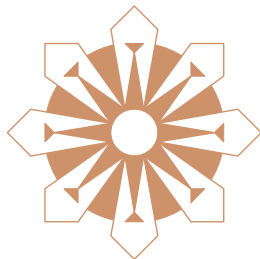


DEMONSTRATING COMPLIANCE WITH VERY LOW AIR PERMIT VOC LIMITS

Mannie L. Carpenter, P.E.

At Gatekeeper Regulatory Roundup Conference

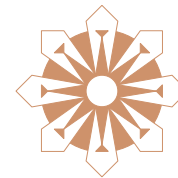
February 15, 2011



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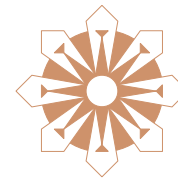
THE TASK

- Demonstrate compliance for natural gas-fired combined cycle turbine generators with air quality permit emission limits of 1.0 ppm and 2.3 pounds per hour VOC emissions.



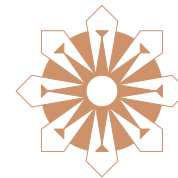
THE TRADITIONAL METHODS

- EPA Method 25A – total hydrocarbons (THC) using flame ionization detector (FID)
- EPA Method 18 – methane content from composite Tedlar bag samples
- EPA Method 19 – flowrate based on fuel use and O₂ concentration
- Numerically subtract methane concentration from THC concentration to obtain non-methane organic carbon (NMOC)



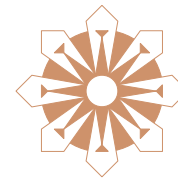
THE “COMPLICATIONS”

- Permit language related issues
- Field analytical equipment limitations
- Laboratory analysis method variations and limitations
- Adaptation of ambient methods to industrial sources



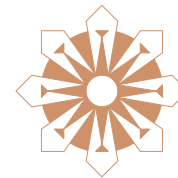
PERMIT ISSUES

- In air emissions parlance ppm = parts per million by volume
- A gram mole of propane and a gram mole of methane occupy the same volume
- A gram mole of propane weighs 44 grams and a gram mole of methane weighs 16 grams
- Dry basis ppm varies from wet basis ppm
- Standard O₂ basis (i.e. ppm @ 15% O₂)



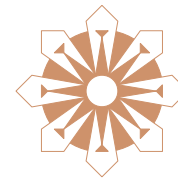
PERMIT ISSUES

- Definition of VOC excludes methane and other non-precursor organic compounds—sometimes
- Many regulatory agencies will not allow subtraction of methane concentrations if greater than THC



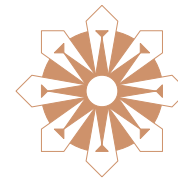
FIELD EQUIPMENT

- Method 25A:
 - *“Span Value means the upper limit of a gas concentration measurement range that is specified for affected source categories in the applicable part of the regulations. The span value is established in the applicable regulation and is usually 1.5 to 2.5 times the applicable emission limit. If no span value is provided, use a span value equivalent to 1.5 to 2.5 times the expected concentration. For convenience, the span value should correspond to 100 percent of the recorder scale.”*



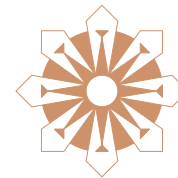
FIELD EQUIPMENT

- Per Method 25A, maximum span of the FID for a 1.0 ppm limit should be no more than 2.5 ppm
- Minimum range for most FID analyzers is 0 – 10 ppm
- One manufacturer lists a 0 – 1.0 ppm range, but with a 0.20 ppm drift specification



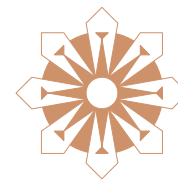
ANALYTICAL METHODS

- “Method 18 analysis” means many different things to many different people
- Original design was to collect composite samples using Tedlar bags in an evacuated canister to be analyzed off-site for methane
- Problems with FID field analyzer resulted in field decision to have composite samples analyzed for NMOC



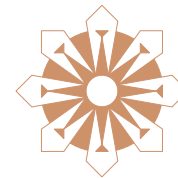
ANALYTICAL METHODS

- Method 18 Analysis:
 - GC to separate compounds by groups
 - Counts each group as if all were ethane, propane, butane, etc.
 - Sample aliquot size typically limited to 1.0 cm³
 - ~1.0 ppm NMOC minimum reporting levels (MRLs)



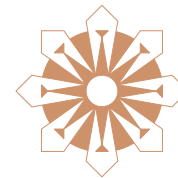
ANALYTICAL METHODS

- Method 25C Analysis:
 - GC to separate compounds
 - Oxidizes all hydrocarbons to CO₂
 - Reduce all CO₂ to methane for analysis by FID
 - Counts carbons without response factor issues
 - Produces <1.0 ppm NMOC MRLs with ambient CO₂



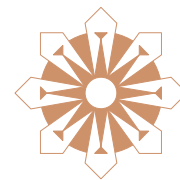
ANALYTICAL METHODS

- Method TO-12 analysis:
 - CO₂ and H₂O removed from sample
 - Cryogenic concentration allows much larger sample volume to be analyzed
 - GC/MS/FID analysis produces characteristic spectra and identifies compounds of interest
 - Produces <50 ppb NMOC MRLs
 - Limited laboratory availability



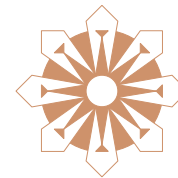
ANALYTICAL RESULTS

- Composite samples were analyzed by outside labs by Method 25C, resulting in 19 of 21 samples analyzed with results of less than the MRLs of 2.75 ppm
- Compliance could not be demonstrated due to high CO₂ content of samples causing the high MRL

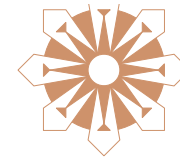
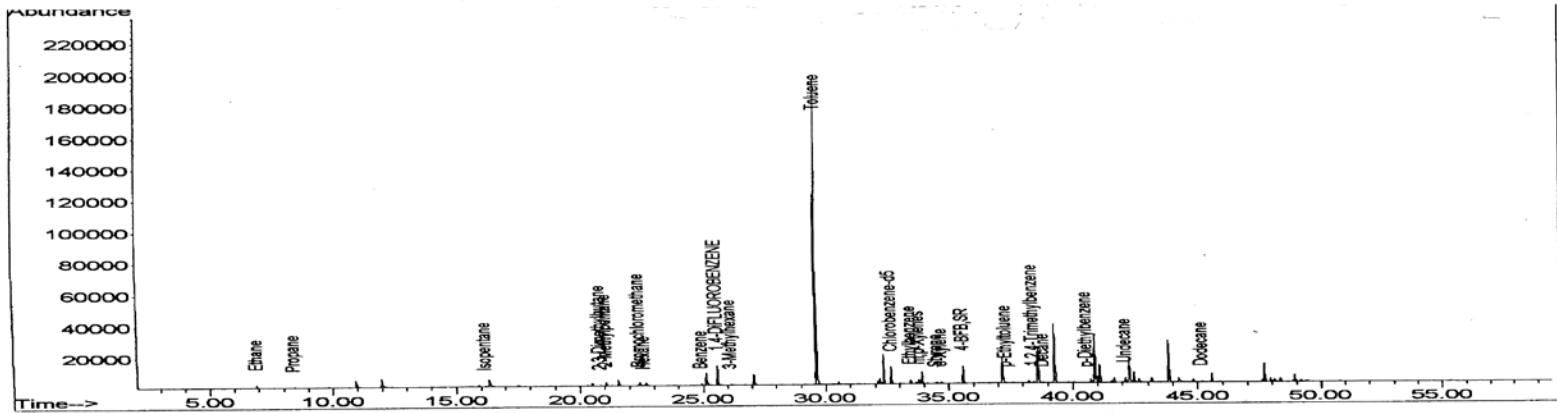
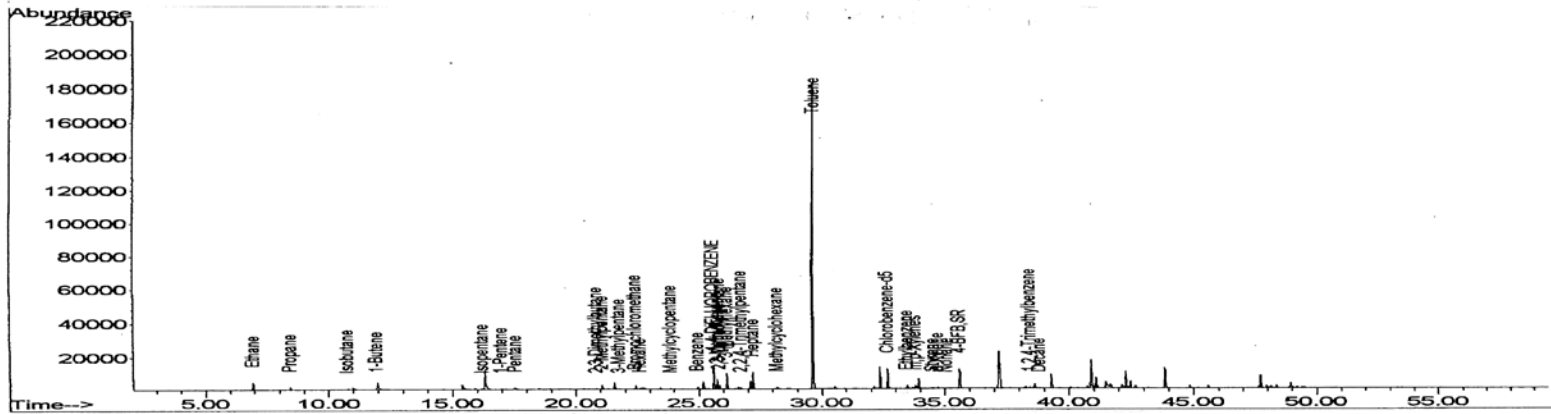


ANALYTICAL RESULTS

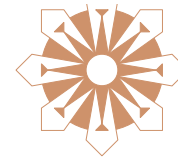
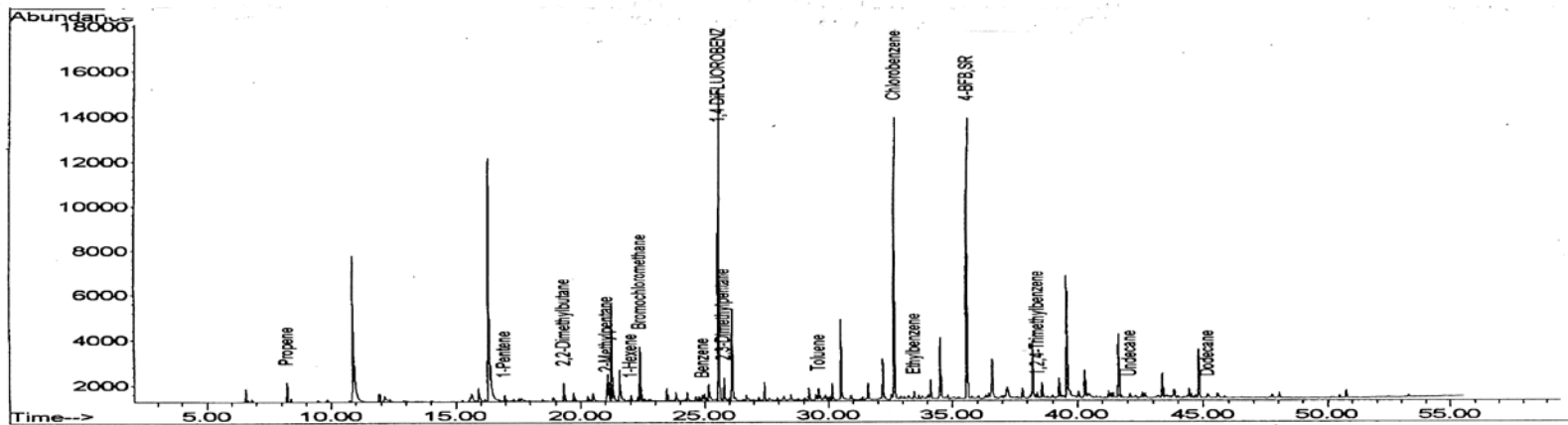
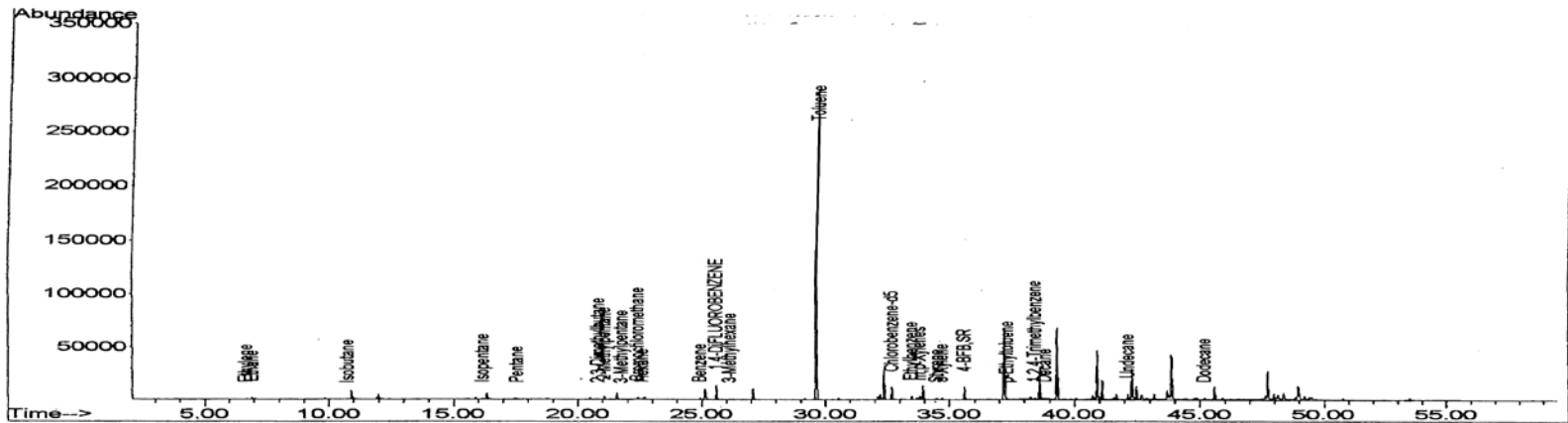
- Repeated duplicate samples were collected using Tedlar bags and Summa canisters
- Both samples analyzed by Method TO-12
- Samples collected in Tedlar bags failed to meet 1.0 ppm limit
- Samples collected in evacuated SS canisters were below 1.0 ppm limit
- Blanks collected in new Tedlar bags analyzed at 1.0 – 1.7 ppm NMOC, primarily toluene



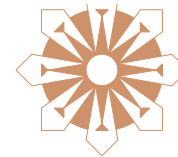
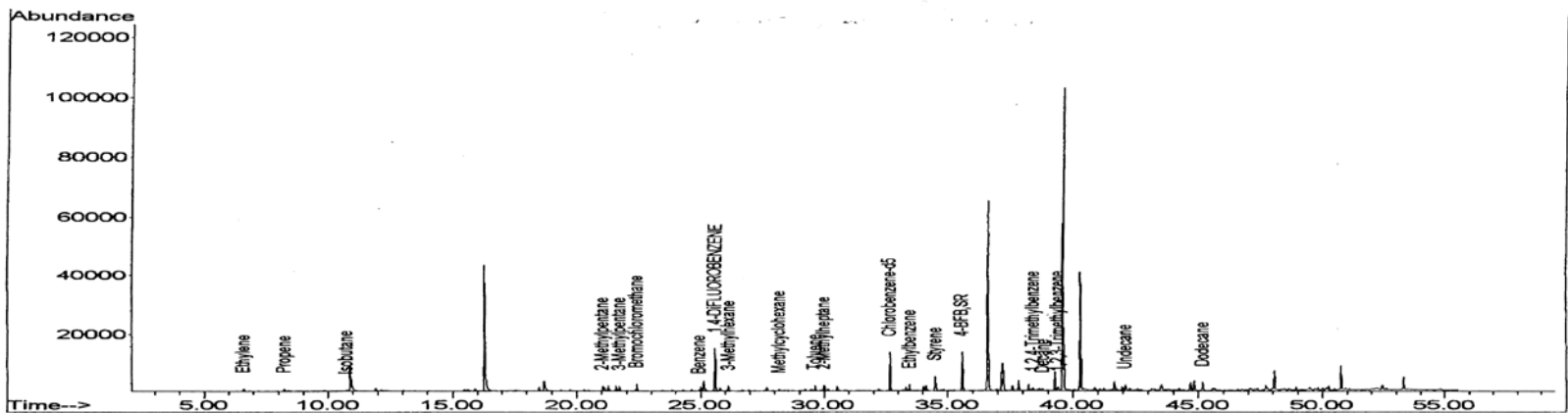
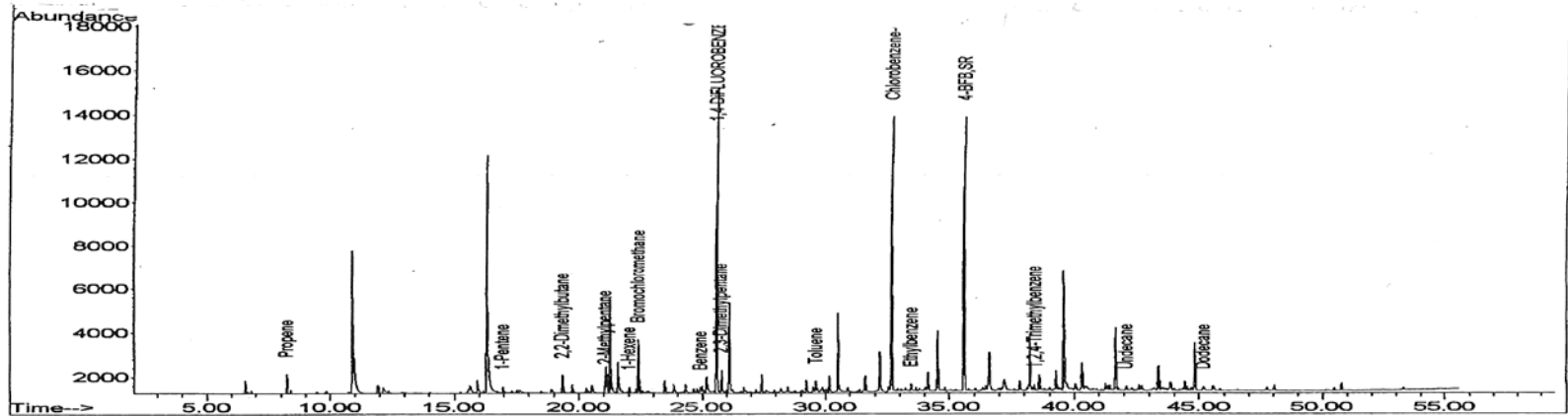
ANALYTICAL RESULTS



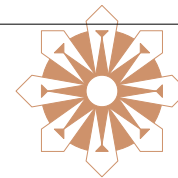
ANALYTICAL RESULTS



ANALYTICAL RESULTS

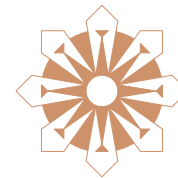


ANALYTICAL RESULTS



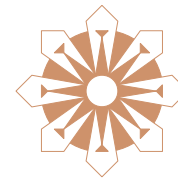
LESSONS LEARNED

- When adapting methodologies, start small to avoid additional expense if things don't work out as planned and alternative approaches are required
- For best results, thorough communication between field and laboratory personnel is required



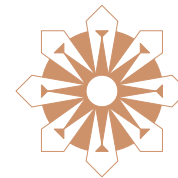
LESSONS LEARNED

- Make sure permit language is clear on limits and methods for demonstrating compliance
- While Method TO-12 can provide a great deal of information, the ability to “see” at much lower levels creates unique challenges
- New technology and/or methodology is required if VOC limits continue to decline

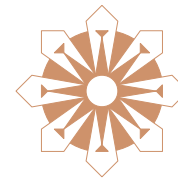


LESSONS LEARNED

- Not all Teflon© is created equal – FEP vs. PTFE
- High moisture and temperature can affect flow controllers
- Method 25A may still be the best available to measure VOC emissions at a reasonable cost, but demonstrating very low emissions may require dedicated test equipment



QUESTIONS?



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