

Laboratory Products Focus

Investigating the Performance and Discussing the Suitability of FTIR for TOC Emissions Monitoring

Fourier transform infrared (FTIR) spectroscopy is becoming increasingly used for emission monitoring applications for a range of inorganic gases. However, where TOC monitoring is also required generally a flame ionisation detector (FID) is used. The standard reference method (SRM) [2] is based on the use of flame ionisation detection. Whilst there are no technical issues in using FTIR and FID in tandem there are the practicalities and cost of the transportation and set-up of two analysers. Consequently, it would be advantageous to be able to measure all the required species by FTIR alone – in addition, the FTIR also has the advantage of providing speciation information. Many UK VOC emissions are regulated and fall under either the waste incineration directive (WID) [3] or large combustion plant directive (LCPD) [4]. Consequently, regulatory monitoring must be carried out following the SRM or with an alternative reference method (ARM) where equivalence to the former has been demonstrated.

Towards assessing the suitability of FTIR for TOC monitoring we have tested the performance of the Gasetm DX4000 (distributed in the UK by Quantitech Ltd) against that of a Sick Bernath FID for measuring VOC compositions generated in NPL's Stack Simulator Facility. The FID is certified under MCERTS for TOC measurements whilst the DX4000 FTIR is certified for a range of inorganic gases (for example, NO, SO₂, HCl) but, at the time of writing this article, no VOC species. Many performance parameters of the FTIR are well characterised due to the original MCERTS testing, for example, noise, drift and temperature sensitivity so for the purposes of this investigation need not be repeated, consequently, we have focussed mainly on responses to different VOC mixtures and cross-sensitivities.

The Stack Simulator Facility developed at NPL was used for the work so that testing was carried out under real stack conditions. The facility has been designed with a cross-stack pathlength of 1.5 m, four 5" BSP sample ports, 300 L capacity and is capable of velocities and temperatures of up to 10 m.s⁻¹ and 200 °C, respectively [5]. These specifications allow testing of instruments [6] and procedures [7], and the carrying out of proficiency testing schemes under real sampling conditions. The approach of the testing was to create test mixtures in the Stack Simulator based on the performance requirements for a low range (0 – 20 mgC.m⁻³) TOC continuous emissions monitor (CEM) as detailed under BS EN 15267-38.

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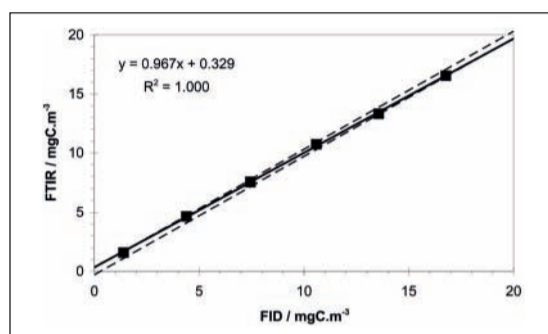


Figure 1. Lack of fit test of Gasetm DX4000 FTIR using test mixtures 1-6 (Table 1). Least squares regression (—), acceptance criteria under BS EN 15267-3 (---).

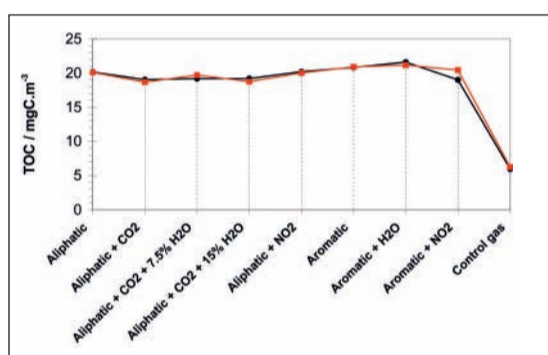


Figure 2. Comparing TOC determinations made by the Gasetm DX4000 FTIR (—■) to those made by the SRM (—●) for compositions based on the performance standard requirements of a low range TOC monitoring CEM under BS EN 15267-3.

EXPERIMENTAL

The Sick Bernath 3006 FID (certified under MCERTS) was operated following the SRM.2 The FTIR used was a Gasetm DX4000 Multicomponent Gas Analyser with a 5 m multipass gas cell heated to 180 °C. The NPL Stack Simulator was heated to 150 °C and the velocity set to 10 m.s⁻¹. Speciation by FID was possible as the VOC component for each test had been mixed in a cylinder and previously certified by NPL, therefore, the ratio of the components was already accurately known and hence the Stack Simulator composition could be derived.

The test compositions (Table 1) were designed to include H₂O and NO₂ as both these species exhibit absorption features in the spectral region where the VOC's are analysed. For wet tests the water vapour content was confirmed using a midget impinger train and carrying out BS EN 147909, sampling times were determined from BS EN ISO 916910.

RESULTS & DISCUSSION

Using the FID to validate the composition of the Stack Simulator for each test it is seen that the FTIR would pass the lack of fit test requirements under MCERTS (Figure 1 & Table 2). Furthermore, we also see that the TOC response to compositions of aromatic and aliphatic hydrocarbons would meet requirements under both wet and dry conditions (Figure 2). With regard to NO₂ cross-sensitivity it is observed that the deviation in the presence of aliphatics is -1.0% whilst in the presence of aromatics it is 7.1%. However, the analyser would still pass the NO₂ cross-sensitivity test under MCERTS. This is due to the fact that the requirement is to test the cross-sensitivity at the span point (a test would also be required at the zero point). The span gas is propane and as seen from the aliphatics test (of which propane is one of the components) the cross-sensitivity is well within acceptable limits. However, it is still of scientific interest to discuss the aromatics + NO₂ result.

It is known that NO₂ is a potential FID interferent and so it's possible that there may have been some suppression in the production of oxidised carbon ions from the sample. However, whilst this might explain some of the deviation it is generally a requirement in equivalence testing to approach the testing assuming that all the error is associated with the alternative method and none with the SRM. With regard to the FTIR the TOC value is found by quantifying each individual hydrocarbon and taking the sum, consequently, the data suggest that the NO₂ has interfered with one (or possibly more) species absorbance features giving an artificially high concentration. The fact that the deviation observed for the aliphatic + NO₂ test was not of the same order evidences that NO₂ is not significantly interfering with the propane channel. Deriving speciation information from the FID TOC value and the mixing ratio of the hydrocarbon Stack Simulator source cylinders it is found (data not shown) that the greatest difference is an increase in the toluene quantification. It is also of note that for the FTIR the aromatics test is more demanding than the aliphatics as, for example, 5 mgC.m⁻³ is equivalent to 9.3 ppm of methane but only 1.3 ppm of toluene, the latter being close to the instruments limit of detection and potentially being affected to a greater extent by noise. Although, it might be expected that this would lead to a random difference in readings rather than the bias as observed here. However, without further work it is not possible to differentiate the true source of the observed deviation.



It is also possible to analyse the data following CEN TS 14793 applying the in-field statistical tests to determine if equivalence could be demonstrated to the SRM (nb. in this investigation only one FTIR analyser is used. As reproducibility for TOC measurements have not been assessed under the MCERTS certification of the DX4000, parallel testing would be required under CEN TS 14793). To test for any systematic deviation between the alternative method (AM) and the SRM repeated determinations of mixtures 1 – 10 from the FTIR are plotted against the FID (data not shown). The orthogonal regression of the plot returns a slope of 1.007 and intercept of -0.164 (Table 3). Both parameters meet the acceptance criteria indicating that if CEN TS 14793 was followed in full (i.e. parallel testing of two analysers) that the FTIR method could ultimately be accepted as an ARM for TOC monitoring. Whilst these data show that in principle FTIR could be used for TOC monitoring there are still a number of issues. For the FTIR data described here the TOC has been determined by summing the responses of the individual hydrocarbon channels on the analyser, in contrast to the FID that directly determines a total response. It is known that the FID response will not always be the same for samples of the same TOC content but with differing hydrocarbon compositions.

Table 1. Nominal concentrations of test mixtures created in NPL's Stack Simulator for testing the performance of the Gasetm DX4000 FTIR against a Sick Bernath 3006 FID. The diluent for all compositions was 11% O₂ / N₂. The BS EN 12619 control gas was sampled directly from the source cylinder and not delivered via the Stack Simulator.

Mix	Propane / mg.m ⁻³	Methane / mg.m ⁻³	n-Hexane / mg.m ⁻³	Benzene / mg.m ⁻³	Toluene / mg.m ⁻³	m-Xylene / mg.m ⁻³	NO ₂ / mg.m ⁻³	CO ₂ / %	H ₂ O / %
1	ro gas: 11% O ₂ / N ₂								
2	4								
3	8								
4	12								
5	16								
6	20								
7	8	8	8						
8	8	8	8					10	
9	8	8	8					10	7.5
10	8	8	8					10	15
11	8	8	8				30		
12	5			5	5	5			
13	5			5	5	5			15
14	5			5	5	5	21		
BS EN 12619 control gas	2 mg.m ⁻³ methane / 1.5 mg.m ⁻³ ethane / 0.5 mg.m ⁻³ toluene / 0.5 mg.m ⁻³ benzene / 0.5 mg.m ⁻³ methylene chloride / 50 mg.m ⁻³ CO / 11% O ₂ / 10% CO ₂ / N ₂								

Table 2. FTIR and FID determinations in lack of fit and response testing.

Mix	Description	FID / mgC.m ⁻³	FTIR / mgC.m ⁻³	Deviation / mgC.m ⁻³	Fraction of full scale / %	BS EN 15267-3 requirement / %
Lack of Fit						
1	n/a	1.4	1.6	0.2	0.9	2.0
2	n/a	4.4	4.6	0.3	1.3	2.0
6	n/a	16.8	16.5	-0.2	-1.1	2.0
3	n/a	7.5	7.5	0.1	0.5	2.0
4	n/a	10.6	10.7	0.1	0.7	2.0
5	n/a	13.6	13.3	-0.2	-1.2	2.0
Response Tests						
7	Aliphatic	20.2	20.1	-0.1	-0.3	2.0
8	Aliphatic + CO ₂	19.0	18.7	-0.4	-1.8	4.0
9	Aliphatic + CO ₂ + 7.5% H ₂ O	19.2	19.7	0.5	2.5	4.0
10	Aliphatic + CO ₂ + 15% H ₂ O	19.2	18.7	-0.4	-2.2	4.0
11	Aliphatic + NO ₂	20.2	20.0	-0.2	-1.0	4.0
12	Aromatic	20.8	20.9	0.1	0.4	2.0
13	Aromatic + H ₂ O	21.6	21.2	-0.4	-2.1	4.0
14	Aromatic + NO ₂	19.0	20.4	1.4	7.1	4.0
	Control Gas	5.9	6.2	0.3	1.4	2.0

Table 3. Results of orthogonal regression between the FTIR (alternative method) and the FID (standard reference method) carrying out CEN TS 14793 using data from measuring mixtures 1 – 10 from Table 2.

	Unit	AM	SRM
Systematic deviation			
Grand averages		13.16	13.23
Repeatability			
Standard Deviation of repeatability		6.79	6.74
Variance of repeatability		46.05	45.40
Total number of measurements		99	99
Non systematic deviation			
Verification of the tests	Value obtained	Critical value	Conclusion
Validation of the test	0.998	=> 0.97	Y
Slope	1.007	=> 0.95 & <=1.05	Y
Intercept	-0.164	=> -0.66 & <=0.66	Y

ACKNOWLEDGEMENTS

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This is due to the fact that carbon atoms bonded to heteroatoms such as oxygen are not ionised as efficiently as those bonded to hydrogen, consequently the response to propanol differs from that for propane.

This is not the case for the FTIR so it might be argued that it's possible to achieve a more accurate TOC reading (with the added benefit of speciation information being available). However, the issue with the FTIR is what happens if a hydrocarbon is present for which it has not been calibrated? In this case many algorithms would attempt to fit the available library spectra resulting in both under- and over-fitting to the sample spectrum, which upon summation could lead to an inaccurate TOC value (or at the very least inaccurate VOC concentration information).

One form of protection from this is the residual spectrum (the result of the fitted library spectra subtracted from the sample spectrum), where features above the noise threshold will appear indicating that the library is insufficient to explain all the sample absorption features. Hence, to have confidence in a TOC value determined in this way it is critical to verify that the library of reference spectra covers all VOC's present in the sample that are above instrumental detection limits. This might mean having application specific libraries, for example, for waste incineration it might be possible to demonstrate that a reference library of methane, ethane, ethylene, propane, hexane and formaldehyde is sufficient.

Alternatively, it has been proposed to analyse the intensity of the C-H stretch in the FTIR spectrum to derive the TOC value directly, in contrast to the method investigated here with the DX4000 where each hydrocarbon is individually quantified followed by summation. However, there are two immediate issues with this, firstly that there doesn't exist a single C-H absorption feature for all conceivable hydrocarbons and secondly, that the FTIR sensitivity is not the same for all species. For the latter it might be argued that this is the current situation with the FID and this has been accepted. However, the difference is that the range of sensitivities is far greater. For example, the FTIR response is related to the cross-sectional area of the absorbing molecule. The cross-sectional area of methane is ~ 48% smaller than benzene, in contrast the FID response to methane is ~14% smaller than benzene (on a per carbon atom basis).

CONCLUSIONS

In using the NPL Stack Simulator Facility to compare the performance of a Gasetm DX4000 FTIR against the SRM for TOC monitoring (FID) it was shown that the FTIR would meet the requirements under MCERTS for linearity, cross-sensitivities to H₂O, CO₂ and NO₂, and for response to VOC mixtures including aliphatic and aromatic hydrocarbons, and methylene chloride. It was also shown that the FTIR could pass the in-field statistical tests of performance under CEN TS 14793 demonstrating equivalence to the SRM. However, whilst the data evidenced that the FTIR would meet many of the requirements under MCERTS and CEN TS 14793 it was argued that for any FTIR used for TOC monitoring it is critical to ensure that the reference library contains spectra for all VOC's likely to be encountered for a given application.

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