CURRENT ISSUES AND METHODOLOGIES FOR DETERMINATION OF HAP EMISSIONS FROM WOOD PRODUCTS SOURCES

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Overview

- List of approved methods
  - Pros, cons, what to watch for, etc.
- Issues
  - Regulators preferring one method over another – how do they compare?
  - FTIR sampling
- Comparison data

EPA Method 25A

- Measures THC using flame ionization analyzer
- Cannot resolve individual HAPs; measures almost all organics in gas steam
- Used as a surrogate for HAP destruction in PCWP MACT
- FIA has limited response to methanol and other oxygenated organic compounds
- FIA has no response to formaldehyde
- Some operating permits require results as WPP1 VOC
  - M25A with methanol and formaldehyde measured separately using approved method in PCWP MACT rule
- Negative bias for high moisture sources
- Only option for PCWP MACT sources demonstrating compliance by HAP_{THC}

EPA Method 18

- Measures gaseous organic compounds by gas chromatography
- Often used with Method 25A to measure methane
  - Methane can be subtracted from THC value
- Can measure individual HAP compounds
- Flexible method
- Most often GC/FID, but other detectors may be used
- Moderately rigorous QA
  - Must demonstrate spike recovery for each compound

EPA Method 308

- Methanol emissions from stationary sources
- Methanol collected in chilled impinger containing DI water and adsorbed on silica gel
- Requires extraction of methanol from silica gel
- Analysis of water sample and extracted silica gel sample on GC/FID
- Limited to only methanol
- Similar to NCASI CI/SG/PULP-94.03 which does not require silica gel

EPA Method 316

- Formaldehyde emissions from stationary sources
- Formaldehyde collected in chilled Greenburg/Smith glass impingers of DI water
- Method claims wide measurement range
  - 0.011 – 23,000 ppm
- Isokinetic sampling with relatively complex setup (adopted Method 5)
- Formaldehyde analyzed through colorimetric method
  - Modified pararosaniline method
  - Potential bias with dirty sample
- Limited to only formaldehyde
- Widely used in fiberglass industry

EPA Method 0011

- Sampling for select aldehyde and ketone emissions
  - Formaldehyde, acetaldehyde, propionaldehyde
  - Not applicable for acrolein
- Aldehydes derivatized with 2,4-nitrophenylhydrazine (DNPH)
- Formaldehyde detection limit of 90 ppb
- Isokinetic sampling with relatively complex procedure (modified Method 5)
- Analyzed by high performance liquid chromatography (HPLC)
- Method requires field and matrix spike
- Limited to only aldehydes (excluding acrolein)
- Acidic/reactive impinger solution can generate formaldehyde from cured resins
- DNPH depletion issues
- DNPH holding times are short
- Most wood products plants avoid this method if possible

NCASI Method CI/WP 98.01

- “Chilled impinger” method to measure formaldehyde, methanol, and phenol
- Compounds collected in chilled midget impingers of DI water
- Methanol analyzed with GC/FID
- Formaldehyde derivatized with acetylacetone and measured by colorimetric analysis
- Simple setup and procedure
- EPA Method 301 validated
- Requires field blank, duplicate, and train spike/ matrix spike

NCASI Method IM/CAN/WP 99.02

- “Impinger/canister” method for selected HAPs and other compounds
- Measures PCWP “total HAPs,” terpenes, and other organics
- Polar compounds collected in chilled midget impingers containing DI water
- Canister following impingers for collection of terpenes and breakthrough
- Four different analyses
  - GC/FID(aqu), GC/MSD(can), GC/FID(can), acetylacetone procedure(form.)

NCASI 99.02 cont.

- Short hold time due to some volatile compounds (e.g., acrolein)
- Self validating method
  - Multiple QA requirements and restrictions
- Much more complicated than 98.01
- Had a time and place once, but not used much anymore
  - For PCWP HAPs, can now be replaced with “BHA method”
- Still used by industry mostly due to benzene sampling requirements

NCASI Method ISS/FP-A105.01

- “BHA” impinger method for selected aldehydes, ketones, and polar compounds
- Designed for measurement of PCWP MACT total HAPs
- Chilled impingers with aqueous solution of o-benzylhydroxylamine (BHA) to derivatize aldehydes and ketones and capture polar compounds
- Analysis of aldehyde oximes with GC/NPD
- Analysis of alcohols with GC/FID

NCASI 105.01 cont.

- Aldehydes stable for longer time in derivatized form
- Self-validating method
  - Multiple QA requirements and restrictions
- Setup and analysis less complicated than 99.02 since there is no canister
- Typical detection limits are about 500 ppb
  - Can be “pushed” down to about 50 ppb (just aldehydes)

EPA Method 320/ASTM Method D 6348-03

- Measurement of gaseous compounds by extractive FTIR spectroscopy
- Uses IR spectroscopy to analyze compounds absorbing in the mid-IR wavelength range
- Capable of measuring PCWP total HAPs and other gaseous compounds
- Measurement of all analytes on single instrument
- If analysis method is already established can obtain instantaneous results
  - Process monitoring, engineering testing

FTIR cont.

- Establishing analysis method is difficult
  - Must define target analytes, interfering compounds, analysis areas
  - Requires knowledge of gas stream composition
- Detection limit levels based on instrument and accuracy of analysis method
- QA spiking required
  - Analyte spiking can be used to evaluate analysis method
  - Should use spike compounds with analysis areas similar to target compounds

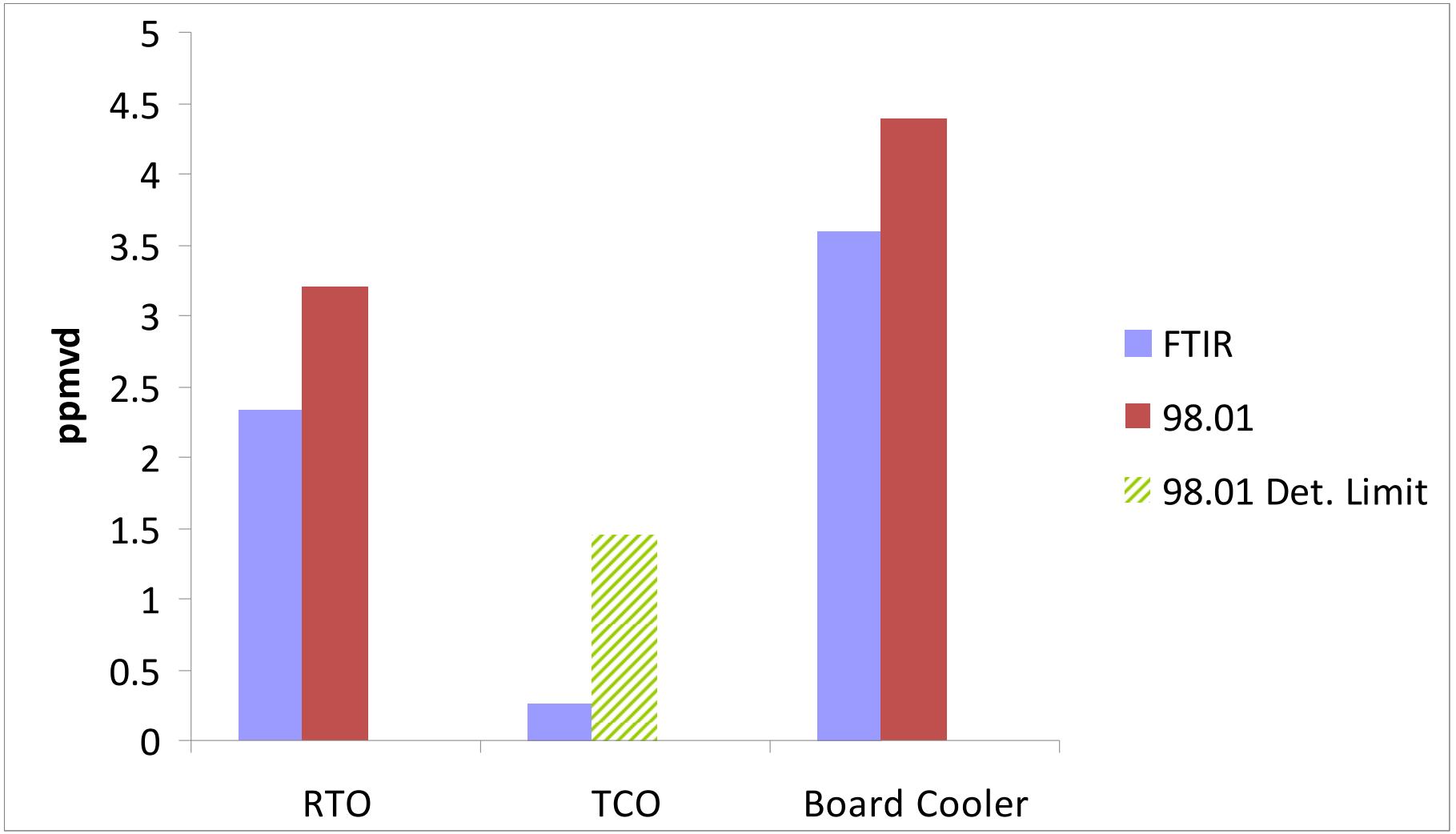
Method Comparison

	25A	18	308	316	0011	98.01	99.02	BHA	320/6348
THC	X								
PCWP Total HAP		X					X	X	X
Methanol		X	X			X	X	X	X
Formaldehyde		X		X	X	X	X	X	X

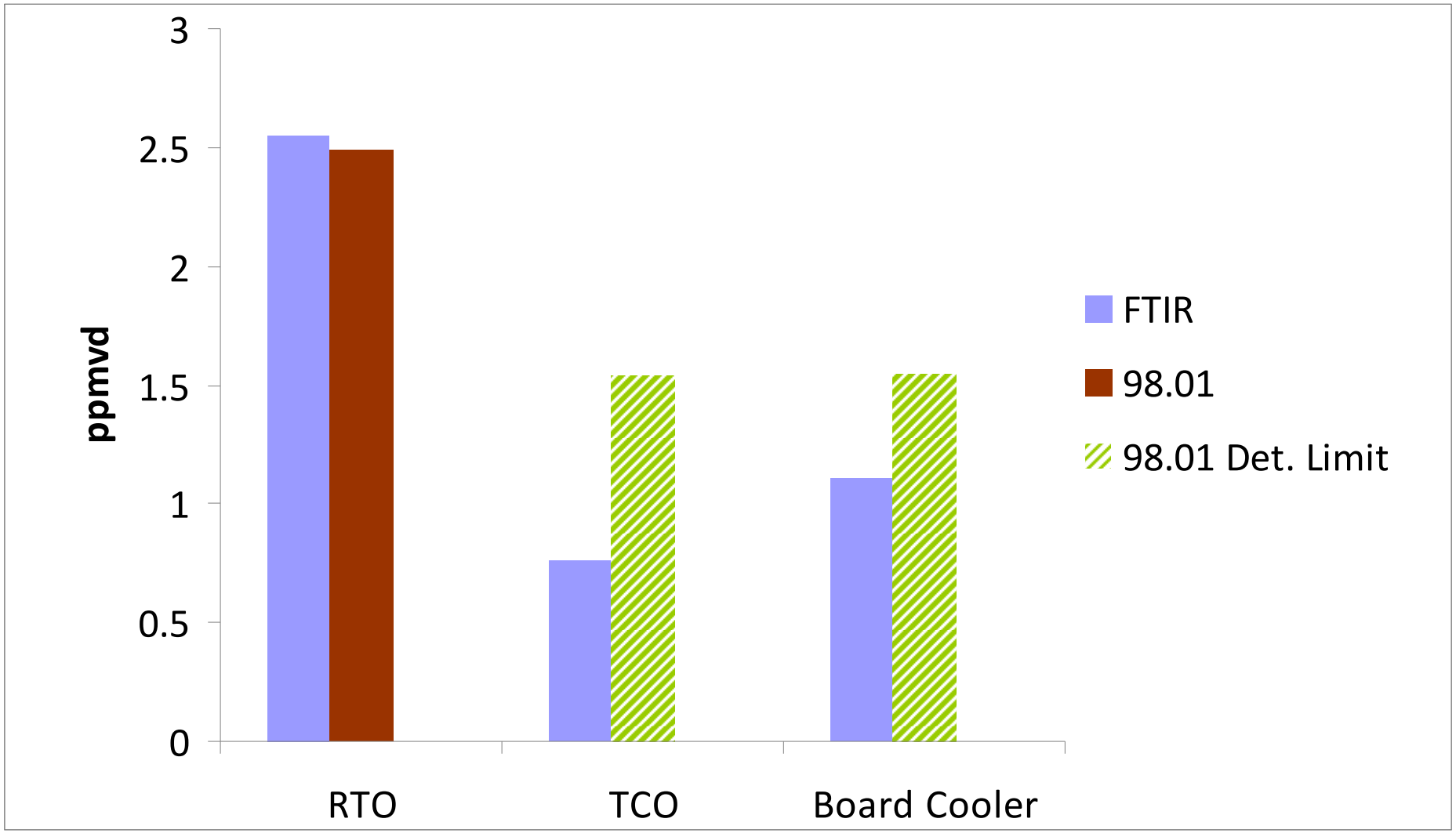
FTIR vs. 98.01

- Facility failed 98.01 QA requirement for methanol and formaldehyde
  - RTO, TCO, Board Cooler
- State strongly suggested the use of FTIR
- FTIR analysis was significantly more expensive for facility
- Facility wanted comparison data to justify the continued use of 98.01
- Contractor – FTIR
- NCASI – 98.01

FTIR vs. 98.01: Methanol



FTIR vs. 98.01: Formaldehyde



FTIR vs. Speciation Trains

- NCASI developed sampling system to speciate VOC from wood products sources
  - TB 991 – Southern pine results
- Gas streams speciated using BHA and impinger/ charcoal setups
  - Chilled impinger/charcoal was a modified 99.02 using a charcoal tube in place of the canister
  - Impinger/charcoal – Alcohols, organic acids, non-polar organic compounds
  - BHA – Aldehydes
- FTIR used initially as additional screening train
- QA for speciation trains according to A105.01
- No dynamic field spiking for FTIR

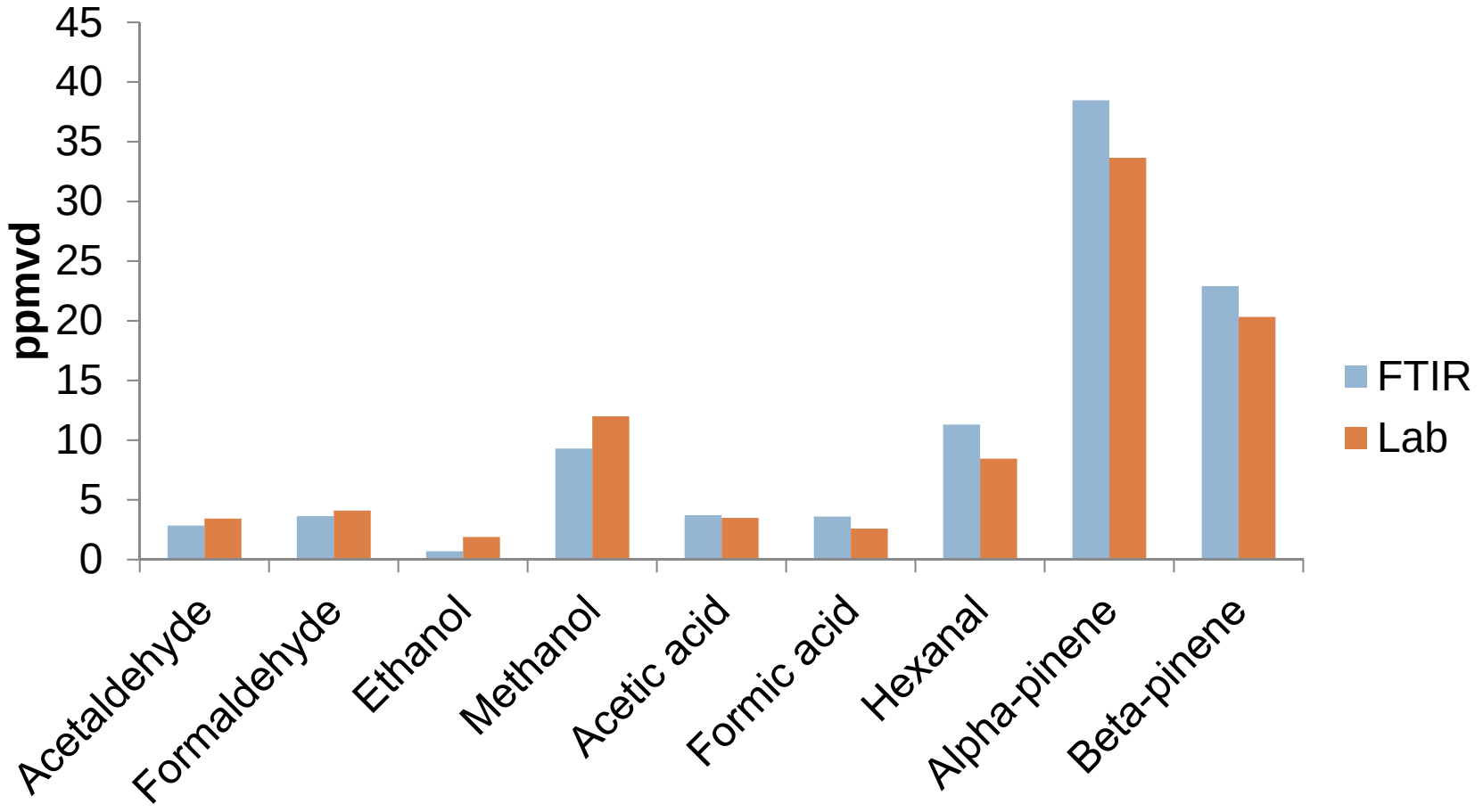
FTIR vs. Speciation Trains – Sources

- Southern pine
  - Small scale kiln
  - OSB (2), particleboard, plywood
    - Batch press/PCD outlet (3)
    - Green dryer/PCD inlet (2) and outlet (2)
    - Dry dryer/PCD outlet
    - Blender (3)
    - Sander
- Hardwood
  - OSB (2)
    - Green dryer/PCD inlet and outlet (2)
    - Former
    - Batch press/PCD outlet
    - Boiler/PCD outlet

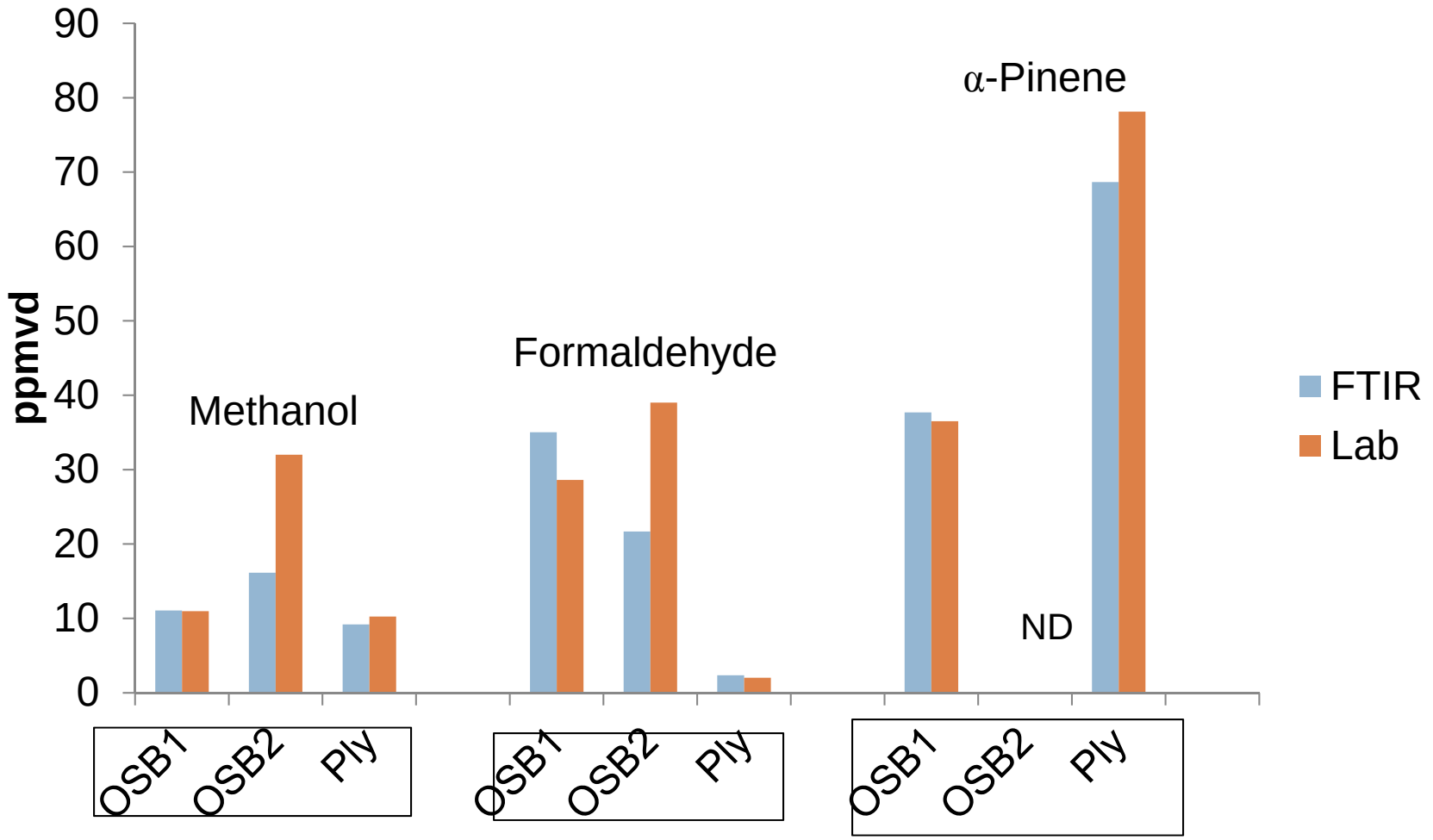
FTIR vs. Speciation Trains – Analytes

- Methanol, Ethanol
- Acetic acid, Formic acid
- Formaldehyde, Acetaldehyde, Hexanal
- Alpha-pinene, Beta-pinene

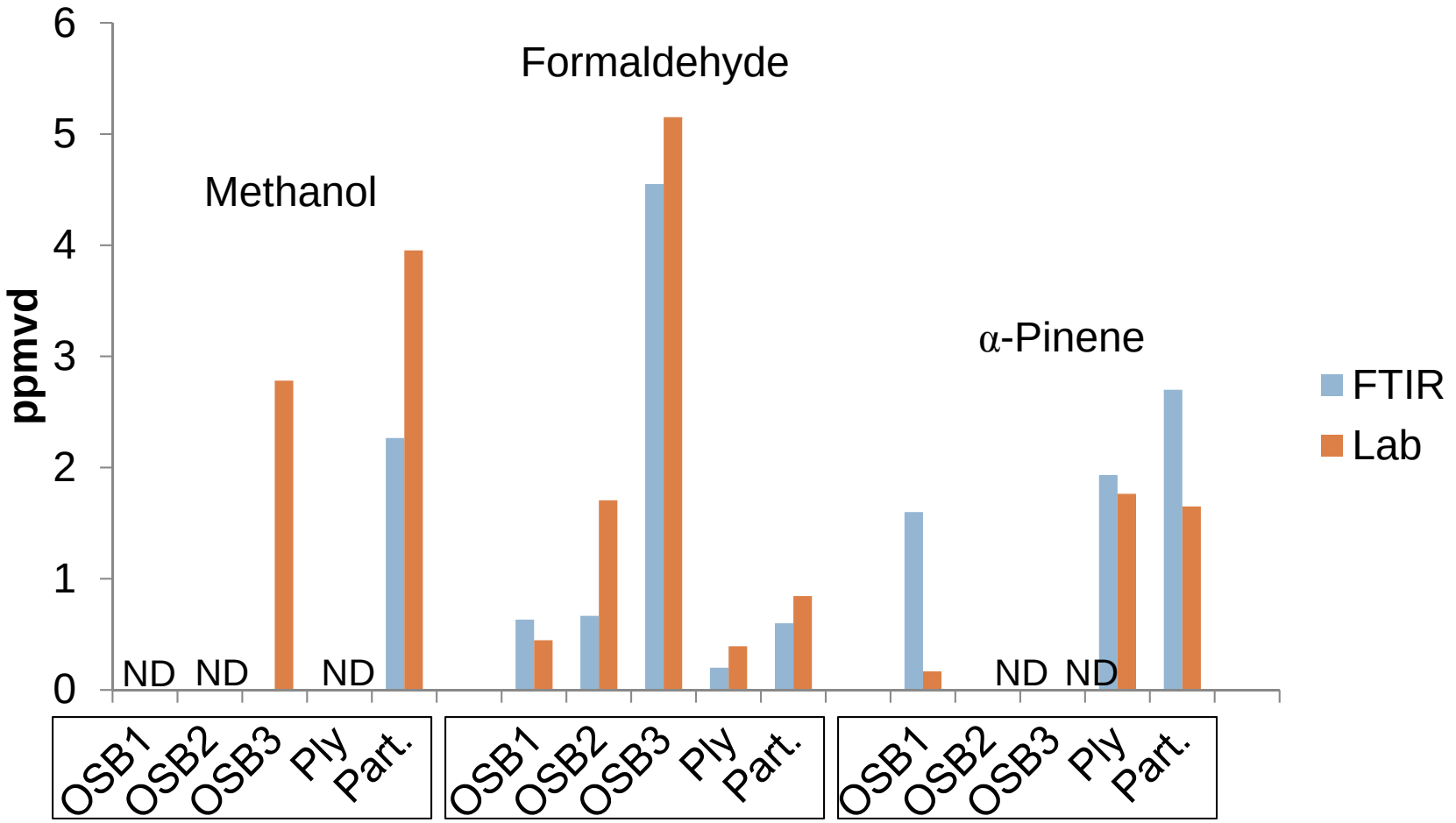
FTIR vs. Speciation Trains: Small-scale Kiln (Southern Pine)



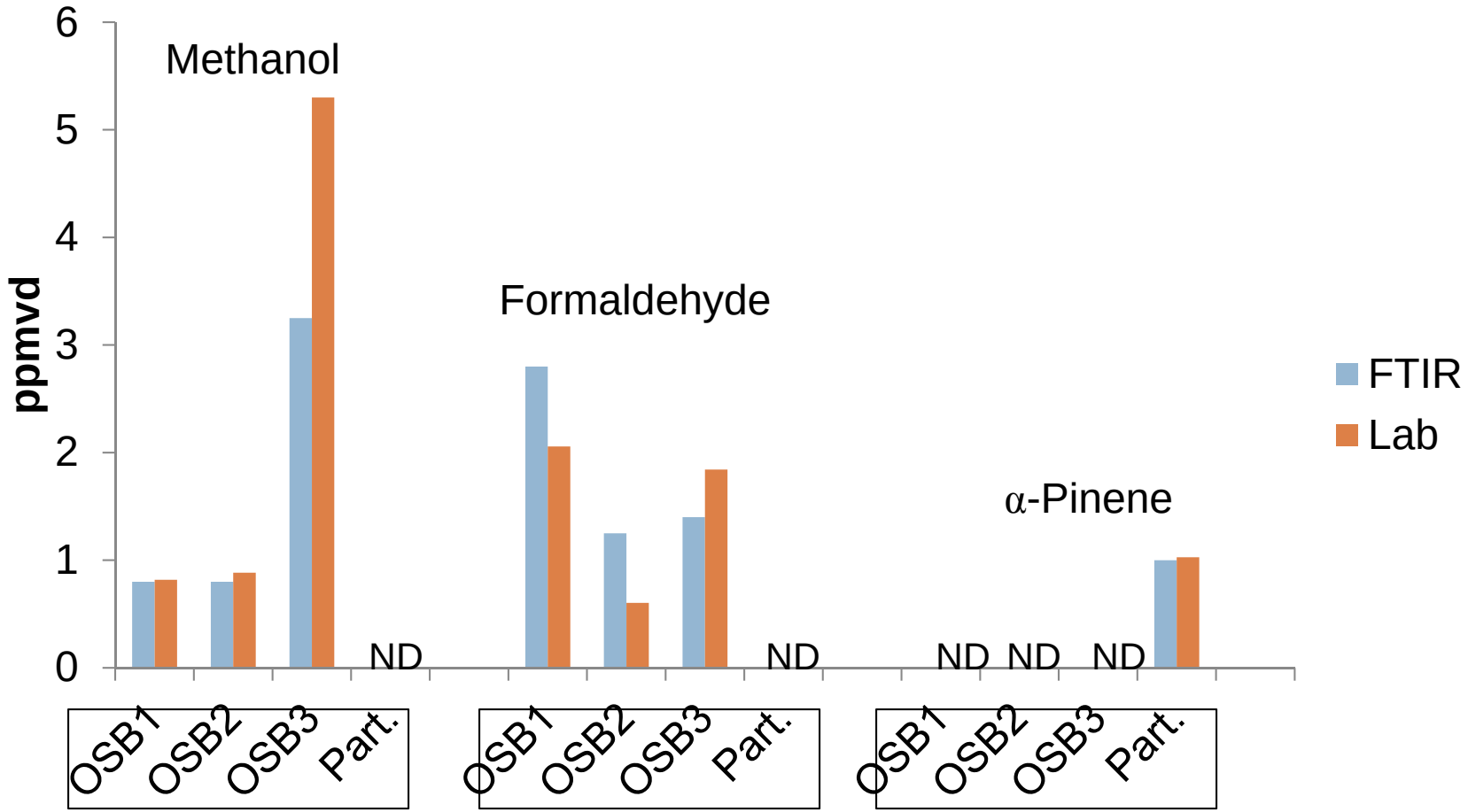
FTIR vs. Speciation Trains: Uncontrolled Dryer Exhaust



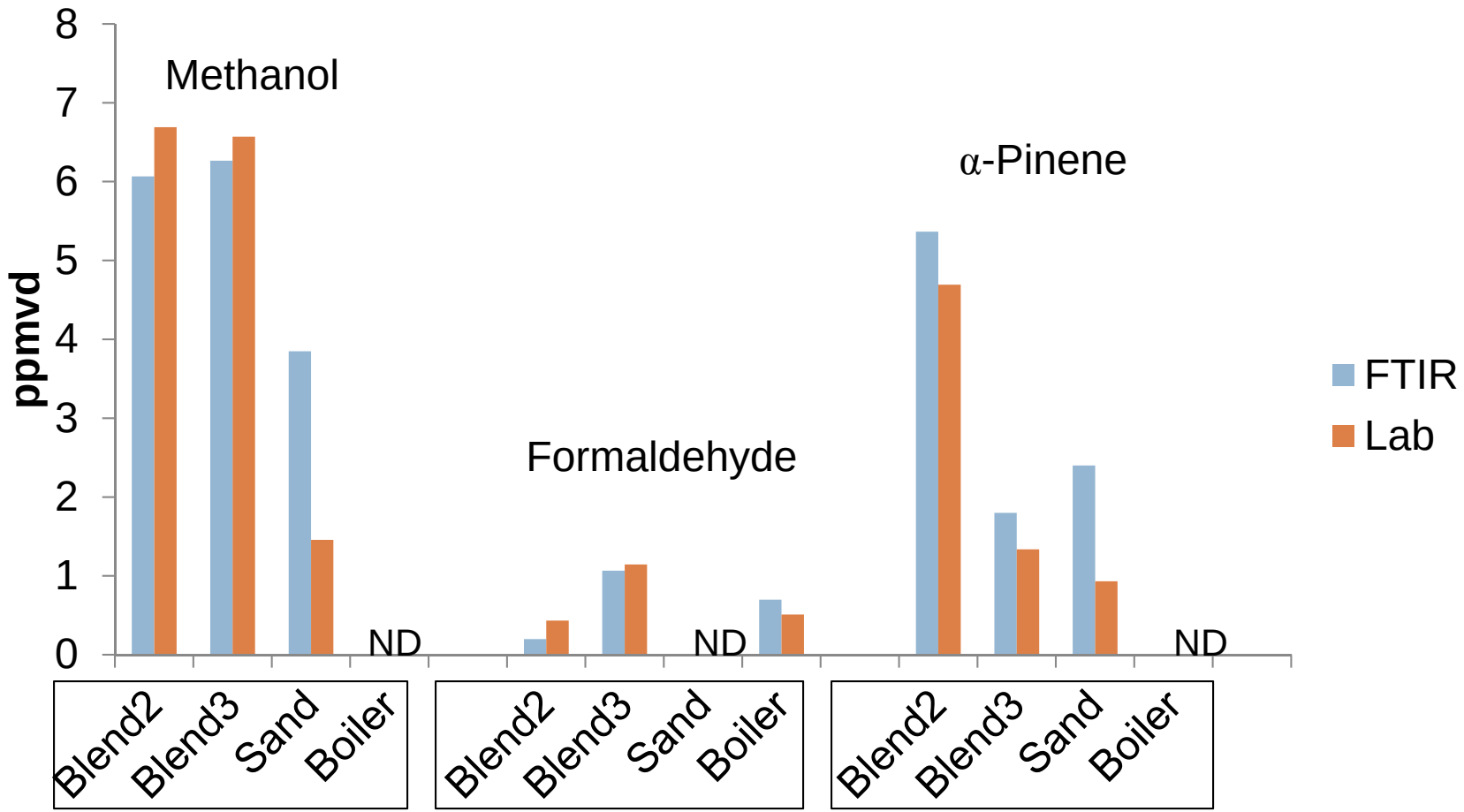
FTIR vs. Speciation Trains: Controlled Dryer Exhaust



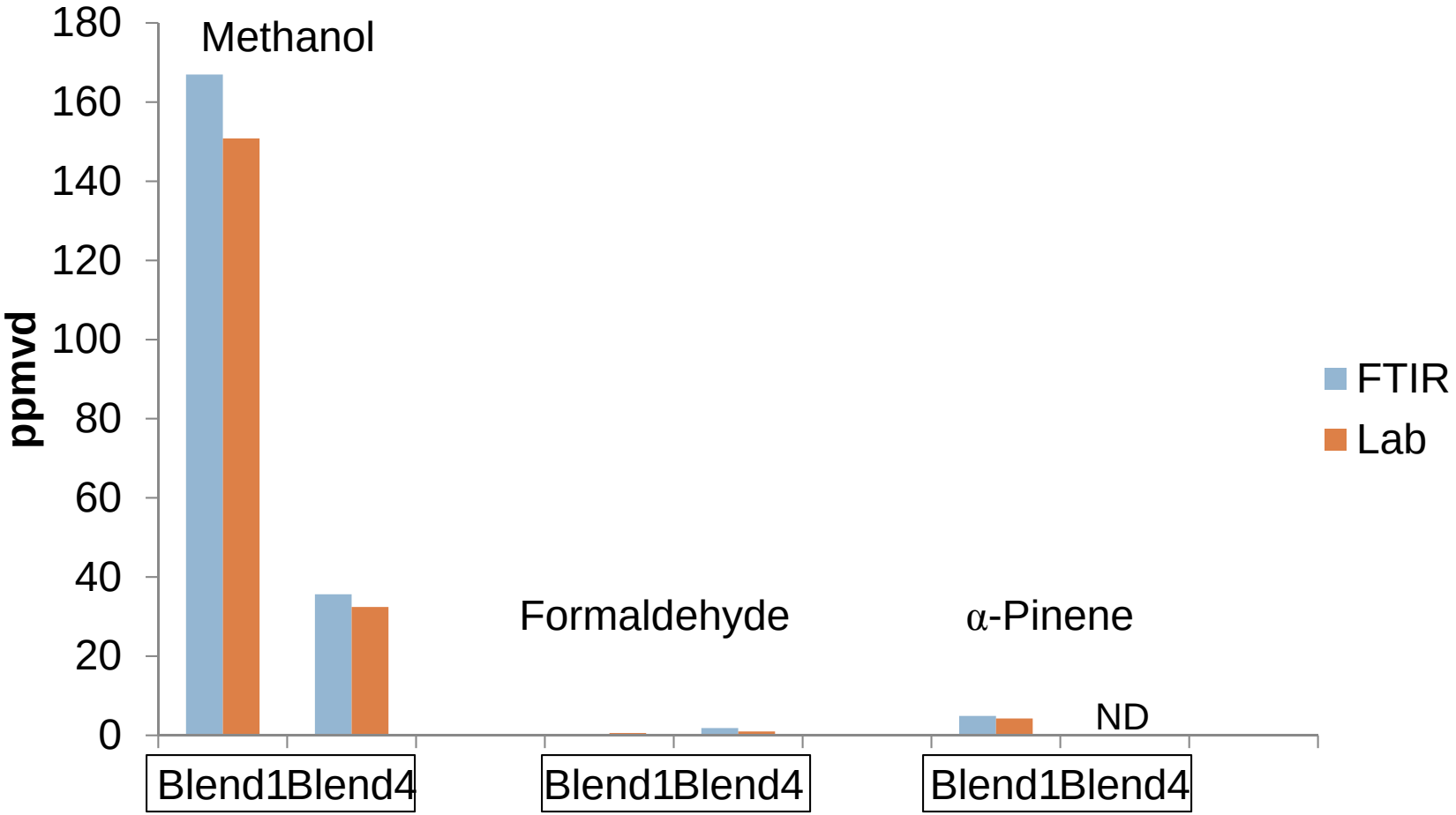
FTIR vs. Speciation Trains: Controlled Press Exhaust



FTIR vs. Speciation Trains: Miscellaneous Sources



FTIR vs. Speciation Trains: Miscellaneous Sources cont.



FTIR Summary

- In field study FTIR showed good agreement to 98.01 results, with lower detection limits
- Small-scale kiln results showed good agreement for 9 compounds in complex gas stream
- Mill results showed FTIR compared reasonably well to other methods
- FTIR can be attractive solution for HAPs sampling
  - Multiple compounds, low detection limits (with the right conditions), instantaneous preliminary data
- FTIR results are only as good as the operator
  - Accurate results depend on how well analysis method is set up
- Any contractor selected for FTIR sampling should have:
  - Experience with instrument
  - Experience with methods and QA spiking
  - Knowledge of process and gas stream characteristics

Questions?

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