different set of conditions, quantitatively compare ''calibration transfer standards'' (CTS) and reference spectra as described in this Protocol. (*Note:* The CTS may, but need not, include analytes of interest.) To effect this, record the absorption spectra of the CTS (a) immediately before and immediately after recording reference spectra and (b) immediately after recording sample spectra.

3.3   Evaluation of FTIR Analyses. The applicability, accuracy, and precision of FTIR measurements are influenced by a number of interrelated factors, which may be divided into two classes:

3.3.1   Sample-Independent Factors. Examples are system configuration and performance (e.g., detector sensitivity and infrared source output), quality and applicability of reference absorption spectra, and type of mathematical analyses of the spectra. These factors define the fundamental limitations of FTIR measurements for a given system configuration. These limitations may be estimated from evaluations of the system before samples are available.

For example, the detection limit for the absorbing compound under a given set of conditions may be estimated from the system noise level and the strength of a particular absorption band. Similarly, the accuracy of measurements may be estimated from the analysis of the reference spectra.

3.3.2   Sample-Dependent Factors. Examples are spectral interferants (e.g., water vapor and CO_2) or the overlap of spectral features of different compounds and contamination deposits on reflective surfaces or transmitting windows. To maximize the effectiveness of the mathematical techniques used in spectral analysis, identification of interferants (a standard initial step) and analysis of samples (includes effect of other analytical errors) are necessary. Thus, the Protocol requires post-analysis calculation of measurement concentration uncertainties for the detection of these potential sources of measurement error.

4.0   Pre-Test Preparations and Evaluations

Before testing, demonstrate the suitability of FTIR spectrometry for the desired application according to the procedures of this section.

4.1   Identify Test Requirements. Identify and record the test requirements described in sections 4.1.1 through 4.1.4 of this addendum. These values set the desired or required goals of the proposed analysis; the description of methods for determining whether these goals are actually met during the analysis comprises the majority of this Protocol.

4.1.1   Analytes (specific chemical species) of interest. Label the analytes from i = 1 to I.

4.1.2   Analytical uncertainty limit (AU_i). The AU_i is the maximum permissible fractional uncertainty of analysis for the ith analyte concentration, expressed as a fraction of the analyte concentration in the sample.

4.1.3   Required detection limit for each analyte (DL_i, ppm). The detection limit is the lowest concentration of an analyte for which its overall fractional uncertainty (OFU_i) is required to be less than its analytical uncertainty limit (AU_i).

4.1.4   Maximum expected concentration of each analyte ($CMAX_i$, ppm).

4.2   Identify Potential Interferants. Considering the chemistry of the process or results of previous studies, identify potential interferants, i.e., the major effluent constituents and any relatively minor effluent constituents that possess either strong absorption characteristics or strong structural similarities to any analyte of interest. Label them 1 through N_j, where the subscript ''j'' pertains to potential interferants. Estimate the concentrations of these compounds in the effluent ($CPOT_j$, ppm).

4.3   Select and Evaluate the Sampling System. Considering the source, e.g., temperature and pressure profiles, moisture content, analyte characteristics, and particulate concentration, select the equipment for extracting gas samples. Recommended are a particulate filter, heating system to maintain sample temperature above the dew point for all sample constituents at all points within the sampling system (including the filter), and sample conditioning system (e.g., coolers, water-permeable membranes that remove water or other compounds from the sample, and dilution devices) to remove spectral interferants or to protect the sampling and analytical components. Determine the minimum absolute sample system pressure (P_{min}, mmHg) and the infrared absorption cell volume (V_{SS}, liter). Select the techniques and/or equipment for the measurement of sample pressures and temperatures.

4.4   Select Spectroscopic System. Select a spectroscopic configuration for the

application. Approximate the absorption pathlength (L_S', meter), sample pressure (P_S', kPa), absolute sample temperature T_S', and signal integration period (t_{SS}, seconds) for the analysis. Specify the nominal minimum instrumental linewidth (MIL) of the system. Verify that the fractional error at the approximate values P_S' and T_S' is less than one half the smallest value AU_i (see section 4.1.2 of this addendum).

4.5 Select Calibration Transfer Standards (CTS's). Select CTS's that meet the criteria listed in sections 4.5.1, 4.5.2, and 4.5.3 of this addendum. (*Note:* It may be necessary to choose preliminary analytical regions (see section 4.7 of this addendum), identify the minimum analyte linewidths, or estimate the system noise level (see section 4.12 of this addendum) before selecting the CTS. More than one compound may be needed to meet the criteria; if so, obtain separate cylinders for each compound.)

4.5.1 The central wavenumber position of each analytical region shall lie within 25 percent of the wavenumber position of at least one CTS absorption band.

4.5.2 The absorption bands in section 4.5.1 of this addendum shall exhibit peak absorbances greater than ten times the value RMS_{EST} (see section 4.12 of this addendum) but less than 1.5 absorbance units.

4.5.3 At least one absorption CTS band within the operating range of the FTIR instrument shall have an instrument-independent linewidth no greater than the narrowest analyte absorption band. Perform and document measurements or cite Studies to determine analyte and CTS compound linewidths.

4.5.4 For each analytical region, specify the upper and lower wavenumber positions (FFU_m and FFL_m, respectively) that bracket the CTS absorption band or bands for the associated analytical region. Specify the wavenumber range, FNU to FNL, containing the absorption band that meets the criterion of section 4.5.3 of this addendum.

4.5.5 Associate, whenever possible, a single set of CTS gas cylinders with a set of reference spectra.

Replacement CTS gas cylinders shall contain the same compounds at concentrations within 5 percent of that of the original CTS cylinders; the entire absorption spectra (not individual spectral segments) of the replacement gas shall be scaled by a factor between 0.95 and 1.05 to match the original CTS spectra.

4.6 Prepare Reference Spectra. (*Note:* Reference spectra are available in a permanent soft copy from the EPA spectral library on the EMTIC (Emission Measurement Technical Information Center) computer bulletin board; they may be used if applicable.)

4.6.1 Select the reference absorption pathlength (L_R) of the cell.

4.6.2 Obtain or prepare a set of chemical standards for each analyte, potential and known spectral interferants, and CTS. Select the concentrations of the chemical standards to correspond to the top of the desired range.

4.6.2.1 Commercially-Prepared Chemical Standards. Chemical standards for many compounds may be obtained from independent sources, such as a specialty gas manufacturer, chemical company, or commercial laboratory. These standards (accurate to within ± 2 percent) shall be prepared according to EPA Traceability Protocol (see Reference D) or shall be traceable to NIST standards. Obtain from the supplier an estimate of the stability of the analyte concentration. Obtain and follow all of the supplier's recommendations for recertifying the analyte concentration.

4.6.2.2 Self-Prepared Chemical Standards. Chemical standards may be prepared by diluting certified commercially prepared chemical gases or pure analytes with ultra-pure carrier (UPC) grade nitrogen according to the barometric and volumetric techniques generally described in Reference A, section A4.6.

4.6.3 Record a set of the absorption spectra of the CTS {R1}, then a set of the reference spectra at two or more concentrations in duplicate over the desired range (the top of the range must be less than 10 times that of the bottom), followed by a second set of CTS spectra {R2}. (If self-prepared standards are used, see section 4.6.5 of this addendum before disposing of any of the standards.) The maximum accepted standard concentration-pathlength product (ASCPP) for each compound shall be higher than the maximum estimated concentration-pathlength products for both analytes and known interferants in the effluent gas. For each analyte, the minimum ASCPP shall be no greater than ten times the concentration-pathlength product of that analyte at its required detection limit.

4.6.4 Permanently store the background and interferograms in digitized form. Document details of the mathematical process for generating the spectra from these interferograms. Record the sample pressure (P_R), sample temperature (T_R), reference absorption pathlength (L_R), and interferogram signal integration period (t_{SR}). Signal integration periods for the background interferograms shall be $\geq t_{SR}$. Values of P_R, L_R, and t_{SR} shall not deviate by more than ±1 percent from the time of recording {R1} to that of recording {R2}.

4.6.5 If self-prepared chemical standards are employed and spectra of only two concentrations are recorded for one or more compounds, verify the accuracy of the dilution technique by analyzing the prepared standards for those compounds with a secondary (non-FTIR) technique in accordance with sections 4.6.5.1 through 4.6.5.4 of this addendum.

4.6.5.1 Record the response of the secondary technique to each of the four standards prepared.

4.6.5.2 Perform a linear regression of the response values (dependant variable) versus the accepted standard concentration (ASC) values (independent variable), with the regression constrained to pass through the zero-response, zero ASC point.

4.6.5.3 Calculate the average fractional difference between the actual response values and the regression-predicted values (those calculated from the regression line using the four ASC values as the independent variable).

4.6.5.4 If the average fractional difference value calculated in section 4.6.5.3 of this addendum is larger for any compound than the corresponding AUi, the dilution technique is not sufficiently accurate and the reference spectra prepared are not valid for the analysis.

4.7 Select Analytical Regions. Using the general considerations in section 7 of Reference A and the spectral characteristics of the analytes and interferants, select the analytical regions for the application. Label them m = 1 to M. Specify the lower, center and upper wavenumber positions of each analytical region (FL_m, FC_m, and FU_m, respectively). Specify the analytes and interferants which exhibit absorption in each region.

4.8 Determine Fractional Reproducibility Uncertainties. Using attachement E of this addendum, calculate the fractional reproducibility uncertainty for each analyte (FRU_i) from a comparison of {R1} and {R2}. If $FRU_i > AU_i$ for any analyte, the reference spectra generated in accordance with section 4.6 of this addendum are not valid for the application.

4.9 Identify Known Interferants. Using attachment B of this addendum, determine which potential interferants affect the analyte concentration determinations. Relabel these potential interferant as ''known'' interferants, and designate these compounds from k = 1 to K. Attachment B to this addendum also provides criteria for determining whether the selected analytical regions are suitable.

4.10 Prepare Computerized Analytical Programs.

4.10.1 Choose or devise mathematical techniques (e.g, classical least squares, inverse least squares, cross-correlation, and factor analysis) based on equation 4 of Reference A that are appropriate for analyzing spectral data by comparison with reference spectra.

4.10.2 Following the general recommendations of Reference A, prepare a computer program or set of programs that analyzes all of the analytes and known interferants, based on the selected analytical regions (section 4.7 of this addendum) and the prepared reference spectra (section 4.6 of this addendum). Specify the baseline correction technique (e.g., determining the slope and intercept of a linear baseline contribution in each analytical region, including all relevant wavenumber positions.

4.10.3 Use programs that provide as output [at the reference absorption pathlength (L_R), reference gas temperature (T_R), and reference gas pressure (P_R)] the analyte concentrations, the known interferant concentrations, and the baseline slope and intercept values. If the sample absorption pathlength (L_S), sample gas temperature (T_S), or sample gas pressure (P_S) during the actual sample analyses differ from L_R, T_R, and P_R, use a program or set of programs that applies multiplicative corrections to the derived concentrations to account for these variations, and that provides as output both the corrected and uncorrected values. Include in the report of the analysis (see section 7.0 of this addendum) the details of any transformations applied to the original reference spectra (e.g., differentiation), in such a fashion that all analytical results may

be verified by an independent agent from the reference spectra and data spectra alone.

4.11 Determine the Fractional Calibration Uncertainty. Calculate the fractional calibration uncertainty for each analyte (FCU_i) according to attachment F of this addendum, and compare these values to the fractional uncertainty limits (AU_i; see section 4.1.2 of this addendum). If $FCU_i > AU_i$, either the reference spectra or analytical programs for that analyte are unsuitable.

4.12 Verify System Configuration Suitability. Using attachment C of this addendum, measure or obtain estimates of the noise level (RMS_{EST}, absorbance) of the FTIR system. Alternatively, construct the complete spectrometer system and determine the values RMS_{Sm} using attachment G of this addendum. Estimate the minimum measurement uncertainty for each analyte (MAU_i, ppm) and known interferant (MIU_k, ppm) using attachment D of this addendum. Verify that (a) $MAU_i < (AU_i) (DL_i)$, $FRU_i < AU_i$, and $FCU_i < AU_i$ for each analyte and that (b) the CTS chosen meets the requirements listed in sections 4.5.1 through 4.5.5 of this addendum.

5.0 Sampling and Analysis Procedure

5.1 Analysis System Assembly and Leak-Test. Assemble the analysis system. Allow sufficient time for all system components to reach the desired temperature. Then, determine the leak-rate (L_R) and leak volume (V_L), where $V_L = L_R t_{SS}$. Leak volumes shall be ≤ 4 percent of V_{SS}.

5.2 Verify Instrumental Performance. Measure the noise level of the system in each analytical region using the procedure of attachment G of this addendum. If any noise level is higher than that estimated for the system in section 4.12 of this addendum, repeat the calculations of attachment D of this addendum and verify that the requirements of section 4.12 of this addendum are met; if they are not, adjust or repair the instrument and repeat this section.

5.3 Determine the Sample Absorption Pathlength. Record a background spectrum. Then, fill the absorption cell with CTS at the pressure P_R and record a set of CTS spectra {R3}. Store the background and unscaled CTS single beam interferograms and spectra. Using attachment H of this addendum, calculate the sample absorption pathlength (L_S) for each analytical region. The values L_S shall not differ from the approximated sample pathlength L_S' (see section 4.4 of this addendum) by more than 5 percent.

5.4 Record Sample Spectrum. Connect the sample line to the source. Either evacuate the absorption cell to an absolute pressure below 5 mmHg before extracting a sample from the effluent stream into the absorption cell, or pump at least ten cell volumes of sample through the cell before obtaining a sample. Record the sample pressure P_S. Generate the absorbance spectrum of the sample. Store the background and sample single beam interferograms, and document the process by which the absorbance spectra are generated from these data. (If necessary, apply the spectral transformations developed in section 5.6.2 of this addendum). The resulting sample spectrum is referred to below as S_S. (*Note:* Multiple sample spectra

may be recorded according to the procedures of section 5.4 of this addendum before performing sections 5.5 and 5.6 of this addendum.)

5.5 Quantify Analyte Concentrations. Calculate the unscaled analyte concentrations RUA_i and unscaled interferant concentrations RUI_k using the programs developed in section 4 of this addendum. To correct for pathlength and pressure variations between the reference and sample spectra, calculate the scaling factor, R_{LPS} using equation A.1,

$$R_{LPS} = (L_R P_R T_S)/(L_S P_S T_R) \quad ((Eq.\ 320{-}A.1)$$

Calculate the final analyte and interferant concentrations RSA_i and RSI_k using equations A.2 and A.3,

$$RSA_i = R_{LPS} RUA_i \quad (Eq.\ 320{-}A.2)$$
$$RSI_k = R_{LPS} RUI_k \quad (Eq.\ 320{-}A.3)$$

5.6 Determine Fractional Analysis Uncertainty. Fill the absorption cell with CTS at the pressure P_S. Record a set of CTS spectra {R4}. Store the background and CTS single beam interferograms. Using appendix H of this addendum, calculate the fractional analysis uncertainty (FAU) for each analytical region. If the FAU indicated for any analytical region is greater than the required accuracy requirements determined in sections 4.1.1 through 4.1.4 of this addendum, then comparisons to previously recorded reference spectra are invalid in that analytical region, and the analyst shall perform one or both of the procedures of sections 5.6.1 through 5.6.2 of this addendum.

5.6.1 Perform instrumental checks and adjust the instrument to restore its performance to acceptable levels. If adjustments are made, repeat sections 5.3, 5.4 (except for the recording of a sample spectrum), and 5.5 of this addendum to demonstrate that acceptable uncertainties are obtained in all analytical regions.

5.6.2 Apply appropriate mathematical transformations (e.g., frequency shifting, zero-filling, apodization, smoothing) to the spectra (or to the interferograms upon which the spectra are based) generated during the performance of the procedures of section 5.3 of this addendum. Document these transformations and their reproducibility. Do not apply multiplicative scaling of the spectra, or any set of transformations that is mathematically equivalent to multiplicative scaling. Different transformations may be applied to different analytical regions. Frequency shifts shall be less than one-half the minimum instrumental linewidth, and must be applied to all spectral data points in an analytical region. The mathematical transformations may be retained for the analysis if they are also applied to the appropriate analytical regions of all sample spectra recorded, and if all original sample spectra are digitally stored. Repeat sections 5.3, 5.4 (except the recording of a sample spectrum), and 5.5 of this addendum to demonstrate that these transformations lead to acceptable calculated concentration uncertainties in all analytical regions.

6.0 Post-Analysis Evaluations

Estimate the overall accuracy of the analyses performed in accordance with

sections 5.1 through 5.6 of this addendum using the procedures of sections 6.1 through 6.3 of this addendum.

6.1 Qualitatively Confirm the Assumed Matrix. Examine each analytical region of the sample spectrum for spectral evidence of unexpected or unidentified interferants. If found, identify the interfering compounds (see Reference C for guidance) and add them to the list of known interferants. Repeat the procedures of section 4 of this addendum to include the interferants in the uncertainty calculations and analysis procedures. Verify that the MAU and FCU values do not increase beyond acceptable levels for the application requirements. Re-calculate the analyte concentrations (section 5.5 of this addendum) in the affected analytical regions.

6.2 Quantitatively Evaluate Fractional Model Uncertainty (FMU). Perform the procedures of either section 6.2.1 or 6.2.2 of this addendum:

6.2.1 Using appendix I of this addendum, determine the fractional model error (FMU) for each analyte.

6.2.2 Provide statistically determined uncertainties FMU for each analyte which are equivalent to two standard deviations at the 95 percent confidence level. Such determinations, if employed, must be based on mathematical examinations of the pertinent sample spectra (not the reference spectra alone). Include in the report of the analysis (see section 7.0 of this addendum) a complete description of the determination of the concentration uncertainties.

6.3 Estimate Overall Concentration Uncertainty (OCU). Using appendix J of this addendum, determine the overall concentration uncertainty (OCU) for each analyte. If the OCU is larger than the required accuracy for any analyte, repeat sections 4 and 6 of this addendum.

7.0 Reporting Requirements

[Documentation pertaining to virtually all the procedures of sections 4, 5, and 6 will be required. Software copies of reference spectra and sample spectra will be retained for some minimum time following the actual testing.]

8.0 References

(A) Standard Practices for General Techniques of Infrared Quantitative Analysis (American Society for Testing and Materials, Designation E 168–88).

(B) The Coblentz Society Specifications for Evaluation of Research Quality Analytical Infrared Reference Spectra (Class II); Anal. Chemistry *47*, 945A (1975); Appl. Spectroscopy *444*, pp. 211–215, 1990.

(C) Standard Practices for General Techniques for Qualitative Infrared Analysis, American Society for Testing and Materials, Designation E 1252–88.

(D) ''EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards,'' U.S. Environmental Protection Agency Publication No. EPA/600/R–93/224, December 1993.

Attachment A to Addendum to Method 320—Definitions of Terms and Symbols

A.1 Definitions of Terms. All terms used in this method that are not defined below have the meaning given to them in the CAA and in subpart A of this part.

Absorption band means a contiguous wavenumber region of a spectrum (equivalently, a contiguous set of absorbance spectrum data points) in which the absorbance passes through a maximum or a series of maxima.

Absorption pathlength means the distance in a spectrophotometer, measured in the direction of propagation of the beam of radiant energy, between the surface of the specimen on which the radiant energy is incident and the surface of the specimen from which it is emergent.

Analytical region means a contiguous wavenumber region (equivalently, a contiguous set of absorbance spectrum data points) used in the quantitative analysis for one or more analytes. (*Note:* The quantitative result for a single analyte may be based on data from more than one analytical region.)

Apodization means modification of the ILS function by multiplying the interferogram by a weighing function whose magnitude varies with retardation.

Background spectrum means the single beam spectrum obtained with all system components without sample present.

Baseline means any line drawn on an absorption spectrum to establish a reference point that represents a function of the radiant power incident on a sample at a given wavelength.

Beers's law means the direct proportionality of the absorbance of a compound in a homogeneous sample to its concentration.

Calibration transfer standard (CTS) gas means a gas standard of a compound used to achieve and/or demonstrate suitable quantitative agreement between sample spectra and the reference spectra; see section 4.5.1 of this addendum.

Compound means a substance possessing a distinct, unique molecular structure.

Concentration (c) means the quantity of a compound contained in a unit quantity of sample. The unit ''ppm'' (number, or mole, basis) is recommended.

Concentration-pathlength product means the mathematical product of concentration of the species and absorption pathlength. For reference spectra, this is a known quantity; for sample spectra, it is the quantity directly determined from Beer's law. The units ''centimeters-ppm'' or ''meters-ppm'' are recommended.

Derivative absorption spectrum means a plot of rate of change of absorbance or of any function of absorbance with respect to wavelength or any function of wavelength.

Double beam spectrum means a transmission or absorbance spectrum derived by dividing the sample single beam spectrum by the background spectrum.(*Note:* The term ''double-beam'' is used elsewhere to denote a spectrum in which the sample and background interferograms are collected simultaneously along physically distinct absorption paths. Here, the term denotes a spectrum in which the sample and background interferograms are collected at different times along the same absorption path.)

Fast Fourier transform (FFT) means a method of speeding up the computation of a discrete FT by factoring the data into sparse matrices containing mostly zeros.

Flyback means interferometer motion during which no data are recorded.

Fourier transform (FT) means the mathematical process for converting an amplitude-time spectrum to an amplitude-frequency spectrum, or vice versa.

Fourier transform infrared (FTIR) spectrometer means an analytical system that employs a source of mid-infrared radiation, an interferometer, an enclosed sample cell of known absorption pathlength, an infrared detector, optical elements that transfer infrared radiation between components, and a computer system. The time-domain detector response (interferogram) is processed by a Fourier transform to yield a representation of the detector response vs. infrared frequency. (*Note:* When FTIR spectrometers are interfaced with other instruments, a slash should be used to denote the interface; e.g., GC/FTIR; HPCL/FTIR, and the use of FTIR should be explicit; i.e., FTIR not IR.)

Frequency, v means the number of cycles per unit time.

Infrared means the portion of the electromagnetic spectrum containing wavelengths from approximately 0.78 to 800 microns.

Interferogram, $I(\sigma)$ means record of the modulated component of the interference signal measured as a function of retardation by the detector.

Interferometer means device that divides a beam of radiant energy into two or more paths, generates an optical path difference between the beams, and recombines them in order to produce repetitive interference maxima and minima as the optical retardation is varied.

Linewidth means the full width at half maximum of an absorption band in units of wavenumbers (cm⁻¹).

Mid-infrared means the region of the electromagnetic spectrum from approximately 400 to 5000 cm⁻¹.

Reference spectra means absorption spectra of gases with known chemical compositions, recorded at a known absorption pathlength, which are used in the quantitative analysis of gas samples.

Retardation, σ means optical path difference between two beams in an interferometer; also known as ''optical path difference'' or ''optical retardation.''

Scan means digital representation of the detector output obtained during one complete motion of the interferometer's moving assembly or assemblies.

Scaling means application of a multiplicative factor to the absorbance values in a spectrum.

Single beam spectrum means Fourier-transformed interferogram, representing the detector response vs. wavenumber. (*Note:* The term ''single-beam'' is used elsewhere to denote any spectrum in which the sample and background interferograms are recorded on the same physical absorption path; such usage differentiates such spectra from those generated using interferograms recorded along two physically distinct absorption paths (see ''double-beam spectrum'' above). Here, the term applies (for example) to the two spectra used directly in the calculation of transmission and absorbance spectra of a sample.)

Standard reference material means a reference material, the composition or properties of which are certified by a recognized standardizing agency or group. (*Note:* The equivalent ISO term is ''certified reference material.'')

Transmittance, T means the ratio of radiant power transmitted by the sample to the radiant power incident on the sample. Estimated in FTIR spectroscopy by forming the ratio of the single-beam sample and background spectra.

Wavenumber, v means the number of waves per unit length. (*Note:* The usual unit of wavenumber is the reciprocal centimeter, cm⁻¹. The wavenumber is the reciprocal of the wavelength, λ, when λ is expressed in centimeters.) *Zero-filling* means the addition of zero-valued points to the end of a measured interferogram. (*Note:* Performing the FT of a zero-filled interferogram results in correctly interpolated points in the computed spectrum.)

A.2 Definitions of Mathematical Symbols. The symbols used in equations in this subpart are defined as follows:

(1) A, absorbance = the logarithm to the base 10 of the reciprocal of the transmittance (T).

$$A = \log_{10}\left(\frac{1}{T}\right) = -\log_{10}T$$

(2) AAI_{im} = band area of the ith analyte in the mth analytical region, at the concentration (CL_i) corresponding to the product of its required detection limit (DL_i) and analytical uncertainty limit (AU_i) .

(3) AAV_{im} = average absorbance of the ith analyte in the mth analytical region, at the concentration (CL_i) corresponding to the product of its required detection limit (DL_i) and analytical uncertainty limit (AU_i) .

(4) ASC, accepted standard concentration = the concentration value assigned to a chemical standard.

(5) ASCPP, accepted standard concentration-pathlength product = for a chemical standard, the product of the ASC and the sample absorption pathlength. The units ''centimeters-ppm'' or ''meters-ppm'' are recommended.

(6) AU_i, analytical uncertainty limit = the maximum permissible fractional uncertainty of analysis for the ith analyte concentration, expressed as a fraction of the analyte concentration determined in the analysis.

(7) AVT_m = average estimated total absorbance in the mth analytical region.

(8) $CKWN_k$ = estimated concentration of the kth known interferant.

(9) $CMAX_i$ = estimated maximum concentration of the ith analyte.

(10) $CPOT_j$ = estimated concentration of the jth potential interferant.

(11) DL_i, required detection limit = for the ith analyte, the lowest concentration of the analyte for which its overall fractional uncertainty (OFU_i) is required to be less than the analytical uncertainty limit (AU_i).

(12) FC_m = center wavenumber position of the mth analytical region.

(13) FAU_i, fractional analytical uncertainty = calculated uncertainty in the measured concentration of the ith analyte because of errors in the mathematical comparison of reference and sample spectra.

(14) FCU$_i$, fractional calibration uncertainty = calculated uncertainty in the measured concentration of the ith analyte because of errors in Beer's law modeling of the reference spectra concentrations.

(15) FFL$_m$ = lower wavenumber position of the CTS absorption band associated with the mth analytical region.

(16) FFU$_m$ = upper wavenumber position of the CTS absorption band associated with the mth analytical region.

(17) FL$_m$ = lower wavenumber position of the mth analytical region.

(18) FMU$_i$, fractional model uncertainty = calculated uncertainty in the measured concentration of the ith analyte because of errors in the absorption model employed.

(19) FN$_L$ = lower wavenumber position of the CTS spectrum containing an absorption band at least as narrow as the analyte absorption bands.

(20) FN$_U$ = upper wavenumber position of the CTS spectrum containing an absorption band at least as narrow as the analyte absorption bands.

(21) FRU$_i$, fractional reproducibility uncertainty = calculated uncertainty in the measured concentration of the ith analyte because of errors in the reproducibility of spectra from the FTIR system.

(22) FU$_m$ = upper wavenumber position of the mth analytical region.

(23) IAI$_{jm}$ = band area of the jth potential interferant in the mth analytical region, at its expected concentration (CPOT$_j$).

(24) IAV$_{im}$ = average absorbance of the ith analyte in the mth analytical region, at its expected concentration (CPOT$_j$).

(25) ISC$_{i \text{ or } k}$, indicated standard concentration = the concentration from the computerized analytical program for a single-compound reference spectrum for the ith analyte or kth known interferant.

(26) kPa = kilo-Pascal (see Pascal).

(27) L$_S$' = estimated sample absorption pathlength.

(28) L$_R$ = reference absorption pathlength.

(29) L$_S$ = actual sample absorption pathlength.

(30) MAU$_i$ = mean of the MAU$_{im}$ over the appropriate analytical regions.

(31) MAU$_{im}$, minimum analyte uncertainty = the calculated minimum concentration for which the analytical uncertainty limit (AU$_i$) in the measurement of the ith analyte, based on spectral data in the mth analytical region, can be maintained.

(32) MIU$_j$ = mean of the MIU$_{jm}$ over the appropriate analytical regions.

(33) MIU$_{jm}$, minimum interferant uncertainty = the calculated minimum concentration for which the analytical uncertainty limit CPOT$_j$/20 in the measurement of the jth interferant, based on spectral data in the mth analytical region, can be maintained.

(34) MIL, minimum instrumental linewidth = the minimum linewidth from the FTIR system, in wavenumbers. (*Note:* The MIL of a system may be determined by observing an absorption band known (through higher resolution examinations) to be narrower than indicated by the system. The MIL is fundamentally limited by the retardation of the interferometer, but is also affected by other operational parameters (e.g., the choice of apodization).)

(35) N$_i$ = number of analytes.

(36) N$_j$ = number of potential interferants.

(37) N$_k$ = number of known interferants.

(38) N$_{scan}$ = the number of scans averaged to obtain an interferogram.

(39) OFU$_i$ = the overall fractional uncertainty in an analyte concentration determined in the analysis (OFU$_i$ = MAX {FRU, FCU$_i$, FAU$_i$, FMU$_i$ }).

(40) Pascal (Pa) = metric unit of static pressure, equal to one Newton per square meter; one atmosphere is equal to 101,325 Pa; 1/760 atmosphere (one Torr, or one millimeter Hg) is equal to 133.322 Pa.

(41) P$_{min}$ = minimum pressure of the sampling system during the sampling procedure.

(42) P$_S$' = estimated sample pressure.

(43) P$_R$ = reference pressure.

(44) P$_S$ = actual sample pressure.

(45) RMS$_{sm}$ = measured noise level of the FTIR system in the mth analytical region.

(46) RMSD, root mean square difference = a measure of accuracy determined by the following equation:

$$RMSD = \sqrt{\left(\frac{1}{n}\right)\sum_{i=1}^{n} e_i^2}$$

Where:

n = the number of observations for which the accuracy is determined.

e$_i$ = the difference between a measured value of a property and its mean value over the n observations.

Note: The RMSD value "between a set of n contiguous absorbance values (A$_i$) and the mean of the values" (A$_M$) is defined as

$$RMSD = \sqrt{\left(\frac{1}{n}\right)\sum_{i=1}^{n} \left(A_i - A_M\right)^2}$$

(47) RSA$_i$ = the (calculated) final concentration of the ith analyte.

(48) RSI$_k$ = the (calculated) final concentration of the kth known interferant.

(49) t$_{scan}$, scan time = time used to acquire a single scan, not including flyback.

(50) t$_S$, signal integration period = the period of time over which an interferogram is averaged by addition and scaling of individual scans. In terms of the number of scans N$_{scan}$ and scan time t$_{scan}$, t$_S$ = N$_{scan}$t$_{scan}$.

(51) t$_{SR}$ = signal integration period used in recording reference spectra.

(52) t$_{SS}$ = signal integration period used in recording sample spectra.

(53) T$_R$ = absolute temperature of gases used in recording reference spectra.

(54) T$_S$ = absolute temperature of sample gas as sample spectra are recorded.

(55) TP, Throughput = manufacturer's estimate of the fraction of the total infrared power transmitted by the absorption cell and transfer optics from the interferometer to the detector.

(56) V$_{SS}$ = volume of the infrared absorption cell, including parts of attached tubing.

(57) W$_{ik}$ = weight used to average over analytical regions k for quantities related to the analyte i; see attachment D of this addendum.

Attachment B to Addendum to Method 320—Identifying Spectral Interferants

B.1 General

B.1.1 Assume a fixed absorption pathlength equal to the value L$_S$'.

B.1.2 Use band area calculations to compare the relative absorption strengths of the analytes and potential interferants. In the mth analytical region (FL$_m$ to FU$_m$), use either rectangular or trapezoidal approximations to determine the band areas described below (see Reference A, sections A.3.1 through A.3.3). Document any baseline corrections applied to the spectra.

B.1.3 Use the average total absorbance of the analytes and potential interferants in each analytical region to determine whether the analytical region is suitable for analyte concentration determinations. (*Note:* The average absorbance in an analytical region is the band area divided by the width of the analytical region in wavenumbers. The average total absorbance in an analytical region is the sum of the average absorbances of all analytes and potential interferants.)

B.2 Calculations

B.2.1 Prepare spectral representations of each analyte at the concentration CL$_i$ = (DL$_i$)(AU$_i$), where DL$_i$ is the required detection limit and AU$_i$ is the maximum permissible analytical uncertainty. For the mth analytical region, calculate the band area (AAI$_{im}$) and average absorbance (AAV$_{im}$) from these scaled analyte spectra.

B.2.2 Prepare spectral representations of each potential interferant at its expected concentration (CPOT$_j$). For the mth analytical region, calculate the band area (IAI$_{jm}$) and average absorbance (IAV$_{jm}$) from these scaled potential interferant spectra.

B.2.3 Repeat the calculation for each analytical region, and record the band area results in matrix form as indicated in Figure B.1.

B.2.4 If the band area of any potential interferant in an analytical region is greater than the one-half the band area of any analyte (i.e., IAI$_{jm}$ >0.5 AAI$_{im}$ for any pair ij and any m), classify the potential interferant as a known interferant. Label the known interferants k = 1 to K. Record the results in matrix form as indicated in Figure B.2.

B.2.5 Calculate the average total absorbance (AVT$_m$) for each analytical region and record the values in the last row of the matrix described in Figure B.2. Any analytical region where AVT$_m$ >2.0 is unsuitable.

FIGURE B.1.—PRESENTATION OF POTENTIAL INTERFERANT CALCULATIONS

	Analytical regions	
	1	M
Analyte Labels		
1	AAI$_{11}$	AAI$_{1M}$
I	AAI$_{I1}$	AAI$_{IM}$
Potential Interferant Labels		
1	IAI$_{11}$	IAI$_{1M}$

FIGURE B.1.—PRESENTATION OF PO-
TENTIAL INTERFERANT CALCULA-
TIONS—Continued

	Analytical regions	
	1	M
J	IAI_{J1}	IAI_{JM}

FIGURE B.2.—PRESENTATION OF
KNOWN INTERFERANT CALCULATIONS

	Analytical regions	
	1	M
Analyte Labels		
1	AAI_{11}	AAI_{1M}
I	AAI_{I1}	AAI_{IM}
Known Interferant Labels		
1	IAI_{11}	IAI_{1M}
K	IAI_{K1}	IAI_{KM}

Total Average Absorbance.	AVT_1	AVT_M

Attachment C to Addendum to Method 320—Estimating Noise Levels

C.1 General

C.1.1 The root-mean-square (RMS) noise level is the standard measure of noise in this addendum. The RMS noise level of a contiguous segment of a spectrum is defined as the RMS difference (RMSD) between the absorbance values which form the segment and the mean value of that segment (see attachment A of this addendum).

C.1.2 The RMS noise value in double-beam absorbance spectra is assumed to be inversely proportional to: (a) the square root of the signal integration period of the sample single beam spectra from which it is formed, and (b) the total infrared power transmitted through the interferometer and absorption cell.

C.1.3 Practically, the assumption of C.1.2 allows the RMS noise level of a complete system to be estimated from the quantities described in sections C.1.3.1 through C.1.3.4:

C.1.3.1 RMS_{MAN}, the noise level of the system (in absorbance units), without the absorption cell and transfer optics, *under those conditions necessary to yield the specified minimum instrumental linewidth,* e.g., Jacquinot stop size.

C.1.3.2 t_{MAN}, the manufacturer's signal integration time used to determine RMS_{MAN}.

C.1.3.3 t_{SS}, the signal integration time for the analyses.

C.1.3.4 TP, the manufacturer's estimate of the fraction of the total infrared power transmitted by the absorption cell and transfer optics from the interferometer to the detector.

C.2 Calculations

C.2.1 Obtain the values of RMS_{MAN}, t_{MAN}, and TP from the manufacturers of the equipment, or determine the noise level by direct measurements with the completely constructed system proposed in section 4 of this addendum.

C.2.2 Calculate the noise value of the system (RMS_{EST}) using equation C.1.

$$RMS_{EST} = RMS_{MAN}\, TP \sqrt{\frac{t_{ss}}{t_{MAN}}} \qquad \text{(Eq. 320-C.1)}$$

Attachment D to Addendum to Method 320—Estimating Minimum Concentration Measurement Uncertainties (MAU and MIU)

D.1 General

Estimate the minimum concentration measurement uncertainties for the ith analyte (MAU_i) and jth interferant (MIU_j) based on the spectral data in the mth analytical region by comparing the analyte band area in the analytical region (AAI_{im}) and estimating or

measuring the noise level of the system (RMS_{EST} or RMS_{Sm}). (*Note:* For a single analytical region, the MAU or MIU value is the concentration of the analyte or interferant for which the band area is equal to the product of the analytical region width (in wavenumbers) and the noise level of the system (in absorbance units). If data from more than one analytical region are used in the determination of an analyte concentration, the MAU or MIU is the mean

of the separate MAU or MIU values calculated for each analytical region.)

D.2 Calculations

D.2.1 For each analytical region, set RMS = RMS_{Sm} if measured (attachment G of this addendum), or set RMS = RMS_{EST} if estimated (attachment C of this addendum).

D.2.2 For each analyte associated with the analytical region, calculate MAU_{im} using equation D.1,

$$MAU_{im} = (RMS)(DL_i)(AU_i)\frac{(FU_m - FL_m)}{AAI_{im}} \qquad \text{(Eq. 320-D.1)}$$

D.2.3 If only the mth analytical region is used to calculate the concentration of the ith analyte, set $MAU_i = MAU_{im}$.

D.2.4 If more than one analytical region is used to calculate the concentration of the ith analyte, set MAU_i equal to the weighted mean of the appropriate MAU_{im} values calculated above; the weight for each term in

the mean is equal to the fraction of the total wavenumber range used for the calculation represented by each analytical region. Mathematically, if the set of analytical regions employed is {m'}, then the MAU for each analytical region is given by equation D.2.

$$MAU_i = \sum_{k \in \{m'\}} W_{ik}\, MAU_{ik} \qquad \text{(Eq. 320-D.2)}$$

Where the weight W_{ik} is defined for each term in the sum as

$$W_{ik} = (FM_k - FL_k)\left(\sum_{p \in \{m'\}}\left[FM_p - FL_p\right]\right)^{-1} \qquad \text{(Eq. 320-D.3)}$$

D.2.5   Repeat sections D.2.1 through D.2.4 of this to calculate the analogous values MIU_j for the interferants j = 1 to J. Replace the value (AU_i) (DL_i) in equation D.1 with $CPOT_j/20$; replace the value AAI_{im} in equation D.1 with IAI_{jm}.

Attachment E to Addendum to Method 320—Determining Fractional Reproducibility Uncertainties (FRU)

E.1   General

To estimate the reproducibility of the spectroscopic results of the system, compare the CTS spectra recorded before and after preparing the reference spectra. Compare the difference between the spectra to their average band area. Perform the calculation for each analytical region on the portions of the CTS spectra associated with that analytical region.

E.2   Calculations

E.2.1   The CTS spectra {R1} consist of N spectra, denoted by S_{1i}, i=1, N. Similarly, the CTS spectra {R2} consist of N spectra, denoted by S_{2i}, i=1, N. Each S_{ki} is the spectrum of a single compound, where i denotes the compound and k denotes the set {Rk} of which S_{ki} is a member. Form the spectra S_3 according to $S_{3i} = S_{2i} - S_{1i}$ for each i. Form the spectra S_4 according to $S_{4i} = [S_{2i}+S_{1i}]/2$ for each i.

E.2.2   Each analytical region m is associated with a portion of the CTS spectra S_{2i} and S_{1i}, for a particular i, with lower and upper wavenumber limits FFL_m and FFU_m, respectively.

E.2.3   For each m and the associated i, calculate the band area of S_{4i} in the wavenumber range FFU_m to FFL_m. Follow the guidelines of section B.1.2 of this addendum for this band area calculation. Denote the result by BAV_m.

E.2.4   For each m and the associated i, calculate the RMSD of S_{3i} between the absorbance values and their mean in the wavenumber range FFU_m to FFL_m. Denote the result by $SRMS_m$.

E.2.5   For each analytical region m, calculate FM_m using equation E.1,

$$FM_m = SRMS_m \left(FFU_m - FFL_m\right)/BAV_m \qquad (Eq.\ 320\text{-}E.1)$$

E.2.6   If only the mth analytical region is used to calculate the concentration of the ith analyte, set $FRU_i = FM_m$.

E.2.7   If a number pi of analytical regions are used to calculate the concentration of the ith analyte, set FRU_i equal to the weighted mean of the appropriate FM_m values calculated according to section E.2.5. Mathematically, if the set of analytical regions employed is {m′}, then FRU_i is given by equation E.2,

$$FRU_i = \sum_{k \in \{m'\}} W_{ik} FM_k \qquad (Eq.\ 320\text{-}E.2)$$

Where the W_{ik} are calculated as described in Attachment D of this addendum.

Attachment F to Addendum to Method 320—Determining Fractional Calibration Uncertainties (FCU)

F.1   General

F.1.1   The concentrations yielded by the computerized analytical program applied to each single-compound reference spectrum are defined as the indicated standard concentrations (ISC's). The ISC values for a single compound spectrum should ideally equal the accepted standard concentration (ASC) for one analyte or interferant, and should ideally be zero for all other compounds. Variations from these results are caused by errors in the ASC values, variations from the Beer's law (or modified Beer's law) model used to determine the concentrations, and noise in the spectra. When the first two effects dominate, the systematic nature of the errors is often apparent and the analyst shall take steps to correct them.

F.1.2   When the calibration error appears non-systematic, apply the procedures of sections F.2.1 through F.2.3 of this appendix to estimate the fractional calibration uncertainty (FCU) for each compound. The FCU is defined as the mean fractional error between the ASC and the ISC for all reference spectra with non-zero ASC for that compound. The FCU for each compound shall be less than the required fractional uncertainty specified in section 4.1 of this addendum.

F.1.3   The computerized analytical programs shall also be required to yield acceptably low concentrations for compounds with ISC = 0 when applied to the reference spectra. The ISC of each reference spectrum for each analyte or interferant shall not exceed that compound's minimum measurement uncertainty (MAU or MIU).

F.2   Calculations

F.2.1   Apply each analytical program to each reference spectrum. Prepare a similar table to that in Figure F.1 to present the ISC and ASC values for each analyte and interferant in each reference spectrum. Maintain the order of reference file names and compounds employed in preparing Figure F.1.

F.2.2   For all reference spectra in Figure F.1, verify that the absolute values of the ISC's are less than the compound's MAU (for analytes) or MIU (for interferants).

F.2.3   For each analyte reference spectrum, calculate the quantity (ASC–ISC)/ASC. For each analyte, calculate the mean of these values (the FCU_i for the ith analyte) over all reference spectra. Prepare a similar table to that in Figure F.2 to present the FCU_i and analytical uncertainty limit (AU_i) for each analyte.

FIGURE F.1.—PRESENTATION OF ACCEPTED STANDARD CONCENTRATIONS (ASC'S) AND INDICATED STANDARD CONCENTRATIONS (ISC'S)

Compound name	Reference spectrum file name	ASC (ppm)	ISC (ppm)			
			Analytes i=1 j=1		Interferants I J	

FIGURE F.2.—PRESENTATION OF FRACTIONAL CALIBRATION UNCERTAINTIES (FCU'S) AND ANALYTICAL UNCERTAINTIES (AU'S)

Analyte name	FCU (%)	AU (%)

Attachment G to Addendum to Method 320—Measuring Noise Levels

G.1 General

The root-mean-square (RMS) noise level is the standard measure of noise. The RMS noise level of a contiguous segment of a spectrum is the RMSD between the absorbance values that form the segment and the mean value of the segment (see appendix A of this addendum).

G.2 Calculations

G.2.1   Evacuate the absorption cell or fill it with UPC grade nitrogen at approximately one atmosphere total pressure.

G.2.2   Record two single beam spectra of signal integration period t_{SS}.

G.2.3   Form the double beam absorption spectrum from these two single beam spectra, and calculate the noise level RMS_{Sm} in the M analytical regions.

Attachment H of Addendum to Method 320—Determining Sample Absorption Pathlength (L_S) and Fractional Analytical Uncertainty (FAU)

H.1 General

Reference spectra recorded at absorption pathlength (L_R), gas pressure (P_R), and gas absolute temperature (T_R) may be used to determine analyte concentrations in samples whose spectra are recorded at conditions different from that of the reference spectra, i.e., at absorption pathlength (L_S), absolute temperature (T_S), and pressure (P_S). This appendix describes the calculations for estimating the fractional uncertainty (FAU) of this practice. It also describes the calculations for determining the sample absorption pathlength from comparison of CTS spectra, and for preparing spectra for further instrumental and procedural checks.

H.1.1   Before sampling, determine the sample absorption pathlength using least squares analysis. Determine the ratio L_S/L_R by comparing the spectral sets {R1} and {R3}, which are recorded using the same CTS at L_S and L_R, and T_S and T_R, but both at P_R.

H.1.2   Determine the fractional analysis uncertainty (FAU) for each analyte by comparing a scaled CTS spectral set, recorded at L_S, T_S, and P_S, to the CTS reference spectra of the same gas, recorded at L_R, T_R, and P_R. Perform the quantitative comparison after recording the sample spectra, based on band areas of the spectra in the CTS absorbance band associated with each analyte.

H.2 Calculations

H.2.1   Absorption Pathlength Determination. Perform and document separate linear baseline corrections to each analytical region in the spectral sets {R1} and {R3}. Form a one-dimensional array A_R containing the absorbance values from all segments of {R1} that are associated with the analytical regions; the members of the array are A_{Ri}, i = 1, n. Form a similar one-dimensional array A_S from the absorbance values in the spectral set {R3}; the members of the array are A_{Si}, i = 1, n. Based on the model $A_S = rA_R + E$, determine the least-squares estimate of r′, the value of r which minimizes the square error E^2. Calculate the sample absorption pathlength, L_S, using equation H.1,

$L_S = r'(T_S/T_R)L_R$ (Eq. 320–H.)

H.2.2   Fractional Analysis Uncertainty. Perform and document separate linear baseline corrections to each analytical region in the spectral sets {R1} and {R4}. Form the arrays A_S and A_R as described in section H.2.1 of this appendix, using values from {R1} to form A_R, and values from {R4} to form A_S. Calculate $NRMS_E$ and IA_{AV} using equations H.2 and H.3,

$$RMS_E = \sqrt{\sum_{i=1}^{n}\left[A_{Si} - \left(\frac{T_R}{T_S}\right)\left(\frac{L_S}{L_R}\right)\left(\frac{P_S}{P_R}\right)A_{Ri}\right]}$$ (Eq. 320-H.2)

$$A_{AV} = \frac{1}{2}\sum_{i=1}^{n}\left[A_{Si} + \left(\frac{T_R}{T_S}\right)\left(\frac{L_S}{L_R}\right)\left(\frac{P_S}{P_R}\right)A_{Ri}\right]$$ (Eq. 320-H.3)

The fractional analytical uncertainty, FAU, is given by equation H.4,

$$FAU = \frac{NRMS_E}{IA_{AV}}$$ (Eq. 320-H.4)

Attachment I to Addendum to Method 320—Determining Fractional Model Uncertainties (FMU)

I.1 General

To prepare analytical programs for FTIR analyses, the sample constituents must first be assumed. The calculations in this, appendix, based upon a simulation of the sample spectrum, shall be used to verify the appropriateness of these assumptions. The simulated spectra consist of the sum of single compound reference spectra scaled to represent their contributions to the sample absorbance spectrum; scaling factors are based on the indicated standard concentrations (ISC) and measured (sample) analyte and interferant concentrations, the sample and reference absorption pathlengths, and the sample and reference gas pressures. No band-shape correction for differences in the temperature of the sample and reference spectra gases is made; such errors are included in the FMU estimate. The actual and simulated sample spectra are quantitatively compared to determine the fractional model uncertainty; this comparison uses the reference spectra band areas and residuals in the difference spectrum formed from the actual and simulated sample spectra.

I.2 Calculations

I.2.1   For each analyte (with scaled concentration RSA_i), select a reference spectrum SA_i with indicated standard concentration ISC_i. Calculate the scaling factors, RA_i, using equation I.1,

$$RA_i = \frac{T_R L_S P_S RSA_i}{T_S L_R P_R ISC_i}$$ (Eq. 320-I.1)

Form the spectra SAC_i by scaling each SA_i by the factor RA_i.

I.2.2   For each interferant, select a reference spectrum SI_k with indicated standard concentration ISC_k. Calculate the scaling factors, RI_k, using equation I.2,

$$RI_k = \frac{T_R L_S P_S RSI_k}{T_S L_R P_R ISC_k} \qquad \text{(Eq. 320-I.2)}$$

Form the spectra SIC_k by scaling each SI_k by the factor RI_k.

I.2.3   For each analytical region, determine by visual inspection which of the spectra SAC_i and SIC_k exhibit absorbance bands within the analytical region. Subtract each spectrum SAC_i and SIC_k exhibiting absorbance from the sample spectrum S_S to form the spectrum SUB_S. To save analysis time and to avoid the introduction of unwanted noise into the subtracted spectrum, it is recommended that the calculation be made (1) only for those spectral data points within the analytical regions, and (2) for each analytical region separately using the original spectrum S_S.

I.2.4   For each analytical region m, calculate the RMSD of SUB_S between the absorbance values and their mean in the region FFU_m to FFL_m. Denote the result by $RMSS_m$.

I.2.5   For each analyte i, calculate FMm, using equation I.3,

$$FM_m = \frac{RMSS_m\left(FFU_m - FFL_m\right)AU_i DL_i}{AAI_i RSA_i} \qquad \text{(Eq. 320-I.3)}$$

for each analytical region associated with the analyte.

I.2.6   If only the mth analytical region is used to calculate the concentration of the ith analyte, set $FMU_i = FM_m$.

I.2.7   If a number of analytical regions are used to calculate the concentration of the ith analyte, set FM_i equal to the weighted mean of the appropriate FM_m values calculated using equation I–3. Mathematically, if the set of analytical regions employed is $\{m'\}$, then the fractional model uncertainty, FMU, is given by equation I.4,

$$FMU_i = \sum_{k \in \{m'\}} W_{ik} FM_k \qquad \text{(Eq. 320-I.4)}$$

Where W_{ik} is calculated as described in Attachment D of this addendum.

Attachment J to Addendum to Method 320—Determining Overall Concentration Uncertainties (OCU)

The calculations in this addendum estimate the measurement uncertainties for various FTIR measurements. The lowest possible overall concentration uncertainty (OCU) for an analyte is its MAU value, which is an estimate of the absolute concentration uncertainty when spectral noise dominates the measurement error. However, if the product of the largest fractional concentration uncertainty (FRU, FCU, FAU, or FMU) and the measured concentration of an analyte exceeds the MAU for the analyte, then the OCU is this product. In mathematical terms, set $OFU_i = MAX\{FRU_i, FCU_i, FAU_i, FMU_i\}$ and $OCU_i = MAX\{RSA_i * OFU_i, MAU_i\}$.

Method 321—Measurement of Gaseous Hydrogen Chloride Emissions At Portland Cement Kilns by Fourier Transform Infrared (FTIR) Spectroscopy

1.0   Introduction

This method should be performed by those persons familiar with the operation of Fourier Transform Infrared (FTIR) instrumentation in the application to source sampling. This document describes the sampling procedures for use in the application of FTIR spectrometry for the determination of vapor phase hydrogen chloride (HCl) concentrations both before and after particulate matter control devices installed at portland cement kilns. A procedure for analyte spiking is included for quality assurance. This method is considered to be self validating provided that the requirements listed in section 9 of this method are followed. The analytical procedures for interpreting infrared spectra from emission measurements are described in the ''Protocol For The Use of Extractive Fourier Transform Infrared (FTIR) Spectrometry in Analyses of Gaseous Emissions From Stationary Industrial Sources'', included as an addendum to proposed Method 320 of this appendix (hereafter referred to as the ''FTIR Protocol''). References 1 and 2 describe the use of FTIR spectrometry in field measurements. Sample transport presents the principal difficulty in directly measuring HCl emissions. This identical problem must be overcome by any extractive measurement method. HCl is reactive and water soluble. The sampling system must be adequately designed to prevent sample condensation in the system.

1.1   Scope and Application.

This method is specifically designed for the application of FTIR Spectrometry in extractive measurements of gaseous HCl concentrations in portland cement kiln emissions.

1.2   Applicability. This method applies to the measurement of HCl [CAS No. 7647–01–0]. This method can be applied to the determination of HCl concentrations both before and after particulate matter control devices installed at portland cement manufacturing facilities. This method applies to either continuous flow through measurement (with isolated sample analysis) or grab sampling (batch analysis). HCl is measured using the mid-infrared spectral region for analysis (about 400 to 4000 cm⁻¹ or 25 to 2.5 μm). Table 1 lists the suggested analytical region for quantification of HCl taking the interference from water vapor into consideration.

TABLE 1.—EXAMPLE ANALYTICAL REGION FOR HCL

Compound	Analytical region (cm⁻¹)	Potential interferants
Hydrogen chloride.	2679–2840	Water.

1.3   Method Range and Sensitivity.

1.3.1   The analytical range is determined by the instrumental design and the composition of the gas stream. For practical purposes there is no upper limit to the range because the pathlength may be reduced or the sample may be diluted. The lower detection range depends on (1) the absorption coefficient of the compound in the analytical frequency region, (2) the spectral resolution, (3) the interferometer sampling time, (4) the detector sensitivity and response, and (5) the absorption pathlength.

1.3.2   The practical lower quantification range is usually higher than the instrument sensitivity allows and is dependent upon (1) the presence of interfering species in the exhaust gas including H_2O, CO_2, and SO_2, (2) analyte losses in the sampling system, (3) the optical alignment of the gas cell and transfer optics, and (4) the quality of the reflective surfaces in the cell (cell throughput). Under typical test conditions (moisture content of up to 30% and CO_2 concentrations from 1 to 15 percent), a 22 meter path length cell with a suitable sampling system may achieve a lower quantification range of from 1 to 5 ppm for HCl.

1.4   Data Quality Objectives.

1.4.1   In designing or configuring the analytical system, data quality is determined by measuring of the root mean square deviation (RMSD) of the absorbance values within a chosen spectral (analytical) region. The RMSD provides an indication of the signal-to-noise ratio (S/N) of the spectral baseline. Appendix D of the FTIR Protocol (the addendum to Method 320 of this appendix) presents a discussion of the relationship between the RMSD, lower detection limit, DL_i, and analytical uncertainty, AU_i. It is important to consider the target analyte quantification limit when performing testing with FTIR instrumentation, and to optimize the system to achieve the desired detection limit.

1.4.2   Data quality is determined by measuring the root mean square (RMS) noise level in each analytical spectral region (appendix C of the FTIR Protocol). The RMS noise is defined as the root mean square deviation (RMSD) of the absorbance values in an analytical region from the mean absorbance value in the same region. Appendix D of the *FTIR Protocol* defines the minimum analyte uncertainty (MAU), and how the RMSD is used to calculate the MAU. The MAU_{im} is the minimum concentration of the ith analyte in the mth analytical region for which the analytical uncertainty limit can be maintained. Table 2 to this method presents example values of AU and MAU using the analytical region presented in Table 1 to this method.

TABLE 2.—EXAMPLE PRE-TEST PRO-
TOCOL CALCULATIONS FOR HYDRO-
GEN CHLORIDE

	HCl
Reference concentration (ppm-meters)/K	11.2
Reference Band Area	2.881
DL (ppm-meters)/K	0.1117
AU	0.2
CL (DL x AU)	0.02234
FL (cm^{-1})	2679.83
FU (cm^{-1})	2840.93
FC (cm^{-1})	2760.38
AAI (ppm-meters)/K	0.06435
RMSD	2.28 E−03
MAU (ppm-meters)/K	1.28E−01
MAU ppm at 22 meters and 250 °F	0.2284

2.0   Summary of Method

2.1   Principle.

See Method 320 of this appendix. HCl can also undergo rotation transitions by absorbing energy in the far-infrared spectral region. The rotational transitions are superimposed on the vibrational fundamental to give a series of lines centered at the fundamental vibrational frequency, 2885 cm^{-1}. The frequencies of absorbance and the pattern of rotational/vibrational lines are unique to HCl. When this distinct pattern is observed in an infrared spectrum of an unknown sample, it unequivocally identifies HCl as a component of the mixture. The infrared spectrum of HCl is very distinctive and cannot be confused with the spectrum of any other compound. See Reference 6.

2.2   Sampling and Analysis. See Method 320 of this appendix.

2.3   Operator Requirements. The analyst must have knowledge of spectral patterns to choose an appropriate absorption path length or determine if sample dilution is necessary. The analyst should also understand FTIR instrument operation well enough to choose instrument settings that are consistent with the objectives of the analysis.

3.0   Definitions

See A of the FTIR Protocol.

4.0   Interferences

This method will not measure HCl under conditions: (1) where the sample gas stream can condense in the sampling system or the instrumentation, or (2) where a high moisture content sample relative to the analyte concentrations imparts spectral interference due to the water vapor absorbance bands. For measuring HCl the first (sampling) consideration is more critical. Spectral interference from water vapor is not a significant problem except at very high moisture levels and low HCl concentrations.

4.1   Analytical Interferences. See Method 320 of this appendix.

4.1.1   Background Interferences. See Method 320 of this appendix.

4.1.2   Spectral interferences. Water vapor can present spectral interference for FTIR gas analysis of HCl. Therefore, the water vapor in the spectra of kiln gas samples must be accounted for. This means preparing at least one spectrum of a water vapor sample where the moisture concentration is close to that in the kiln gas.

4.2   Sampling System Interferences. The principal sampling system interferant for measuring HCl is water vapor. Steps must be taken to ensure that no condensation forms anywhere in the probe assembly, sample lines, or analytical instrumentation. Cold spots anywhere in the sampling system must be avoided. The extent of sampling system bias in the FTIR analysis of HCl depends on concentrations of potential interferants, moisture content of the gas stream, temperature of the gas stream, temperature of sampling system components, sample flow rate, and reactivity of HCl with other species in the gas stream (e.g., ammonia). For measuring HCl in a wet gas stream the temperatures of the gas stream, sampling components, and the sample flow rate are of primary importance. Analyte spiking with HCl is performed to demonstrate the integrity of the sampling system for transporting HCl vapor in the flue gas to the FTIR instrument. See section 9 of this method for a complete description of analyte spiking.

5.0   Safety

5.1   Hydrogen chloride vapor is corrosive and can cause irritation or severe damage to respiratory system, eyes and skin. Exposure to this compound should be avoided.

5.2   This method may involve sampling at locations having high positive or negative pressures, or high concentrations of hazardous or toxic pollutants, and can not address all safety problems encountered under these diverse sampling conditions. It is the responsibility of the tester(s) to ensure proper safety and health practices, and to determine the applicability of regulatory limitations before performing this test method. Leak-check procedures are outlined in section 8.2 of Method 320 of this .

6.0   Equipment and Supplies.

(**Note:** Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.)

6.1   FTIR Spectrometer and Detector. An FTIR Spectrometer system (interferometer, transfer optics, gas cell and detector) having the capability of measuring HCl to the predetermined minimum detectable level required (see section 4.1.3 of the FTIR Protocol). The system must also include an accurate means to control and/or measure the temperature of the FTIR gas analysis cell, and a personal computer with compatible software that provides real-time updates of the spectral profile during sample and spectral collection.

6.2   Pump. Capable of evacuating the FTIR cell volume to 1 Torr (133.3 Pascals) within two minutes (for batch sample analysis).

6.3   Mass Flow Meters/Controllers. To accurately measure analyte spike flow rate, having the appropriate calibrated range and a stated accuracy of ± 2 percent of the absolute measurement value. This device must be calibrated with the major component of the calibration/spike gas (*e.g.,* nitrogen) using an NIST traceable bubble meter or equivalent. Single point calibration checks should be performed daily in the field. When spiking HCl, the mass flow meter/controller should be thoroughly purged before and after introduction of the gas to prevent corrosion of the interior parts.

6.4   Polytetrafluoroethane tubing. Diameter and length suitable to connect cylinder regulators.

6.5   Stainless Steel tubing. Type 316 of appropriate length and diameter for heated connections.

6.6   Gas Regulators. Purgeable HCl regulator.

6.7   Pressure Gauge. Capable of measuring pressure from 0 to 1000 Torr (133.3 Pa=1 Torr) within ± 5 percent.

6.8   Sampling Probe. Glass, stainless steel or other appropriate material of sufficient length and physical integrity to sustain heating, prevent adsorption of analytes and capable of reaching gas sampling point.

6.9   Sampling Line. Heated 180 °C (360 °F) and fabricated of either stainless steel, polytetrafluoroethane or other material that prevents adsorption of HCl and transports effluent to analytical instrumentation. The extractive sample line must have the capability to transport sample gas to the analytical components as well as direct heated calibration spike gas to the calibration assembly located at the sample probe. It is important to minimize the length of heated sample line.

6.10   Particulate Filters. A sintered stainless steel filter rated at 20 microns or greater may be placed at the inlet of the probe (for removal of large particulate matter). A heated filter (Balston® or equivalent) rated at 1 micron is necessary for primary particulate matter removal, and shall be placed immediately after the heated probe. The filter/filter holder temperature should be maintained at 180 °C (360 °F).

6.11   Calibration/Analyte Spike Assembly. A heated three-way valve assembly (or equivalent) to introduce surrogate spikes into the sampling system at the outlet of the probe before the primary particulate filter.

6.12   Sample Extraction Pump. A leak-free heated head pump (KNF® Neuberger or equivalent) capable of extracting sample effluent through entire sampling system at a rate which prevents analyte losses and minimizes analyzer response time. The pump should have a heated by-pass and may be placed either before the FTIR instrument or after. If the sample pump is located upstream of the FTIR instrument, it must be fabricated from materials non-reactive to HCl. The sampling system and FTIR measurement system shall allow the operator to obtain at least six sample spectra during a one-hour period.

6.13   Barometer. For measurement of barometric pressure.

6.14   Gas Sample Manifold. A distribution manifold having the capabilities listed in sections 6.14.1 through 6.14.4;

6.14.1   Delivery of calibration gas directly to the analytical instrumentation;

6.14.2   Delivery of calibration gas to the sample probe (system calibration or analyte spike) via a heated traced sample line;

6.14.3   Delivery of sample gas (kiln gas, spiked kiln gas, or system calibrations) to the analytical instrumentation;

6.14.4   Delivery (optional) of a humidified nitrogen sample stream.

6.15 Flow Measurement Device. Type S Pitot tube (or equivalent) and Magnahelic® set for measurement of volumetric flow rate.

7.0 Reagents and Standards

HCl can be purchased in a standard compressed gas cylinder. The most stable HCl cylinder mixture available has a concentration certified at ±5 percent. Such a cylinder is suitable for performing analyte spiking because it will provide reproducible samples. The stability of the cylinder can be monitored over time by periodically performing direct FTIR analysis of cylinder samples. It is recommended that a 10–50 ppm cylinder of HCl be prepared having from 2–5 ppm SF6 as a tracer compound. (See sections 7.1 through 7.3 of Method 320 of this for a complete description of the use of existing HCl reference spectra. See section 9.1 of Method 320 of this for a complete discussion of standard concentration selection.)

8.0 Sample Collection, Preservation and Storage

See also Method 320 of this appendix.

8.1 Pretest. A screening test is ideal for obtaining proper data that can be used for preparing analytical program files. Information from literature surveys and source personnel is also acceptable. Information about the sampling location and gas stream composition is required to determine the optimum sampling system configuration for measuring HCl. Determine the percent moisture of the kiln gas by Method 4 of appendix A to part 60 of this chapter or by performing a wet bulb/dry bulb measurement. Perform a preliminary traverse of the sample duct or stack and select the sampling point(s). Acquire an initial spectrum and determine the optimum operational pathlength of the instrument.

8.2 Leak-Check. See Method 320 of this appendix, section 8.2 for direction on performing leak-checks.

8.3 Background Spectrum. See Method 320 of this appendix, section 8.5 for direction in background spectral acquisition.

8.4 Pre-Test Calibration Transfer Standard (Direct Instrument Calibration). See Method 320 of this appendix, section 8.3 for direction in CTS spectral acquisition.

8.5 Pre-Test System Calibration. See Method 320 of this appendix, sections 8.6.1 through 8.6.2 for direction in performing system calibration.

8.6 Sampling.

8.6.1 Extractive System. An extractive system maintained at 180 °C (360 °F) or higher which is capable of directing a total flow of at least 12 L/min to the sample cell is required (References 1 and 2). Insert the probe into the duct or stack at a point representing the average volumetric flow rate and 25 percent of the cross sectional area. Co-locate an appropriate flow monitoring device with the sample probe so that the flow rate is recorded at specified time intervals during emission testing (*e.g.,* differential pressure measurements taken every 10 minutes during each run).

8.6.2 Batch Samples. Evacuate the absorbance cell to 5 Torr (or less) absolute pressure before taking first sample. Fill the cell with kiln gas to ambient pressure and record the infrared spectrum, then evacuate the cell until there is no further evidence of infrared absorption. Repeat this procedure, collecting a total of six separate sample spectra within a 1-hour period.

8.6.3 Continuous Flow Through Sampling. Purge the FTIR cell with kiln gas for a time period sufficient to equilibrate the entire sampling system and FTIR gas cell. The time required is a function of the mechanical response time of the system (determined by performing the system calibration with the CTS gas or equivalent), and by the chemical reactivity of the target analytes. If the effluent target analyte concentration is not variable, observation of the spectral up-date of the flowing gas sample should be performed until equilibration of the sample is achieved. Isolate the gas cell from the sample flow by directing the purge flow to vent. Record the spectrum and pressure of the sample gas. After spectral acquisition, allow the sample gas to purge the cell with at least three volumes of kiln gas. The time required to adequately purge the cell with the required volume of gas is a function of (1) cell volume, (2) flow rate through the cell, and (3) cell design. It is important that the gas introduction and vent for the FTIR cell provides a complete purge through the cell.

8.6.4 Continuous Sampling. In some cases it is possible to collect spectra continuously while the FTIR cell is purged with sample gas. The sample integration time, t_{ss}, the sample flow rate through the gas cell, and the sample integration time must be chosen so that the collected data consist of at least 10 spectra with each spectrum being of a separate cell volume of flue gas. Sampling in this manner may only be performed if the native source analyte concentrations do not affect the test results.

8.7 Sample Conditioning

8.7.1 High Moisture Sampling. Kiln gas emitted from wet process cement kilns may contain 3- to 40 percent moisture. Zinc selenide windows or the equivalent should be used when attempting to analyze hot/wet kiln gas under these conditions to prevent dissolution of water soluble window materials (*e.g.,* KBr).

8.7.2 Sample Dilution. The sample may be diluted using an in-stack dilution probe, or an external dilution device provided that the sample is not diluted below the instrument's quantification range. As an alternative to using a dilution probe, nitrogen may be dynamically spiked into the effluent stream in the same manner as analyte spiking. A constant dilution rate shall be maintained throughout the measurement process. It is critical to measure and verify the exact dilution ratio when using a dilution probe or the nitrogen spiking approach. Calibrating the system with a calibration gas containing an appropriate tracer compound will allow determination of the dilution ratio for most measurement systems. The tester shall specify the procedures used to determine the dilution ratio, and include these calibration results in the report.

8.8 Sampling QA, Data Storage and Reporting. See the FTIR Protocol. Sample integration times shall be sufficient to achieve the required signal-to-noise ratio, and all sample spectra should have unique file names. Two copies of sample interferograms and processed spectra will be stored on separate computer media. For each sample spectrum the analyst must document the sampling conditions, the sampling time (while the cell was being filled), the time the spectrum was recorded, the instrumental conditions (path length, temperature, pressure, resolution, integration time), and the spectral file name. A hard copy of these data must be maintained until the test results are accepted.

8.9 Signal Transmittance. Monitor the signal transmittance through the instrumental system. If signal transmittance (relative to the background) drops below 95 percent in any spectral region where the sample does not absorb infrared energy, then a new background spectrum must be obtained.

8.10 Post-test CTS. After the sampling run completion, record the CTS spectrum. Analysis of the spectral band area used for quantification from pre-and post-test CTS spectra should agree to within ±5 percent or corrective action must be taken.

8.11 Post-test QA. The sample spectra shall be inspected immediately after the run to verify that the gas matrix composition was close to the assumed gas matrix, (this is necessary to account for the concentrations of the interferants for use in the analytical analysis programs), and to confirm that the sampling and instrumental parameters were appropriate for the conditions encountered.

9.0 Quality Control

Use analyte spiking to verify the effectiveness of the sampling system for the target compounds in the actual kiln gas matrix. QA spiking shall be performed before and after each sample run. QA spiking shall be performed after the pre-and post-test CTS direct and system calibrations. The system biases calculated from the pre-and post-test dynamic analyte spiking shall be within ±30 percent for the spiked surrogate analytes for the measurements to be considered valid. See sections 9.3.1 through 9.3.2 for the requisite calculations. Measurement of the undiluted spike (direct-to-cell measurement) involves sending dry, spike gas to the FTIR cell, filling the cell to 1 atmosphere and obtaining the spectrum of this sample. The direct-to-cell measurement should be performed before each analyte spike so that the recovery of the dynamically spiked analytes may be calculated. Analyte spiking is only effective for assessing the integrity of the sampling system when the concentration of HCl in the source does not vary substantially. Any attempt to quantify an analyte recovery in a variable concentration matrix will result in errors in the expected concentration of the spiked sample. If the kiln gas target analyte concentrations vary by more than ±5 percent (or 5 ppm, whichever is greater) in the time required to acquire a sample spectrum, it may be necessary to: (1) use a dual sample probe approach, (2) use two independent FTIR measurement systems, (3) use alternate QA/QC procedures, or (4) postpone testing until stable emission concentrations are achieved. (See section 9.2.3 of this method).

It is recommended that a laboratory evaluation be performed before attempting to employ this method under actual field conditions. The laboratory evaluation shall include (1) performance of all applicable calculations in section 4 of the FTIR Protocol; (2) simulated analyte spiking experiments in dry (ambient) and humidified sample matrices using HCl; and (3) performance of bias (recovery) calculations from analyte spiking experiments. It is not necessary to perform a laboratory evaluation before every field test. The purpose of the laboratory study is to demonstrate that the actual instrument and sampling system configuration used in field testing meets the requirements set forth in this method.

9.1 Spike Materials. Perform analyte spiking with an HCl standard to demonstrate the integrity of the sampling system.

9.1.1 An HCl standard of approximately 50 ppm in a balance of ultra pure nitrogen is recommended. The SF_6 (tracer) concentration shall be 2 to 5 ppm depending upon the measurement pathlength. The spike ratio (spike flow/total flow) shall be no greater than 1:10, and an ideal spike concentration should approximate the native effluent concentration.

9.1.2 The ideal spike concentration may not be achieved because the target concentration cannot be accurately predicted prior to the field test, and limited calibration standards will be available during testing. Therefore, practical constraints must be applied that allow the tester to spike at an anticipated concentration. For these tests, the analyte concentration contributed by the HCl standard spike should be 1 to 5 ppm or should more closely approximate the native concentration if it is greater.

9.2 Spike Procedure

9.2.1 A spiking/sampling apparatus is shown in Figure 2. Introduce the spike/tracer gas mixture at a constant flow (±2 percent) rate at approximately 10 percent of the total sample flow. (For example, introduce the surrogate spike at 1 L/min ±20 cc/min, into a total sample flow rate of 10 L/min). The spike must be pre-heated before introduction into the sample matrix to prevent a localized condensation of the gas stream at the spike introduction point. A heated sample transport line(s) containing multiple transport tubes within the heated bundle may be used to spike gas up through the sampling system to the spike introduction point. Use a calibrated flow device (*e.g.,* mass flow meter/controller), to monitor the spike flow as indicated by a calibrated flow meter or controller, or alternately, the SF_6 tracer ratio may be calculated from the direct measurement and the diluted measurement. It is often desirable to use the tracer approach in calculating the spike/total flow ratio because of the difficulty in accurately measuring hot/wet total flow. The tracer technique has been successfully used in past validation efforts (Reference 1).

9.2.2 Perform a direct-to-cell measurement of the dry, undiluted spike gas. Introduce the spike directly to the FTIR cell, bypassing the sampling system. Fill cell to 1 atmosphere and collect the spectrum of this sample. Ensure that the spike gas has

equilibrated to the temperature of the measurement cell before acquisition of the spectra. Inspect the spectrum and verify that the gas is dry and contains negligible CO_2. Repeat the process to obtain a second direct-to-cell measurement. Analysis of spectral band areas for HCl from these duplicate measurements should agree to within ±5 percent of the mean.

9.2.3 Analyte Spiking. Determine whether the kiln gas contains native concentrations of HCl by examination of preliminary spectra. Determine whether the concentration varies significantly with time by observing a continuously up-dated spectrum of sample gas in the flow-through sampling mode. If the concentration varies by more than ±5 percent during the period of time required to acquire a spectra, then an alternate approach should be used. One alternate approach uses two sampling lines to convey sample to the gas distribution manifold. One of the sample lines is used to continuously extract unspiked kiln gas from the source. The other sample line serves as the analyte spike line. One FTIR system can be used in this arrangement. Spiked or unspiked sample gas may be directed to the FTIR system from the gas distribution manifold, with the need to purge only the components between the manifold and the FTIR system. This approach minimizes the time required to acquire an equilibrated sample of spiked or unspiked kiln gas. If the source varies by more than ±5 percent (or 5 ppm, whichever is greater) in the time it takes to switch from the unspiked sample line to the spiked sample line, then analyte spiking may not be a feasible means to determine the effectiveness of the sampling system for the HCl in the sample matrix. A second alternative is to use two completely independent FTIR measurement systems. One system would measure unspiked samples while the other system would measure the spiked samples. As a last option, (where no other alternatives can be used) a humidified nitrogen stream may be generated in the field which approximates the moisture content of the kiln gas. Analyte spiking into this humidified stream can be employed to assure that the sampling system is adequate for transporting the HCl to the FTIR instrumentation.

9.2.3.1 Adjust the spike flow rate to approximately 10 percent of the total flow by metering spike gas through a calibrated mass flowmeter or controller. Allow spike flow to equilibrate within the sampling system before analyzing the first spiked kiln gas samples. A minimum of two consecutive spikes are required. Analysis of the spectral band area used for quantification should agree to within ±5 percent or corrective action must be taken.

9.2.3.2 After QA spiking is completed, the sampling system components shall be purged with nitrogen or dry air to eliminate traces of the HCl compound from the sampling system components. Acquire a sample spectra of the nitrogen purge to verify the absence of the calibration mixture.

9.2.3.3 Analyte spiking procedures must be carefully executed to ensure that meaningful measurements are achieved. The requirements of sections 9.2.3.3.1 through 9.2.3.3.4 shall be met.

9.2.3.3.1 The spike must be in the vapor phase, dry, and heated to (or above) the kiln gas temperature before it is introduced to the kiln gas stream.

9.2.3.3.2 The spike flow rate must be constant and accurately measured.

9.2.3.3.3 The total flow must also be measured continuously and reliably or the dilution ratio must otherwise be verified before and after a run by introducing a spike of a non-reactive, stable compound (i.e., tracer).

9.2.3.3.4 The tracer must be inert to the sampling system components, not contained in the effluent gas, and readily detected by the analytical instrumentation. Sulfur hexafluoride (SF_6) has been used successfully (References 1 and 2) for this purpose.

9.3 Calculations

9.3.1 Recovery. Calculate the percent recovery of the spiked analytes using equations 1 and 2.

$\%R = (S_m/C_e) \times 100$ (Eq. 321–1).

S_m = Mean concentration of the analyte spiked effluent samples (observed).
C_e = Expected concentration of the spiked samples (theoretical).
$C_e = D_f C_s + S_u (1 - D_f)$ (Eq. 321–2)
D_f = dilution Factor (Spike flow/Total flow). total flow = spike flow plus effluent flow.
C_s = cylinder concentration of spike gas.
S_u = native concentration of analytes in unspiked samples.

The spike dilution factor may be confirmed by measuring the total flow and the spike flow directly. Alternately, the spike dilution can be verified by comparing the concentration of the tracer compound in the spiked samples (diluted) to the tracer concentration in the direct (undiluted) measurement of the spike gas.

If SF_6 is the tracer gas, then

$D_f = [SF_6]_{spike}/ [SF_6]_{direct}$ (Eq. 321–3)
$[SF_6]_{spike}$ = the diluted SF6 concentration measured in a spiked sample.
$[SF_6]_{direct}$ = the SF_6 concentration measured directly.

9.3.2 Bias. The bias may be determined by the difference between the observed spike value and the expected response (i.e., the equivalent concentration of the spiked material plus the analyte concentration adjusted for spike dilution). Bias is defined by section 6.3.1 of EPA Method 301 of this (Reference 8) as,

$B = S_m — C_e$ (Eq. 321–4)
where:
B = Bias at spike level.
S_m = Mean concentration of the analyte spiked samples.
C_e = Expected concentration of the analyte in spiked samples.

Acceptable recoveries for analyte spiking are ±30 percent. Application of correction factors to the data based upon bias and recovery calculations is subject to the approval of the Administrator.

10.0 Calibration and Standardization

10.1 Calibration transfer standards (CTS). The EPA Traceability Protocol gases or NIST traceable standards, with a minimum accuracy of ±2 percent shall be used. For

other requirements of the CTS, see the FTIR Protocol section 4.5.

10.2   Signal-to-Noise Ratio (S/N). The S/N shall be less than the minimum acceptable measurement uncertainty in the analytical regions to be used for measuring HCl.

10.3   Absorbance Pathlength. Verify the absorbance path length by comparing CTS spectra to reference spectra of the calibration gas(es).

10.4   Instrument Resolution. Measure the line width of appropriate CTS band(s) to verify instrumental resolution.

10.5   Apodization Function. Choose the appropriate apodization function. Determine any appropriate mathematical transformations that are required to correct instrumental errors by measuring the CTS. Any mathematical transformations must be documented and reproducible. Reference 9 provides additional information about FTIR instrumentation.

11.0   Analytical Procedure

A full description of the analytical procedures is given in sections 4.6—4.11, sections 5, 6, and 7, and the appendices of the FTIR Protocol. Additional description of quantitative spectral analysis is provided in References 10 and 11.

12.0   Data Analysis and Calculations

Data analysis is performed using appropriate reference spectra whose concentrations can be verified using CTS spectra. Various analytical programs (References 10 and 11) are available to relate sample absorbance to a concentration standard. Calculated concentrations should be verified by analyzing spectral baselines after mathematically subtracting scaled reference spectra from the sample spectra. A full description of the data analysis and calculations may be found in the FTIR Protocol (sections 4.0, 5.0, 6.0 and appendices).

12.1   Calculated concentrations in sample spectra are corrected for differences in absorption pathlength between the reference and sample spectra by

$$C_{corr} = (L_r/L_s) \times (T_s/T_r) \times (C_{calc}) \quad (Eq.\ 321\text{--}5)$$

Where:

C_{corr} = The pathlength corrected concentration.

C_{calc} = The initial calculated concentration (output of the multicomponent analysis program designed for the compound).

L_r = The pathlength associated with the reference spectra.

L_s = The pathlength associated with the sample spectra.

T_s = The absolute temperature (K) of the sample gas.

T_r = The absolute temperature (K) at which reference spectra were recorded.

12.2   The temperature correction in equation 5 is a volumetric correction. It does not account for temperature dependence of rotational-vibrational relative line intensities. Whenever possible, the reference spectra used in the analysis should be collected at a temperature near the temperature of the FTIR cell used in the test to minimize the calculated error in the measurement (FTIR Protocol, appendix D). Additionally, the analytical region chosen for the analysis should be sufficiently broad to minimize errors caused by small differences in relative line intensities between reference spectra and the sample spectra.

13.0   Method Performance

A description of the method performance may be found in the FTIR Protocol. This method is self validating provided the results meet the performance specification of the QA spike in sections 9.0 through 9.3 of this method.

14.0   Pollution Prevention

This is a gas phase measurement. Gas is extracted from the source, analyzed by the instrumentation, and discharged through the instrument vent.

15.0   Waste Management

Gas standards of HCl are handled according to the instructions enclosed with the material safety data sheet.

16.0   References

1.   ''Laboratory and Field Evaluation of a Methodology for Determination of Hydrogen Chloride Emissions From Municipal and Hazardous Waste Incinerators,'' S. C. Steinsberger and J. H. Margeson. Prepared for U.S. Environmental Protection Agency, Research Triangle Park, NC. NTIS Report No. PB89–220586. (1989).

2.   ''Evaluation of HCl Measurement Techniques at Municipal and Hazardous Waste Incinerators,'' S.A. Shanklin, S.C. Steinsberger, and L. Cone, Entropy, Inc. Prepared for U.S. Environmental Protection Agency, Research Triangle Park, NC. NTIS Report No. PB90–221896. (1989).

3.   ''Fourier Transform Infrared (FTIR) Method Validation at a Coal Fired-Boiler,'' Entropy, Inc. Prepared for U.S. Environmental Protection Agency, Research Triangle Park, NC. EPA Publication No. EPA–454/R95–004. NTIS Report No. PB95–193199. (1993).

4.   ''Field Validation Test Using Fourier Transform Infrared (FTIR) Spectrometry To Measure Formaldehyde, Phenol and Methanol at a Wool Fiberglass Production Facility.'' Draft. U.S. Environmental Protection Agency Report, Entropy, Inc., EPA Contract No. 68D20163, Work Assignment I–32.

5.   Kinner, L.L., Geyer, T.G., Plummer, G.W., Dunder, T.A., Entropy, Inc. ''Application of FTIR as a Continuous Emission Monitoring System.'' Presentation at 1994 International Incineration Conference, Houston, Tx. May 10, 1994.

6.   ''Molecular Vibrations; The Theory of Infrared and Raman Vibrational Spectra,'' E. Bright Wilson, J.C. Decius, and P.C. Cross, Dover Publications, Inc., 1980. For a less intensive treatment of molecular rotational-vibrational spectra see, for example, ''Physical Chemistry,'' G.M. Barrow, chapters 12, 13, and 14, McGraw Hill, Inc., 1979.

7.   ''Laboratory and Field Evaluations of Ammonium Chloride Interference in Method 26,'' U.S. Environmental Protection Agency Report, Entropy, Inc., EPA Contract No. 68D20163, Work Assignment No. I–45.

8.   40 CFR 63, A. Method 301—Field Validation of Pollutant Measurement Methods from Various Waste Media.

9.   ''Fourier Transform Infrared Spectrometry,'' Peter R. Griffiths and James de Haseth, Chemical Analysis, 83, 16–25,(1986), P.J. Elving, J.D. Winefordner and I.M. Kolthoff (ed.), John Wiley and Sons.

10.   ''Computer-Assisted Quantitative Infrared Spectroscopy,'' Gregory L. McClure (ed.), ASTM Special Publication 934 (ASTM), 1987.

11.   ''Multivariate Least-Squares Methods Applied to the Quantitative Spectral Analysis of Multicomponent Mixtures,'' Applied Spectroscopy, 39(10), 73–84, 1985.
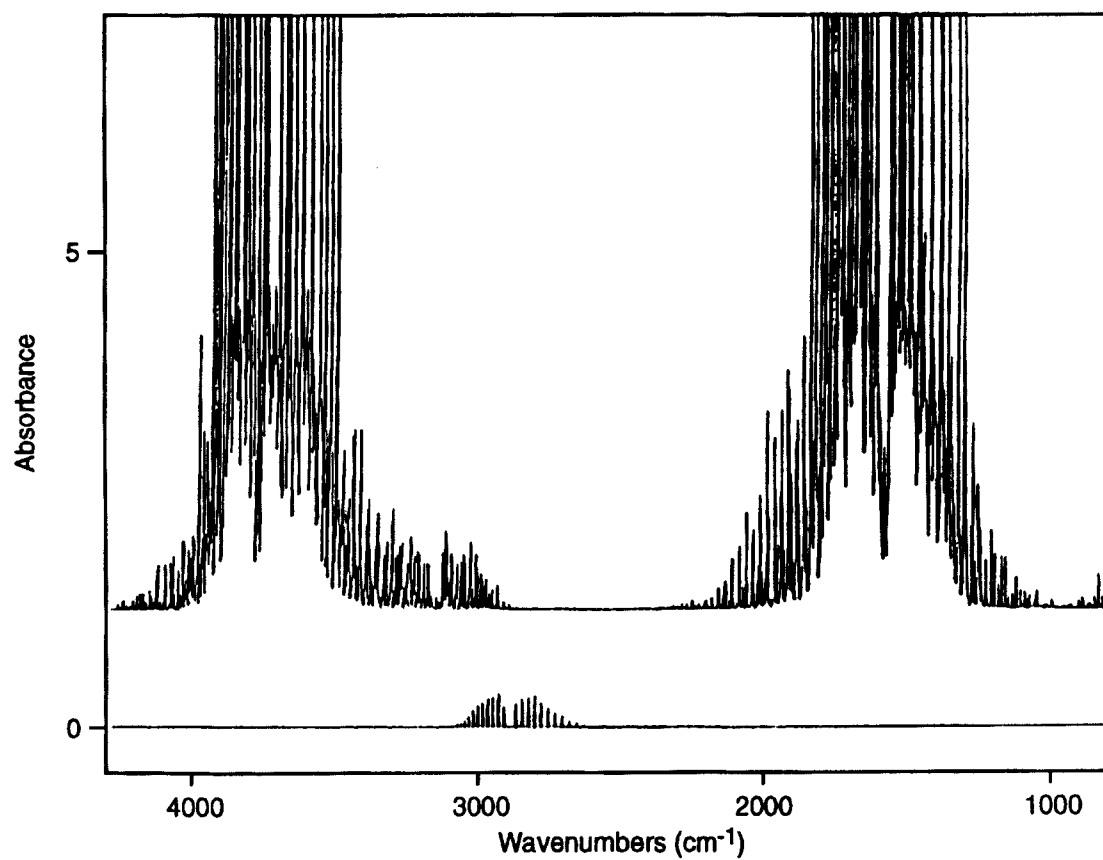
Top, water vapor (194hsub); Bottom, HCl at 11.4 (ppm-M)/K.
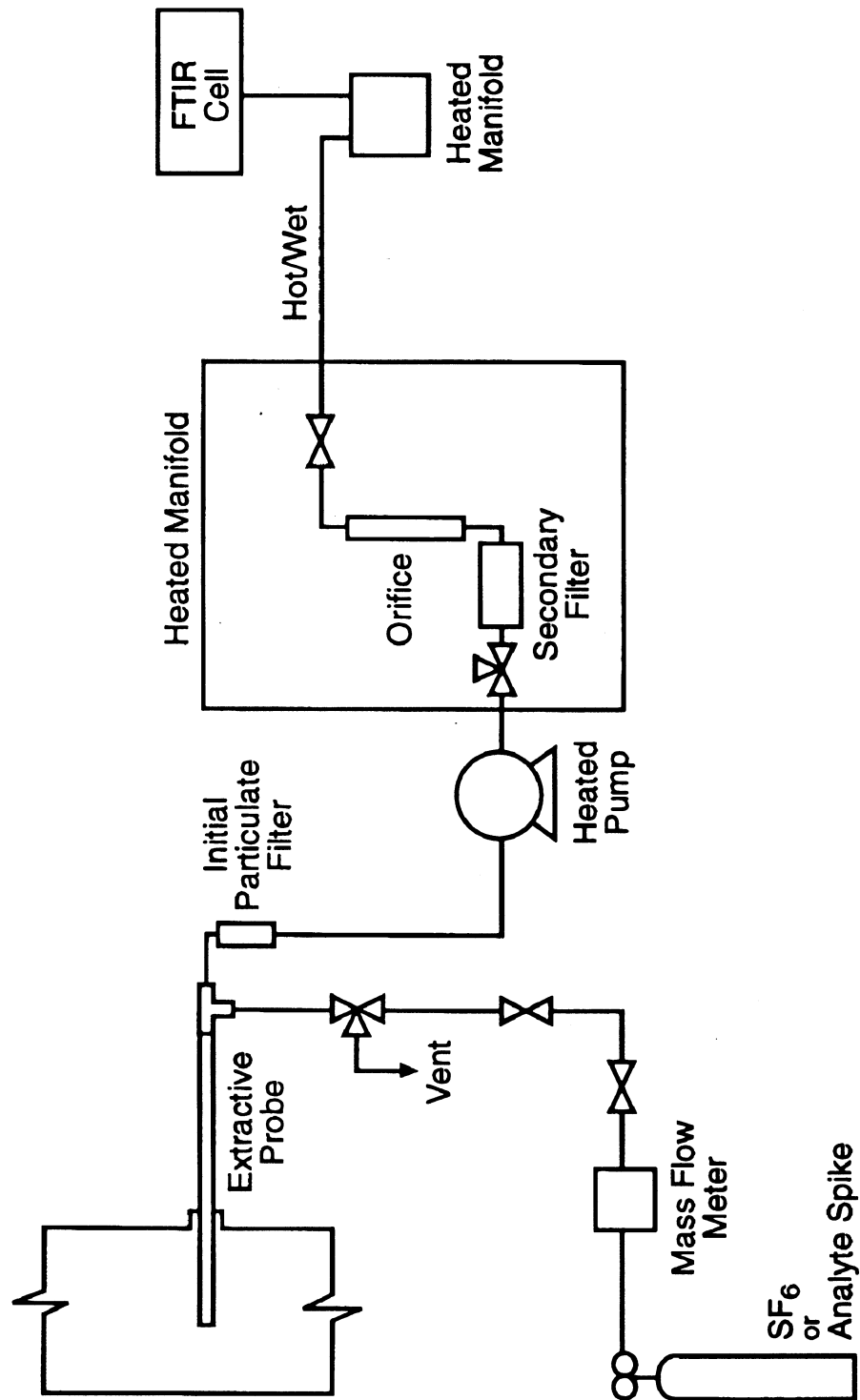
Figure 1. FTIR Spectra of HCl and Water.

Figure 2. FTIR Sampling/Spiking System.

Method 322—Measurement of Hydrogen Chloride Emissions From Portland Cement Kilns by GFCIR

1.0 Applicability and Principle

1.1 Applicability. This method is applicable to the determination of hydrogen chloride (HCl) concentrations in emissions from portland cement kilns. This is an instrumental method for the measurement of HCl using an extractive sampling system and an infrared (IR) gas-filter correlation (GFC) analyzer. This method is intended to provide the cement industry with a direct interface instrumental method. A procedure for analyte spiking is included for quality assurance. This method is considered to be self-validating provided that the requirements in section 9 of this method are followed.

1.2 Principle. A gas sample is continuously extracted from a stack or duct over the test period using either a source-level hot/wet extractive subsystem or a dilution extractive subsystem. A nondispersive infrared gas filter correlation (NDIR–GFC) analyzer is specified for the measurement of HCl in the sample. The total measurement system is comprised of the extractive subsystem, the analyzer, and the data acquisition subsystem. Test system performance specifications are included in this method to provide for the collection of accurate, reproducible data.

1.3 Test System Operating Range. The measurement range (span) of the test system shall include the anticipated HCl concentrations of the effluent and spiked samples. The range should be selected so that the average of the effluent measurements is between 25 and 75 percent of span. If at any time during a test run, the effluent concentration exceeds the span value of the test system, the run shall be considered invalid.

2.0 Summary of Method

2.1 Sampling and Analysis. Kiln gas is continuously extracted from the stack or duct using either a source level, hot/wet extractive system, or an in-situ dilution probe or heated out-of-stack dilution system. The sample is then directed by a heated sample line maintained above 350 °F to a GFC analyzer having a range appropriate to the type of sampling system. The gas filter correlation analyzer incorporates a gas cell filled with HCl. This gas cell is periodically moved into the path of an infrared measurement beam of the instrument to filter out essentially all of the HCl absorption wavelengths. Spectral filtering provides a reference from which the HCl concentration of the sample can be determined. Interferences are minimized in the analyzer by choosing a spectral band over which compounds such as CO_2 and H_2O either do not absorb significantly or do not match the spectral pattern of the HCl infrared absorption.

2.2 Operator Requirements. The analyst must be familiar with the specifications and test procedures of this method and follow them in order to obtain reproducible and accurate data.

3.0 Definitions

3.1 Measurement System. The total equipment required for the determination of gas concentration. The measurement system consists of the following major subsystems:

3.1.1 Sample Interface. That portion of a system used for one or more of the following: sample acquisition, sample transport, sample conditioning, or protection of the analyzers from the effects of the stack gas.

3.1.2 Gas Analyzer. That portion of the system that senses the gas to be measured and generates an output proportional to its concentration.

3.1.3 Data Recorder. A strip chart recorder, analog computer, or digital recorder for recording measurement data from the analyzer output.

3.2 Span. The upper limit of the gas concentration measurement range displayed on the data recorder.

3.3 Calibration Gas. A known concentration of a gas in an appropriate diluent gas (i.e., N_2).

3.4 Analyzer Calibration Error. The difference between the gas concentration exhibited by the gas analyzer and the known concentration of the calibration gas when the calibration gas is introduced directly to the analyzer.

3.5 Sampling System Bias. The sampling system bias is the difference between the gas concentrations exhibited by the measurement system when a known concentration gas is introduced at the outlet of the sampling probe and the known value of the calibration gas.

3.6 Response Time. The amount of time required for the measurement system to display 95 percent of a step change in gas concentration on the data recorder.

3.7 Calibration Curve. A graph or other systematic method of establishing the relationship between the analyzer response and the actual gas concentration introduced to the analyzer.

3.8 Linearity. The linear response of the analyzer or test system to known calibration inputs covering the concentration range of the system.

3.9 Interference Rejection. The ability of the system to reject the effect of interferences in the analytical measurement processes of the test system.

4.0 Interferences

4.1 Sampling System Interferences. An important consideration in measuring HCl using an extractive measurement system is to ensure that a representative kiln gas sample is delivered to the gas analyzer. A sampling system interferant is a factor that inhibits an analyte from reaching the analytical instrumentation. Condensed water vapor is a strong sampling system interferant for HCl and other water soluble compounds. ''Cold spots'' in the sampling system can allow water vapor in the sample to condense resulting in removal of HCl from the sample stream. The extent of HCl sampling system bias depends on concentrations of potential interferants, moisture content of the gas stream, temperature of the gas stream, temperature of sampling system components, sample flow rate, and reactivity of HCl with other species in the gas stream. For measuring HCl in a wet gas stream, the temperatures of the gas stream and sampling system components and the sample flow rate are of primary importance. In order to prevent problems with condensation in the sampling system, these parameters must be closely monitored.

4.1.1 System Calibration Checks. Performing these calibration checks where HCl calibration gas is injected through the entire system both before and after each test run demonstrates the integrity of the sampling system and capability of the analyzer for measuring this water soluble and otherwise unstable compound under ideal conditions (i.e., HCl in N_2).

4.1.2 Analyte Spiking Checks. For analyte spiking checks, HCl calibration gas is quantitatively added to the sample stream at a point upstream of the particulate filter and all other sample handling components both before and after each test run. The volume of HCl spike gas should not exceed 10 percent of the total sample volume so that the sample matrix is relatively unaffected. Successfully performing these checks demonstrates the integrity of the sampling system for measuring this water soluble and reactive compound under actual sample matrix conditions. Successfully performing these checks also demonstrates the adequacy of the interference rejection capability of the analyzer. (See section 9.3 of this method.)

4.2 Analytical Interferences. Analytical interferences are reduced by the GFC spectroscopic technique required by the method. The accuracy of HCl measurements provided by some GFC analyzers is known to be sensitive to the moisture content of the sample. This must be taken into account in order to acquire accurate results. These analyzers must be calibrated for the specific moisture content of the samples.

5.0 Safety

This method may involve sampling at locations having high positive or negative pressures, or high concentrations of hazardous or toxic pollutants, and cannot address all safety problems encountered under these diverse sampling conditions. It is the responsibility of the tester(s) to ensure proper safety and health practices, and to determine the applicability of regulatory limitations before performing this test method. Because HCl is a respiratory irritant, it is advisable to limit exposure to this compound.

6.0 Equipment and Supplies.

(Note: Mention of company or product names does not constitute endorsement by the U. S. Environmental Protection Agency.)

6.1 Measurement System. Use any GFC measurement system for HCl that meets the specifications of this method. All sampling system components must be maintained above the kiln gas temperature, when possible, or at least 350 °F. The length of sample transport line should be minimized and sampling rate should be as high as possible to minimize adsorption of HCl. The essential components of the measurement system are described in sections 6.1.1 through 6.1.12.

6.1.1 Sample Probe. Glass, stainless steel, Hastalloy™, or equivalent, of sufficient

length to traverse the sample points. The sampling probe shall be heated to a minimum of 350 °F to prevent condensation. Dilution extractive systems must use a dilution ratio such that the average diluted concentrations are between 25 to 75 percent of the selected measurement range of the analyzer.

6.1.2   Calibration Valve Assembly. Use a heated, three-way valve assembly, or equivalent, for selecting either sample gas or introducing calibration gases to the measurement system or introducing analyte spikes into the measurement system at the outlet of the sampling probe before the primary particulate filter.

6.1.3   Particulate Filter. A coarse filter or other device may be placed at the inlet of the probe for removal of large particulate (10 microns or greater). A heated (Balston® or equivalent) filter rated at 1 micron is necessary for primary particulate removal, and shall be placed immediately after the heated probe. The filter/filter holder shall be maintained at 350 °F or a higher temperature. Additional filters at the inlet of the gas analyzer may be used to prevent accumulation of particulate material in the measurement system and extend the useful life of components. All filters shall be fabricated of materials that are nonreactive with HCl. Some types of glass filters are known to react with HCl.

6.1.4   Sample Transport Lines. Stainless steel or polytetrafluoroethylene (PTFE) tubing shall be heated to a minimum temperature of 350 °F (sufficient to prevent condensation and to prevent HCl and NH_3 from combining into ammonium chloride in the sampling system) to transport the sample gas to the gas analyzer.

6.1.5   Sample Pump. Use a leak-free pump to pull the sample gas through the system at a flow rate sufficient to minimize the response time of the measurement system. The pump components that contact the sample must be heated to a temperature greater than 350 °F and must be constructed of a material that is nonreactive to HCl.

6.1.6   Sample Flow Rate Control. A sample flow rate control valve and rotameter, or equivalent, must be used to maintain a constant sampling rate within ±10 percent. These components must be heated to a temperature greater than 350 °F. (**Note**: The tester may elect to install a back-pressure regulator to maintain the sample gas manifold at a constant pressure in order to protect the analyzer(s) from over-pressurization, and to minimize the need for flow rate adjustments.)

6.1.7   Sample Gas Manifold. A sample gas manifold, heated to a minimum of 350 °F, is used to divert a portion of the sample gas stream to the analyzer and the remainder to the by-pass discharge vent. The sample gas manifold should also include provisions for introducing calibration gases directly to the analyzer. The manifold must be constructed of material that is nonreactive to the gas being sampled.

6.1.8   Gas Analyzer. Use a nondispersive infrared analyzer utilizing the gas filter correlation technique to determine HCl concentrations. The analyzer shall meet the applicable performance specifications of

section 8.0 of this method. (**Note:** Housing the analyzer in a clean, thermally-stable, vibration free environment will minimize drift in the analyzer calibration.) The analyzer (system) shall be designed so that the response of a known calibration input shall not deviate by more than ±3 percent from the expected value. The analyzer or measurement system manufacturer may provide documentation that the instrument meets this design requirement. Alternatively, a known concentration gas standard and calibration dilution system meeting the requirements of Method 205 of appendix M to part 51 of this chapter, ''Verification of Gas Dilution Systems for Field Calibrations'' (or equivalent procedure), may be used to develop a multi-point calibration curve over the measurement range of the analyzer.

6.1.9   Gas Regulators. Single stage regulator with cross purge assembly that is used to purge the CGA fitting and regulator before and after use. (This purge is necessary to clear the calibration gas delivery system of ambient water vapor after the initial connection is made, or after cylinder changeover, and will extend the life of the regulator.) Wetted parts are 316 stainless steel to handle corrosive gases.

6.1.10   Data Recorder. A strip chart recorder, analog computer, or digital recorder, for recording measurement data. The data recorder resolution (i.e., readability) shall be 0.5 percent of span. Alternatively, a digital or analog meter having a resolution of 0.5 percent of span may be used to obtain the analyzer responses and the readings may be recorded manually. If this alternative is used, the readings shall be obtained at equally-spaced intervals over the duration of the sampling run. For sampling run durations of less than 1 hour, measurements at 1-minute intervals or a minimum of 30 measurements, whichever is less restrictive, shall be obtained. For sampling run durations greater than 1 hour, measurements at 2-minute intervals or a minimum of 96 measurements, whichever is less restrictive, shall be obtained.

6.1.11   Mass Flow Meters/Controllers. A mass flow meter having the appropriate calibrated range and a stated accuracy of ±2 percent of the measurement range is used to measure the HCl spike flow rate. This device must be calibrated with the major component of the calibration spike gas (e.g., nitrogen) using an NIST traceable bubble meter or equivalent. When spiking HCl, the mass flow meter/controller should be thoroughly purged before and after introduction of the gas to prevent corrosion of the interior parts.

6.1.12   System Flow Measurement. A measurement device or procedure to determine the total flow rate of sample gas within the measurement system. A rotameter, or mass flow meter calibrated relative to a laboratory standard to within ±2 percent of the measurement value at the actual operating temperature, moisture content, and sample composition (molecular weight) is acceptable. A system which ensures that the total sample flow rate is constant within ±2 percent and which relies on an intermittent measurement of the actual flow rate (e.g., calibrated gas meter) is also acceptable.

6.2   HCl Calibration Gases. The calibration gases for the gas analyzer shall be HCl in N_2.

Use at least three calibration gases as specified below:

6.2.1   High-Range Gas. Concentration equivalent to 80 to 100 percent of the span.

6.2.2   Mid-Range Gas. Concentration equivalent to 40 to 60 percent of the span.

6.2.3   Zero Gas. Concentration of less than 0.25 percent of the span. Purified ambient air may be used for the zero gas by passing air through a charcoal filter or through one or more impingers containing a solution of 3 percent H_2O_2.

6.2.4   Spike Gas. A calibration gas of known concentration (typically 100 to 200 ppm) used for analyte spikes in accordance with the requirements of section 9.3 of this method.

7.0   Reagents and Standards

7.1   Hydrogen Chloride. Hydrogen Chloride is a reactive gas and is available in steel cylinders from various commercial gas vendors. The stability is such that it is not possible to purchase a cylinder mixture whose HCl concentration can be certified at better than ±5 percent. The stability of the cylinder may be monitored over time by periodically analyzing cylinder samples. The cylinder gas concentration must be verified within 1 month prior to the use of the calibration gas. Due to the relatively high uncertainty of HCl calibration gas values, difficulties may develop in meeting the performance specifications if the mid-range and high-range calibration gases are not consistent with each other. Where problems are encountered, the consistency of the test gas standards may be determined: (1) By comparing analyzer responses for the test gases with the responses to additional certified calibration gas standards, (2) by reanalysis of the calibration gases in accordance with sections 7.2.1 or 7.2.2 of this method, or (3) by other procedures subject to the approval of EPA.

7.2   Calibration Gas Concentration Verification. There are two alternatives for establishing the concentrations of calibration gases. Alternative No. 1 is preferred.

7.2.1   Alternative No. 1. The value of the calibration gases may be obtained from the vendor's certified analysis within 1 month prior to the test. Obtain a certification from the gas manufacturer that identifies the analytical procedures and date of certification.

7.2.2   Alternative No. 2. Perform triplicate analyses of the gases using Method 26 of A to part 60 of this chapter. Obtain gas mixtures with a manufacturer's tolerance not to exceed ±5 percent of the tag value. Within 1 month of the field test, analyze each of the calibration gases in triplicate using Method 26 of appendix A to part 60 of this chapter. The tester must follow all of the procedures in Method 26 (e.g., use midget impingers, heated Pallflex TX40H175 filter (TFE-glass mat), etc. if this analysis is performed. Citation 3 in section 13 of this method describes procedures and techniques that may be used for this analysis. Record the results on a data sheet. Each of the individual HCl analytical results for each calibration gas shall be within 5 percent (or 5 ppm, whichever is greater) of the triplicate set average; otherwise, discard the entire set and

repeat the triplicate analyses. If the average of the triplicate analyses is within 5 percent of the calibration gas manufacturer's cylinder tag value, use the tag value; otherwise, conduct at least three additional analyses until the results of six consecutive runs agree within 5 percent (or 5 ppm, whichever is greater) of the average. Then use this average for the cylinder value.

7.3 Calibration Gas Dilution Systems. Sample flow rates of approximately 15 L/min are typical for extractive HCl measurement systems. These flow rates coupled with response times of 15 to 30 minutes will result in consumption of large quantities of calibration gases. The number of cylinders and amount of calibration gas can be reduced by the use of a calibration gas dilution system in accordance with Method 205 of appendix M to part 51 of this chapter, ''Verification of Gas Dilution Systems for Field Instrument Calibrations.'' If this option is used, the tester shall also introduce an undiluted calibration gas approximating the effluent HCl concentration during the initial calibration error test of the measurement system as a quality assurance check.

8.0 Test System Performance Specifications

8.1 Analyzer Calibration Error. This error shall be less than ±5 percent of the emission standard concentration or ±1 ppm, (whichever is greater) for zero, mid-, and high-range gases.

8.2 Sampling System Bias. This bias shall be less than ±7.5 percent of the emission standard concentration or ±1.5 ppm (whichever is greater) for zero and mid-range gases.

8.3 Analyte Spike Recovery. This recovery shall be between 70 to 130 percent of the expected concentration of spiked samples calculated with the average of the before and after run spikes.

9.0 Sample Collection, Preservation, and Storage

9.1 Pretest. Perform the procedures of sections 9.1.1 through 9.1.3.3 of this method before measurement of emissions (procedures in section 9.2 of this method). It is important to note that after a regulator is placed on an HCl gas cylinder valve, the regulator should be purged with dry N2 or dry compressed air for approximately 10 minutes before initiating any HCl gas flow through the system. This purge is necessary to remove any ambient water vapor from within the regulator and calibration gas transport lines; the HCl in the calibration gas may react with this water vapor and increase system response time. A purge of the system should also be performed at the conclusion of a test day prior to removing the regulator from the gas cylinder. Although the regulator wetted parts are corrosion resistant, this will reduce the possibility of corrosion developing within the regulator and extend the life of the equipment.

9.1.1 Measurement System Preparation. Assemble the measurement system by following the manufacturer's written instructions for preparing and preconditioning the gas analyzer and, as applicable, the other system components. Introduce the calibration gases in any sequence, and make all necessary adjustments to calibrate the analyzer and the data recorder. If necessary, adjust the instrument for the specific moisture content of the samples. Adjust system components to achieve correct sampling rates.

9.1.2 Analyzer Calibration Error. Conduct the analyzer calibration error check in the field by introducing calibration gases to the measurement system at any point upstream of the gas analyzer in accordance with sections 9.1.2.1 and 9.1.2.2 of this method.

9.1.2.1 After the measurement system has been prepared for use, introduce the zero, mid-range, and high-range gases to the analyzer. During this check, make no adjustments to the system except those necessary to achieve the correct calibration gas flow rate at the analyzer. Record the analyzer responses to each calibration gas. (**Note**: A calibration curve established prior to the analyzer calibration error check may be used to convert the analyzer response to the equivalent gas concentration introduced to the analyzer. However, the same correction procedure shall be used for all effluent and calibration measurements obtained during the test.

9.1.2.2 The analyzer calibration error check shall be considered invalid if the difference in gas concentration displayed by the analyzer and the concentration of the calibration gas exceeds ±5 percent of the emission standard concentration or ±1 ppm, (whichever is greater) for the zero, mid-, or high-range calibration gases. If an invalid calibration is exhibited, cross-check or recertify the calibration gases, take corrective action, and repeat the analyzer calibration error check until acceptable performance is achieved.

9.1.3 Sampling System Bias Check. For nondilution extractive systems, perform the sampling system bias check by introducing calibration gases either at the probe inlet or at a calibration valve installed at the outlet of the sampling probe. For dilution systems, calibration gases for both the analyzer calibration error check and the sampling system bias check must be introduced prior to the point of sample dilution. For dilution and nondilution systems, a zero gas and either a mid-range or high-range gas (whichever more closely approximates the effluent concentration) shall be used for the sampling system bias check.

9.1.3.1 Introduce the upscale calibration gas, and record the gas concentration displayed by the analyzer. Then introduce zero gas, and record the gas concentration displayed by the analyzer. During the sampling system bias check, operate the system at the normal sampling rate, and make no adjustments to the measurement system other than those necessary to achieve proper calibration gas flow rates at the analyzer. Alternately introduce the zero and upscale gases until a stable response is achieved. The tester shall determine the measurement system response time by observing the times required to achieve a stable response for both the zero and upscale gases. Note the longer of the two times and note the time required for the measurement system to reach 95 percent of the step change in the effluent concentration as the response time.

9.1.3.2 For nondilution systems, where the analyzer calibration error test is performed by introducing gases directly to the analyzer, the sampling system bias check shall be considered invalid if the difference between the gas concentrations displayed by the measurement system for the sampling system bias check and the known gas concentration standard exceeds ±7.5 percent of the emission standard or ±1.5 ppm, (whichever is greater) for either the zero or the upscale calibration gases. If an invalid calibration is exhibited, take corrective action, and repeat the sampling system bias check until acceptable performance is achieved. If adjustment to the analyzer is required, first repeat the analyzer calibration error check, then repeat the sampling system bias check.

9.1.3.3 For dilution systems (and nondilution systems where all calibration gases are introduced at the probe), the comparison of the analyzer calibration error results and sampling system bias check results is not meaningful. For these systems, the sampling system bias check shall be considered invalid if the difference between the gas concentrations displayed by the analyzer and the actual gas concentrations exceed ±7.5 percent of the emission standard or ±1.5 ppm, (whichever is greater) for either the zero or the upscale calibration gases. If an invalid calibration is exhibited, take corrective action, and repeat the sampling system bias check until acceptable performance is achieved. If adjustment to the analyzer is required, first repeat the analyzer calibration error check.

9.2 Emission Test Procedures

9.2.1 Selection of Sampling Site and Sampling Points. Select a measurement site and sampling points using the same criteria that are applicable to Method 26 of A to part 60 of this chapter.

9.2.2 Sample Collection. Position the sampling probe at the first measurement point, and begin sampling at the same rate as used during the sampling system bias check. Maintain constant rate sampling (i.e., ±10 percent) during the entire run. Field test experience has shown that conditioning of the sample system is necessary for approximately 1-hour prior to conducting the first sample run. This conditioning period should be repeated after particulate filters are replaced and at the beginning of each new day or following any period when the sampling system is inoperative. Experience has also shown that prior to adequate conditioning of the system, the response to analyte spikes and/or the change from an upscale calibration gas to a representative effluent measurement may be delayed by more than twice the normal measurement system response time. It is recommended that the analyte spikes (see section 9.3 of this method) be performed to determine if the system is adequately conditioned. The sampling system is ready for use when the time required for the measurement system to equilibrate after a change from a representative effluent measurement to a representative spiked sample measurement approximates the calibration gas response time observed in section 9.1.3.1 of this method.

9.2.3   Sample Duration. After completing the sampling system bias checks and analyte spikes prior to a test run, constant rate sampling of the effluent should begin. For each run, use only those measurements obtained after all residual response to calibration standards or spikes are eliminated and representative effluent measurements are displayed to determine the average effluent concentration. At a minimum, this requires that the response time of the measurement system has elapsed before data are recorded for calculation of the average effluent concentration. Sampling should be continuous for the duration of the test run. The length of data collection should be at least as long as required for sample collection by Method 26 of part 60 of this chapter. One hour sampling runs using this method have provided reliable data for cement kilns.

9.2.4   Validation of Runs. Before and after each run, or if adjustments are necessary for the measurement system during the run, repeat the sampling system bias check procedure described in section 9.1.3 of this method. (Make no adjustments to the measurement system until after the drift checks are completed.) Record the analyzer's responses.

9.2.4.1   If the post-run sampling system bias for either the zero or upscale calibration gas exceeds the sampling system bias specification, then the run is considered invalid. Take corrective action, and repeat both the analyzer calibration error check procedure (section 9.1.2 of this method) and the sampling system bias check procedure (section 9.1.3 of this method) before repeating the run.

9.2.4.2   If the post-run sampling system bias for both the zero and upscale calibration gas are within the sampling system bias specification, then construct two 2-point straight lines, one using the pre-run zero and upscale check values and the other using the post-run zero and upscale check values. Use the slopes and y-intercepts of the two lines to calculate the gas concentration for the run in accordance with equation 1 of this method.

9.3   Analyte Spiking—Self-Validating Procedure. Use analyte spiking to verify the effectiveness of the sampling system for the target compounds in the actual kiln gas matrix. Quality assurance (QA) spiking should be performed before and after each sample run. The spikes may be performed following the sampling system bias checks (zero and mid-range system calibrations) before each run in a series and also after the last run. The HCl spike recovery should be within ±30 percent as calculated using equations 1 and 2 of this method. Two general approaches are applicable for the use of analyte spiking to validate a GFC HCl measurement system: (1) Two independent measurement systems can be operated concurrently with analyte spikes introduced to one of the systems, or (2) a single measurement system can be used to analyze consecutively, spiked and unspiked samples in an alternating fashion. The two-system approach is similar to Method 301 of this appendix and the measurement bias is determined from the difference in the paired concurrent measurements relative to the

amount of HCl spike added to the spiked system. The two-system approach must employ identical sampling systems and analyzers and both measurement systems should be calibrated using the same mid- and high-range calibration standards. The two-system approach should be largely unaffected by temporal variations in the effluent concentrations if both measurement systems achieve the same calibration responses and both systems have the same response times. (See Method 301 of this appendix for appropriate calculation procedures.) The single measurement system approach is applicable when the concentration of HCl in the source does not vary substantially during the period of the test. Since the approach depends on the comparison of consecutive spiked and unspiked samples, temporal variations in the effluent HCl concentrations will introduce errors in determining the expected concentration of the spiked samples. If the effluent HCl concentrations vary by more than ±10 percent (or ±5 ppm, whichever is greater) during the time required to obtain and equilibrate a new sample (system response time), it may be necessary to: (1) Use a dual sampling system approach, (2) postpone testing until stable emission concentrations are achieved, (3) switch to the two-system approach [if possible] or, (4) rely on alternative QA/QC procedures. The dual-sampling system alternative uses two sampling lines to convey sample to the gas distribution manifold. One of the sample lines is used to continuously extract unspiked kiln gas from the source. The other sample line serves as the analyte spike line. One GFC analyzer can be used to alternately measure the HCl concentration from the two sampling systems with the need to purge only the components between the common manifold and the analyzer. This minimizes the time required to acquire an equilibrated sample of spiked or unspiked kiln gas. If the source varies by more than ±10 percent or ±5 ppm, (whichever is greater) during the time it takes to switch from the unspiked sample line to the spiked sample line, then the dual-sampling system alternative approach is not applicable. As a last option, (where no other alternatives can be used) a humidified nitrogen stream may be generated in the field which approximates the moisture content of the kiln gas. Analyte spiking into this humidified stream can be employed to assure that the sampling system is adequate for transporting the HCl to the GFC analyzer and that the analyzer's water interference rejection is adequate.

9.3.1   Spike Gas Concentration and Spike Ratio. The volume of HCl spike gas should not exceed 10 percent of the total sample volume (i.e., spike to total sample ratio of 1:10) to ensure that the sample matrix is relatively unaffected. An ideal spike concentration should approximate the native effluent concentration, thus the spiked sample concentrations would represent approximately twice the native effluent concentrations. The ideal spike concentration may not be achieved because the native HCl concentration cannot be accurately predicted prior to the field test, and limited calibration gas standards will be available during the field test. Some flexibility is available by

varying the spike ratio over the range from 1:10 to 1:20. Practical constraints must be applied to allow the tester to spike at an anticipated concentration. Thus, the tester may use a 100 ppm calibration gas and a spike ratio of 1:10 as default values where information regarding the expected HCl effluent concentration is not available prior to the tests. Alternatively, the tester may select another calibration gas standard and/or lower spike ratio (e.g., 1:20) to more closely approximate the effluent HCl concentration.

9.3.2   Spike Procedure. Introduce the HCl spike gas mixture at a constant flow rate (±2 percent) at less than 10 percent of the total sample flow rate. (For example, introduce the HCl spike gas at 1 L/min (±20 cc/min) into a total sample flow rate of 10 L/min). The spike gas must be preheated before introduction into the sample matrix to prevent a localized condensation of the gas stream at the spike introduction point. A heated sample transport line(s) containing multiple transport tubes within the heated bundle may be used to spike gas up through the sampling system to the spike introduction point. Use a calibrated flow device (e.g., mass flow meter/controller) to monitor the spike flow rate. Use a calibrated flow device (e.g., rotameter, mass flow meter, orifice meter, or other method) to monitor the total sample flow rate. Calculate the spike ratio from the measurements of spike flow and total flow. (See equation 2 and 3 in section 10.2 of this method.)

9.3.3   Analyte Spiking. Determine the approximate effluent HCl concentrations by examination of preliminary samples. For single-system approaches, determine whether the HCl concentration varies significantly with time by comparing consecutive samples for the period of time corresponding to at least twice the system response time. (For analyzers without sample averaging, estimate average values for two to five minute periods by observing the instrument display or data recorder output.) If the concentration of the individual samples varies by more than ±10 percent relative to the mean value or ±5 ppm, (whichever is greater), an alternate approach may be needed.

9.3.3.1   Adjust the spike flow rate to the appropriate level relative to the total flow by metering spike gas through a calibrated mass flow meter or controller. Allow spike flow to equilibrate within the sampling system for at least the measurement system response time and a steady response to the spike gas is observed before recording response to the spiked gas sample. Next, terminate the spike gas flow and allow the measurement system to sample only the effluent. After the measurement system response time has elapsed and representative effluent measurements are obtained, record the effluent unspiked concentration. Immediately calculate the spike recovery.

9.3.3.2   If the spike recovery is not within acceptable limits and a change in the effluent concentration is suspected as the cause for exceeding the recovery limit, repeat the analyte spike procedure without making any adjustments to the analyzer or sampling system. If the second spike recovery falls within the recovery limits, disregard the first

attempt and record the results of the second spike.

9.3.3.3 Analyte spikes must be performed before and after each test run. Sampling system bias checks must also be performed before and after each test run. Depending on the particular sampling strategy and other constraints, it may be necessary to compare effluent data either immediately before or immediately after the spike sample to determine the spike recovery. Either method is acceptable provided a consistent approach is used for the test program. The average spike recovery for the pre-and post-run spikes shall be used to determine if spike recovery is between 70 and 130 percent.

10.0 Data Analysis and Emission Calculations

The average gas effluent concentration is determined from the average gas concentration displayed by the gas analyzer and is adjusted for the zero and upscale sampling system bias checks, as determined in accordance with section 9.2.3 of this method. The average gas concentration displayed by the analyzer may be determined by integration of the area under the curve for chart recorders, or by averaging all of the effluent measurements. Alternatively, the average may be calculated from measurements recorded at equally spaced intervals over the entire duration of the run. For sampling run durations of less than 1-hour, average measurements at 2-minute intervals or less, shall be used. For sampling run durations greater than 1-hour, measurements at 2-minute intervals or a minimum of 96 measurements, whichever is less restrictive, shall be used. Calculate the effluent gas concentration using equation 1.

$$C_{gas} = \frac{(m_i + m_f)\left[\dfrac{(C_{avg} - b_c)}{m_c}\right] + (b_i + b_f)}{2} \quad \text{(Eq. 322-1)}$$

Where:

b_c=Y-intercept of the calibration least-squares line.

b_f=Y-intercept of the final bias check 2-point line.

b_i=Y-intercept of the initial bias check 2-point line.

C_{gas}=Effluent gas concentration, as measured, ppm.

C_{avg}=Average gas concentration indicated by gas analyzer, as measured, ppm.

m_c=Slope of the calibration least-squares line.

m_f=Slope of the final bias check 2-point line.

m_i=Slope of the initial bias check 2-point line.

The following equations are used to determine the percent recovery (%R) for analyte spiking:

%R=$(S_M/C_E) \times 100$ (Eq. 322–2)

Where:

S_M=Mean concentration of duplicate analyte spiked samples (observed).

C_E=Expected concentration of analyte spiked samples (theoretical).

$C_E = C_S(Q_S/Q_T) + S_U(1 - Q_S/Q_T)$ (Eq. 322–3)

Where:

C_S=Concentration of HCl spike gas (cylinder tag value).

Q_S=Spike gas flow rate.

Q_T=Total sample flow rate (effluent sample flow plus spike flow).

S_U=Native concentration of HCl in unspiked effluent samples.

Acceptable recoveries for analyte spiking are ±30 percent.

11.0 Pollution Prevention

Gas extracted from the source and analyzed or vented from the system manifold shall be either scrubbed, exhausted back into the stack, or discharged into the atmosphere where suitable dilution can occur to prevent harm to personnel health and welfare or plant or personal property.

12.0 Waste Management

Gas standards of HCl are handled as according to the instructions enclosed with the materials safety data sheets.

13.0 References

1. Peeler, J.W., Summary Letter Report to Ann Dougherty, Portland Cement Association, June 20, 1996.

2. Test Protocol, Determination of Hydrogen Chloride Emissions from Cement Kilns (Instrumental Analyzer Procedure) Revision 4; June 20, 1996.

3. Westlin, Peter R. and John W. Brown. Methods for Collecting and Analyzing Gas Cylinder Samples. Source Evaluation Society Newsletter. *3*(3):5–15. September 1978.

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