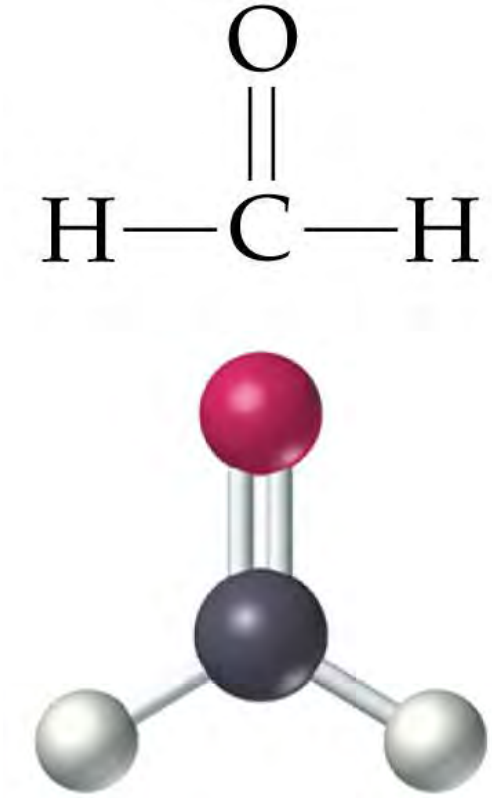
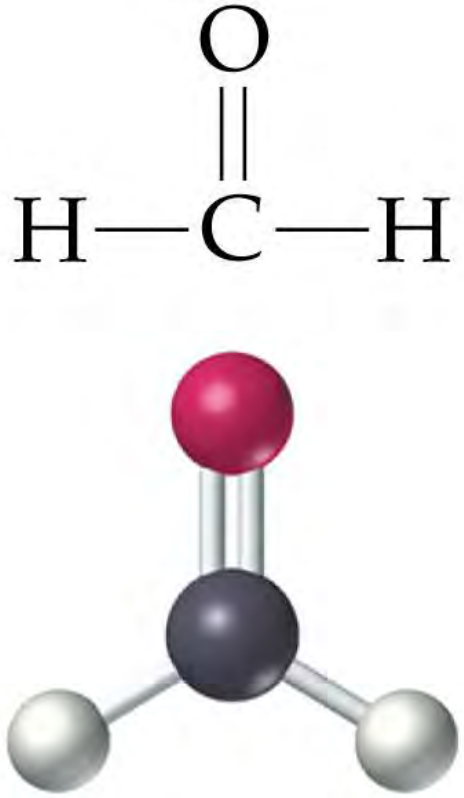


Air Toxics Testing: *Formaldehyde*



Council of Industrial Boiler Owners
December 7, 2016

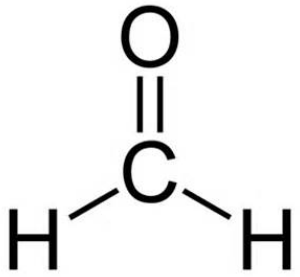
Joseph Macak
Mostardi Platt

Purpose of the Presentation

- Why should I care about formaldehyde testing?
- Discuss the various emissions test methods used for formaldehyde.
- Provide a better understanding of sources of concern regarding low levels being quoted by EPA.
- Example results.

General Comments

- USEPA Emission Factors from early testing for air toxics like formaldehyde were often at detection limits.
- The minimum detection limit in the laboratory for pure samples (e.g. formaldehyde in ultra pure water) cannot be achieved in the field.
  - Don’t be fooled by **lab detection** limits.
  - You could always do better in a lab.
- Formaldehyde is usually one of the listed HAPs for plant wide emission calculations for the demonstration of whether or not the facility is a major HAP source.
  - AP-42 could make you become a major HAP source.



USEPA AP-42 Emission Factor Example – Combustion Turbines

Formaldehyde Equivalents - Gas Turbines

Information Source	Fuel	Factor (lb/million Btu, HHV)	ppmvd @ 15% O2	PPB
USEPA AP-42	Gas	7.10E-04	0.309	308.5
USEPA AP-42	#2 Oil	2.80E-04	0.115	115.3
GE DLN Data	Gas	3.58E-05	0.016	15.6

GE level data is not easily measured.

USEPA AP-42 Emission Factor Example – Combustion Turbines for 3 Units

Three Combustion Turbines - NATURAL GAS FIRING ONLY

Natural Gas Operation

Maximum Operating Hours (11, 12 combined)	8,760	hours
Maximum Operating Hours (21)	8,760	hours
Emission Units 11, 12 Max Heat Inut	1,734	million Btu/hr, HHV
Emission Unit 21 Max Heat Input	1,901	million Btu/hr, HHV
Total Heat Input (plant)	31,843,471	million Btu/year, HHV

Single HAP > 10 TPY

Pollutant	CAS #	Emission Factor Basis	AP-42 Emission Factor (lb/mmBtu)	Plant Total Maximum Emissions (tons/year)
1,3-Butadiene	106-99-0	EPA AP-42	4.30E-07	**0.0068**
Acetaldehyde	75-07-0	EPA AP-42	4.00E-05	**0.6369**
Acrolein	107-02-8	EPA AP-42	6.40E-06	**0.1019**
Benzene	71-43-2	EPA AP-42	1.20E-05	**0.1911**
Ethylbenzene	100-41-4	EPA AP-42	3.20E-05	**0.5095**
Formaldehyde	50-00-0	EPA AP-42	**7.10E-04**	**11.3044**
Naphthalene	91-20-3	EPA AP-42	1.30E-06	**0.0207**
Polycyclic Aromatic Hydrocarbons	N590	EPA AP-42	2.20E-06	**0.0350**
Propylene Oxide	115-07-1	EPA AP-42	2.90E-05	**0.4617**
Toluene	108-88-3	EPA AP-42	1.30E-04	**2.0698**
Xylenes	1330-20-7	EPA AP-42	6.40E-05	**1.0190**
Annual HAP Emissions for Three Combustion Turbines (Tons) - Natural Gas Firing Only				**16.36**

USEPA AP-42 Emission Factor Example – Combustion Turbines for 3 Units with GE Factor

Three Combustion Turbines - NATURAL GAS FIRING ONLY

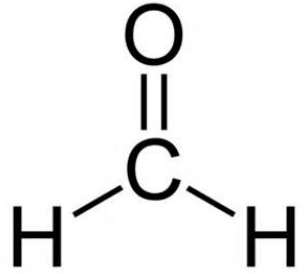
Natural Gas Operation

Maximum Operating Hours (11, 12 combined)	8,760	hours
Maximum Operating Hours (21)	8,760	hours
Emission Units 11, 12 Max Heat Inut	1,734	million Btu/hr, HHV
Emission Unit 21 Max Heat Input	1,901	million Btu/hr, HHV
Total Heat Input (plant)	31,843,471	million Btu/year, HHV

No single HAP above 10 TPY

Pollutant	CAS #	Emission Factor Basis	AP-42 Emission Factor (lb/mmBtu)	Plant Total Maximum Emissions (tons/year)
1,3-Butadiene	106-99-0	EPA AP-42	4.30E-07	**0.0068**
Acetaldehyde	75-07-0	EPA AP-42	4.00E-05	**0.6369**
Acrolein	107-02-8	EPA AP-42	6.40E-06	**0.1019**
Benzene	71-43-2	EPA AP-42	1.20E-05	**0.1911**
Ethylbenzene	100-41-4	EPA AP-42	3.20E-05	**0.5095**
Formaldehyde	50-00-0	GE DLN	**3.58E-05**	**0.5700**
Naphthalene	91-20-3	EPA AP-42	1.30E-06	**0.0207**
Polycyclic Aromatic Hydrocarbons	N590	EPA AP-42	2.20E-06	**0.0350**
Propylene Oxide	115-07-1	EPA AP-42	2.90E-05	**0.4617**
Toluene	108-88-3	EPA AP-42	1.30E-04	**2.0698**
Xylenes	1330-20-7	EPA AP-42	6.40E-05	**1.0190**
Annual HAP Emissions for Three Combustion Turbines (Tons) - Natural Gas Firing Only				**5.62**

Typical Formaldehyde Test Methods



Method	Description
EPA Method 316	Sampling and Analysis for Formaldehyde Emissions in Fiberglass Industry (used for other sources as well)
EPA Method 320	Measurement of Vapor Phase Organic and Inorganic Emissions Using Extractive Fourier Transform Infrared (FTIR) Spectroscopy
EPA Method 323	Measurement of Formaldehyde Emissions From Natural Gas-Fired Stationary Sources-Acetyl Acetone Derivitization Method
EPA SW-846 Test Method 0011	Sampling for Selected Aldehyde and Ketone Emissions from Stationary Sources (Solid Waste Source Method) – Not presented.
CARB Method 430	Determination of Formaldehyde and Acetaldehyde in Emissions from Stationary Sources

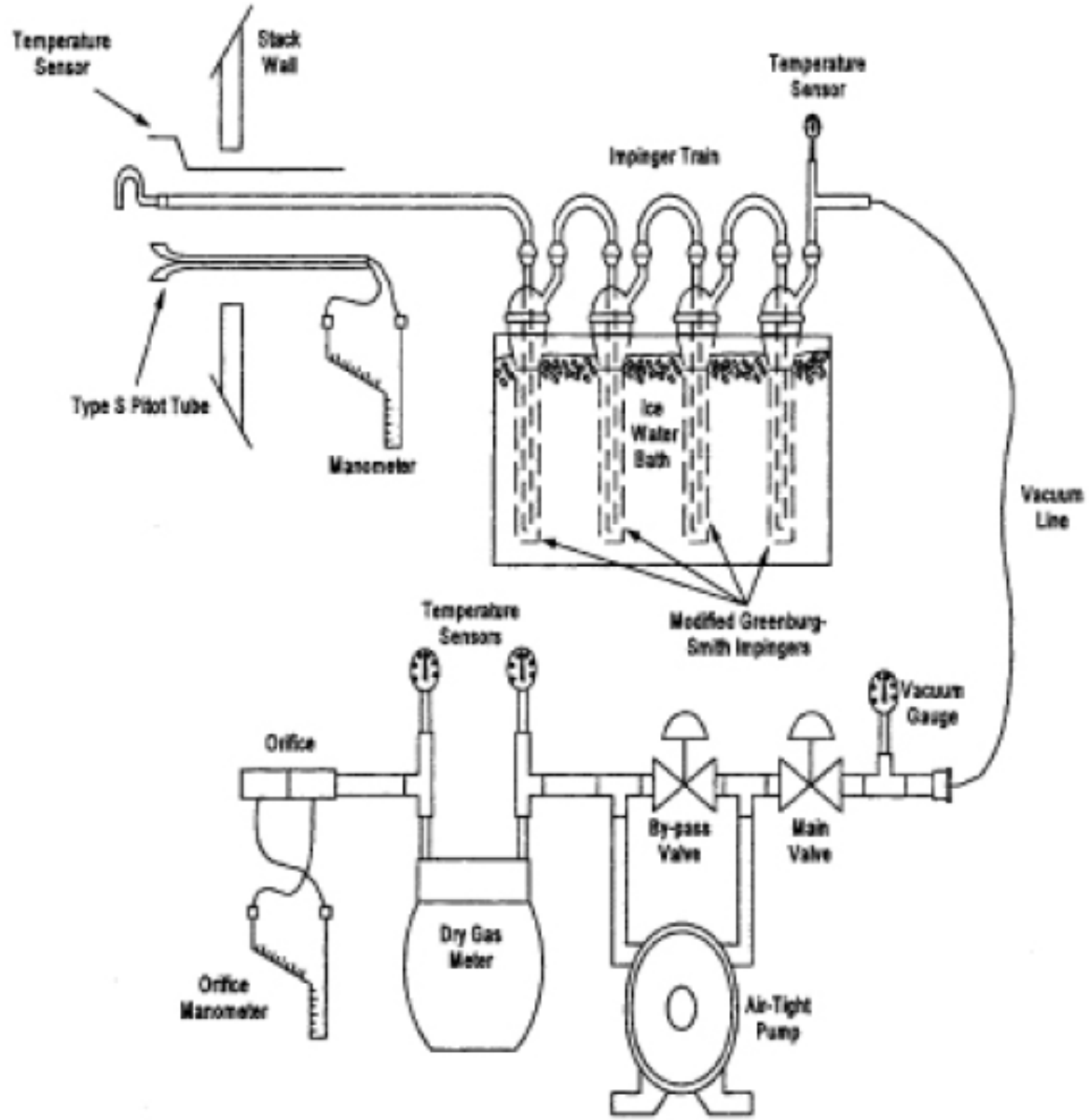
Method 316 Methodology

- High purity water is used to collect formaldehyde.
- Collected samples are developed and measured in spectrophotometer.
- Isokinetic sampling method similar to Method 5 particulates.
- Stack is traversed from multiple ports.
- Sample 30 cubic feet of gas over 1 hour period.
- LAB detection of 11.3 PPB, with no other interferences.

Method 316 Methodology (2)

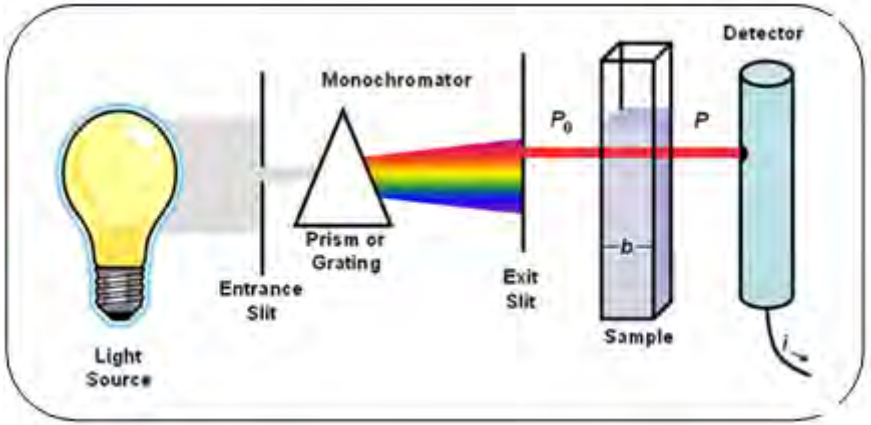
- Probe nozzle and lining is quartz or borosilicate glass. Must be ultra clean (note tape on end of probe tip to keep it clean until use).
- First two glass impingers filled with 100 ml "ULTRA PURE" water. Formaldehyde gets collected in the water.
- End of test, sample recovery includes rinsing the probe and collecting the rinse water.

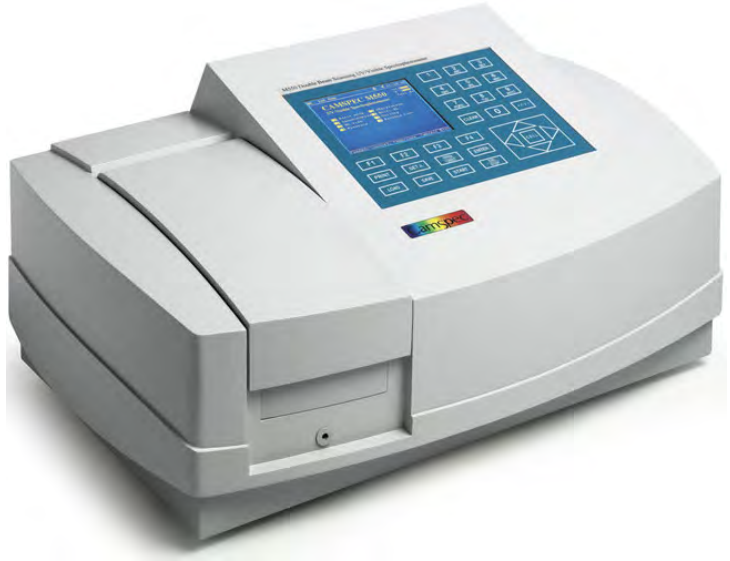
Method 316 Methodology



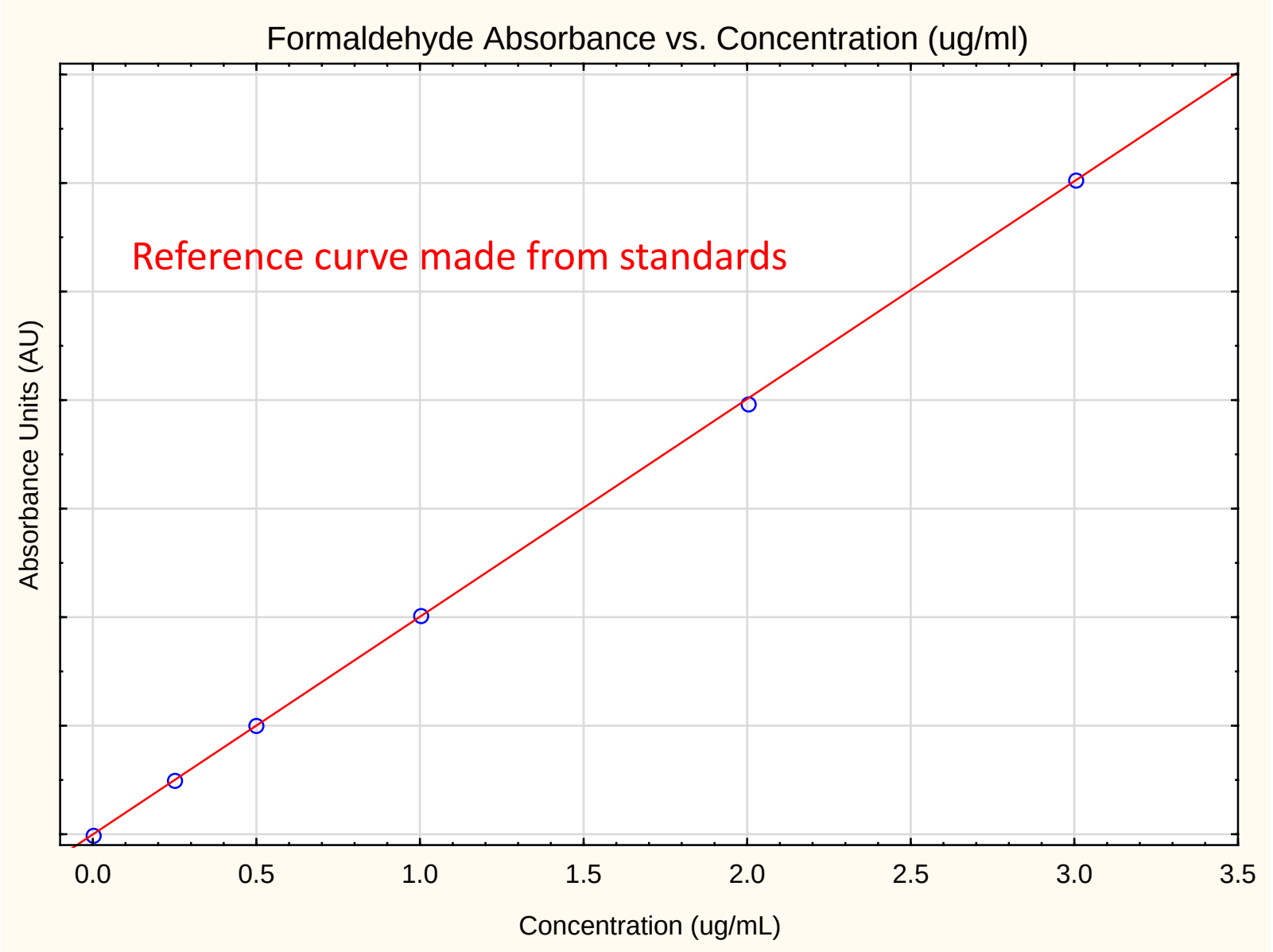
Method 316 Methodology (3)

- Working standards of formaldehyde are prepared in the lab. 0.25, 0.5, 1.0, 2.0, and 3.0 ug/mL. Curve established.
- Collected sample is developed and compared to the standard curve.
- If the results are outside the range of the curve, the sample is diluted and retested until it is in the range.

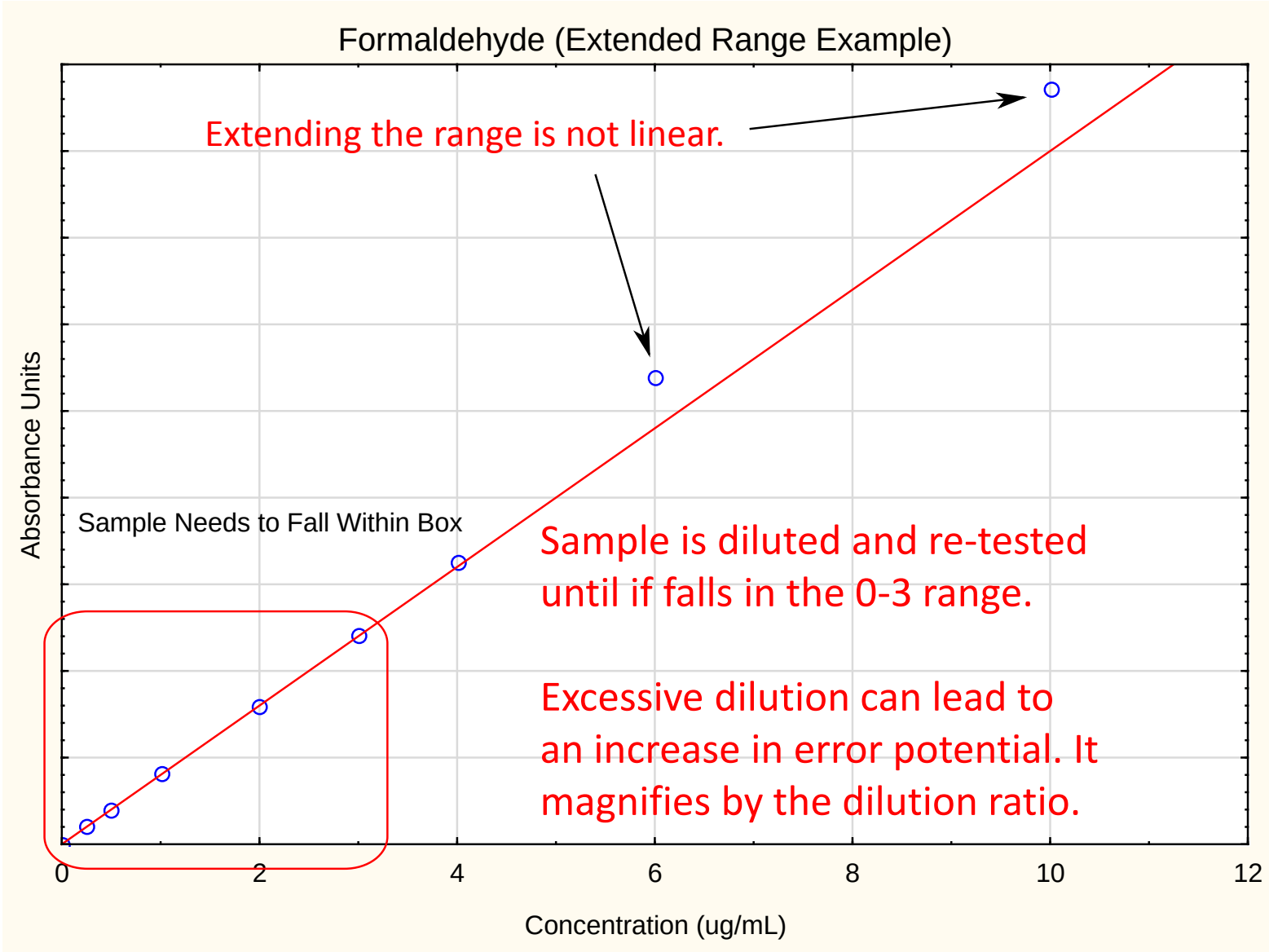




Method 316 Methodology (4)



Method 316 Methodology (5)



Method 316 – Example Results

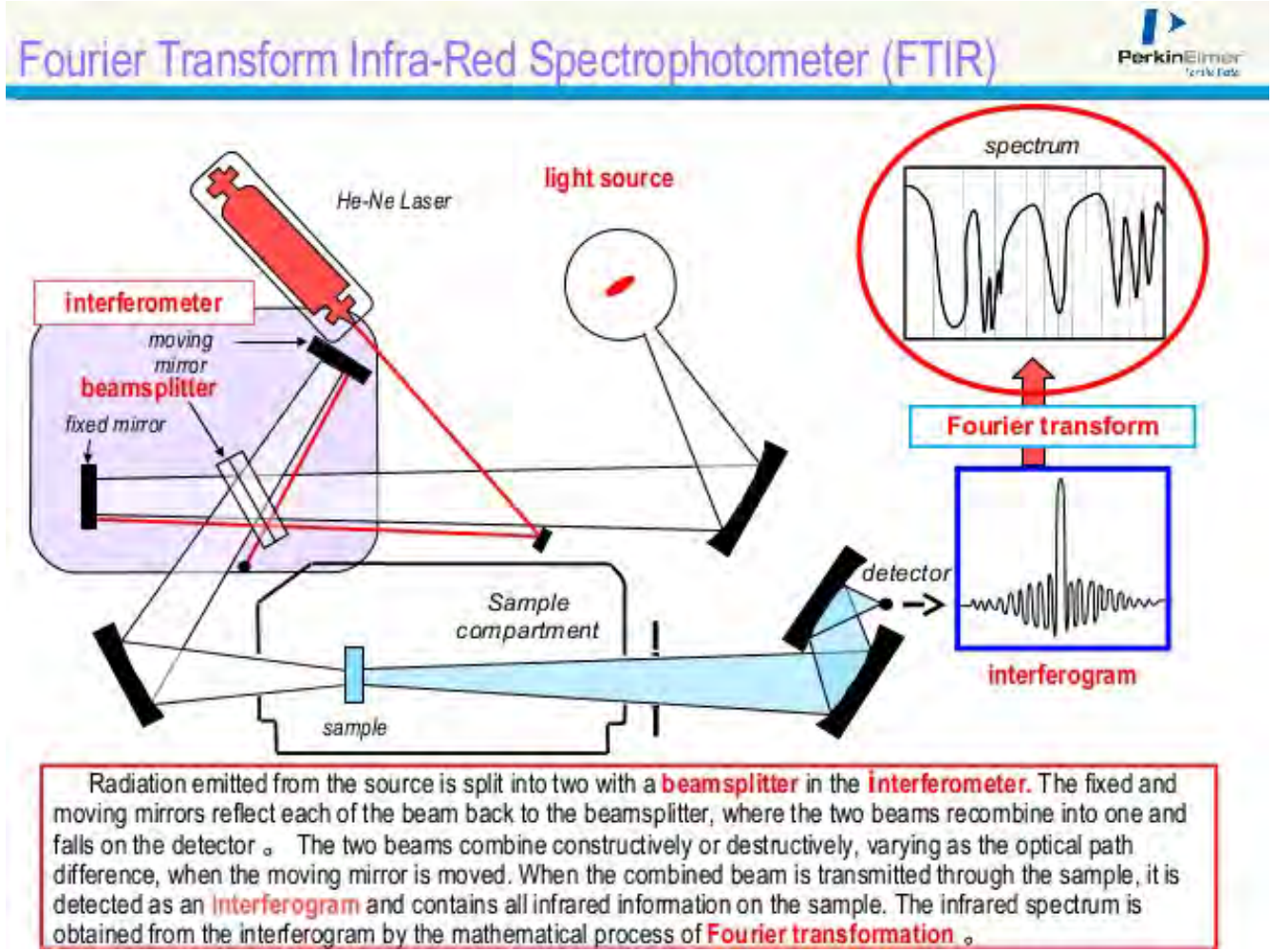
Test Location: Coke Battery No. 2 Underfire Stack
Test Method: 316

Source Condition		Normal		Normal		Normal		
Date		9/7/16		9/7/16		9/8/16		
Start Time		9:07		12:30		8:30		
End Time		11:16		14:39		10:39		
		Run 1		Run 2		Run 3		Average
Stack Conditions								
Average Gas Temperature, °F		454.7		455.5		452.6		454.3
Flue Gas Moisture, percent by volume		18.1%		18.5%		18.2%		18.3%
Average Flue Pressure, in. Hg		29.17		29.17		29.08		29.14
Gas Sample Volume, dscf		79.124		76.234		76.308		77.222
Average Gas Velocity, ft/sec		22.044		21.957		22.010		22.004
Gas Volumetric Flow Rate, acfm		218,408		217,541		218,067		218,005
Gas Volumetric Flow Rate, dscfm		100,594		99,696		100,278		100,189
Gas Volumetric Flow Rate, scfm		122,894		122,295		122,603		122,597
Average $\%CO_2$ by volume, dry basis		6.3		6.4		6.1		6.3
Average $\%O_2$ by volume, dry basis		8.4		8.2		8.8		8.5
Isokinetic Variance		104.9		102.0		101.5		102.8
Formaldehyde Emissions (Method 316)								
ug of sample collected	≤	17.00	≤	17.00	≤	18.00	≤	17.33
ppm	≤	0.01	≤	0.01	≤	0.01	≤	0.01
mg/dscm	≤	1.00E-02	≤	1.00E-02	≤	1.00E-02	≤	1.00E-02
lb/hr	≤	2.90E-03	≤	2.90E-03	≤	3.10E-03	≤	2.97E-03

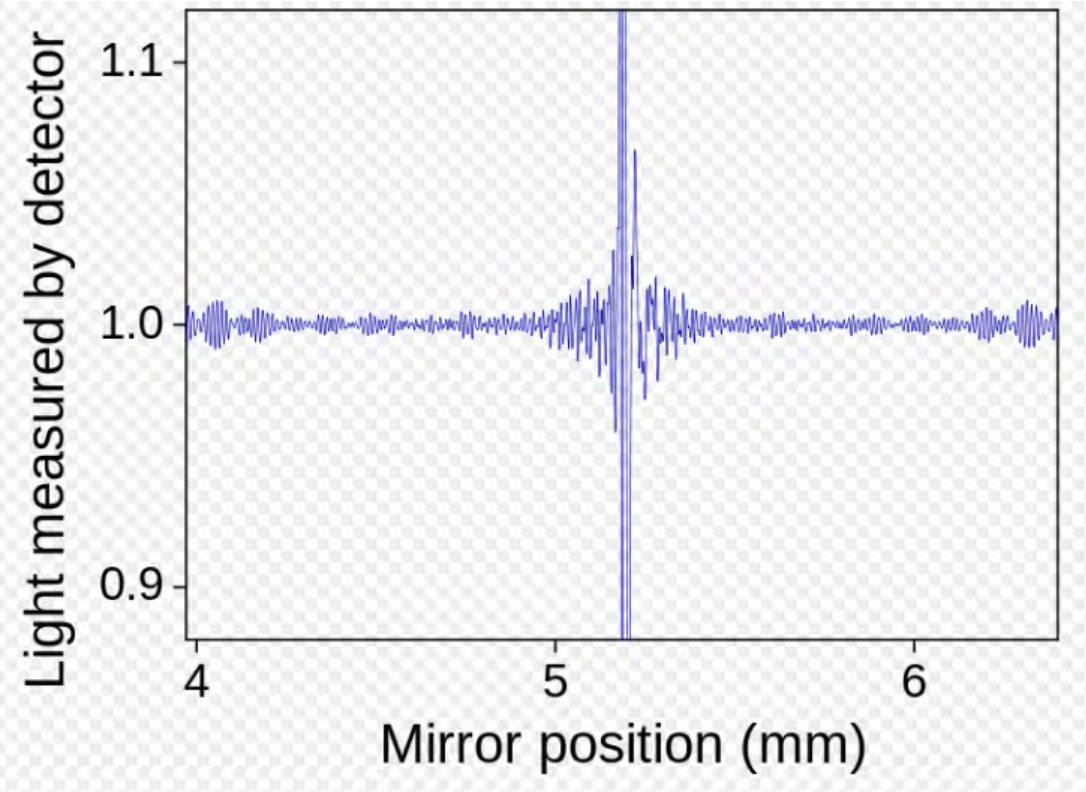
<10 PPB

Method 320 FTIR Methodology

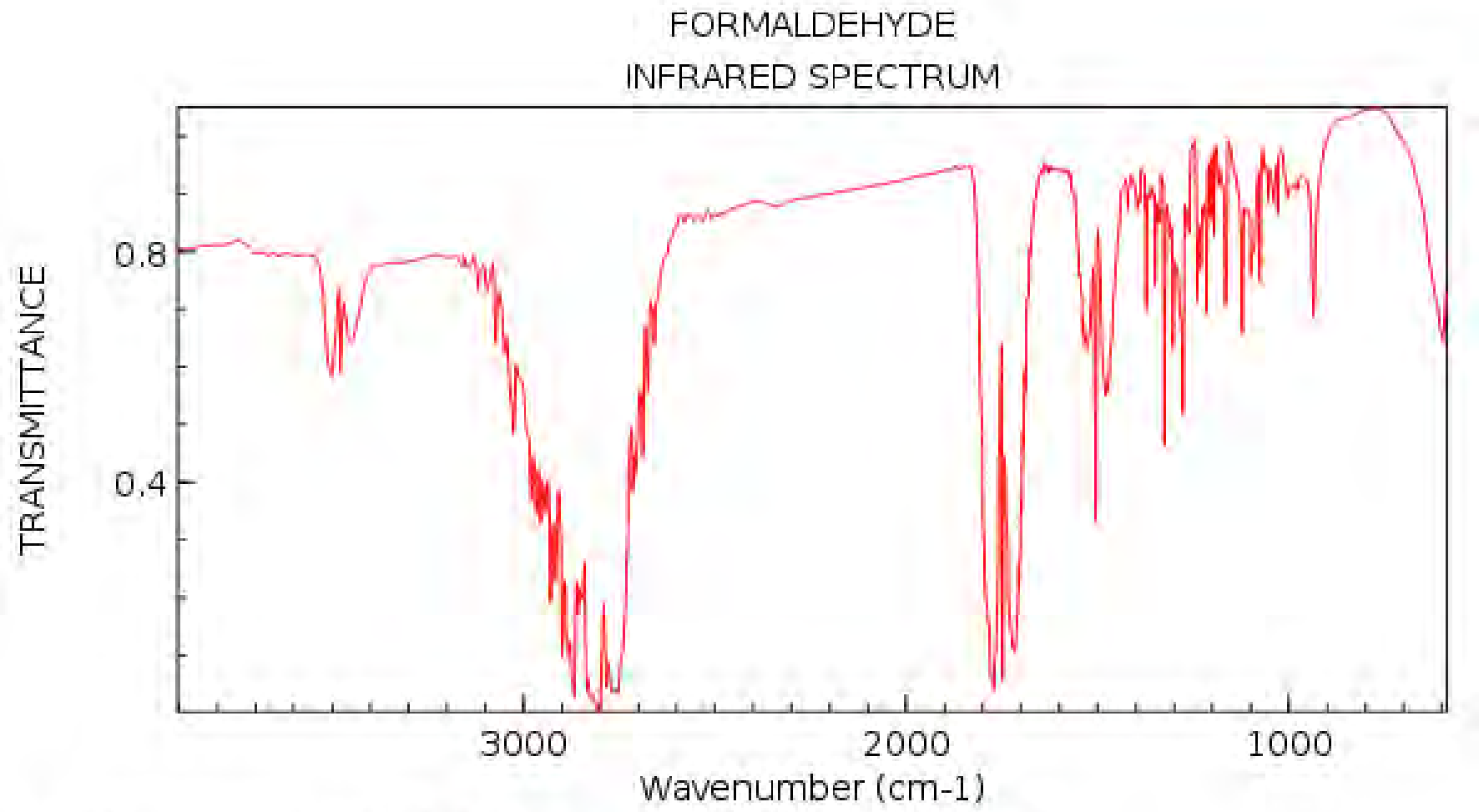
- Measures vapor phase organics and inorganic compounds in the IR spectral region (25 to 2.5 um).
- Not all FTIR systems are equivalent.
- Sample detection limits depend on gas characteristics such as moisture in the gas and/or presence of interferants.
- Test single point in stack.



Method 320 FTIR – Before Transformation

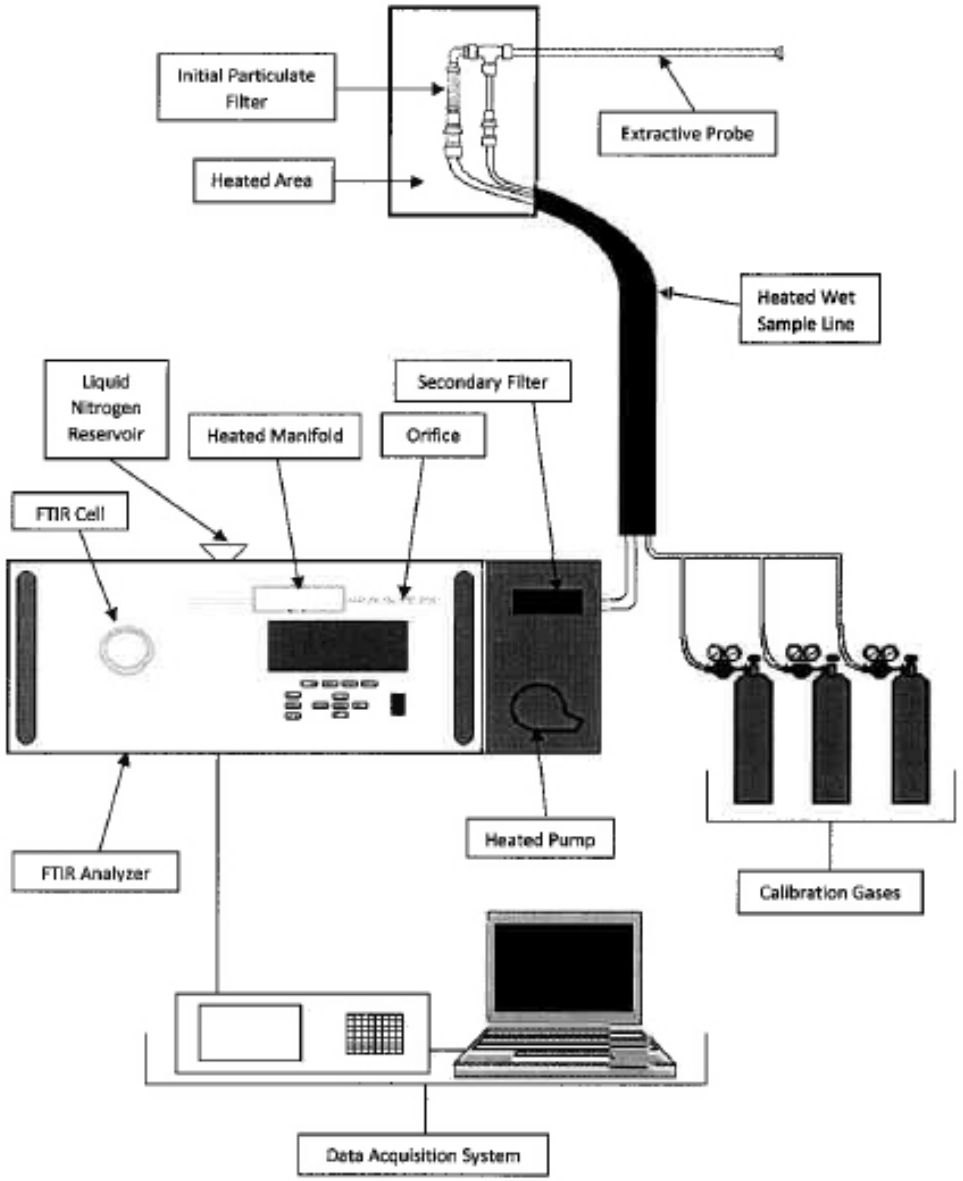


Method 320 FTIR – After Transformation Example



NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

Method 320 FTIR Methodology

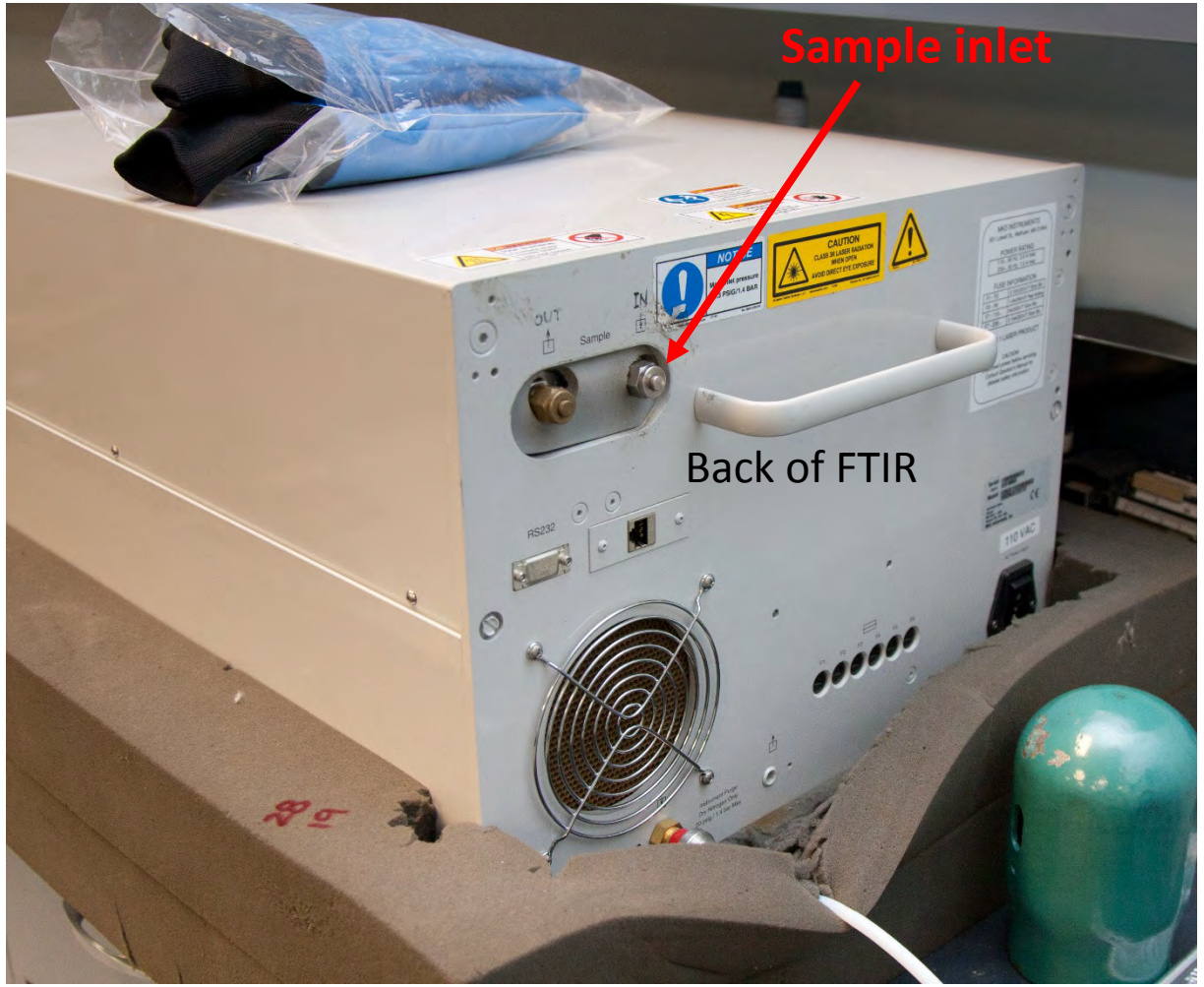


Method 320 FTIR Methodology (2)

- Measures vapor phase organics and inorganic compounds in the IR spectral region (25 to 2.5 um).
- Sample detection limits depend on gas characteristics such as moisture in the gas and/or presence of interferants.
- Each compound has a “fingerprint” spectra.

Method 320 FTIR Methodology (3)

- Analyzer and software has reference spectra from EPA FTIR library.
- An “interferant” is a compound whose IR spectrum overlaps part of the spectrum that you are measuring.
- A surrogate is used in a QA spike for instrument calibration.



Method 320 FTIR Methodology (4) – Example of Calibration Gas for Engines

Table 3 – Calibration Gas Standards

Source	Components	Concentration (ppm)	Vendor	Cylinder #	Standard Type
Unit 11	Ethylene	100.5	Airgas	CC469309	Primary +/- 1%
Unit 17	Acetaldehyde, Methanol, SF_6	200.3/201.1/4.149	Airgas	CC467194	Certified Standard +/- 2%
Unit 18	Nitrogen	zero gas	Airgas	n/a	UHP Grade

FTIR QA/QC Calculations

Method 320: Analyte Spiking

Acetaldehyde/methanol spiking was performed on each source prior to testing to verify the ability of the sampling system to quantitatively deliver a sample containing both acetaldehyde and

Note the high concentrations used in the method.

Testing requires matrix spikes with dilution to calibrate.

How accurate is the vendor calibration gas? Amount of dilution?

Method 320 FTIR Methodology (5)
Detection Limits from Test Program

Detection Limit

The detection limit of each analyte was calculated following Annex A2 of ASTM D6348-12 procedure using spectra that contained similar amounts of moisture.

Table 7 - FTIR Detection Limits

Analyte	Detection Limit (ppmv wet)	Detection Limit (%v)
Formaldehyde	0.10	-
Acetaldehyde	0.5	-
Methanol	0.3	-
Water	-	0.1

0.10 ppmv is 100 parts per billion (PPB)

Method 320 FTIR Methodology (6)
Example of Actual Run Data

Unit 11 - Run 1

Spectrum	Date	Time	Formaldehyde (ppmv wet)	Acetaldehyde (ppmv wet)	Methanol (ppmv wet)	H2O (%v)	FTIR Gas Cell Temp (C)	FTIR Gas Cell Pressure (Atm)
U11_001216.LAB	9/14/2016	10:50:01	0.19	< 0.5	< 0.3	10.1	190.4	1.010
U11_001217.LAB	9/14/2016	10:51:01	< 0.10	< 0.5	< 0.3	10.1	190.4	1.012
U11_001218.LAB	9/14/2016	10:52:01	0.13	< 0.5	< 0.3	10.1	190.4	1.015
U11_001219.LAB	9/14/2016	10:53:01	0.16	< 0.5	< 0.3	10.2	190.4	1.012
U11_001220.LAB	9/14/2016	10:54:02	< 0.10	< 0.5	< 0.3	10.1	190.4	1.012
U11_001221.LAB	9/14/2016	10:5	0.21	< 0.5	< 0.3	10.1	190.4	1.010
U11_001222.LAB	9/14/2016	10:56:02	0.17	< 0.5	< 0.3	10.1	190.4	1.009
U11_001223.LAB	9/14/2016	10:57:02	0.19	< 0.5	< 0.3	10.1	190.4	1.011
U11_001224.LAB	9/14/2016	10:58:02	0.19	< 0.5	< 0.3	10.2	190.4	1.012
U11_001225.LAB	9/14/2016	10:59:02	0.18	< 0.5	< 0.3	10.1	190.4	1.013
U11_001226.LAB	9/14/2016	11:00:02	< 0.10	< 0.5	< 0.3	10.1	190.4	1.013
U11_001227.LAB	9/14/2016	11:01:02	< 0.10	< 0.5	< 0.3	10.1	190.4	1.011
U11_001228.LAB	9/14/2016	11:02:02	0.14	< 0.5	< 0.3	10.1	190.4	1.010
U11_001229.LAB	9/14/2016	11:03:03	0.14	< 0.5	< 0.3	10.2	190.4	1.012
U11_001230.LAB	9/14/2016	11:04:03	0.18	< 0.5	< 0.3	10.2	190.4	1.012
U11_001231.LAB	9/14/2016	11:05:03	0.15	< 0.5	< 0.3	10.2	190.4	1.011
U11_001232.LAB	9/14/2016	11:06:03	0.14	< 0.5	< 0.3	10.2	190.4	1.015
U11_001233.LAB	9/14/2016	11:07:03	0.15	< 0.5	< 0.3	10.1	190.4	1.015
U11_001234.LAB	9/14/2016	11:08:03	< 0.10	< 0.5	< 0.3	10.1	190.4	1.013
U11_001235.LAB	9/14/2016	11:09:03	0.15	< 0.5	< 0.3	10.2	190.4	1.012
[illegible]	[illegible]	[illegible]	0.11	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

0.10 ppmv is 100 PPB

Method 320 FTIR Methodology (7)
Run Averages

Table 4 – Unit 18 Summary of Testing

Test run	Calculation	Formaldehyde (ppmv wet)	Acetaldehyde (ppmv wet)	Methanol (ppmv wet)	H_2O (%v)
9/13/2016 –Unit 18 Run 1 13:15 – 14:15	Minimum	< 0.10		< 0.3	9.5
	Maximum	0.41	< 0.5	< 0.3	9.7
	Average*	0.15	< 0.5	< 0.3	9.6
9/13/2016 – Unit 18 Run 2 14:25 - 15:25	Minimum	< 0.10	< 0.5	< 0.3	9.5
	Maximum	0.31	< 0.5	< 0.3	9.6
	Average*	0.17	< 0.5	< 0.3	9.6
9/13/2016 – Unit 18 Run 3 15:35 – 16:35	Minimum	< 0.10	< 0.5	< 0.3	9.5
	Maximum	0.25	< 0.5	< 0.3	9.6
	Average*	0.14	< 0.5	< 0.3	9.6

*When calculating averages, any value less than the determined detection limit will be assigned the detection limit value.

Table 5 – Unit 17 Summary of Testing

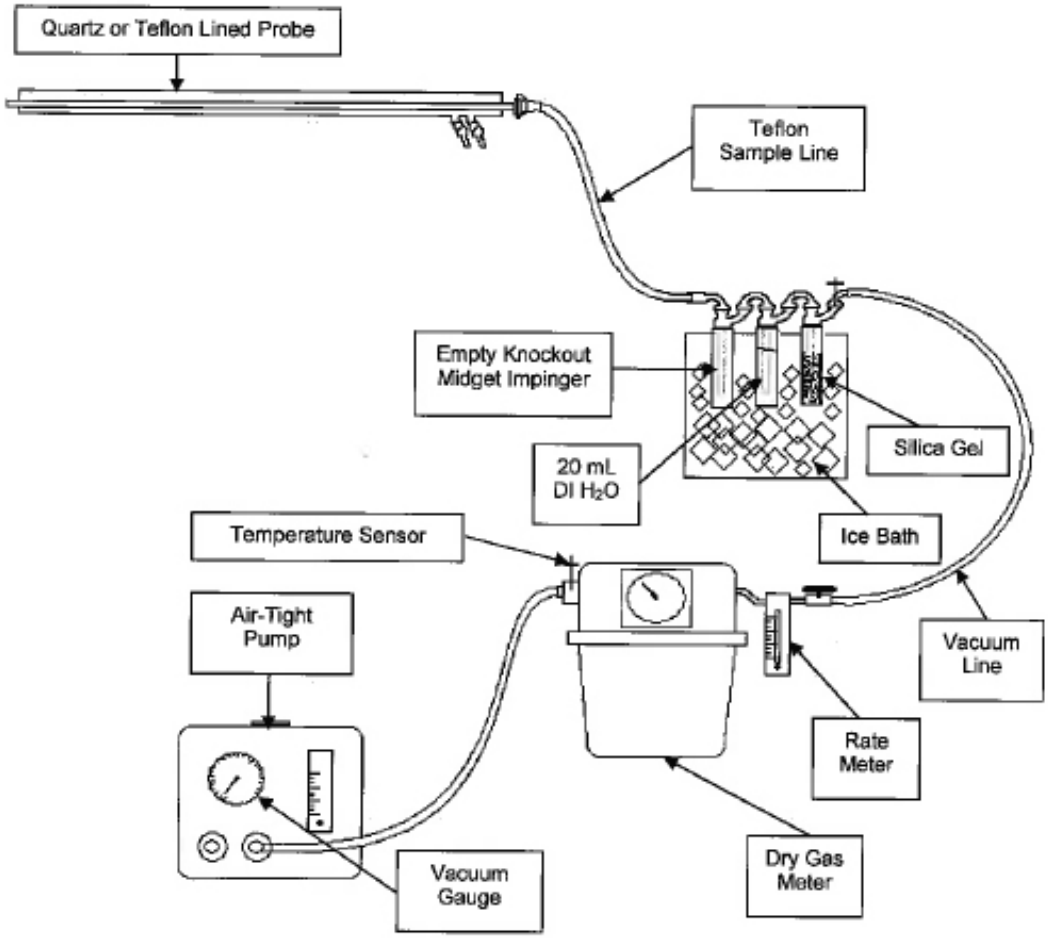
Test run	Calculation	Formaldehyde (ppmv wet)	Acetaldehyde (ppmv wet)	Methanol (ppmv wet)	H_2O (%v)
9/13/2016 – Unit 17 Run 1 9:00 – 10:00	Minimum	< 0.10	< 0.5	< 0.3	9.6
	Maximum	0.17	< 0.5	< 0.3	9.8
	Average*	0.10	< 0.5	< 0.3	9.7
9/13/2016 – Unit 17 Run 2 10:10 – 11:10	Minimum	< 0.10	< 0.5	< 0.3	9.6
	Maximum	0.19	< 0.5	< 0.3	9.8

Method 323 - Measurement of Formaldehyde Emissions From Natural Gas-Fired Stationary Sources-Acetyl Acetone Derivitization Method

- A colorimetric procedure for measuring formaldehyde from natural gas-fired sources.
- Test in one location in the stack with quartz lined probe.
- Use of midget impingers for sample collection.
  - 20 mL of reagent water
- Probe and sample line rinsed and included in analysis. 10 mL.
- Field duplicate concurrently.

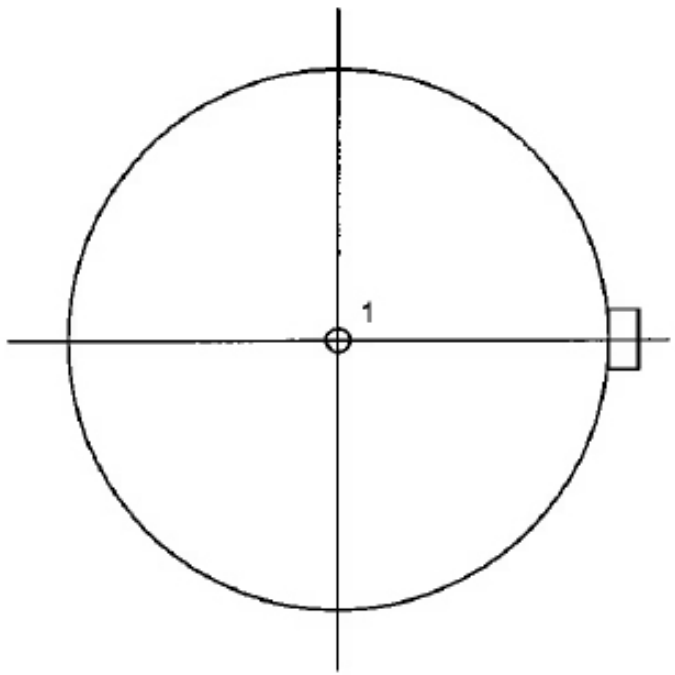
Very small sample volume collected.

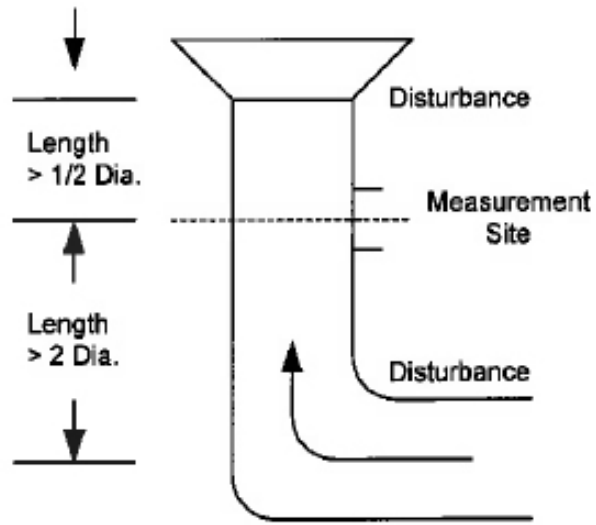
USEPA Method 323- Formaldehyde Sample Train Diagram



Method 323 Sampling Point

EQUAL AREA TRAVERSE FOR ROUND DUCTS





Method 323 Example Results

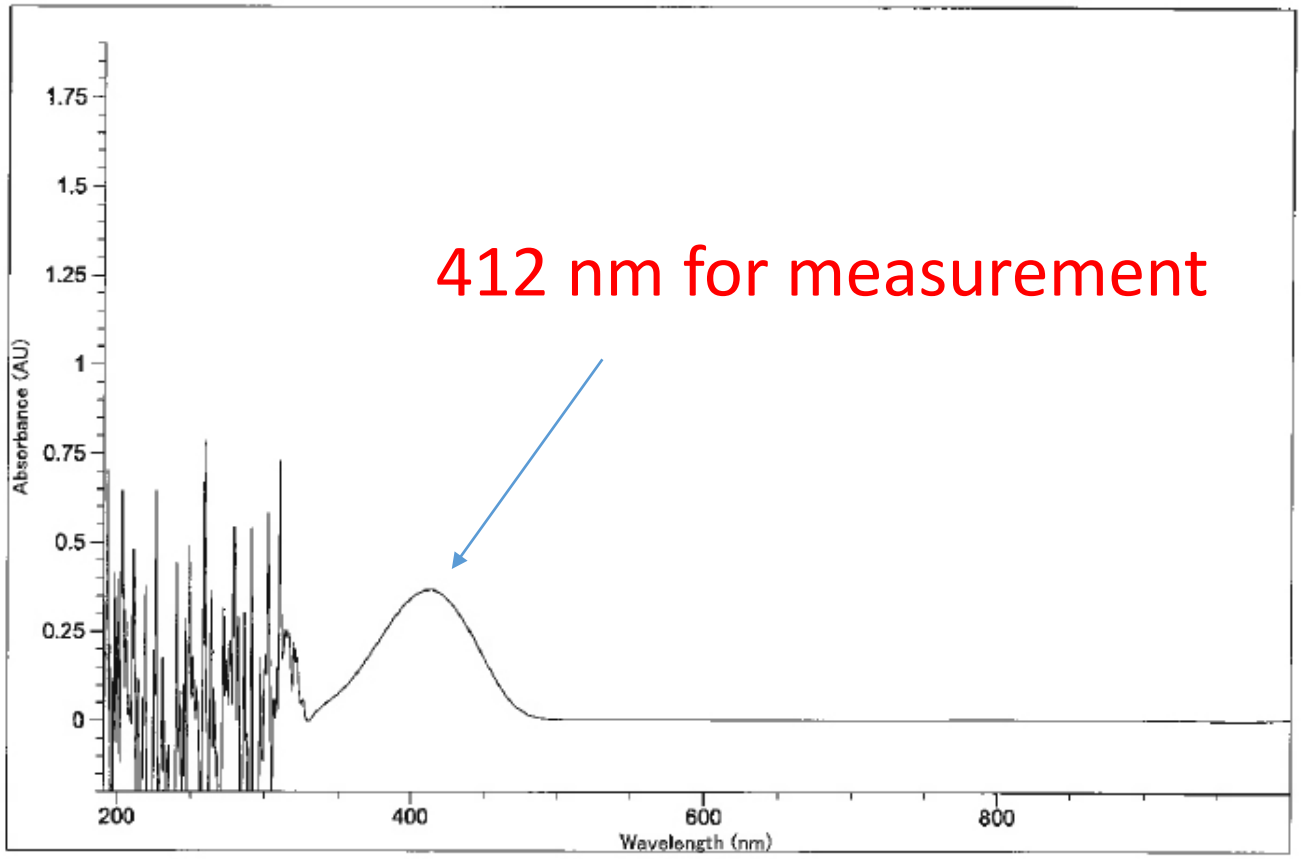
USEPA METHOD 323 RESULTS SUMMARY

[redacted] **Power Plant**

Run No.	Date	Time	Meter Volume, standard liters	Formaldehyde detected, ug	Formaldehyde Concentration, ppmvd	DSCFM	Formaldehyde Emission Rate, lbs/hr
1A	6/22/2016	7:17-9:17	33.757	≤ 0.967	≤ 0.023	754,399	≤ 0.081
1B	6/22/2016	7:17-9:17	33.626	≤ 0.992	≤ 0.024	754,399	≤ 0.083
Run 1 Average			**33.691**	**≤ 0.980**	**≤ 0.023**	**754,399**	**≤ 0.082**
2A	6/22/2016	9:50-11:50	33.476	1.040	0.025	740,992	0.086
3A	6/22/2016	12:12-14:12	33.511	≤ 1.040	≤ 0.025	738,486	≤ 0.086
Overall Average			**33.559**	**≤ 1.020**	**≤ 0.024**	**744625.67**	**≤ 0.085**

Method 323 Spectrum

Sample Spectrum



Data Analysis Results

#	Analyte Name	Value	Unit	Std. Dev.
1	Formaldehyde	2.81311	ug/mL	0.02073

Method 323 Example Results

Company: Mostardi Platt - Elmhurst
Job No.: 0616-168 – EPA Method 323
Client No.: M161506

LOQ = Limit of Quantification

MDL 0.0248 (µg/mL)
LOQ 0.496 (µg/mL)
Compound Formaldehyde

Lower Curve Limit 0.496 (µg/mL)
Upper Curve Limit 7.45 (µg/mL)

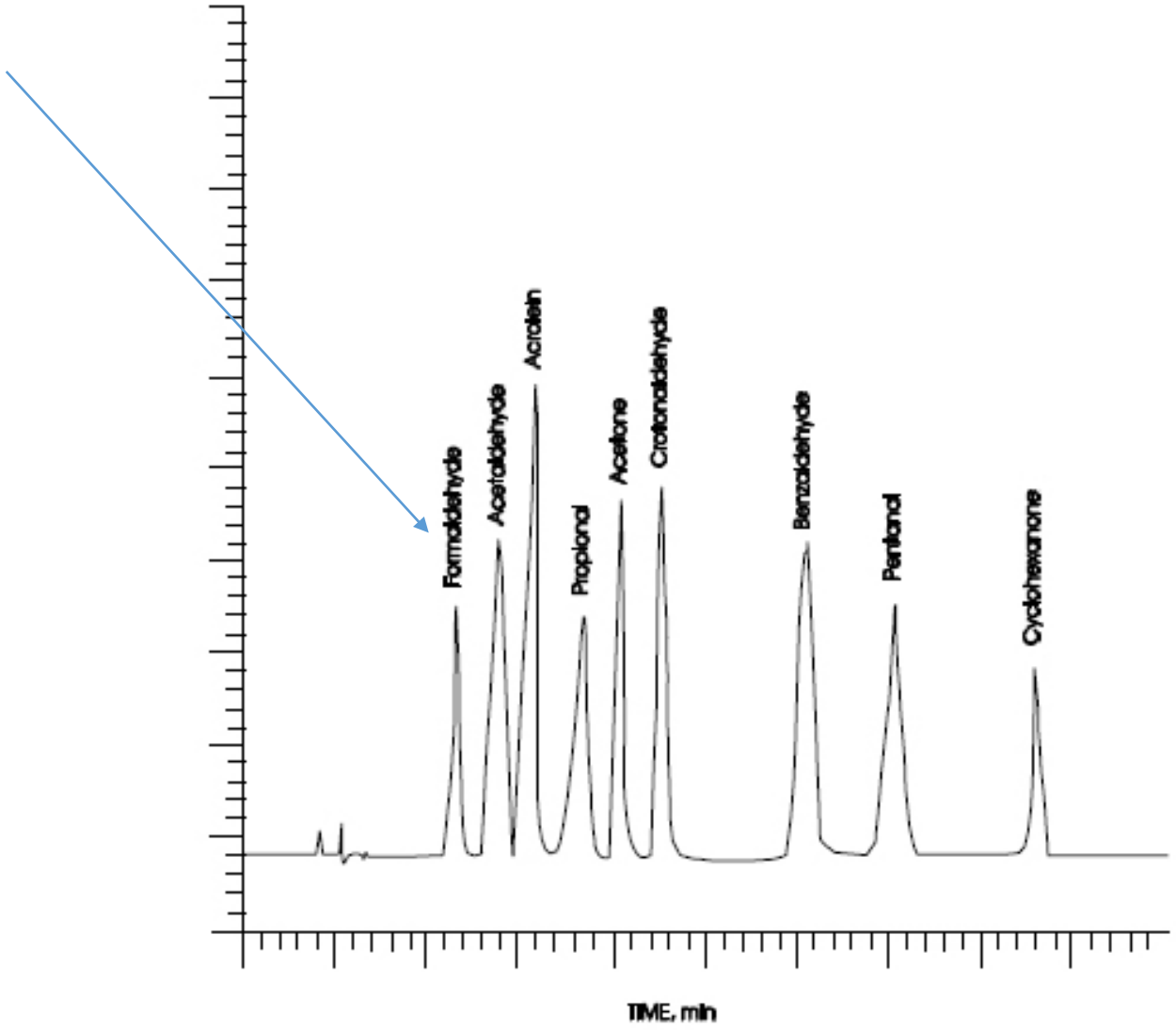
Below the LOQ, the LAB cannot guarantee analyte results within the criteria of the test method.

Sample ID	Lab ID	Absorbance	Analytical Concentration (µg/mL)	Dilution	Volume (mL)	Catch Weight (µg)	Qual
001-CT21 Run 1A	4	0.0030	0.0248	1	39.0	0.967	ND
002-CT21 Run 1B	7	0.0014	0.0248	1	40.0	0.992	ND
003-CT21 Run 2A	8	0.0033	0.0253	1	41.0	1.04	J
005-CT21 Run 3A	10	0.0025	0.0248	1	42.0	1.04	ND
007-CT22 Run 1A	4	0.0025	0.0248	1	41.0	1.02	ND
008-CT22 Run 1B	7	0.0023	0.0248	1	41.0	1.02	ND
009-CT22 Run 2A	8	0.0030	0.0248	1	38.0	0.942	ND
011-CT22 Run 3A	10	0.0028	0.0248	1	38.0	0.942	ND
013-DI Blank	12	0.0027	0.0248	1	158	3.92	ND
Method Blank #1	10	0.0014	0.0248	1	1.00	0.0248	ND
Method Blank #2	3	0.0006	0.0248	1	1.00	0.0248	ND
Method Blank #3	3	0.0002	0.0248	1	1.00	0.0248	ND
LD / 001-CT21 Run 1A	5	0.0021	0.0248	1	39.0	0.967	ND
					% Difference	NA	

CARB Method 430 - Formaldehyde

- Method adopted by CARB in 1989.
- Use of high performance liquid chromatography (HPLC) in the lab.
  - HPLC is not a field instrument.
- Not validated for high moisture nor high particulate gas streams.
- Use of midget impingers in series with 10 mL of liquid.
- Use of 2,4-dinitrophenylhydrazine (DNPH)

CARB Method 430 - HPLC



CARB Method 430 - HPLC

Maxxam ID		DCG579	DCG580	DCG581	DCG582			
Sampling Date		2016/09/13	2016/09/13	2016/09/13	2016/09/13			
COC Number		001	002	003	004			
	UNITS	CARB 430- E17-R1	CARB 430- E17-R2	CARB 430- E17-R3	CARB 430- E18-R1	RDL	MDL	QC Batch
Formaldehyde (Methanal)	ug/Tot.	3.4	2.3	2.9	6.4	0.2	0.1	4673732
Acrolein	ug/Tot.	<2	<2	<2	<2	2	0.4	4673732

RDL = Reportable Detection Limit

QC Batch = Quality Control Batch

Note: Minimum detectable limit (MDL) is not equal to Reportable detectable limit (RDL).

CARB Method 430 - HPLC

Test Number:	1	**Time:**		10:50-11:50
Pressure, Barometric(Hg"):	28.350	**Formaldehyde**	**(ug, impinger catch)**	3.8
Initial Volume (liters)	0	**Formaldehyde**	**(ppm, impinger catch):**	0.1364
Final Volume (liters)	24.121	**Formaldehyde**	**(lb/hr, Impinger catch):**	0.0168
Meter Temperature (°F)	79.17	**Acrolein**	**(ug, impinger catch)**	≤ 2.0
Meter Volume (standard liters)	22.292	**Acrolein**	**(ppm, impinger catch):**	≤ 0.0385
Meter Calibration (Y)	0.996	**Acrolein**	**(lb/hr, Impinger catch):**	≤ 0.0088
Dry Standard Flow Rate (dscfm):	26,273	**Formaldehyde**	**(lb/mmBtu, impinger catch):**	0.000200
Water Vapor in Flue Gas (Bws):	0.000	**Acrolein**	**(lb/mmBtu, Impinger catch):**	≤ 0.000105
O2, % dry	11.2			
CO2, % dry	5.6			
Fuel Factor Fd (mmBtu/dscf)	8,710			

3.8 ug impinger catch resulted in 136.4 PPB of Formaldehyde

RDL was 0.2 ug … approximately 7 PPB.

Comments

- FTIR methodology allows for instantaneous results, although you cannot achieve levels as low as the wet chemistry.
  - Often used in parallel with wet chemistry methods to provide an indication of where you are to ensure you will pass using wet chemistry.
  - DRAWBACK … FTIR is very expensive to run.
- Running longer test runs for wet chemistry methods does not necessarily mean you will have better results. Small sample sizes and then you collect additional moisture in impingers that dilutes the results.
- How much stratification do you have in the stack??? Sampling in one location for all but Method 316.
- Advantage of single point is the probe is less susceptible to contamination by keeping the probe in a single test port.

Comments (2)

- Extremely low levels of formaldehyde are DIFFICULT to measure accurately.
  - USEPA doesn’t always take into account the detection levels.
  - Many compounds could interfere with detection.
- Very low sample volume collected to represent source emissions.
  - Susceptible to contamination in sample handling, and probe rinsing.
  - How clean is the equipment? How good is the QA/QC?
  - How pure is your Ultra-Pure water?
- When attempting to measure in the PPB level, the results can vary widely.

Comments (3)

- Any errors in the dilution of samples will be magnified by the dilution ratio. 1:10 dilution results in a 10X multiplier of the result.
  - 10X the potential for error
- Even with FTIR, you may see swings of over 100% of reading from one minute to the next (e.g. <100 ppb to over 210 ppb, then back down).
  - Does it really change that abruptly?
- In general, combustion sources for formaldehyde are extremely low.
  - If VOC levels are less than 1 ppm, what are you accomplishing by looking for even lower levels of formaldehyde?
- Push back on EPA proposed emission levels if the test results do not support their numbers.

For further information …

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