

# On-Line Flare BTU Monitoring with Process Mass Spec for RSR compliance

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S C I E N T I F I C

# Regulatory Background



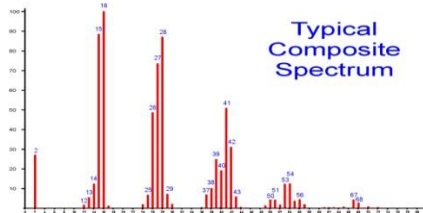
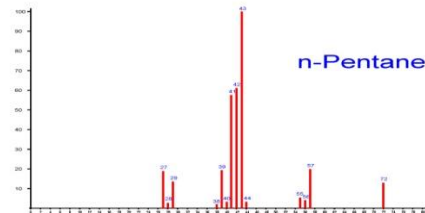
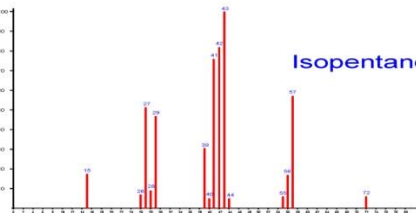
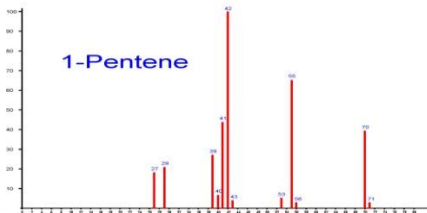
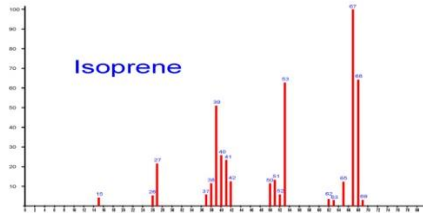
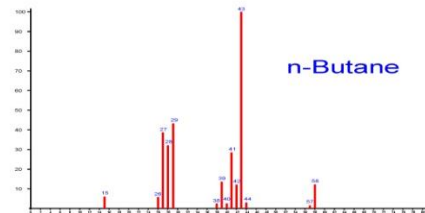
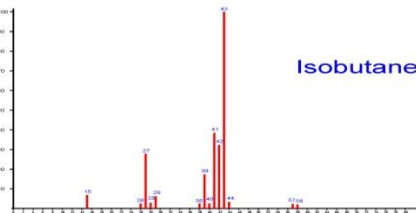
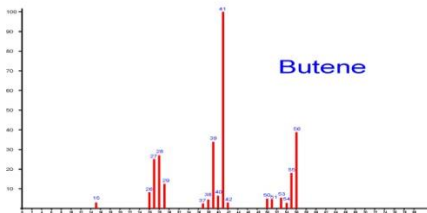
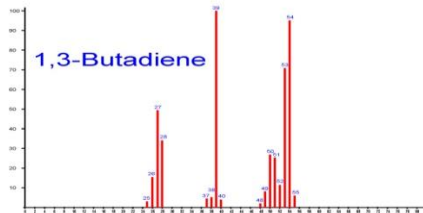
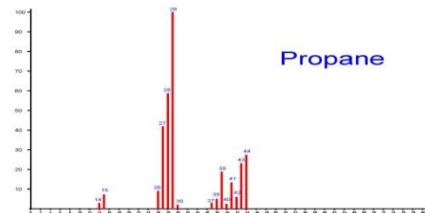
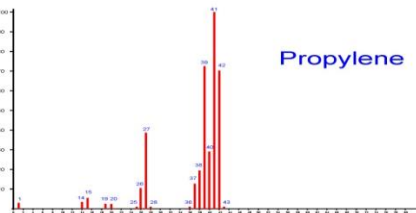
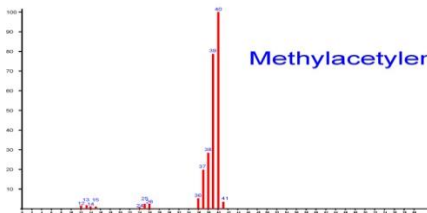
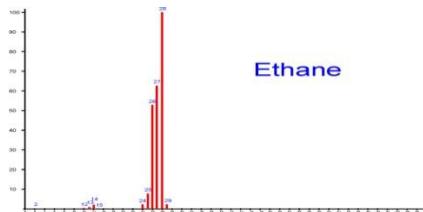
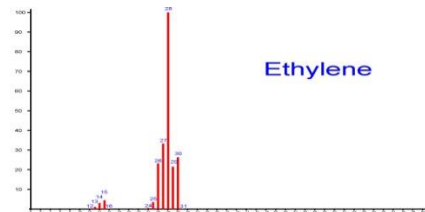
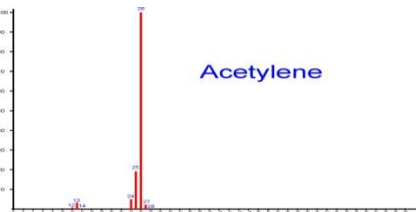
Refinery Sector Rule - The final rule is based on the risk and technology review of two refinery emissions standards:

- National Emission Standards for Hazardous Air Pollutants From Petroleum Refineries (40 CFR Part 63 Subpart CC, "Refinery MACT 1" – Max. Achievable Control Technology)
- National Emission Standards for Hazardous Air Pollutants for Petroleum Refineries: Catalytic Cracking Units, Catalytic Reforming Units, and Sulfur Recovery Units (40 CFR Part 63 Subpart UUU, "Refinery MACT 2").

# What is Process Mass Spectrometry?

- It is NOT GC/MS
- All molecules in the stream are ionized and fragmented
- Each compound produces a signature fragmentation pattern (fingerprint)
- Separation and quantitation are solution to mathematical matrix
- Matrix must have as many equations as unknowns
- Process mass spec only quantifies those compounds that you tell it to look for

# Example mass spectra



# Background

- In a flare, vented gases are combined with steam and/or air and burned to produce water vapor, carbon dioxide, trace NOX & SOX compounds
- Flaring occurs during start-up, shut-down and during unplanned operational interruptions and upsets
- Increasing regulatory control on flares
  - *US EPA 40 CFR Part 63 subpart CC – must measure flare vent gas to determine Net Heating Value (BTU/SCF)*
  - May use GC (63.670 (j1)), Calorimeters (63.670 (j1)), or Process Mass Spectrometers (EPA Generally Applicable AMP, Feb. 5<sup>th</sup>, 2018)
  - *Component analysis (GC & Mass Spec) assists with root-cause analysis by identifying individual components that are present in the flare g*
- Net Heating Value
$$X_1 * \text{Ideal Net Heating Value}_1 + X_2 * \text{Ideal Net Heating Value}_2 + X_3 * \text{Ideal Net Heating Value}_3 \dots + X_n * \text{Ideal Net Heating Value}_n$$



# RSR for Flare - Specifics

## Reductions in Flare Emissions

Under the new rule, provisions have been implemented to assure 98% combustion efficiency, superseding the flare General Provision requirements. Flares must now meet the following operating conditions:

- Continuously lit pilot flame at all times
- No visible emissions when flare vent gas is below the smokeless capacity of the flare
- Net heating value for the combustion zone gas (NHVcz),  $\geq 270$  BTU/ft<sup>3</sup> on a 15-minute average, calculated using flare vent gas composition monitoring
- Compliance with one of two options for measuring flare tip velocity

# Monitoring System Requirements – 40 CFR 63.671

Owner shall install, operate, calibrate and maintain the Continuous Process Monitoring System (CPMS)

1. ... readout for compliance is readily accessible by operator (sic)
2. . . . must complete a minimum of one cycle (sampling, analyzing and data recording) for each successive 15-minute cycle
3. Except for periods of malfunction, repairs, & QA/QC activities, owner shall operate & collect data continuously when emissions are routed to flare
4. Operate, maintain & calibrate according to part (b)
5. Must comply with out of control procedures in (c)
6. Reduce data as specified in (d)
7. CPMS must be capable of measuring appropriate parameter over range expected at that location

## Section (e) – addn. requirements for GC

For monitors used to determine compositional analysis:

1. Q/A requirements are in table 13 of 63.671
2. Cal Gases must meet one of 2 options:
  - a) Must include all of Hydrogen, Methane, Ethane, Ethylene, Propane, Propylene, n-Butane, iso-Butane, Butenes, 1,3-Butadiene, n-Pentane
  - b) or may calibrate according to surrogate method
3. Owner may choose a compound list based on what is reasonably expected to be present
4. Thermo Scientific recommends target compound list calibration for mass specs



# Table 13

## Net heating Value by Gas Chromatograph.

- As specified in [Performance Specification 9](#) of 40 CFR part 60, appendix B
  - Follow the procedure in Performance Specification 9 of 40 CFR part 60, appendix B, except that a single daily midlevel calibration check can be used (rather than triplicate analysis), the multi-point calibration (linearity validation) can be conducted quarterly (rather than monthly), and the sampling line temperature must be maintained at a minimum temperature of 60 °C (rather than 120 °C).

## Hydrogen Analyzer

- +/- 2 percent over the concentration measured or 0.1 volume percent, whichever is greater.
  - Specify calibration requirements in your site specific CPMS monitoring plan. Calibration requirements should follow manufacturer's recommendations at a minimum.

# Performance Spec 9

Calibration precision, calibration error, and performance audit tests are conducted to determine conformance of the CPMS with specifications. Daily calibration maintenance requirements are also specified

- 6.2 Sampling System – shall be heat traced with no cold spots.
- 7.1 Calibration Gases. Obtain three concentrations certified within 2%. Performance test in Meth. 205 shall be repeated quarterly. Concentrations shall be: Low level. 40-60% of measured concentration Mid level. 90-110% of measured concentration High level. 140-160% of measured concentration
- 8.3 7-Day Calibration Error Test. At beginning of each 24 hr period, set instr setpts by conducting a (multipoint) calibration for each compound. Throughout the 24 hr per., analyze the stack gas. At end of 24 hrs., analyze each of 3 initial cal standards in triplicate, determine avg instrument response. Each CE for all compounds must be  $\leq 10\%$ . Repeat procedure for a total of 7 consecutive days.

## Performance Spec 9 (cont)

8.4 Performance Audit Test Periods. Conduct the performance audit once during the initial 7-day CE test and quarterly thereafter. Analyze EPA audit gas three times, and calculate the average instr response (if using a gas mixture, report the certified concentration of each compound)

10.1 Initial (Multi-point) Calibration. After routine maintenance, or at least once per month (subst. quarter), conduct a multipoint calibration of the analyzer for each target analyte. Calibration shall meet requirements in section 13.3 (sample to be analyzed shall flow continuously through the sample system).

10.2 Daily Calibration. Once every 24 hours, analyze the mid-level standard in triplicate. Average analyte response cannot vary by more than 10% from the certified value.

# EPA Alternate Measurement Protocol 119

EPA approves substitution of continuous mass spectrometry for continuous gas chromatography.

Must meet requirements in 40 CFR63.671 (e1 & e2), including Table 13.

May use alternative sampling line temp (60° C)

Must meet applicable Performance Spec 9

- Multi point calibration check at three concentrations
- Periodic mass spec calibrations as directed in Table 13
- May use n-Pentane response for unknowns and compounds with higher molecular weight than Pentane

**. . . "we will announce on EPA's website that the alternative method is broadly applicable to determination of NHV under this subpart"**

# Example 1: Flare Gas Application Summary

Name	Formula	Molecular Weight	Conc %mol	precision (standard deviation) %mol
Hydrogen	H <sub>2</sub>	2	Bal	≤0.1
Methane	CH <sub>4</sub>	16	10	≤0.02
Water	H <sub>2</sub> O	18	10	≤0.05
Carbon Monoxide	CO	28	10	≤0.05
Nitrogen	N <sub>2</sub>	28	1	≤0.005
Ethane	C <sub>2</sub> H <sub>6</sub>	30	0.1	≤0.005
Methanol	CH <sub>3</sub> OH	32	1	≤0.005
Carbon Dioxide	CO <sub>2</sub>	44	1	≤0.005
Propane	C <sub>3</sub> H <sub>8</sub>	44	1	≤0.005
i- & n- Butane	i- & n-C <sub>4</sub> H <sub>10</sub>	58	1	≤0.005
i- & n- Pentane	i- & n-C <sub>5</sub> H <sub>12</sub>	72	0.5	≤0.005
NHV				0.3% rel

# Why use process mass spec?

- Speed – measurement of all components in under 30 seconds
- Stability – some clients run their mass specs for >1 yr without needing recalibration
- Excellent linearity - many components exhibit  $R^2$  of 1.0
- Flexible application – software based
- Versatility – can provide measurement of multiple sample points with the same analyzer

# Mass spec drawbacks

- Cost
- Low level of industry adoption
- Perceived as “complex”
- Persistent negative stereotypes from >30 years ago
- Lots of calibration cylinders required
- If you perform maintenance, must allow vacuum to be attained before the analyzer can be returned to service

# Thank you!!

## Questions??