

Measurement of Hydrogen Cyanide Air Emissions in Refinery Operations

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roduction

A 2011 ICR for Refinery Sector requested HCN emissions from FCCU

- Requested Method was EPA Other Test Method (OTM)-029
 - Other Methods used were EPA Conditional Test Method (CTM)-033
 - Carb Method 426
 - FTIR Methods: EPA Method 320 and ASTM D3648
- EPA reviewed data from 22 Reports
 - 12 Reports were from existing report no early than 2005
 - 10 Reports from requested tests



Draft Results of Refinery ICR

y 9 of the 22 reports were considered useable data

- Included data from 8 units
- 13 reports were unsuitable to use according to EPA guidance
 - Wrong Method used
 - pH too low in last impinger

ving data sets

- Methods for valid data included OTM-029 and CTM-033(that used stronger NaOH Impinger solutions (pH12)
- Emissions varied (0.001 to 0.022 lb. HCN/BBL Feed)

asons of varying data

- Operation of FCC
- Test Method Variation



Formation of HCN in FCCU



- FCCU takes higher molecular hydrocarbon and “cracks” them into more valuable lighter hydrocarbon compounds for gas and diesel
- Much of the HCN comes during the burning of carboneous coke
 - Nitrogen species are reduced to HCN mostly during the burn
 - HCN is then thermally decomposed into NO
 - Similar in Coal Combustion
- FCCU Operating Parameters that effect HCN
 - Full Burn (O_2 rich) vs Partial Burn (O_2 Lean)
 - Use of CO Boilers –conversion of HCN to NO_x
 - Use of PT and Non-PT Catalyst- speeds conversion of HCN
 - ESP and Scrubber units unknown effects to HCN removal



A OTM-029

Impinger based Method

A manual, impinger based method that captures HCN in a strongly basic NaOH solution as illustrated in the sample train diagram below. The impinger contents are analyzed off-site by Ion Chromatography (IC).

OTM-033

Similar to OTM-029 but used a different concentration of NaOH for the impinger solutions

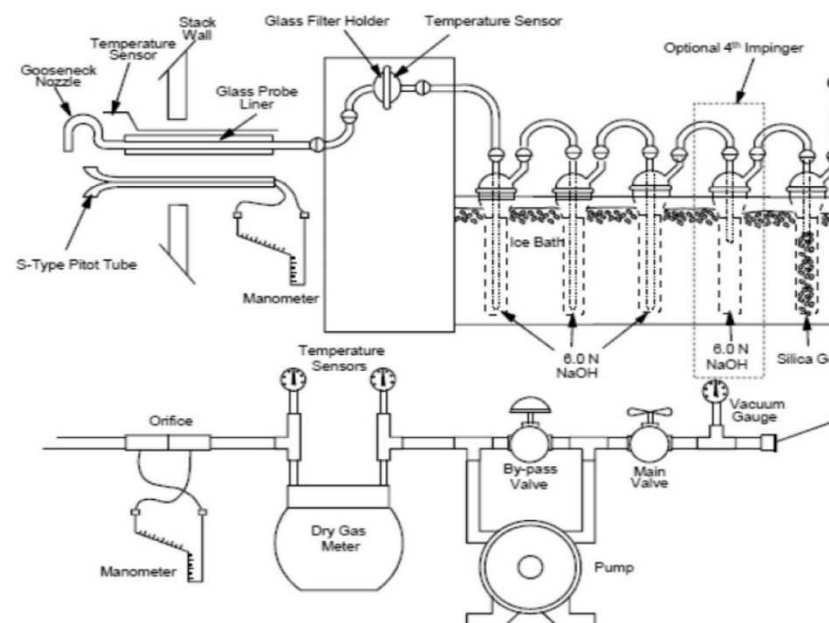
OTM-029 replaced CTM-033

IC Highlights

Manual Equipment Checks and Calibrations

IC Analysis Checks

- linearity of detector, batch spiking, internal standard





M-029 Sources of Bias

OH solutions pH

- OTM-029 doubled the strength of the solution over CTM-033
- CO_2 in the stack effluent will neutralize the NaOH base
- H_2O could dilute solution

ides in solution

- >25mg/sample interfere by converting HCN to SCN

oxidizing Compounds

- Potential to oxidize HCN to other forms

Limitations on testing for ICR using OTM-029

- Limit total sample volume to 1 cubic meter
- Use of Lead Acetate impinger for sulfides
- Must check pH of last NaOH impinger



Method EPA Method 320 and ASTM Method 348

- These instrumental methods measures HCN and other gases using extractive FT
 - Stack gas is transported to the analyzer using a heated sampling system where it is measured in real-time on a wet basis.
 - M320 and D6348 have very similar procedural requirements.
 - Data bias correction required for both methods.
 - EPA Method 320 relies on Method 301 Bias Correction
 - ASTM D6348 relies on Spiking procedures (EPA requirement)
- QAQC Highlights
 - Daily CTS and N2 Checks (direct and system)
 - Analyte Spiking
 - Source Specific detection limits (MDC)





ns for FTIR Methods

Sample System Bias

- Cold Spots in Sample Lines
 - Keep all component hot and hot
- In-line Filters for Particulate Matter
- Gas Manufacturers for spiking gases

Analytical Bias

- IR Spectra of H_2O as interferant
- Both HCN and H_2O absorb in the same spectral region





Final Thoughts

h methods present challenges

- Bias in each of the methods
- Need for experience emission testers for both methods

A Requesting a one-time test in 40CFR63, Subpart UUU

- Why??
 - Use of FTIR methods only
 - Collect data on all FCCU's
 - Readdress the emission factor with more data????

a Refineries control HCN through existing operations

- Current data (9 tests) does not support a lot of trends for operators



Credits to the following:

- Thomas A. Dunder, Ph.D.
- “HCN and NO_x control strategies in the FCC” by Xunhua Mo, Bart De Graaf, Charles Radcliffe and Paul Diddams
- The EPA “DRAFT Review of Emissions Test Reports for Emissions Factors Development for Flares and Certain Refinery Operations”



Thank you

Questions?

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