



Holcim EMR
List of USEPA Methods usable for
Discontinuous Measurements in
Cement Plants

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(HGRS-JW-04-27s)

HGRS-CTS/MT

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SUMMARY

	USEPA Method	Use for measurements in cement plants
Velocity	1	Yes
	2	Yes
Carbon Dioxide, Oxygen, Molecular Weight	3	Yes
	3A	Yes
	3B	Yes (only Orsat)
Moisture	4	Yes
Particulate Matter (Dust) High concentrations	5	Yes
Particulate Matter (Dust) Low concentrations	5i	Yes
	17	Yes
Dust - Particle Size Selective	201A	Yes
Heavy Metals	29	Yes
Mercury (Hg)	29	Yes
	101A	No
Sulfur Dioxide (SO ₂)	6	No
	6A	Yes
	6B	Yes
	6C	No
	8	No
Nitrogen Oxides (NO _x)	7	No
	7A	No
	7B	No
	7C	No
	7D	No
	7E	Yes
Basic Nitrogen Compounds	6A/B modified	Yes
Hydrogen Chloride (HCl) Hydrogen Fluoride (HF)	26	Yes
	26A	Yes in special cases
	321	Yes in special cases
Volatile Organic Compounds (VOC)	25	No
	25A	Yes
	25B	No
Dioxins and Furans	23	Yes

1. **VELOCITY, VOLUMETRIC RATE, ETC.**

	USEPA Method	Use for measurements in cement plants
Velocity	1	Yes
	2	Yes
Carbon Dioxide, Oxygen, Molecular Weight	3	Yes
	3A	Yes
	3B	Yes (only Orsat)
Moisture	4	Yes

1.1 **Remarks to the Methods**

Determination of Velocity

- The methods are designed to aid in the representative measurement of pollutant emissions and/or total volumetric flow rate from a stationary source.
- In cement plants usually method with Pitot tubes are used (e.g. method 2)
- The methods are applicable to gas streams flowing in ducts, stacks, and flues. These method cannot be used when: (1) the flow is cyclonic or swirling; or (2) a stack is smaller than 0.30 meter (12 in.) in diameter, or 0.071 m² (113 in.²) in cross-sectional area.
- When unacceptable conditions exist, alternative procedures must be employed to produce accurate flow rate determinations. An example of such an alternative procedure is to calculate the total volumetric flow rate stoichiometrically.
- In any case with the proceeding indicated in the EMR guidelines the determination of the velocity and the volume stream must be controlled.

1.2 **Methods**

- 1) **METHOD 1 - Sample and Velocity Traverses for Stationary Sources**
 - This method is designed to aid in the representative measurement of pollutant emissions and/or total volumetric flow rate from a stationary source. A measurement site where the effluent stream is flowing in a known direction is selected, and the cross-section of the stack is divided into a number of equal areas. Traverse points are then located within each of these equal areas.

- 2) METHOD 2 - Determination of Stack Gas Velocity and Volumetric Flow Rate (Type S Pitot Tube)
- The average gas velocity in a stack is determined from the gas density and from measurement of the average velocity head with a Type S (Stausscheibe or reverse type) pitot tube.
- 3) METHOD 3 - Gas Analysis for the Determination of the Dry Molecular Weight
- This method is applicable for the determination of CO₂ and O₂ concentrations and dry molecular weight of a sample from an effluent gas stream of a fossil fuel combustion process or other process. Other methods, as well as modifications to the procedure described herein, are also applicable for all of the above determinations.
 - A gas sample is extracted from a stack by one of the following methods: (1) single-point, grab sampling; (2) single-point, integrated sampling; or (3) multi-point, integrated sampling. The gas sample is analyzed for percent CO₂ and percent O₂. For dry molecular weight determination, either an Orsat or a Fyrite analyzer may be used for the analysis.
- 3A) Method 3A - Determination of Oxygen and Carbon Dioxide Concentrations in Emissions from Stationary Sources (Instrumental Analyzer Procedure)
- A gas sample is continuously extracted from a stack, and a portion of the sample is conveyed to an instrumental analyzer for determination of O₂ and or CO₂ gas concentration. Any measurement system for O₂ or CO₂ that meets the specifications of this method is acceptable.
 - A refrigerator-type condenser or similar device (e.g., permeation dryer), to remove condensate continuously from the sample gas can be used.
- 3B) METHOD 3B - Gas Analysis for the Determination of Emission Rate Correction Factor or Excess Air
- Only the part with "Orsat Analysis" shall be used.
 - The fuel factor, etc. of exhaust gases from cement plants cannot be calculated with this method.

- 4) METHOD 4 - Determination of Moisture Content in Stack Gases
- This method is applicable for the determination of the moisture content of stack gas.
 - A gas sample is extracted at a constant rate from the source; moisture is removed from the sample stream and determined either volumetrically or gravimetrically. The method contains two possible procedures: a reference method and an approximation method.
 - The reference method is used for accurate determinations of moisture content (such as are needed to calculate emission data).
 - The approximation method provides estimates of percent moisture to aid in setting isokinetic sampling rates prior to a pollutant emission measurement run.

2. **DUST**

	USEPA Method	Use for measurements in cement plants
Particulate Matter (Dust) High concentrations	5	Yes
Particulate Matter (Dust) Low concentrations	5i	Yes
	17	Yes
Dust - Particle Size Selective	201A	Yes

- 5) METHOD 5 - Determination of particulate matter from stationary sources
- 5i) METHOD 5i - Determination of Low Level Particulate Matter Emissions From Stationary Sources
- This method is applicable for the determination of low-level particulate matter (PM) emissions from stationary sources. The method is most effective for total PM catches of 50 [mg] or less. This method was initially developed for performing correlation of manual PM measurements to PM continuous emission monitoring systems (CEMS).
 - New kilns with bag filter have dust emissions clearly below 20 [mg/m³]. With a total volume extraction in the range of 1 to 2 [m³] the total PM accumulated on the filter is below 40 [mg].
 - **Method 5i is the only method for the determination of particulate matter emissions of less than approximately 20 to 30 [mg/m³].**
- 17) METHOD 17 - Determination of particulate matter emissions from stationary sources
- This method is applicable for the determination of PM emissions, where PM concentrations are known to be independent of temperature over the normal range of temperatures characteristic of emissions from a specified source category.
 - **The method should be used with a small for concentrations < 30 [mg/m³].**
- 201A) METHOD 201A - Determination of PM₁₀ Emissions (Constant Sampling Rate Procedure)
- This method applies to the in-stack measurement of particulate matter (PM) emissions equal to or less than an aerodynamic diameter of nominally 10 µm (PM₁₀) from stationary sources.

3. **INORGANIC SUBSTANCES MAINLY AS DUST PARTICLES**

(Heavy Metals)

	USEPA Method	Use for measurements in cement plants
Heavy Metals	29	Yes
Mercury	29 101A	Yes No

29) **METHOD 29 - Determination of Metals Emissions from stationary Sources**

- This method is applicable to the determination of the following metals emissions from stationary sources: Antimony (Sb), Arsenic (As), Barium (Ba), Beryllium (Be), Cadmium (Cd), Chromium (Cr), Cobalt (Co), Copper (Cu), Lead (Pb), Manganese (Mn), Mercury (Hg), Nickel (Ni), Phosphorus (P), Selenium (Se), Silver (Ag), Thallium (Tl), Zinc (Zn)
- Remark: Hg emissions can be measured, alternatively, using EPA Method 101A. The Method 101-A measures only Hg but it can be of special interest to sources, which need to measure both Hg and Mn emissions.

101A) **METHOD 101A - Determination of Particulate and Gaseous Mercury Emissions from Sewage Sludge Incinerators**

- This method is applicable for the determination of Hg emissions from sewage sludge incinerators and other sources as specified in an applicable subpart of the regulations.
- Remark: Method 110 is applicable for the determination of Hg emissions, including both particulate and gaseous Hg, from chlor-alkali plants and other sources (as specified in the regulations) where the carrier-gas stream in the duct or stack is principally air.
- **This method shall not be used for stack measurements.**

4. INORGANIC GASEOUS COMPOUNDS

	USEPA Method	Use for measurements in cement plants
Sulfur Dioxide (SO ₂)	6	No
	6A	Yes
	6B	Yes
	6C	No
	8	No
Nitrogen Oxides (NO _x)	7	No
	7A	No
	7B	No
	7C	No
	7D	No
	7E	Yes
Basic Nitrogen Compounds	6A/B modified	Yes
Hydrogen Chloride (HCl)	26	Yes
Hydrogen Fluoride (HF)	26A	Yes in special cases
	321	Yes in special cases

4.1 Remarks to the Methods

Determination of SO₂

- Exhaust gases from cement plants do not contain sulfur acid mist and no or only a negligible amount of sulfur trioxide (SO₃). Therefore it is recommended to omit all proceedings which determine or remove these compounds.
- Method 6 and 8 shall not be used
Method 6A should be used with empty isopropanol bubbler as described in method 6B

Determination of NO_x

- The determination of nitrogen oxide emissions by absorptive methods fails.
Reasons:
 - The nitrates, nitrites and certain organic nitrogenous compounds entrained in the form of vapors or suspended matter may substantially and systematically impair the result in the direction of higher values. In high concentrations, sulfur dioxide and other oxidizable substances greatly impede complete oxidation of the nitrogen monoxide.

- Biased results have also been observed when sampling under conditions of high sulfur dioxide concentrations and ammonia (NH₃).
- All absorptive methods (method 7, 7A, 7B, 7C, 7D) shall not be used for the measurement of nitrogen oxide emissions in exhaust gases from cement plants.

Determination of NH₃

At the moment no method for the determination of ammonia exist. Therefore Holcim recommend making the following measurement.

- The amount of gaseous ammonia is much greater than the ammonia in form of dust or adsorbed on dust. Therefore only the gaseous ammonia should be measured. For the extraction the sampling train of method 6A or 6B shall be used.
- In cement plants the emission of basic nitrogen compounds consists mainly of ammonia. Other compounds like high-volatile amines are not present or present in absolute negligible concentrations. Therefore the absorption of ammonia can be made in sulfuric acid (2 wash bottles with 0.05 M sulfuric acid)
- The analysis of the solutions is made by a hydro-distillation followed by a titrimetric determination according to the indophenol method.
- Example of a Guideline: VDI 3496 / part 1; Gaseous emission measurement; determination of basic nitrogen compounds seizable by absorption in sulphuric acid (available only in German)

Determination of HCl

- In general the gaseous HCl emission of a kiln is very low, exceptions are preheater kilns with chlorine bypass and wet or long dry kilns with a high chlorine input (low-alkali-clinker).
The German VDZ¹ published 2002 the following measurements. The emission values between 15 and 30 [mg/m³] are from cement kilns with chlorine bypass systems.

Number of measurements	127 measurements on 35 kilns
Emission < 2 [mg/m ³]	90 measurements
Emission between 2 and 10 [mg/m ³]	32 measurements
Emission between 15 and 30 [mg/m ³]	5 measurements

- In general the dust collected at the main stack of a cement plant has a very low Cl concentration. Reasons:

¹ Environmental Data of the German Cement Industry 2001; Verein Deutscher Zementwerke e.V., Düsseldorf

- The total Cl input (via fuels and raw material) to a preheater kiln should not exceed 0.05 % (related to clinker); otherwise severe kiln problems occur.
 - Assuming an unrealistic Cl accumulation of factor 10 in the filter system, the dust concentration can never exceed a concentration of 0.3 [%].
 - A kiln with a relative high dust emission of 50 [mg/m³] would emit less than 0.15 [mgCl/m³] in form of particles; at least factor 10 below the detection limit (2 [mg/m³]) for gaseous Cl emissions.
 - **Therefore only Non-Isokinetic method shall be used for the determination of the HCl emission at the main stack.**
- In so-called chlorine bypasses the amount of Cl in form of dust may be higher and isokinetic methods may be justified.

Determination of HF

- The same argumentation as for chlorine applies also for the element fluorine.

Determination of Cl₂ and F₂

- Gaseous chlorine (Cl₂) and gaseous fluorine (F₂) react in wet gases for instance with sulfur dioxide.
- **All methods shall not be used for the determination of the Cl₂ and F₂ emission in cement plants.**

4.2 Methods

- 6) METHOD 6 - Determination of Sulfur Dioxide Emissions from stationary Sources
- A gas sample is extracted from the sampling point in the stack. The SO₂ and the sulfur trioxide, including those fractions in any sulfur acid mist, are separated. The SO₂ fraction is measured by the barium-thorin titration method.
 - **The method shall not be used for the measurement of exhaust gases from cement plants**
- 6A) METHOD 6A - Determination of Sulfur Dioxide, Moisture, and Carbon Dioxide From fossil Fuel Combustion
- This method is applicable for the determination of sulfur dioxide (SO₂) emissions from fossil fuel combustion sources in terms of concentration (mg/dscm or lb/dscf) and in terms of emission rate (ng/J or lb/106 Btu) and for the determination of carbon dioxide (CO₂) concentration (percent). Moisture content (percent), if desired, may also be determined by this method.
 - A gas sample is extracted from a sampling point in the stack. The SO₂ and the sulfur trioxide, including those fractions in any sulfur acid mist, are separated. The SO₂ fraction is measured by the barium-thorin titration method. Moisture and CO₂ fractions

are collected in the same sampling train, and are determined gravimetrically.

- It is recommended not to include the isopropanol bubbler in the sampling train.

6B) METHOD 6B - Determination of Sulfur Dioxide and Carbon Dioxide Daily Average Emissions from Fossil Fuel Combustion Sources

- A gas sample is extracted from the sampling point in the stack intermittently over a 24-hour or other specified time period. The SO₂ fraction is measured by the barium-thorin titration method. Moisture and CO₂ fractions are collected in the same sampling train, and are determined gravimetrically.
- The sampling train is assembled as shown in Method 6A, except that the isopropanol bubbler is not included. An empty bubbler for the collection of liquid droplets, that does not allow direct contact between the collected liquid and the gas sample, may be included in the sampling train.

6C) METHOD 6C - Determination of Sulfur Dioxide Emissions from Stationary Sources (Instrumental Analyzer Procedure)

- A gas sample is continuously extracted from a stack, and a portion of the sample is conveyed to an instrumental analyzer for determination of SO₂ gas concentration using an ultraviolet (UV), nondispersive infrared (NDIR), or fluorescence analyzer.
- **Analyzing with moisture removal facilities shall not be used** (so-called cold analyzing systems)
- Hot analyzing systems or system with gas dilution can be used.

8) METHOD 8 - Determination of Sulfuric Acid and Sulfur Dioxide Emissions from Stationary Sources

- This method is applicable for the determination of H₂SO₄ (including H₂SO₄ mist and SO₃) and gaseous SO₂ emissions from stationary sources.
- A gas sample is extracted isokinetically from the stack. The H₂SO₄ and the SO₂ are separated, and both fractions are measured separately by the barium-thorin titration method.
- **The method shall not be used for the measurement of exhaust gases from cement plants**

7) METHOD 7 - Determination of Nitrogen Oxide Emissions from Stationary Sources

- A grab sample is collected in an evacuated flask containing a dilute sulfuric acid-hydrogen peroxide absorbing solution, and the nitrogen oxides, except nitrous oxide, are measured colorimetrically using the phenoldisulfonic acid (PDS) procedure.
- Biased results have been observed when sampling under conditions of high sulfur dioxide concentrations (above 2000 ppm). Other experiences: The nitrates, nitrites and certain organic nitrogenous compounds entrained in the form of vapors or suspended matter may substantially and systematically impair the

result in the direction of higher values. In high concentrations, sulfur dioxide and other oxidizable substances greatly impede complete oxidation of the nitrogen monoxide.

- **The method shall not be used for the measurement of exhaust gases from cement plants**

7A) METHOD 7A - Determination of Nitrogen Oxide Emissions from Stationary Sources (Ion Chromatographic Method)

- A grab sample is collected in an evacuated flask containing a dilute sulfuric acid-hydrogen peroxide absorbing solution. The nitrogen oxides, excluding nitrous oxide (N₂O), are oxidized to nitrate and measured by ion chromatography.
- **The method shall not be used for the measurement of exhaust gases from cement plants**

7B) METHOD 7B - Determination of Nitrogen Oxide Emissions from stationary Sources (Ultraviolet Spectrophotometric Method)

- A grab sample is collected in an evacuated flask containing a dilute sulfuric acid-hydrogen peroxide absorbing solution; the NO_x, excluding nitrous oxide (N₂O), are measured by ultraviolet spectrophotometry.
- **The method shall not be used for the measurement of exhaust gases from cement plants**

7C) METHOD 7C - Determination of Nitrogen Oxide Emissions from Stationary Sources (Alkaline Permanganate/Colorimetric Method)

- An integrated gas sample is extracted from the stack and passed through impingers containing an alkaline potassium permanganate solution; NO_x (NO + NO₂) emissions are oxidized to NO₂ and NO₃. Then NO₃ is reduced to NO₂ with cadmium, and the NO₂ is analyzed colorimetrically.
- **The method shall not be used for the measurement of exhaust gases from cement plants**

7D) METHOD 7D - Determination of Nitrogen Oxide Emissions from Stationary Sources (Alkaline-Permanganate/Ion Chromatographic Method)

- An integrated gas sample is extracted from the stack and passed through impingers containing an alkaline potassium permanganate solution; NO_x (NO + NO₂) emissions are oxidized to NO₂ and NO₃. Then NO₃ is analyzed by ion chromatography.
- **The method shall not be used for the measurement of exhaust gases from cement plants**

7E) METHOD 7E - Determination of Nitrogen Oxides Emissions from Stationary Sources (Instrumental Analyzer Procedure)

- A sample is continuously extracted from the effluent stream; a portion of the sample stream is conveyed to an instrumental chemiluminescent analyzer for determination of NO concentration.

- A refrigerator-type condenser or similar device (e.g., permeation dryer), to remove condensate continuously from the sample gas can be used.
 - Generally the amount of NO₂ of exhaust gases from cement kilns is less than 5 % of the total NO_x. Therefore the integration of a "NO₂ to NO Converter" is not absolutely necessary.
- 26) METHOD 26 - Determination of Hydrogen Halide and Halogen Emissions from Stationary Sources; Non-Isokinetic Method
- This method is applicable for determining emissions of hydrogen halides (HX) [HCl, HBr, and HF] and halogens (X₂) [Cl₂ and Br₂] from stationary sources
 - An integrated sample is extracted from the source and passed through a prepurged heated probe and filter into dilute sulfuric acid and dilute sodium hydroxide solutions, which collect the gaseous hydrogen halides and halogens, respectively. The filter collects particulate matter including halide salts but is not routinely recovered and analyzed. The hydrogen halides are solubilized in the acidic solution and form chloride (Cl⁻), bromide (Br⁻), and fluoride (F⁻) ions.
 - **The method can be used for the measurement of HCl and HF in exhaust gases from cement plants**
- 26A) METHOD 26A - Determination of Hydrogen Halide and Halogen Emissions from Stationary Sources; Isokinetic Method
- The isokinetic method shall only be used in special cases, e.g. measurement of chlorine bypass with high dust emission
- 321) METHOD 321 - Measurement of Gaseous Hydrogen Chloride Emissions At Portland Cement Kilns by Fourier Transform Infrared (FTIR) Spectroscopy
- This method should be performed by specialists familiar with the operation of Fourier Transform Infrared (FTIR) instrumentation in the application to source sampling.
 - 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.
 - **Not recommended for "normal" emission measurements in cement plants. Applicable for specific investigations.**

5. **ORGANIC COMPOUNDS**

	USEPA Method	Use for measurements in cement plants
Volatile Organic Compounds (VOC)	25	No
	25A	Yes
	25B	No
Benzene	N1501	Yes
Dioxins and Furans	23	Yes

25) METHOD 25 - Determination of Total Gaseous Non Methane Organic Emissions as Carbon

- **The method shall not be used for the measurement of exhaust gases from cement plants**

Reason:

When carbon dioxide (CO₂) and water vapor are present together in the stack, they can produce a positive bias in the sample. The magnitude of the bias depends on the concentrations of CO₂ and water vapor. As a guideline, multiply the CO₂ concentration, expressed as volume percent, times the water vapor concentration. If this product does not exceed 100 the bias can be considered insignificant.

In stack gases of cement plants this product exceeds at least the value of 200!

25A) METHOD 25A - Determination of Total Gaseous Organic Concentration using a Flame Ionization Analyzer

- This method is applicable for the determination of total gaseous organic concentration of vapors consisting primarily of alkanes, alkenes, and/or arenes (aromatic hydrocarbons). The concentration is expressed in terms of propane (or other appropriate organic calibration gas) or in terms of carbon.
- EPA: All sampling components leading to the analyzer shall be heated > 110 [°C] (220 [°F]). The flame ionization detector block shall be heated >120 [°C] (250 [°F]).
Our experience: All sampling components leading to the analyzer and the detector block shall be heated > 180 [°C] (360 [°F]).
- EPA - Calibration Gases: The calibration gases for the gas analyzer shall be propane in air or propane in nitrogen.
Our recommendation: Propane in nitrogen
- EPA - Zero Gas: High purity air with less than 0.1 part per million by volume (ppmv) of organic material (propane or carbon equivalent) or less than 0.1 percent of the span value, whichever is greater.
Our recommendation: High purity nitrogen and check of a possi-

ble cross-sensitivity of the analyzer to oxygen - Check with high gas containing oxygen.

- **Only this method can be used to measure the volatile organic emission of a cement kiln.**

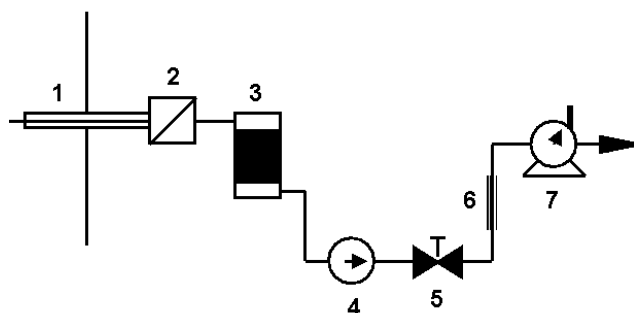
25B) METHOD 25B - Determination of Total Gaseous Organic Concentration using a Non-Dispersive Infrared Analyzer

- A gas sample is extracted from the source through a heated sample line, if necessary, and glass fiber filter to a non-dispersive infrared analyzer (NDIR).
- This method is applicable for the determination of total gaseous organic concentration of vapors consisting primarily of alkanes. With this method only a part of the volatile organic compounds are measured.
The method shall not be used for the measurement of exhaust gases from cement plants

N1501) NIOSH method 1501² can be used for non-continuous benzene measurement in cement-plant exhaust gases. This method is based on adsorptive enrichment in activated carbon followed by liquid desorption and analysis by gas chromatography. The method is also suitable for the following compounds: cumene, a-methyl-styrene, styrene, vinyl-toluene, p-tert-butyl-toluene, ethyl-benzene, naphthalene, toluene, and xylene.

- **Sampling**

The water must be removed prior to absorption by activated carbon. The following Figure shows the scheme of an example sampling system.



- 1 Heated gas-extraction tube (>120 [°C])
- 2 Heated filter (>120 [°C])
- 3 Condensate collector (measuring-gas cooler, ...)
- 4 Gas-sample pump
- 5 Regulator and shut-off valve

²

NIOSH Manual of Analytical Methods, 3rd Ed., US Department of Health and Human Services, National Institute for Occupational Safety and Health, Cincinnati, USA, (1994)
<http://www.cdc.gov/niosh/nmam/nmammenu.html>

