

Measuring Total VOC via FTIR

Current Total VOC Measurements

The most common, and current standard, method for measuring Total Volatile Organic Compounds (VOC) is the use of a Flamed Ionisation Detector (FID). This gives a representative value of the total carbon content of a gas stream, as the FID cannot tell which specific organic compounds are present.

Waste Incineration plants are required to report Total VOC levels, often at levels of 50mg/m³ or less.

Speciated Organic Measurements

Protea has used FTIR technology for many years on batch chemical processes where there can be dozens of different organic compounds present in a gas stream. This experience has been led by the successful application of chemometric analysis techniques to spectroscopic data. This is imperative for multi-variate and large concentration range analysis. As well as this, excellent calibration facilities and full traceability of reference standards has further backed up the quality of measurements.

atmosFTIR Solution

Protea has designed the atmosFIR FTIR gas analyser specifically to meet the requirements of test houses in carrying out compliance monitoring on WID and LCPD installations.

As well as the common inorganic measurements (CO, NO_x, SO₂, HCl etc.), Protea's in-house FTIR software (PAS) comes with a number of speciated organic measurements built-in. These include CH₄ to C₅H₁₂, Formaldehyde and Benzene. With the software pre-programmed for these species, measurement of a number of individual VOCs is very easy.



Quantifying Total VOC

The common methodology to generating a Total VOC figure from FTIR readings is to simply sum the results of the measured organic species. Indeed this can be done, and Protea's software allows this to be done, even assigning factor weightings to each species to give a result "as Carbon".

However, this methodology has problems when we consider the number of possible individual species that should be considered. For example, the minimum species that an FID should respond to are methane, ethane, benzene, toluene and dichloromethane. For WID applications, there are another approx. 25 organic species.

Whenever we make a measurement with any analytical equipment it has an uncertainty. For a Total VOC measurement made up from the summation of separate VOC concentrations, the total uncertainty increases as we add the VOCs as shown below.

$$\sigma_{VOC}^2 = \sqrt{\sigma_{CH_4}^2 + \sigma_{C_2H_6}^2 + \sigma_{C_6H_6}^2 + \sigma_{C_7H_8}^2 + \sigma_{CH_2Cl_2}^2}$$

$$\sigma_{VOC}^2 = \sqrt{20} = 4.5\%$$

As well as the uncertainty of measurement, if we are to sum all the individual organic species, we in turn should sum the LDLs of each. With 5 species each with detection limits of 0.5mg/m³, this means our total realistic LDL would be 2.5mg/m³. This is above the allowable LDL for a Total VOC emissions system. Likewise, the total measurement uncertainty for a sum of readings will be higher than the allowable uncertainty for a single measurement.

Modelling the process

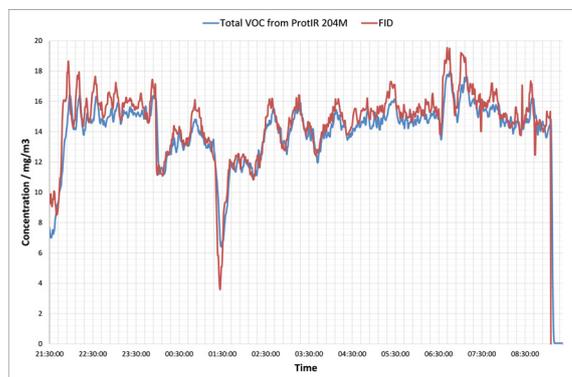


Figure 1 - Total VOC via FTIR vs. FID (data taken from cement kiln running under WID)

Protea have developed a novel solution to the measurement of Total VOC by modelling the response from an FID analyser against typical WID installation gas streams.

Rather than trying to speciate individual organics, of which there can be dozens at low levels, Protea compared parallel FID measurement data with FTIR spectra. Different tests were run on different “types” of incineration – medical waste, municipal waste, cement kiln – and different types of incinerator - stepped hearth, rotary kiln and pulsed hearth.

This has produced results from the FTIR which are based on a single transferable PLS model. This factor-based multi-variate analysis is able to accommodate variances due to many IR responses i.e. many organic gas species.

It enables us to give a single measurement value with a single detection limit (<0.5mg/m³) and a single uncertainty value.

Linearity

As this method is in effect giving readings as a FID would read, it does mean that the reported value is not an absolute “true” reading, but one that has different responses for different gas species.

The response is linear for each gas, however just as with a FID there

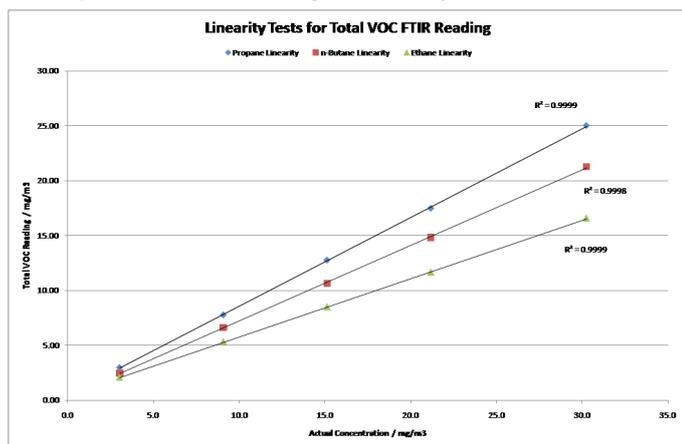


Figure 2 - Linearity response for FTIR Total VOC model for 3 common organic species

is a different response to each. This response could be identified with a correction like a FID, however we wouldn't need to as if we were measuring a known VOC - the FTIR can identify this individually!

Supplier:

Like having another analyser!

So, with Protea's Total VOC analysis as part of the analysis package with the atmosFIR analyser the user has the luxury of speciated organics when needed but also a single Total VOC measurement. This could remove the need for a separate FID analyse if Total VOC readings are required alongside inorganic gases. The associated costs and time of running another analyser would be removed.

Added to this the ability of the FTIR to measure water vapour and oxygen (via built in ZrO₂ cell) and atmosFIR turns into a truly complete transportable CEM system.