



## **Concerns with the use of EPA Method 320 for the Portland Cement NESHAP**

### **New standard may require FTIR testing for HAPs:**

On Aug 6, 2010 EPA published amendments to 40 CFR 64 Parts F and LLL – *NESHAP from the Portland Cement Manufacturing Industry and Standards of Performance for Portland Cement Plants*. Contained within the rule is a requirement to monitor THC with a limit of 24 ppmv as propane. Alternately, organic HAPs may be monitored with a limit of 9 ppmv @ 7% O<sub>2</sub>. Organic HAPs must be measured by FTIR using EPA Method 320 or ASTM Method D6348-03 [63.1349 (b) 4 (iii)]. Organic HAPs are defined in this rule as benzene, toluene, styrene, o,m,p-xylene, formaldehyde, acetaldehyde, and naphthalene. The rule also has limits for hydrogen chloride (HCl).

Enthalpy believes there are serious problems with requiring the use of EPA Method 320 to determine total organic HAP concentration. We believe that using Method 320 will provide limits of detection that are up to 100 times higher for organic HAPS than can be obtained using EPA Method 18.

Sources may not be able to use the THC limit if feed to the unit is likely to cause significant methane or ethane in the outlet. Sources in this situation have the option to use the alternative approach of measuring organic HAPs. In order to use the alternative approach, the facility must establish a relationship between THC and organic HAPs by conducting a performance test using both methods simultaneously. Each test run must be 3 hours long and 3 runs are required.

### **A problem with the monitoring requirements:**

The difficulty lies in achieving appropriate detection limits for some of the compounds when testing a typical Portland cement matrix. Portland cement stacks typically contain 30% moisture and 15% CO<sub>2</sub>. Both of these compounds absorb infrared at many different wavelengths. Because they are present at very high concentrations, they absorb a great deal of energy making it difficult to quantify compounds that absorb at wavelengths similar to those characteristic of water or carbon dioxide.

Formaldehyde can be quantified at relatively low concentrations because its absorbance wavelengths can be separated from those of water and CO<sub>2</sub>. Acetaldehyde can be quantified at slightly higher concentrations. However, aromatic compounds absorb at regions that are highly affected by water and CO<sub>2</sub>.

Any compound, with the exception of homonuclear diatomic compounds, has two mechanisms that will result in absorbing infrared energy. Those mechanisms are rotation and vibration. Aromatic compounds (such as benzene, toluene, styrene, o,m,p-xylene, formaldehyde, acetaldehyde, and naphthalene) have strong rotational and vibrational absorbance. Unfortunately, most of these absorbance bands are masked by water. Aromatic compounds also have absorbance regions caused by stretching vibrations that are not masked by water or CO<sub>2</sub>. However, these bands are not strong and are indistinguishable from the stretching bands of other organics. The net result is that aromatic compounds are difficult to quantify in the presence of water and CO<sub>2</sub>.

**The data processing mechanism yields uncertain results:**

In a clean dry matrix, compounds are quantified by comparison to reference spectra of the target compound. When significant interferences are present, the analyst uses FTIR software to model the absorbance of the interference. The model is scaled to match the concentration of the interferent in the sample. The response predicted by the model is subtracted from the sample response on a wavelength by wavelength basis. The resulting subtracted absorbance pattern is then compared against the reference spectra of the target analyte. If the world were perfect this would work well all the time. In reality, the modeled response for the interferant is likely to be slightly different than the actual response. Thus, when the modeled response is subtracted, errors are created in the residual absorbance pattern. It is these errors that complicate the process of quantifying the target compounds. As the concentration of the interferent, e.g. water increases the magnitude of the modeling errors will generally increase as well.

Like many other compounds, water and CO<sub>2</sub> have both strong and weak absorbance bands. As the concentration of these compounds increases, weaker bands suddenly become important and further interfere when trying to detect aromatic compounds at low concentrations. Ammonia is also found in some Portland cement matrices, which adds to the complexity of modeling the interferences.

The minimum detectable concentration (MDC) of any compound is a function of the uncertainty associated with quantifying the compound at low concentrations. When the uncertainty is larger than the predicted concentration the compound cannot be definitively determined to be present. Uncertainty is created by detector noise and modeling uncertainty. Of these factors, modeling uncertainty is a much larger issue.

**An Analogy:**

Imagine standing in Kansas and looking toward the western horizon with the intent of determining if there is a cottonwood tree in the distance. This is analogous to finding a target compound in a matrix with little water or CO<sub>2</sub>. The cottonwood is easy to spot when present. Now, imagine moving a little farther West and trying to find the cottonwood with the Rocky Mountains in the background. The cottonwood has not gotten smaller, but the amount of information that has to be processed to find the cottonwood has increased dramatically, so much so that one cannot find the tree without some help. In our FTIR analogy, the help comes by creating a model of the Rocky Mountains and subtracting the assumed peak height at each degree of horizon. You are now trying to find a 50 ft. tree by subtracting 14,000 ft. peaks. A 1% error in the model leaves you with an error larger than your tree. So, on a flat plain the presence of a 50 ft. tree is easy to determine, but when back-dropped by the Rocky Mountains the tree would have to be 300 ft high to be definitively sure the tree is there.

Dr. Grant Plummer, Enthalpy staff member, was instrumental in developing and promulgating EPA Method 320. He estimates that one would have to achieve 99.99% accuracy modeling water and CO<sub>2</sub> to achieve the desired MDCs in a Portland cement plant effluent.

**Our Conclusion:**

FTIR methods allow several different calculations to determine the minimum detectable concentration of target analytes. Some are simply a measurement of the detector noise, such a technique would be equivalent to taking your measurement in Kansas. If you are testing at a Portland cement plant, your matrix is full of Rocky Mountain sized interferences and the MDC you determined in clean matrix is simply not applicable. In clean matrix 0.25 ppmv MDCs are possible for aromatic compounds. However, when considering the uncertainty introduced by a matrix high in water, CO<sub>2</sub>, and ammonia, MDCs are likely to be 5 to 20 ppmv per compound.

If you are only presented with the result of the most favorable MDC determination you may decide that FTIR is an appropriate tool. However, if you were also presented with the alternate MDC calculations, you may make a different decision.

**Alternative Approach:**

Formaldehyde, acetaldehyde, and hydrochloric acid have FTIR MDCs low enough to make FTIR a useful tool to measure HAPs at Portland cement plants. Benzene, toluene, styrene, (o-, m-, p-)xylene, and naphthalene can be measured by EPA Method 18. Within Method 18 there are two options. Both options allow method detection limits of well less than 1 ppm. EPA Method 18 is called out as an option in the standard [63.1353 (b)].

The combination of Method 320 and Method 18 meets all of the requirements of the task at hand. In this case sample is extracted from the stack and delivered to the FTIR cell with a sample line heated to 180°C. The sample is drawn through the cell, and the effluent is sampled by Method 18. Dynamic spiking using HCl assures that the sampling system is leak-free and not prone to adsorbing analytes during transport.

If adsorbent tubes are used for Method 18 the detection limits for the aromatic compounds will be on the order of 10 to 20 ppb, thus the need for low detection limits will be met. However, the results of the adsorbent tube analysis may not be available for two weeks (standard laboratory turnaround schedule). If direct interface GC is used as the Method 18 option, the detection limit for the aromatic compounds will be on the order of 100 to 150 ppb, but the results will be available on-site.

Compounds	Estimated MDCs (ppmv)		
	EPA M320 only	M320 / M18 Adsorbent Tubes	M320 / M18 Direct Interface
HCl	1	1	1
Formaldehyde	0.15	0.15	0.15
Acetaldehyde	1.5	1.5	1.5
Benzene	22	0.02	0.15
Toluene	23	0.02	0.15
Styrene	18	0.02	0.15
Xylenes	23 (69)*	.02 (.06)*	.15 (.45)*
Naphthalene	25	0.015	0.1

\* Sum of all three Xylene isomers

**Final Conclusion:**

While FTIR is a powerful tool for characterizing a gas stream, it has its limitations. Due to the concerns highlighted in this paper, and the presentation of a suitable alternative that provides increased sensitivity, Enthalpy Analytical, Inc. strongly recommends the inclusion of EPA Method 18 with these tests. Without Method 18, it is our belief that HAP results will be biased high, and it will be very difficult for facilities to comply with the limits presented in the new rule. Enthalpy Analytical, Inc. is putting forth this alternative because we believe we have a professional responsibility to inform clients when our technical knowledge and expertise can generate higher quality data.