A.4 Monitoring
This module will focus on monitoring of air pollution control equipment. The flow diagram presented in this slide shows schematically a process that might be the subject of MACT EEE, the hazardous waste combustor MACT. The process would be one such as a chemical process. The treatment would be the part of the air pollution control that combusted the hazardous waste, such as an incinerator, solid or liquid fuel boiler, or cement or light aggregate kiln. The air pollution control device would be one that follows the combustion device to remove hazardous constituents from the gas stream before being released to the atmosphere. The monitors could be measuring parameters in the inlet or outlet of the treatment or in the stack prior to release to the atmosphere.
Before getting into the slides on monitoring, review of acronyms used in monitoring would be helpful. The acronym for Continuous Monitoring Systems is CMS. A Continuous Emissions Monitoring Systems also is referred to as CEMS. A Continuous Opacity Monitoring Systems also is called a COMS. A Parametric Emissions Monitoring Systems can be referred to as PEMS. Total Hydrocarbons is sometimes called THC.
MACT EEE has regulations requiring monitoring by continuous monitoring systems. These are Total Hydrocarbon, Carbon Monoxide and Oxygen CEMS and a COMS for Opacity.
Other Continuous Monitoring Systems (CMS)

- Temperature – Thermocouples
- Pressure – Pressure Transducers
- Flow Rate – Flow Meters

Other Continuous Monitoring Systems required by MACT EEE measure Temperature with Thermocouples, Pressure with Pressure Transducers, and Flow Rate with Flow Meters.
Temperature Measurement

- Consist of sensor, transmitter, external power supply (for some systems), and wiring that connects these components
- Sensors most commonly used are thermocouples, resistance temperature detectors (RTD’s), and infrared (IR) thermometers
- Integrated circuit (IC) temperature transducers and thermistors also are used but have more limitations than thermocouples, RTD’s, and IR thermometers

Temperature measurement consists of sensor, transmitter, external power supply (for some systems), and wiring that connects these components. The sensors most commonly used for temperature measurement are thermocouples, resistance temperature detectors (RTD’s), and infrared (IR) thermometers. Integrated circuit (IC) temperature transducers and thermistors also are used but have more limitations than thermocouples, RTD’s, and IR thermometers.
This slide lists the advantages of a thermocouple, RTD, Infrared thermometer, integrated circuit sensor and thermistor.
### Temperature Monitoring Systems Characteristics

<table>
<thead>
<tr>
<th>Thermocouple</th>
<th>RTD</th>
<th>IR Thermometer</th>
<th>IC sensor</th>
<th>Thermistor</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Disadvantages</strong> – all can be affected by radiation from flame</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>• Nonlinear output signal</td>
<td>• Expensive</td>
<td>• Expensive</td>
<td>• Nonlinear</td>
<td></td>
</tr>
<tr>
<td>• Low voltage</td>
<td>• Self-heating</td>
<td>• Must be protected</td>
<td>• Limited temperature range</td>
<td></td>
</tr>
<tr>
<td>• Reference required</td>
<td>• Lower temperature range</td>
<td>• Affected by emissivity of target</td>
<td>• Fragile</td>
<td></td>
</tr>
<tr>
<td>• Accuracy is function of two separate measurements</td>
<td></td>
<td></td>
<td>• Current source required</td>
<td></td>
</tr>
<tr>
<td>• Least sensitive</td>
<td></td>
<td></td>
<td>• Self-heating</td>
<td></td>
</tr>
<tr>
<td>• Sensor cannot be recalibrated</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>• Least stable</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T &lt; 200°C</td>
<td>Slower response</td>
<td>Self-heating</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

This slide lists the disadvantages of a thermocouple, RTD, Infrared thermometer, integrated circuit sensor and thermistor.
This slide illustrates the components of a thermocouple. The thermocouple is made up of the sensor that is covered by a sheath, which is in the gas stream being measured, a transition to a lead wire that is connect to the thermocouple head.
<table>
<thead>
<tr>
<th>Sensor Types</th>
<th>Pressure range, kPa (psi)</th>
<th>Temperature range, ºC (ºF)</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bourdon</td>
<td>83 to 690,000 (12 to 100,000)</td>
<td>-40 to 190 (-40 to +375)</td>
<td>Low cost; field replaceable; variety of materials for media and range</td>
<td>Slow response; large sensor volume sensitive to shock and vibration</td>
</tr>
<tr>
<td>Diaphragm</td>
<td>35 to 103 (5 to 15)</td>
<td>-40 to 190 (-40 to +375)</td>
<td>Variety of materials for media and range; field replaceable; large force</td>
<td>Limited capacity; position sensitive in low ranges</td>
</tr>
<tr>
<td>Bellows</td>
<td>3.4 to 207 (0.5 to 30)</td>
<td>-40 to 190 (-40 to +375)</td>
<td>Compact, accurate, field replaceable</td>
<td>Limited material; may be position sensitive</td>
</tr>
</tbody>
</table>

This slide lists the characteristics, advantages and disadvantages of bourdon tube, diaphragm and bellows pressure measurement methods.
This slide lists the characteristics, advantages and disadvantages of Strain Gauge, Linear Variable Differential Transducer, or LVDT, Capacitance and Piezoelectric pressure measurement devices.

<table>
<thead>
<tr>
<th>Sensor Types</th>
<th>Pressure range, kPa (psi)</th>
<th>Temperature range, ºC (ºF)</th>
<th>Accuracy, %</th>
<th>Shock-Vibration Sensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strain Gauge</td>
<td>4 to 69,000 (0.5 to 10,000)</td>
<td>-40 to 315 (-40 to +600)</td>
<td>0.25</td>
<td>Good</td>
</tr>
<tr>
<td>Linear Variable Differential Transducer (LVDT)</td>
<td>207 to 69,000 (30 to 10,000)</td>
<td>-18 to 74 (0 to +165)</td>
<td>0.05</td>
<td>Poor</td>
</tr>
<tr>
<td>Capacitance</td>
<td>0.07 to 69,000 (0.01 to 10,000)</td>
<td>-18 to 815 (0 to +1,500)</td>
<td>0.05 to 0.5</td>
<td>Poor to Good</td>
</tr>
<tr>
<td>Piezoelectric</td>
<td>0.07 to 69,000 (0.01 to 10,000)</td>
<td>-268 to 204 (-450 to +400)</td>
<td>1</td>
<td>Excellent</td>
</tr>
</tbody>
</table>
This slide illustrates the operation of a bourdon-tube pressure gauge.
The bellows-type pressure gauge operation is demonstrated in this slide.
The operation of a diaphragm-type pressure gauge is demonstrated in this slide.
This slide lists the permissible error of pressure gauges according to the grade of the pressure gauge.

<table>
<thead>
<tr>
<th>Grade</th>
<th>Permissible error ±% of span</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>First 25%</td>
</tr>
<tr>
<td>4A</td>
<td>0.1</td>
</tr>
<tr>
<td>3A</td>
<td>0.25</td>
</tr>
<tr>
<td>2A</td>
<td>0.5</td>
</tr>
<tr>
<td>A</td>
<td>2.0</td>
</tr>
<tr>
<td>B</td>
<td>3.0</td>
</tr>
<tr>
<td>C</td>
<td>4.0</td>
</tr>
<tr>
<td>D</td>
<td>5.0</td>
</tr>
</tbody>
</table>
Operation of the strain gauge pressure transducer is illustrated in this slide.
A capacitance pressure transducer is illustrated in this slide.
Operation of a linear variable differential transducer is depicted in this slide.
This slide lists various types of flow measurement methods. Those that are mainly used are a venturi tube, flow nozzle, orifice plate, and pitot tube.
The type of measurement, whether used in liquid or gas service, flow rate range, the net pressure loss, accuracy and restrictions of venturi tube, flow nozzle, orifice plate and magnetic flow measurement devices are listed in this slide.

<table>
<thead>
<tr>
<th>Type of flow meter</th>
<th>Venturi tube</th>
<th>Flow nozzle</th>
<th>Orifice plate</th>
<th>Magnetic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of measurement</td>
<td>Volumetric</td>
<td>Volumetric</td>
<td>Volumetric</td>
<td>Velocity</td>
</tr>
<tr>
<td>Liquid, Gas</td>
<td>L, G</td>
<td>L, G</td>
<td>L, G</td>
<td>L (not petroleum)</td>
</tr>
<tr>
<td>Applicable flow rate</td>
<td>Limited to ~4:1 flow range</td>
<td>Limited to ~4:1 flow range</td>
<td>Limited to ~4:1 flow range</td>
<td>0.0008 to 9,500 L/min (0.002 to 2,500 gal/min)</td>
</tr>
<tr>
<td>Net pressure loss</td>
<td>10 to 20% of ΔP</td>
<td>30 to 85% of ΔP</td>
<td>Slightly more than flow nozzle</td>
<td>None</td>
</tr>
<tr>
<td>Accuracy</td>
<td>±0.75% flow rate w/o cal.</td>
<td>±1.0% flow rate w/o cal.</td>
<td>±0.6% flow rate w/o calibration</td>
<td>±1% flow rate</td>
</tr>
<tr>
<td>Restrictions</td>
<td>Eliminate swirl and pulsations</td>
<td>Eliminate swirl and pulsations</td>
<td>Eliminate swirl and pulsations</td>
<td>Conductive liquid only</td>
</tr>
</tbody>
</table>
This slide lists the type of measurement, whether used in liquid or gas service, flow rate range, the net pressure loss, accuracy and restrictions for the flow measurement devices lobed impeller, slide-vane rotary, turbine and rotameter.

<table>
<thead>
<tr>
<th>Type of measurement</th>
<th>Lobed impeller</th>
<th>Slide-vane rotary</th>
<th>Turbine</th>
<th>Rotameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of measurement</td>
<td>Volumetric</td>
<td>Volumetric</td>
<td>Volumetric</td>
<td>Velocity</td>
</tr>
<tr>
<td>Liquid, Gas</td>
<td>L, G</td>
<td>L</td>
<td>L, G</td>
<td>L, G</td>
</tr>
<tr>
<td>Applicable flow rate</td>
<td>L: 8 to 18,000 gpm</td>
<td>L: 50,000 gpm G: 230,000 scfm</td>
<td>L: Up to 750 L/min (200 gpm G: unlimited)</td>
<td></td>
</tr>
<tr>
<td>Net pressure loss</td>
<td>Low</td>
<td>5 to 6 psi @ 20 fps water</td>
<td>Low</td>
<td></td>
</tr>
<tr>
<td>Accuracy</td>
<td>±0.2% flow rate</td>
<td>±0.1 to 0.2% flow rate</td>
<td>±0.5% flow rate</td>
<td>±1 to 2% full scale</td>
</tr>
<tr>
<td>Restrictions</td>
<td>Best used at high flow rates</td>
<td>Straightening vanes - do not exceed max. flow</td>
<td>Mounted vertically</td>
<td></td>
</tr>
</tbody>
</table>
This slide illustrates a venturi tube flow measurement device. The taps shown on the lower side of the flow inlet and smallest diameter are measured. The ratio of these pressures are calibrated to the flow rate of the gas.
This slide illustrates a flow nozzle flow measurement device. The taps shown on the either side of the nozzle are measured. The reduction of pressure across the nozzle is calibrated to the flow rate of the gas.
This slide illustrates a orifice plate flow measurement device. The taps shown on the either side of the orifice are measured. The reduction of pressure across the orifice is calibrated to the flow rate of the gas.
This slide illustrates a pitot tube flow measurement device. The taps shown on the pitot tube are measured. The ratio of these pressures is calibrated to the flow rate of the gas.
This slide illustrates a magnetic flow meter flow measurement device.
This slide illustrates a lobed impeller flow measurement device. The flow rate is proportional to the speed of the lobed impellers.
This slide illustrates a slide-vane rotary flow measurement device. The flow rate is proportional to the speed of the rotor.
Turbine Flow Meter

This slide illustrates a turbine flow measurement device.
This slide illustrates a vortex precision flow measurement device.
This slide illustrates a rotameter flow measurement device. The gas flowing up through the meter causes the element to rise proportional to the rate of flow.
Continuous emission monitoring systems, or CEMS, and continuous opacity monitoring systems, or COMS, are equipment for determination of concentration or emission rate of gas or particulate matter. Each system uses pollutant analyzer measurements and a conversion equation, graph, or computer program to produce results in units of the applicable emission limitation or standard. CEMS and COMS are required under some of EPA regulations for either continual compliance determination or determination of exceedances of standards. EPA rules specify reference methods that must be used to substantiate a CEMS or COMS accuracy and precision.
A parametric emission monitoring system, or PEMS, is another means for the determination of concentration or emission rate of pollutant. A PEMS uses processor control device operating parameter measurements and a conversion equation, graph, or computer program to produce results in units of the applicable emission limitation or standard. EPA is studying the applicability of PEMS for NOx compliance determinations for various sources. EPA has a protocol for assessing accuracy and precision of PEMS.
CEMS Calibration Testing

- Zero Drift (ZD) – difference between instrument zero reading and simulated zero device
- Calibration Drift (CD) – difference between instrument upscale reading and the simulated upscale device
- Relative Accuracy (RA) – absolute mean difference between gas concentration or emission rate and the value determined by reference method

Terms used for CEMS calibration testing are Zero Drift, Calibration Drift, and Relative Accuracy. Zero Drift, sometimes identified as ZD, is the difference between the instrument zero reading and the simulated zero device. Calibration Drift, identified as CD, is the difference between the instrument upscale reading and the simulated upscale device. Relative Accuracy, or RA, is the absolute mean difference between the gas concentration or the emission rate and the value determined by reference method.
MACT EEE Calibrations

- **Zero Drift (ZD)** – difference in CEMS output readings at zero pollutant level after stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

- **Calibration Drift (CD)** – difference in CEMS output readings from the established reference value after stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

More specific to MACT EEE calibrations, Zero Drift, or ZD, is the difference in the CEMS output readings at zero pollutant level after the stated period of operation during which no unscheduled maintenance, repair, or adjustment took place. Calibration Drift, or CD, is the difference in CEMS output readings from the established reference value after the stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.
MACF EEE Relative Accuracy

• Relative Accuracy (RA) – absolute mean difference between pollutant concentration determined by CEMS and value determined by reference method (RM) plus 2.5 % error confidence coefficient of series of test divided by mean of RM tests or applicable emission limit

• Relative Accuracy Test Audit (RATA) – comparison of CEMS measurements to reference method measurements to evaluate relative accuracy in appropriate performance specification

MACF EEE definitions for Relative Accuracy, or RA, is the absolute mean difference between the pollutant concentration determined by the CEMS and the value determined by the reference method (RM) plus a 2.5 % error confidence coefficient of the series of test divided by the mean of RM tests or the applicable emission limit. Relative Accuracy Test Audit, RATA, is the comparison of the CEMS measurements to the reference method measurements to evaluate the relative accuracy in the appropriate performance specification.
Performance Specifications

- 40 CFR 60, Appendix B [refer to MACT EEE Appendix first]
- Requirements to develop QC procedures for specific activities
- “Out of Control” limits on daily zero and calibration drift check results to determine if data can be used
- Quarterly accuracy assessment (audit) procedures and “Out of Control” criteria

Performance specifications are contained in Appendix B of 40 CFR 60, however, because of changes to the specifications made within MACT EEE, reference to the MACT EEE Appendix is required to ensure the correct specifications are being used.

MACT EEE contains requirements to develop QC procedures for specific activities. “Out of Control” limits on daily zero and calibration drift check results to determine if data can be used. Quarterly accuracy assessment (audit) procedures and “Out of Control” criteria
This slide lists the referenced performance specification, allowed drift, the RA or the percent mean of the test divided by the percent of standard for relative accuracy, and the reference method or methods for the various continuous monitoring systems.
Other CMS Performance Specifications (PS)

- GC CEMS – Performance Specification 9
- PM CEMS – Performance Specification 11
- FTIR – Performance Specification 15
- TRS CEMS – Performance Specification 5
- H₂S CEMS – Performance Specification 7
- Proposed:
  - Hg CEMS – Performance Specification 12, 12A
  - HCl CEMS – Performance Specification 13A
  - Cl₂ CEMS – Performance Specification 14A
  - Predictive CEMS – Performance Specification 16

Performance specifications, including those proposed by EPA, for other continuous monitoring systems are listed in this slide.
CEMS – Continuous Emissions Monitoring Systems Types

• **Extractive** – representative sample withdrawn from stack, conditions, and then analyzed
• **In-Situ** – not extracted but monitored directly in stack by analyzer
• **Parameter** – indirect monitoring of operational or control equipment parameters correlated to emissions by manual or instrument reference methods

**Extractive** CEMS is performed by a representative sample being withdrawn from stack, conditioned, and then analyzed. An **In-Situ** CEMS is not extracted but monitored directly in the stack by the analyzer. A **Parameter** CEMS is the indirect monitoring of operational or control equipment parameters correlated to the emissions by manual or instrument reference methods.
CEMS – Continuous Emissions Monitoring Systems Types

- **Extractive** – Dry or Wet Source, In-stack or Out of Stack Dilution
- **In-Situ** – Point, Single or Double Pass
- **Parameter** – Parameter Surrogates or Theory-based or Empirical Predictive Models

An **Extractive** CEMS can operate in a dry or wet source, in-stack or out of stack dilution. An **In-Situ** CEMS can be a point, single or double pass. **Parameter** CEMS uses parameter surrogates or theory-based or empirical predictive models.
This slide lists several spectroscopic absorption techniques, the type of system of the technique and the gas monitored. Methods listed are non-dispersive infrared, gas filter correlation, differential absorption, and second derivative.

<table>
<thead>
<tr>
<th>Method</th>
<th>System Type</th>
<th>Gas Monitored</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-Dispersive Infrared</td>
<td>Extractive</td>
<td>SO₂, NO, NO₂, HCl, CO, CO₂</td>
</tr>
<tr>
<td>Gas Filter Correlation</td>
<td>Extractive</td>
<td>HCl</td>
</tr>
<tr>
<td></td>
<td>In-situ</td>
<td>SO₂, NO, CO, CO₂</td>
</tr>
<tr>
<td>Differential Absorption</td>
<td>Extractive, In-situ</td>
<td>SO₂, NO₂</td>
</tr>
<tr>
<td>Second Derivative</td>
<td>In-situ</td>
<td>SO₂, NO₂</td>
</tr>
</tbody>
</table>
Luminescence techniques are listed in this slide. Ultra-violet fluorescence, chemiluminescence, and flame photometry are the methods listed with the type of system and the gas that the technique monitors.

<table>
<thead>
<tr>
<th>Method</th>
<th>System Type</th>
<th>Gas Monitored</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultra-Violet Fluorescence</td>
<td>Extractive</td>
<td>SO₂</td>
</tr>
<tr>
<td>Chemiluminescence</td>
<td>Extractive</td>
<td>NO, NO₂, NH₃</td>
</tr>
<tr>
<td>Flame Photometry</td>
<td>Extractive</td>
<td>Gases containing Sulfur</td>
</tr>
</tbody>
</table>
Electro-analytical techniques listed in this slide with the system type and gas monitored. The methods listed are polarography and electrocatalysis.

<table>
<thead>
<tr>
<th>Method</th>
<th>System Type</th>
<th>Gas Monitored</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polarography</td>
<td>Extractive</td>
<td>O₂, SO₂, NO, CO₂</td>
</tr>
<tr>
<td>Electrocatalysis</td>
<td>Extractive, In-situ</td>
<td>O₂, SO₂</td>
</tr>
</tbody>
</table>
Paramagnetic techniques for measurement of oxygen by extraction are thermomagnetic, magnetodynamic and magnetopneumatic methods.
Sampling conditioning is used to provide a clean, dry gas sample to analytical section of instrument. A primary filter is used to remove particulate and a secondary filter to remove any remaining particulate. Moisture is removal by condensation, permeation or dilution with clean, dry air. Sample lines usually are heated to prevent condensation that might lead to blockage of the sample line.
CEMS Measurement Methods

- FTIR – **Fourier Transform Infrared**: CO, CO₂, CH₄, C₃H₈, NO₂, N₂O, SO₂, NH₃, others
- **Chemiluminescence**: NO, NOₓ, NO₂ and NH₃
- **Ultra-Violet Fluorescence**: SO₂
- NDIR: **Non-Dispersive Infrared Spectroscopy**: CO, CO₂, CH₄, C₃H₈, NO, NOₓ, N₂O, SO₂, THC
- Transmissometer - Opacity

Other CEMS measurement methods used and the gas that they measure are FTIR, or Fourier Transform infrared method, chemi-luminescence, ultra-violet fluorescence, and non-dispersive infrared spectroscopy. A transmissometer for measurement of opacity is used for COMS measurements.
Methods for measuring and analyzing air pollutants can be characterized as gravimetric, atomic absorption spectrometry, or spectrophotometry. This slide discusses the principle on which the method is based.

<table>
<thead>
<tr>
<th>Method</th>
<th>Measured</th>
<th>Principle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravimetric</td>
<td>PM$<em>{10}$, PM$</em>{2.5}$</td>
<td>Particles are trapped or collected on filters, and the filters are weighed to determine the volume of the pollutant.</td>
</tr>
<tr>
<td>Atomic absorption spectrometry (AAS)</td>
<td>more than 60 metals or metalloid elements (e.g. Pb, Hg, Zn)</td>
<td>Technique operates by measuring energy changes in atomic state of analyte. Emitted radiation is function of atoms present in sample.</td>
</tr>
<tr>
<td>Spectrophotometry</td>
<td>SO$_2$, O$_3$</td>
<td>Measure amount of light that sample absorbs. Amount of light absorbed indicates amount of analyte present in sample.</td>
</tr>
</tbody>
</table>
Methods of Measuring and Analyzing Air Pollutants

<table>
<thead>
<tr>
<th>Method</th>
<th>Measured</th>
<th>Principle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemiluminescence</td>
<td>NO$_2$, O$_3$</td>
<td>Based upon emission spectrum of an excited species that is formed in chemical reaction</td>
</tr>
<tr>
<td>Gas Chromatography (GC) - Flame Ionization Detector (FID)</td>
<td>VOC</td>
<td>Responds in proportion to number of carbon atoms in gas sample</td>
</tr>
<tr>
<td>Gas Chromatography-Mass Spectrometry (GC-MS)</td>
<td>VOC</td>
<td>Mass Spec uses difference in mass-to-charge ratio of ionized atoms-molecules to separate them</td>
</tr>
<tr>
<td>Fourier Transform Infrared Spectroscopy (FTIR)</td>
<td>CO, VOC, CH$_4$</td>
<td>Sample absorbs infrared radiation and difference in absorption is measured</td>
</tr>
</tbody>
</table>

The principles on which Chemi-luminescence, Gas Chromatography (GC) - Flame Ionization Detector (FID) and Gas Chromatography-Mass Spectrometry (GC-MS) are listed in this slide.
Spectrophotometry

- Useful and widely used tools available for quantitative analysis
- Measures amount of light that sample absorbs
- Passes beam of light through sample and measures intensity of light reaching detector
- Relies on colorimetric principles
- Commonly used to measure sulfur dioxide (SO₂) concentrations
- Chemicals are combined with a solution containing SO₂ such that the color of the solution results in different amounts of light being absorbed, therefore, the amount of light absorbed indicates the amount of sulfur dioxide

Spectrophotometry is a useful and widely used tool available for quantitative analysis. This method measures the amount of light that a sample absorbs by passing a beam of light through sample and measuring the intensity of light reaching the instrument’s detector. This method relies on colorimetric principles and is commonly used to measure sulfur dioxide (SO₂) concentrations. Chemicals are combined with a solution containing SO₂ such that the color of the solution results in different amounts of light being absorbed, therefore, the amount of light absorbed indicates the amount of sulfur dioxide.
Spectrophotometry

- Ozone can also be analyzed using monochromatic ultraviolet absorption spectrophotometry principle
- As ultraviolet light at 253.7 nm is passed through the optic bench, a fixed quantity of "zero air" and ambient air are drawn into the bench
- Intensity of ultraviolet radiation traversing the optics bench is attenuated by the ozone present in the sample
- This attenuated signal is detected and compared with the unattenuated signal from the "zero air" cycle
- This difference in intensity is electronically translated into a reading of ozone present

With Spectrophotometry, ozone can also be analyzed using the monochromatic ultraviolet absorption spectrophotometry principle. As ultraviolet light at 253.7 nanometers is passed through the optic bench, a fixed quantity of "zero air" and ambient air are drawn into the bench. The Intensity of ultraviolet radiation traversing the optics bench is attenuated by the ozone present in the sample. This attenuated signal is detected and compared with the unattenuated signal from the "zero air" cycle. This difference in intensity is electronically translated into a reading of ozone present.
Methods for determining components of gases originated with the need for a highly sensitive means for determining atmospheric pollutants such as ozone, oxides of nitrogen, and sulfur compounds. This method is based upon the emission spectrum of excited species that are formed in the course of chemical reaction. Oxides of nitrogen can be determined by gas phase reaction of NO with ozone. A sample is mixed with excess ozone in a special sample cell. A portion of NO present is converted to activated NO\textsubscript{2} which returns to a lower energy state and emits light. This phenomenon is called chemiluminescence. The intensity of light can be measured with photomultiplier tube and is proportional to the amount of NO in sample. A second reaction measures total oxides of nitrogen in the sample and in turn, the concentration of NO\textsubscript{2} can be calculated.
Gas Chromatography (GC)

• Gas chromatography coupled with Flame Ionization Detector (FID) is used for qualitative identification and quantitative VOC determination
• GC consists of a column, oven and detector
• Sample goes to the column, separates into individual compounds and proceeds through hydrogen FID
• Flame in FID is produced by combustion of hydrogen and air

Gas chromatography, or GC, coupled with Flame Ionization Detector, or FID, is used for qualitative identification and quantitative VOC determination. The GC consists of a column, oven and detector. The sample goes through the column, separates into individual compounds and proceeds through the hydrogen-fired FID. A flame in the FID is produced by combustion of hydrogen and air.
Gas Chromatography (GC)

- When sample is introduced, hydrocarbons are combusted and ionized, releasing electrons
- Collector with polarizing voltage located near flame attracts free electrons, producing a current that is proportional to amount of hydrocarbons in sample
- Signal from FID is amplified and output to display or external device

When the sample is introduced to the GC, hydrocarbons are combusted and ionized, releasing electrons. A collector with polarizing voltage located near flame attracts free electrons, producing a current that is proportional to the amount of hydrocarbons in the sample. The signal from the FID is amplified and output to a display or external device.
Gas Chromatography-Mass Spectrometry (GC-Mass Spec)

• GC-MS instruments used for identification of volatile organic compounds
• Mass spec uses the difference in mass-to-charge ratio (m/z) of ionized atoms or molecules to separate them from each other
• Mass spec is useful for quantification of atoms or molecules and also for determining chemical and structural information about molecules
• Molecules have distinctive fragmentation patterns that provide information to identify structural components, oven and detector

A GC-MS instrument can be used for identification of volatile organic compounds. The mass spec uses the difference in the mass-to-charge ratio (m/z) of ionized atoms or molecules to separate them from each other. The mass spec is useful for quantification of atoms or molecules and also for determining chemical and structural information about molecules. Molecules have distinctive fragmentation patterns that provide the information to identify structural components, oven and detector.
The Fourier Transform Infrared Spectroscopy, or FTIR, method can detect and measure both criteria pollutants and toxic pollutants in air. This method can directly measure more than 120 gaseous pollutants in the air, such as carbon monoxide, sulfur dioxide, and ozone. It also can measure toxic pollutants, such as toluene, benzene, and methanol. The method is based on the fact that every gas has its own "fingerprint," or absorption spectrum. The FTIR sensor monitors the entire infrared spectrum and reads the different fingerprints of gases present.
This slide is a photograph of a total hydrocarbon analyzer.
THC Analyzer – Method of Operation

- Detector responds to carbon mass, not specific compound; does not respond well to oxygenated compounds
- Uses Flame Ionization Detection (FID) principle to determine total hydrocarbons in gaseous sample
- FID analyzer has heated burner (550C) with pump

A total hydrocarbon detector responds to carbon mass, not a specific compound; and does not respond well to oxygenated compounds. It uses the Flame Ionization Detection principle to determine total hydrocarbons in a gaseous sample. The instrument’s FID analyzer has a heated burner, capable of temperatures to 550 degrees Celsius, with pump to pull the sample from the stack.
THC Analyzer – Method of Operation

- Small flame of burner is elevated and sustained by regulated flows of air and either pure hydrogen or 40/60 mixture of hydrogen and helium, or nitrogen
- Split ring detector contains 2 electrodes
- One electrode is negatively polarized using a precision power supply and the other electrode, known as the “collector” is connected to an amplifier

A small flame of the total hydrocarbon burner is elevated and sustained by regulated flows of air and either pure hydrogen or 40/60 mixture of hydrogen and helium, or nitrogen. A split ring detector contains 2 electrodes, where one electrode is negatively polarized using a precision power supply and the other electrode, known as the “collector” is connected to an amplifier.
The 2 electrodes establish an electrostatic field. When introduced to the burner, the gaseous sample is ionized in the flame and the electrostatic field causes charged particles, ions, to migrate to their respective electrodes. This migration creates a small current between electrodes, measured by electrometer amplifier, that is directly proportional to hydrocarbon concentration of the sample.
THC FID Analyzer

- **Ranges:** Four User Definable ranges from 0-3 to 0-30,000 ppm
- **Readout:** As ppm CH₄ or C₃H₈
- **Fuel Requirements:** 40/60 H₂/He (120CC/min) or 100% H₂ (60cc/min)
- **Sample Temperature:** 50°C, Non-condensing
- **Ambient Temperature:** 5°C to 40°C

This slide lists the ranges, readout, fuel requirements, sample temperature and ambient temperature specifications for a total hydrocarbon FID-type analyzer.
This slide is a photograph of a NDIR and oxygen analyzer.
Non-Dispersive Infrared (NDIR) Detection of CO

• CO is monitored continuously by analyzers that operate on infrared absorption principle.
• Sample gas drawn into sample chamber and beam of infrared light is passed through it.
• CO absorbs infrared radiation, and any decrease in intensity of beam is due to presence of CO molecules.
• Decrease in intensity is directly related to CO concentration.

Using a Non-Dispersive Infrared (NDIR) method, carbon monoxide is monitored continuously by analyzers that operate on the infrared absorption principle. Sample gas drawn into the sample chamber and a beam of infrared light is passed through it. Carbon monoxide absorbs infrared radiation, and any decrease in intensity of beam is due to presence of carbon monoxide molecules. Any decrease in intensity is directly related to the carbon monoxide concentration.
With the non-dispersive infrared method, a special detector measures the difference in radiation between the beam and a duplicate beam passing through reference chamber with no carbon monoxide present. The difference in intensity is electronically translated into a reading of carbon monoxide measured in ppm.
NDIR + Oxygen Analyzer – Method of Operation

- Based on infrared absorption characteristics of gases
- Using single infrared beam to measure gas concentrations, analyzer produces highly stable and reliable results
- Single infrared light beam is modulated by chopper system and passed through sample cell of predetermined length containing gas sample to be analyzed

The NDIR method is based on the infrared absorption characteristics of gases. Using a single infrared beam to measure gas concentrations, the NDIR analyzer produces highly stable and reliable results. The single infrared light beam is modulated by a chopper system and passed through a sample cell of predetermined length containing the gas sample to be analyzed.
NDIR + Oxygen Analyzer – Method of Operation

- As beam passes through cell, sample gas absorbs some of its energy
- Attenuated beam (transmittance) emerges from cell and is introduced to front chamber of two-chamber infrared micro-flow detector
- The detector is filled with gas component of interest and consequently beam experiences further energy absorption

As the beam passes through cell, the sample gas absorbs some of its energy. An attenuated beam (transmittance) emerges from the cell and is introduced to the front chamber of a two-chamber infrared micro-flow detector. The detector is filled with the gas component of interest and consequently the beam experiences further energy absorption.
NDIR + Oxygen Analyzer – Method of Operation

• Absorption process increases pressure in both chambers
• Differential pressure between front and rear chambers of detector causes slight gas flow
• This flow is detected by mass-flow sensor and converted into output signal

The absorption process increases the pressure in both chambers. The differential pressure between the front and rear chambers of the detector causes a slight gas flow. This flow is detected by the mass-flow sensor and converted into an output signal.
The Oxygen analyzer section uses either a paramagnetic or a fuel cell method to determine the percent level of oxygen contained in the sample gas. The oxygen level is displayed on an LCD panel in percent concentration.
NDIR + Oxygen Analyzer Specs

- **O₂ Ranges:** 0-1% (Paramagnetic Only) up to 0-100% O₂ Full Scale, Four Definable Ranges
- **Ambient Temperature:** 5° to 40° C
- **Ambient Humidity:** Less than 90% RH (Non-condensing)
- **Sample Temperature:** Up to 50° C

This slide lists the oxygen ranges, ambient temperature, ambient humidity and sample temperature specification for a NDIR and oxygen analyzer.
This slide is a photograph of an oxygen sensor and oxygen analyzer.
The sensor of an oxygen analyzer is made from zirconium dioxide. The sensor surface is positioned in direct contact with the flue gases and the oxygen content is the difference between the atmosphere and flue gases. The temperature range of the sensor is 1110 – 2550 degrees Fahrenheit or 600 – 1400 degrees Celsius. The life of the sensor probe is reduced in flue gas streams above 1250 degrees Celsius.
This slide shows a schematic of a double pass transmissometer for measuring opacity in the stack. A light beam is projected from the lamp through the half-silvered mirror, through the window, through the stack, through the window of the reflector unit, to the retro-reflector that reflects the beam back to the sending unit, through the stack gas, to the mirror, and to the detector. The amount of the light beam that is measured at the detector is less than the amount of light sent through the stack because of the particulate in the gas diffuses the light. Since the light passes through the stack twice, the measurement is actually twice the amount intended so the measured amount must be adjusted for this situation. Since both sending and reflecting units have windows, high moisture content in the gas can result in condensation on the window that will distort the opacity reading.
This is another schematic of an opacity monitor.
This slide shows the results from FTIR monitoring. You can see that the results are responsive to the concentration of the compound being measured, in this case formaldehyde, methanol, and alpha-pinene.
This slide shows the response output from a gas chromatograph. From the peaks one can determine the compounds that are present and the relative concentration.
This slide shows a schematic of a flame ionization detector. The flame ionizes the compounds and the ionization is measured by the electric circuit created.
The slide illustrates a schematic of a CEMS unit. The sample probe in the stack draws a sample from the gas stream and the sample flows to the sample cooling unit inside the CEMS cabinet. The sample stream then goes through a catch pot to remove moisture, then through a particulate filter, then to a flow indicator. Depending on the type of measuring unit, air may be introduced to dilute the gas stream after flow measurement of the sample gas. The gas then flows a sample pump, and to the sensor units before being exhausted.
This slide is a photograph of an analyzer panel on a stack testing site.

This ends the presentation of this module.