

How to Measure Formaldehyde at Lowest Detection Levels Using the MultiGas™ FTIR Analyzer – Preliminary Recommendations

Summary

Per 40 CFR Part 63, Subpart YYYY, the emissions limit in turbine exhaust for formaldehyde is 91 ppb. In order to measure formaldehyde at steady state at the lowest possible levels, the MultiGas FTIR equipped with a LN2 detector can be used with a custom water calibration (done in the field right before the test), 10-min spectra (average of 10 x 1 min scans) and an optimized formaldehyde calibration. A detection limit as low as ~ 30 ppb (as 3-sigma) can be achieved under these optimal conditions (applicable to each 10-min spectrum). Although MKS cannot guarantee that any instrument in the field can meet this detection limit, guidelines are provided below to reach the lowest possible detection limit.

Step by step instructions to measure formaldehyde at the lowest level (steady state only)

- 1) **Use a Multigas with low noise / high SNR** - Use a MultiGas FTIR gas analyzer with SNR (in N₂) > 800 in the 2900-3000 cm⁻¹ region. SNR measurements settings used should be: 0.5 cm⁻¹, MNB, 4 sec measurement time, gas cell at 191°C. Do not use any other settings to check the SNR. If the SNR is lower than 800, the lowest detection limit mentioned above might not be met.
- 2) **Use clean lines of appropriate material** - It is imperative to use thoroughly cleaned sampling lines as formaldehyde can “stick” to lines. Follow sampling materials recommendations below for formaldehyde sampling.

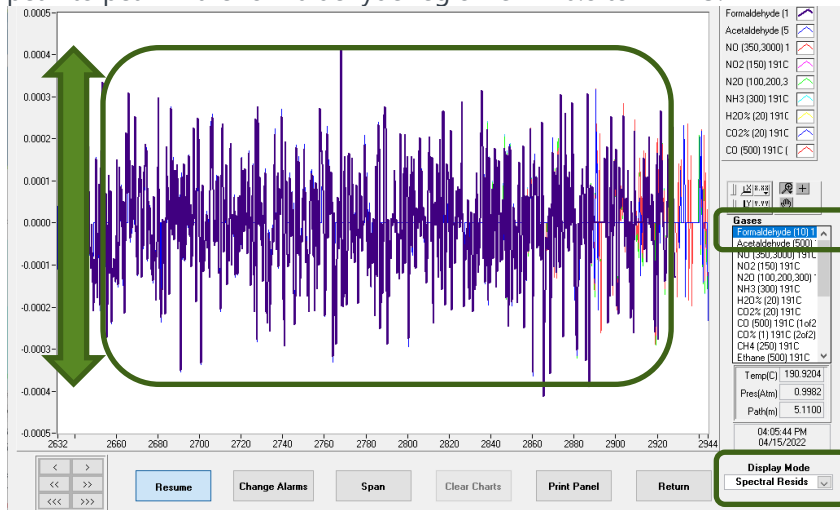
Gas Component	Calibration Line (Unheated)				Sample Line (Heated)			
	PTFE	PFA	HDPE	Stainless Steel	PTFE	PFA	Stainless Steel	Dursan® Stainless Steel
CH ₂ O	Good	Very Good	Very Good	Not Recommended	Very Good	Very Good	Very Good	Very Good

Gas Component	Sample Probe		Filter Material			
	Stainless Steel	Dursan® Stainless Steel	PTFE	Borosilicate Glass	Stainless Steel	Dursan® Stainless Steel
CH ₂ O	Very Good	Very Good	Very Good	Good	Very Good	Very Good

- 3) **Ensure instrument is stable and optics thoroughly purged (~ Few hours)** - Ensure that the MultiGas is at temperature, has a stable signal, and is purged (temporarily increase the optics purge N₂ flow rate from 0.2 LPM to 0.5 LPM to speed up the purging process if necessary) which might take a few hours. Ensure that the optics flow is back at 0.2 LPM before taking measurements. It is important that the level of moisture in the optics

remains constant during the tests eg that the H₂O measured in the HCU (Health Check Utility) is constant within a few ppm.

- 4) **Use MKS latest recipe** - MGRef-YYYY "Turbine Formaldehyde YYYY R1" recipe with "Formaldehyde (10) 191C" calibration and "Delta H₂O" calibration. Recipe uses 1 min sample scan time and 5 min background scan time.
- 5) **Take a background in N₂ (~15 min)** – Run N₂ for 5 or 10 min to ensure readings (including H₂O) are stable, then take a 5 min background. A long background is important in order to reduce the noise on each sample spectrum. Measure 5 to 10 spectra in N₂ with the 1 min scan time after taking the background, and check that the peak to peak in the formaldehyde region is <~ 0.8 to 1 mAU.



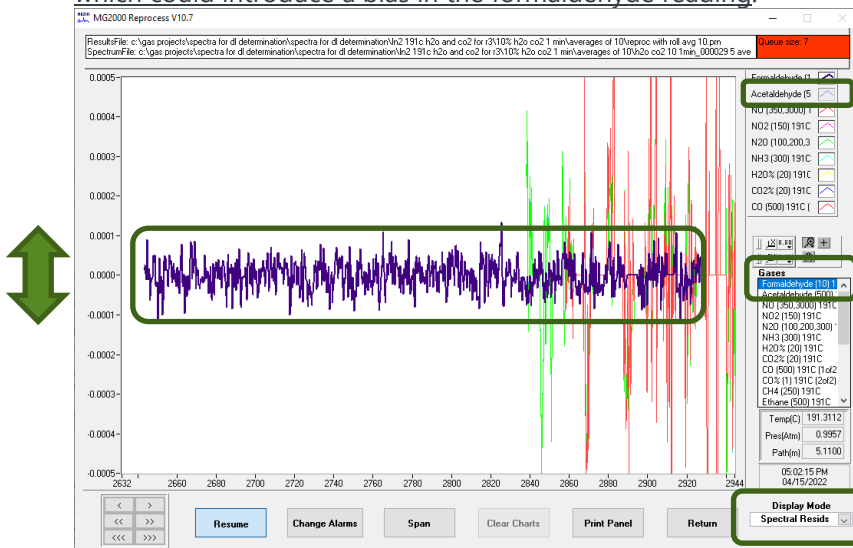
Typical spectral residuals spectrum (dark purple) for formaldehyde as shown in MG2000 for a 1-min spectrum in N₂.

In order to get the smallest y-scale, change the number of significant figures (precision) in the Y scale by clicking on Y.YY, selecting a Precision of 4.



- 6) **Measure turbine sample gas to determine level of H₂O (~ 30 min)** – As H₂O is the main interferent, you will need to collect H₂O spectra at the same level as present in the turbine exhaust, and at the same sampling pressure, so these need to be measured before we create the H₂O calibration. Collect 1 min spectra for at least 30 min of turbine at steady state, and create 10 spectra averages to get 10-min spectra (if collecting for 30 min, 3 10-min spectra can be created). Collecting 1 min spectra allows to double check that the sample is truly at steady state. Averaging is done using MG2000 > Spectrum Utilities > Average Spectra, and the 10-min spectra can be reprocessed later using the REPROCESS function.
- 7) **Reprocess 10-min Turbine Spectra and Check Spectral Residuals**
- 8) **Collect H₂O Spectra on-site (~30 min)** - Collect steady-state H₂O spectra on your instrument using a water delivery system providing H₂O in clean air or N₂ or 3% CO₂ in N₂ cylinder at the same level as the sample stream (within 0.2 mol% water) e.g. if sample has 7% water, use 6.8% to 7.2% water. Collect at the same flow rate as the sample (e.g. 1 LPM) and at the same pressure condition as the sample (within ~ 0.01 atm). Collect 1-min spectra at for at least 10 min and average these spectra to get a 10-min spectrum which represents the interference from H₂O. Collecting at 1 min ensures that the sampling is at steady state, and that there is no "drop" in H₂O concentration. Rename the spectrum with a name such as "H₂O x.xx% SNxxx location yy-mm-dd.lab". Use "x.xx%" to label the H₂O concentration level, eg in this example "7.00%". SN = Instrument serial number. Location = customer/location information. Yy-mm-dd = year-month-day.

- 9) **Create a custom H2O interference “Delta H2O” calibration** - Create a custom H2O interference calibration “Delta H2O” in the recipe by loading the “H2O x.xx% SNxxx location yy-mm-dd.lab” spectrum in the “Delta H2O” calibration from the recipe (MG2000 > Gas Calibration Tab > Create Gas Calibration > Load Calibration > Select “Delta H2O” calibration > Load spectra > select H2O x.xx% SNxxx location yy-mm-dd.lab > Save Calibration > Use name for new calibration such as “Delta H2O x.xx% SN location yy-mm-dd” > Goto MG2000 SETUP screen > Select Gases > use the new “Delta H2O x.xx% SN location yy-mm-dd” instead of the generic “Delta H2O” calibration.
- 10) **Reprocess the three turbine 10-min sample spectra collected earlier to determine the spectral residuals.** Spectral residuals for each 10-min sample spectra in the formaldehyde region should be similar or less than 0.0003 AU (peak to peak, green arrow), as shown below in the “Spectral Resids” screen of MG2000). It is important to have very low spectral residuals because it proves that there are no remaining interfering peaks which could introduce a bias in the formaldehyde reading.



Typical spectral residuals spectrum (dark purple) for formaldehyde as shown in MG2000 for the reprocessing of a 10-min spectrum (average of 10 x 1 min spectra), on same scale as the previous figure. The figure shows an acceptable level of residuals which is below 0.0003 AU peak to peak. The acetaldehyde plot was hidden (as it overlaps the formaldehyde) for clarity. Formaldehyde residuals are lower than for other gases because the custom “Delta H2O” calibration is using the formaldehyde region only.

If spectral residuals are higher than 0.0003 peak to peak, the uncertainty on the formaldehyde reading might be too high and another background + H2O calibration might be necessary.

- 11) **Establish Formaldehyde Detection Limit using multiple repeat measurements of H2O using updated recipe (~ 2 hours)**- Establish the instrument detection limit and check that there is no bias in the formaldehyde reading due to H2O by repeating measurements of a synthetic sample of interference-only gas (H2O in N2 or H2O in air or H2O and CO2 in N2 / air at the same level as in the sample). Use the same pressure condition as the sample (within 0.01 atm). EPA detection limit determination involves taking 7 independent measurements (each independent measurement here is a 10-min spectrum), with preferably taking a 5-min background in N₂ every time between each measurement. In this case, since such a procedure would imply repeatedly placing and removing the water generating device which is not very convenient, taking consecutive H2O spectra can be used (eg for 70 min). The average formaldehyde reading of the 7 x 10-min measurements, which is the bias (B), should be < 10 ppb. Calculate your instrument detection limit (DL) as 3 * standard deviation of formaldehyde readings for the 7 10-min spectra. We expect a standard deviation for formaldehyde readings of < 10 ppb for 10-min spectra, which corresponds to a DL (as 3-sigma) of ~ 30 ppb or less.

- 12) Collect Sample Spectra (90 min/run, 3 runs, ~5 hours)** - Use 1 min scan time, so that it can be confirmed that the sample is at steady-state. We recommend the collection time of 1.5 hours for each run instead of the standard 1 hour run in order to be able to do more averaging. If runs of 1 hour only are allowed (as per EPA m320 or ASTM 6348), create 7-min average samples instead of 10-min samples, such that there are a minimum of 8 samples / hour, but detection limit will increase slightly. Note that when collecting at 1 min scan time and viewing in the Spectral Resid window, the spectral residuals shown in MG2000 will be 2 to 3 times larger than the spectral residuals from a 10-min spectrum. Run at least 10 min N₂ between each run, and double check that the formaldehyde reading remains low when running N₂ (< 10 ppb).
- 13) Average Sample spectra and Reprocess** - Calculate 10-min spectra as explained above (will yield 9 x 10-min spectra for a 1.5 hour run). Reprocess these 10-min spectra. Again, spectral residuals for each 10-min sample spectra in the formaldehyde region should be similar or less than 0.0003 AU, as shown in the "Spectral Resids" screen of MG2000. If the spectral residuals are much higher, it might be that the source is variable, or not at the same H₂O or CO₂ conditions, or that there are instrument or sampling issues. Check that the standard deviation from the multiple 10-min formaldehyde readings is close to the value determined when using the interference-only stream (e.g. < ~ 10 ppb). The average formaldehyde reading of the 9 10-min spectra would be the quantity to be reported.

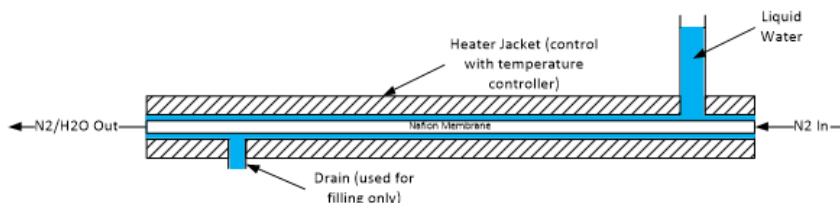
FAQs

Do we really need to perform a water calibration on-site ?

Yes, as even small changes in instrument condition can have an effect on the formaldehyde bias. The instrument also needs to be at thermal equilibrium and with a constant H₂O level in the optics (eg H₂O reading in HCU is constant within a few ppm).

What water delivery system do you recommend ?

Temperature controlled impingers, heated permature membranes, Hovacal are typical water delivery systems. See figure below as an example using a Permapure system.



Can we collect 10-min scans instead of collecting 1 min scans and performing a manual average ?

Yes, however 1-min scans allow to ensure that the stream is truly at steady state. Note that the spectral residuals in the "Spectral Resids" screen for a 10-min scan should very low, e.g. 0.0003 AU or less peak to peak or less.

Can we collect a 10-min background instead of a 5-min background ?

Yes.

Does MKS have instruments with lower detection limits for formaldehyde ?

MKS offers more sensitive detectors (eg 5 micron detector, 2000-4000 cm^{-1} wavenumber region) which will improve the sensitivity (eg detection limit as 3σ) by a factor of ~ 1.5 . In that case, a detection limit of ~ 15 -20 ppb can be expected. The same procedure with a spectrum for H_2O taken before the test would still be needed. Note that a 5 microns detector cannot measure NO_x , but is very well suited for formaldehyde measurements.

Does it make sense to have a dedicated instrument for formaldehyde testing ?

Yes, we recommend to have a dedicated instrument and sampling lines for formaldehyde testing.

What formaldehyde cylinder is appropriate ?

Customers have reported that they are using a 0.5 ppm formaldehyde cylinder with N_2O tracer for spiking, with spiking in the range of 30-50 ppb (45 ppb is 50% of the limit of 91 ppb).

Can I use multiple "Delta H_2O " calibrations ?

It is possible that using multiple "Delta H_2O " calibrations might help in reducing the spectral residuals, but more investigation is needed as there is a risk of increased white noise. The main end-criteria for acceptable performance is having less than 0.0003 AU (peak to peak) in the spectral residuals of the formaldehyde of a 10-min spectrum when measuring turbine exhaust.

If needed, how can I improve the performance of my current instrument ?

Although mirrors and windows performance can be recovered through cleaning, use of new mirrors and windows may be required to achieve optimal performance.