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TGN M22 Measuring Stack Gas Emissions using FTIR Instruments: Testing Equivalence to H_2O, CO, NO, SO_2 and HCl SRMs in Accordance with CEN/TS 14793

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National Measurement System

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1 INTRODUCTION

Technical Guidance Note (TGN) M22 *Measuring Stack Gas Emissions using FTIR Instruments* [1] is an Environment Agency document that provides a method for using Fourier Transform Infrared (FTIR) instruments to monitor gaseous emissions from stacks and flues. The document was originally drafted by a sub-group created by the Source Testing Association (STA), which was chaired by the National Physical Laboratory (NPL) and included key FTIR users from the UK stack monitoring community, instrument manufacturers, regulators (the Environment Agency - EA) and those involved in accreditation (United Kingdom Accreditation Service – UKAS). The document was drafted in response to the need to regulate FTIR based monitoring and the lack of an applicable CEN (Comité Européen du Normalisation) standard. TGN M22 was first published in 2009 and in accordance with EA requirements the stack monitoring community was permitted 18 months grace in order to successfully obtain accreditation. Hence, since 2010 all FTIR based regulated emissions monitoring in England has been carried out in accordance with TGN M22, as required by the EA. Since this time the stack monitoring community's use of TGN M22 and FTIR has been monitored through both UKAS surveillance visits and EA site visits (both informally as fact finding missions and also formerly as part of site audits). In addition, there has also been a forum for the community to discuss issues, namely the STA's FTIR Users' group. However, whilst these activities provide much assurance there is also a need to acquire test data under controlled stack conditions in order to further build confidence in the M22 method and FTIR. This has been the motivation for the work described here, which utilises NPL's Stack Testing Facility: a facility able to simulate real stack conditions, where test matrices are precisely known.

The EU's Industrial Emissions Directive (IED) [2] requires monitoring of pollutants including CO, NO, SO_2 and HCl, and that emissions, for a number of processes, are reported under dry conditions, hence the need to also monitor water vapour. CEN have provided a series of Standard Reference Methods (SRMs – see section 3) that stack monitoring organisations must follow and hold accreditation for. However, an Alternative Method (AM) may be used in place of an SRM where equivalency has been demonstrated to the satisfaction of the local competent authority (e.g. the EA for England). In England (and some other EU member states) monitoring using instrumental techniques, of what by convention have become called, "directive species" (i.e. CO, NO, SO_2, HCl) must be carried out by instruments type approved in accordance with EN 15267-3 [3]: both MCERTS[a] and TUV type approval testing were harmonised under this standard in 2007. However, this does not mean that in other EU member states there is no requirement to characterise an instrument, the only difference is that stack testing organisations are permitted to test the performance characteristics of each analyser as opposed to a manufacturer submitting an instrument model for type approval. Under the MCERTS Performance Standard for Organisations [4] the EA has stipulated that an instrumental technique (e.g. FTIR, UVA, etc.) used with an appropriate technical procedure is considered equivalent to the applicable SRM if it has been certified under EN 15267-3 across the appropriate range (e.g. for an SO_2 emission limit value (ELV) of 50 $mg.m^{-3}$ on a waste incinerator the appropriate range would be 75 $mg.m^{-3}$, as the appropriate range is defined as 1.5 x ELV).

[a] The Environment Agency's Monitoring Certification Scheme (MCERTS) provides a framework for businesses to meet quality requirements ensuring confidence in the monitoring of emissions into the environment. MCERTS is used for the approval of instruments, people and laboratories.

However, the type approval does not extend to the method used to operate the instrument: in the work described here TGN M22 which provides a method by which to operate an FTIR. In order to test if the combined performance of method and instrumental technique (i.e. the AM) is equivalent to the SRM, testing following CEN/TS 14793 [5] must be carried out. This document requires parallel measurements on either a stack or a national test bench able to simulate real stack conditions. The testing requires measuring the stack gas using at least two SRMs and at least two AMs. There are then a series of statistical tests to determine if results can be considered equivalent. The details of these are beyond the scope of this report but there are essentially three key parameters considered:

1. Is the repeatability between the two SRMs within the repeatability limit (since the acquired SRM data must be valid to make any comparison fair)?
2. Is the repeatability between the two AMs within the repeatability limit?
3. Does the correlation between the mean SRM and mean AM readings give a correlation coefficient and slope close to unity, and a y-axis intercept close to zero?

2 DESCRIPTION OF TGN M22

TGN M22 is available along with the full series of EA TGNs from http://www.environment-agency.gov.uk/business/regulation/31831.aspx and www.mcerts.net . For specific details the reader should refer to TGN M22 directly, however, the key steps in the method are summarised below.

Table 1 Key procedural requirements of TGN M22.

Test	Description	Requirement (% of range)
Annually		
Lack of Fit[a]	5 concentration points evenly distributed across each certified[b] and supplementary[c] range for each analyte	< ±2%
Zero[a]	Passing zero gas (N_2) directly into analyser to confirm a zero reading on each analyte channel	< ±2%
Start of measurement period		
Zero	(as above)	< ±2%
Limit of Detection	2 x STD determined from the concentration reported on each channel for 10 repeat measurements of zero gas	< ±2%
Check Gas	Passing a reference gas standard through the analyser and comparing the reading to the certified value	< ±5%[d]
Response Time	Time taken after switching from zero to Check Gas to reach 90% of final value (T90)	< 200s (excluding HCl, NH_3 & HF)
Sampling System Check	Standard of the most reactive gas to be monitored (hierarchy of reactivity defined in TGN M22) applied via 1 of 4 options: 1) As part of Check Gas test described above except including the entire sampling system 2) Difference between passing standard directly into analyser and then through entire sampling system 3) Injecting a known amount of analyte using a wet gas injection system through entire sampling system 4) During stack sampling spiking a known amount of analyte into the front of the probe (commonly referred to as analyte spiking)	 < ±5%[d] ≤ ±10%[e] ≤ ±10%[e] ≤ ±30%[e]
Daily checks		
Sampling Zero	Pass zero gas down entire sampling system and analyser	< ±2%
Interference Check	Carried out at least once per day for every analyte being monitored. 1) Maximum absolute residual value expressed as a percentage of the maximum absorbance value in the measurand spectrum. [The residual being the difference between the measurand spectrum and the fitted reference spectrum in the analytical wavenumber window used for the analyte]	< 5% of measurand peak absorbance

	At low concentrations test (1) can fail even if residuals are acceptable, however, interference check is passed if below can be satisfied 2) Residual peak-to-peak noise not more than twice the peak-to-peak noise of a zero gas measurement across the analytes' analytical window	<2 x peak-to-peak spectral noise in a measurement of zero gas
End of measurement period		
Sampling Zero	Pass zero gas down entire sampling system and analyser	< ±2%
Sampling System Check	Repeat of same method (options 1-4) as was employed at start of measurement period	(same criteria as above)
Check Gas	(as start of measurement period)	< ±5%[d]
Drift	Percentage change of end of measuring period check gas readings from start of measurement period	< 2% = pass ≥ 2% & <5% = drift correct data ≥ 5% =fail, reject data

[a] Shall also be carried out after annual service and significant repair.
[b] Range certified under EN 15267-3.
[c] Range in excess of the certified range.
[d] Expressed as percentage of standard certified value where the concentration of the standard approximates the ELV of the stack to be monitored.
[e] Expressed as percentage of analyser reading / amount injected / amount spiked.

3 TECHNIQUES & INSTRUMENTS EMPLOYED

The table below details the species studied in this project, associated SRM methods and the relevant certification details for the type approved (EN 15267-3) ProtIR 204m FTIR employed in the study.

Table 2 Standard reference methods and associated techniques, and EN 15267-3 certification ranges of the type approved ProtIR 204m FTIR.

Species	SRM	Associated Technique	ProtIR FTIR EN 15267-3 certified range / $mg.m^{-3}$
CO	EN 15058 [6]	Non-Dispersive Infrared (NDIR)	75
NO	EN 14792 [7]	Chemiluminescence	200
SO_2	EN 14791 [8]	Passing extracted stack gas through $H_2O_{2(aq)}$ filled impingers followed by analysis for sulphate ions via either ion chromatography or titration	75
HCl	EN 1911 [9]	Passing extracted stack gas through deionised water filled impingers followed by analysis for chloride ions via either ion chromatography or titration or spectrophotometry	15
H_2O	EN 14790 [10]	Condensation out of extracted gas passed through impingers. Determination via weight difference. May be performed as part of either SO_2 or HCl SRMs	40%vol

It should be noted that the ProtIR 204m FTIR is also certified under EN 15267-3 for other species not listed above and that the on-board algorithms are capable of analysing at concentrations significantly in excess of the certified ranges.

In general, type approval certification is usually carried out at relatively low concentration ranges as extending to supplementary ranges (i.e. greater) requires significantly fewer additional tests than extending to decreased ranges. This is because at greater ranges many percentage uncertainties decrease (as expressions are as percentage of range), whereas at decreased ranges the opposite occurs. Hence, in order to demonstrate that the technique / instrument still meets uncertainty requirements much of the testing from EN 15267-3 must be repeated for decreased ranges.

4 DESCRIPTION OF STACK SIMULATOR

Figure 1 shows a schematic of NPL's Stack Simulator Facility. The facility has been described in detail elsewhere [11], however, for brevity some specifications are provided here. The facility consists of 2 m tall, re-circulating stack with 127 mm BSP (British Standard Piping) ports able to accommodate standard heated sample probes connected to gas pumping and conditioning equipment commonly used in stack monitoring. Temperatures of up to 180 °C are possible, as are flow rates of 12 $m.s^{-1}$, due to an internal re-circulating fan. Up to 25 %vol of water vapour can be introduced using a heated injection system along with a host of common emission species, via mass flow controllers.

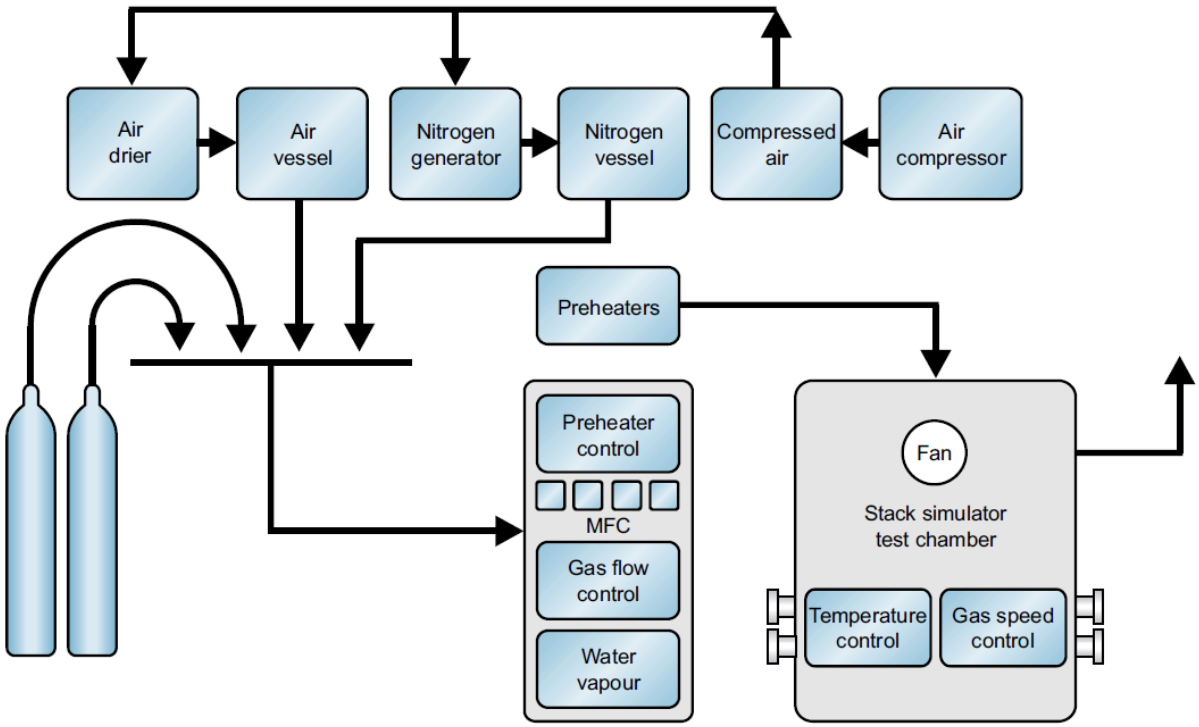

Figure 1 Schematic of NPL's Stack Simulator Facility.

Simulating emissions rather than a using a real process plant has a number of advantages, including:

- Concentrations can be carefully controlled and varied over broad ranges;
- Concentrations can be altered anti-correlated;
- Potential interferent species specific to the AM can be added and then removed;
- Water vapour can be varied or removed.

Consequently, in principle it's possible to create even more challenging conditions than would be found on a single process plant.

The test concentrations were chosen to provide a large number of points both within the range required under the IED for monitoring waste incinerators (200 $mg.m^{-3}$ NO, 75 $mg.m^{-3}$ SO_2, 15 $mg.m^{-3}$ HCl) and at elevated values applicable to the emissions possible from large combustion plants. ELVs of 200 $mg.m^{-3}$ SO_2 are found under the IED for combustion of coal, biomass, peat, other solid fuels and liquid fuels for plants of >300 MW thermal input. Whilst for NO ELVs (expressed as NO_2 equivalent) as high as 450 $mg.m^{-3}$ can be found for combustion of liquid fuels on plants with a 50-100 MW thermal input. There are no IED stipulated ELVs for CO for combustion of solid or liquid fuels, only for gas where the limit is 100 $mg.m^{-3}$. Whilst there are no IED stipulated ELVs for HCl, some plants in the UK that incinerate waste are actually licensed as combustion plants and the EA have set ELVs of 25 $mg.m^{-3}$. However, whilst most HCl test concentrations were of this range a small number were increased to greater values (~50 $mg.m^{-3}$) for academic interest.

Cross-interferent species were chosen that are found on a number of different processes and from the perspective of the operating principle of the AM, i.e. those with the potential to cause spectroscopic interference (e.g. NH_3 absorbs radiation in a similar part of the electromagnetic spectrum to SO_2). The concentrations used for the interferents were the same as would be required under EN 15267-3 in type approval testing. Whilst in principle such species should not cause any issues as the ProtIR 204m FTIR is type approved (i.e. tested for such cross-interference sensitivity), it is, however, important to demonstrate equivalency (or otherwise) to the SRM over as broad a range of conditions as possible in

order to understand the performance of the AM. The test mixtures used to demonstrated (or otherwise) equivalency for each species are detailed in the following sections.

5 APPARATUS USED FOR SRMs & AMs

The wet chemistry SRMs (SO_2, HCl, H_2O) were run by using Apex heated probes with titanium liner, insulated PTFE lines and Method 5 pumping systems to extract a sample from the Stack Simulator through sets of borosilicate glass impingers. Two complete sets of apparatus were used to simultaneously measure from two ports (for equivalency testing parallel runs of both the SRM and AM are required). Similarly, in order to provide CO & NO SRM data two Horiba PG250 analysers were interfaced with the Stack Simulator via, an M & C PSS-5 gas conditioning system and pump. With respect to H_2O this was determined in-situ (i.e. at the Stack Simulator Facility) by impinger train weight difference in accordance with EN14790.

NPL holds ISO 17025 [12] accreditation for all procedures used to implement the SRM standards listed above in Table 2. Furthermore, all the SRMs were operated by two members of NPL's stack team certified under the EA's Personnel Competency Standard [13] to MCERTS Level 2 (MCERTS certification applies to certification of personnel, as well as the certification of instrumentation). All the collected sulphate and chloride samples were analysed by NPL by ion chromatography, using an ISO 17025 accredited procedure in accordance with EN 14791 and EN 1911, respectively.

For comparison against the SRMs there were two ProtIR 204m FTIR systems employed, one supplied by NPL and the other by Protea Ltd. (the manufacturer). Both instruments were operated by NPL following an ISO 17025 accredited procedure in accordance with TGN M22. As summarised in Table 1 annual zero, response time and lack of fit testing was carried out on each analyser before commencing monitoring of the Stack Simulator. All test criteria were met, as was also the case for the two PG250 instruments which were tested in accordance with EN 15058 and EN 14792. All start of measurement period tests as defined in TGN M22 were carried out and all criteria met. All the instruments were interfaced using titanium probes, M & C PS4000 heated filters with ceramic filters and M & C heated lines. As required under TGN M22 daily system zero and residual checks were performed across the equivalency testing. Once all sampling of the Stack Simulator was complete (approximately a two week interval) the end of measurement period checks were carried out. All criteria were met and drift in all cases was < 2%, hence no corrections were required.

6 TEST PLAN & CEN/TS 14793 EQUIVALENCY STATISTICS

In equivalency testing CEN/TS 14793 stipulates a number of statistical tests and provides a template for summarising the results as shown below in Table 3.

Table 3 Template for summarising equivalency statistical tests under CEN/TS 14793.

Verification tests	Value obtained	Critical value	Conclusion
Non-systematic deviation			
Validation of the test	r	$r \geq 0.97$	Acceptable Y / N?
Slope	C_1	$1 - \frac{S_R(\bar{z})}{(\bar{z})} \leq C_1 \leq 1 + \frac{S_R(\bar{z})}{(\bar{z})}$	Acceptable Y / N?
Intercept	C_0	$\lvert C_0 \rvert \leq S_R(\bar{z})$	Acceptable Y / N?
Repeatability			
Standard uncertainty of SRM	$s_r(\bar{z})$	$s_r(\bar{z}) \leq s_{rlimit}(\bar{z})$	Acceptable Y / N?
Standard uncertainty of AM	$s_r(\bar{x})$	$s_r(\bar{x}) \leq s_{rlimit}(\bar{z})$	Acceptable Y / N?

Where

r	is the correlation coefficient for an orthogonal regression between the average AM and average SRM measurements;
C_1	is the slope of the orthogonal regression;
C_0	is the intercept of the orthogonal regression;
$s_R(\bar{z})$	is the standard deviation of reproducibility of the SRM;
$\bar{z}$	is the mean of the SRM measurements;
$s_r(\bar{z})$	is the repeatability variance of the SRM measurements;
$s_r(\bar{x})$	is the repeatability variance of the AM measurements;
$s_{rlimit}(\bar{z})$	is the maximum allowable standard deviation of repeatability for the SRM.

Acceptance criteria for repeatability and reproducibility are defined in the applicable SRM since (with the exception of HCl) these standards along with CEN/TS 14793 have all been produced by the same CEN working group (CEN/TC264/WG16 *Reference measurement methods for NOx, SO_2, O_2, CO and water vapour*) facilitating harmonisation. For example, section 14 of EN 14791 details that the required repeatability and reproducibility for SO_2 measurements are,

$$s_r = 0.051\alpha + 2.3$$

and

$$s_R = 0.0514\alpha + 2$$

where, α is the concentration in $mg.m^{-3}$.

The HCl standard has not been produced by CEN/TC264/WG16 and hence does not directly interface with CEN/TS 14793, i.e. no repeatability or reproducibility criteria are provided. Consequently, for the purposes of this study requirements are taken from the type approval standard (EN 15267-3), where any technique for monitoring HCl is required to meet repeatability and reproducibility of 2% and 3.3% of range, respectively.

7 H_2O RESULTS & DISCUSSION

Table 4 shows the mixtures used to test equivalence of the AM to the SRM for H_2O whilst Figure 2 shows the reported concentrations as a function of test number. Greater readings are seen for AM 2 than AM 1, however, in general the repeatability between the two AMs appears similar to that between the two SRMs. The AMs respond similarly to the SRMs to changes in concentration with both reporting satisfactory zeros when H_2O is removed from the stack simulator.

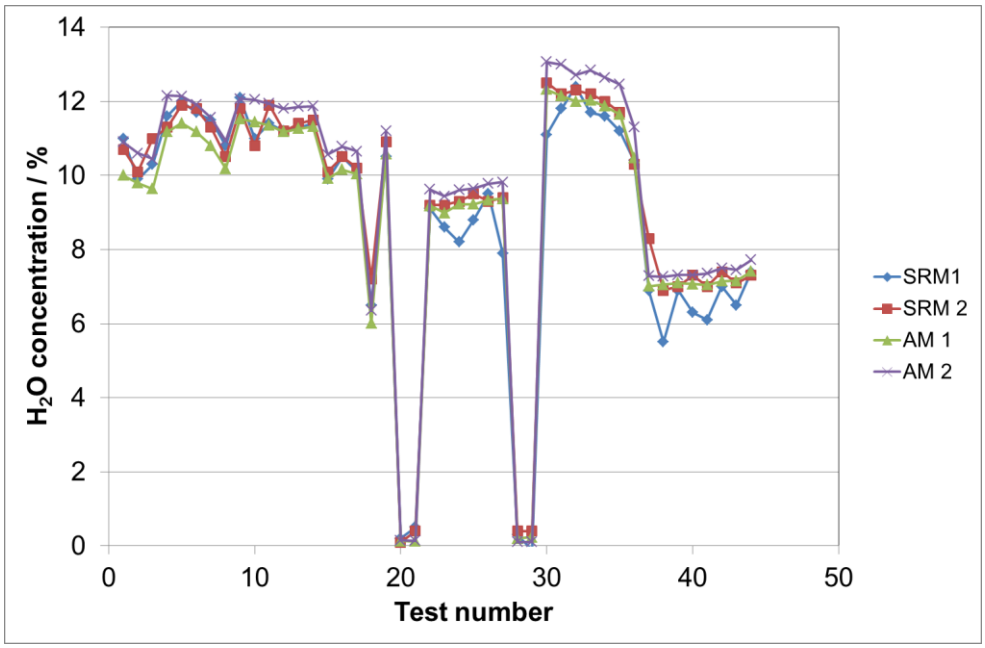

Figure 2 H_2O determinations as a function of test number.

Table 4 Test mixtures generated in NPL's Stack Simulator Facility to test equivalence of TGN M22/FTIR to EN 14790/gravimetric for H_2O.

Test	Comment	[CO] / mg.m^{-3}	[SO_2] / mg.m^{-3}	[HCl] / mg.m^{-3}	[NO] / mg.m^{-3}	[H_2O] / %	[CO_2] / %	[NO_2] / mg.m^{-3}	[NH_3] / mg.m^{-3}	[CH_4] / mg.m^{-3}	[C_2H_6] / mg.m^{-3}	[C_3H_8] / mg.m^{-3}
1		60	190	15	268	11.2						
2		18	57	15	100	11.2						
3		18	57	15	100	11.2						
4		30	95	10	200	11.2						
5	NH_3 interferent	30	95	10	200	11.2			15			
6	NH_3 interferent	30	95	10	200	11.2			15			
7	NH_3 interferent	30	95	10	200	11.2			15			
8		30	95	10	200	11.2						
9		21	66	20	41	11.4						
10		21	66	20	41	11.4						
11		21	66	20	41	11.4						
12		21	66	20	41	11.4						
13	NO_2 interferent	21	66	20	41	11.4		31				
14	NO_2 interferent	21	66	20	41	11.4		31				
15		7	22	5	160	9						
16		25	80	20	130	9						
17		25	80	20	130	9						
18	H_2O only test					9						
19	H_2O only test					9						
20	Zero											
21	Zero											
22		16	51	5	70	9						
23		16	51	5	70	9						
24		7	22	50	130	9						
25		7	22	50	130	9						
26		11	35	30	100	9						
27		11	35	30	100	9						
28	Dry test	11	35	30	100	0						
29	Dry test	11	35	30	100	0						
30		100	317	50	330	11.2						
31		100	317	50	330	11.2						
32	CO_2 interferent	50	159	50	330	11.2	10					
33	CO_2 interferent	50	159	50	330	11.2	10					
34	CO_2 interferent	80	254	50	330	11.2	10					
35	CO_2 interferent	80	254	50	330	11.2	10					
36		50	159	50	330	11.2						
37		5	16	5	30	7						
38		5	16	5	30	7						
39		5	16	5	30	7						
40		5	16	5	30	7						
41		5	16	5	170	7						
42		7	22	3	170	7						
43		7	22	3	170	7						
44	VOC interferent	7	22	3	170	7				9	8	8.5

Carrying out the equivalency statistics (Table 5) it is seen that the SRM meets the repeatability requirement from EN 14790 (≤ 0.44), which confirms that the SRM dataset is valid and that comparison can justifiably be made. The same repeatability is found for the AM and with regard to the orthogonal regression (Fig. 3) all requirements (correlation, slope & intercept) are met, hence equivalency of TGN M22/FTIR to EN 14790/gravimetric has been demonstrated.

Table 5 Equivalency tests for H_2O comparing TGN M22/FTIR to EN 14790/gravimetric.

Verification tests	Value obtained	Critical value	Conclusion
Non-systematic deviation			
Validation of the test	0.995	=> 0.97	Y
Slope	0.987	0.929 <= & <= 1.071	Y
Intercept	0.306	-0.64 <= & <= 0.64	Y
Repeatability			
Standard uncertainty of the SRM	0.42	<= 0.44	Y
Standard uncertainty of the AM	0.42	<= 0.44	Y

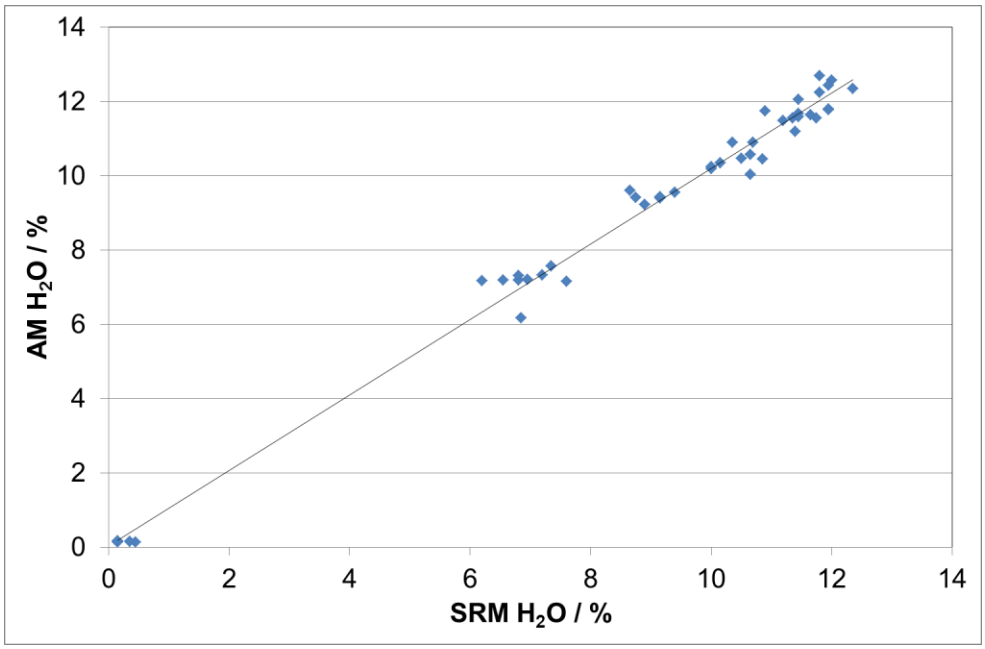

Figure 3 Orthogonal regression of AM vs SRM determinations for H_2O.

Having demonstrated equivalence of the AM for H_2O determination each FTIR analysers' respective water vapour reading is used to correct all remaining analyte channels to dry conditions for comparison to the applicable SRM readings. Alternatively, an equally valid approach would be to use the SRM water vapour data for dry correction, however, in terms of how monitoring is actually carried out this is a less common approach, since from a stack monitoring organisations' perspective it is far more favourable to take one technique into the field rather than two.

8 CO RESULTS & DISCUSSION

In general there is a close correlation across the SRMs and AMs (Fig. 4) with the individual instruments all responding similarly with changing concentrations and interferents. AM 2 shows some decreased readings compared to the SRMs at concentrations around 100 mg.m^{-3}, however, there is no obvious explanation for this deviation, as AM 1 shows no such deviation and no interferent species are present during these tests. When only air (tests 26 & 27) or only air and water vapour (tests 24 & 25) are present in the Stack Simulator, negative readings are seen for SRM 1, however, these readings are still within 2% of range and hence are considered valid zero data.

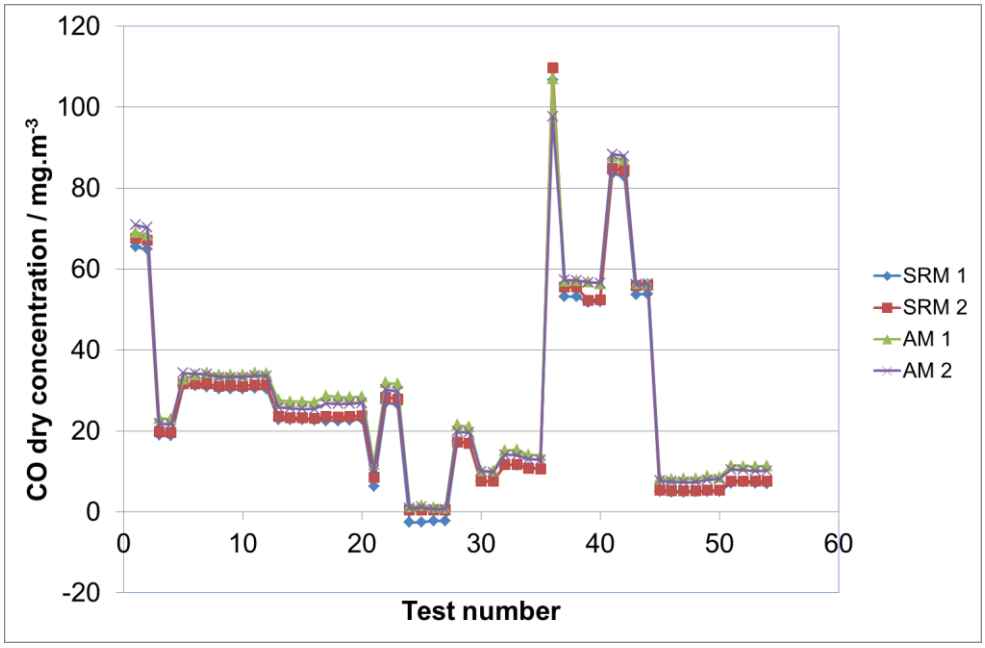

Figure 4 CO determinations as a function of test number.

Table 6 Test mixtures generated in NPL's Stack Simulator Facility to test equivalence of TGN M22/FTIR to EN 15058/NDIR for CO.

Test	Comment	[CO] / $mg.m^{-3}$	[SO_2] / $mg.m^{-3}$	[HCl] / $mg.m^{-3}$	[NO] / $mg.m^{-3}$	[H_2O] / %	[CO_2] / %	[NO_2] / $mg.m^{-3}$	[NH_3] / $mg.m^{-3}$	[CH_4] / $mg.m^{-3}$	[C_2H_6] / $mg.m^{-3}$	[C_3H_8] / $mg.m^{-3}$
1		60	190	15	268	11.2						
2		60	190	15	268	11.2						
3		18	57	15	100	11.2						
4		18	57	15	100	11.2						
5		30	95	10	200	11.2						
6		30	95	10	200	11.2						
7	NH_3 interferent	30	95	10	200	11.2			15			
8	NH_3 interferent	30	95	10	200	11.2			15			
9	NH_3 interferent	30	95	10	200	11.2			15			
10	NH_3 interferent	30	95	10	200	11.2			15			
11		30	95	10	200	11.2						
12		30	95	10	200	11.2						
13		21	66	20	41	11.4						
14		21	66	20	41	11.4						
15		21	66	20	41	11.4						
16		21	66	20	41	11.4						
17	NO_2 interferent	21	66	20	41	11.4		31				
18	NO_2 interferent	21	66	20	41	11.4		31				
19	NO_2 interferent	21	66	20	41	11.4		31				
20	NO_2 interferent	21	66	20	41	11.4		31				
21		7	22	5	160	9						
22		25	80	20	130	9						
23		25	80	20	130	9						
24	H_2O only test					9						
25	H_2O only test					9						
26	Zero											
27	Zero											
28		16	51	5	70	9						
29		16	51	5	70	9						
30		7	22	50	130	9						
31		7	22	50	130	9						
32		11	35	30	100	9						
33		11	35	30	100	9						
34	Dry test	11	35	30	100	0						
35	Dry test	11	35	30	100	0						
36		100	317	50	330	11.2						
37		50	159	50	330	11.2						
38		50	159	50	330	11.2						
39	CO_2 interferent	50	159	50	330	11.2	10					
40	CO_2 interferent	50	159	50	330	11.2	10					
41	CO_2 interferent	80	254	50	330	11.2	10					
42	CO_2 interferent	80	254	50	330	11.2	10					
43		50	159	50	330	11.2						
44		50	159	50	330	11.2						
45		5	16	5	30	7						
46		5	16	5	30	7						
47		5	16	5	30	7						
48		5	16	5	30	7						
49		5	16	5	170	7						
50		5	16	5	170	7						
51		7	22	3	170	7						
52		7	22	3	170	7						
53	VOC interferent	7	22	3	170	7				9	8	8.5
54	VOC interferent	7	22	3	170	7				9	8	8.5

Whilst within the acceptance criterion, the intercept of the regression line (Table 7) is relatively high, however, this can be rationalised by a combination of negative SRM readings when CO was removed

from the Stack Simulator (see effect on lowest concentration point in Fig. 5) and AM 2 reporting lower readings than the SRM at high concentrations (see highest concentration point in Fig. 5).

Table 7 Equivalency tests for CO comparing TGN M22/FTIR to EN 15058/NDIR.

Verification tests	Value obtained	Critical value	Conclusion
Non-systematic deviation			
Validation of the test	1.00	=> 0.97	Y
Slope	0.99	0.87 <= & <= 1.13	Y
Intercept	3.09	-3.31 <= & <= 3.31	Y
Repeatability			
Standard uncertainty of the SRM	1.0	<= 3.3	Y
Standard uncertainty of the AM	1.2	<= 3.3	Y

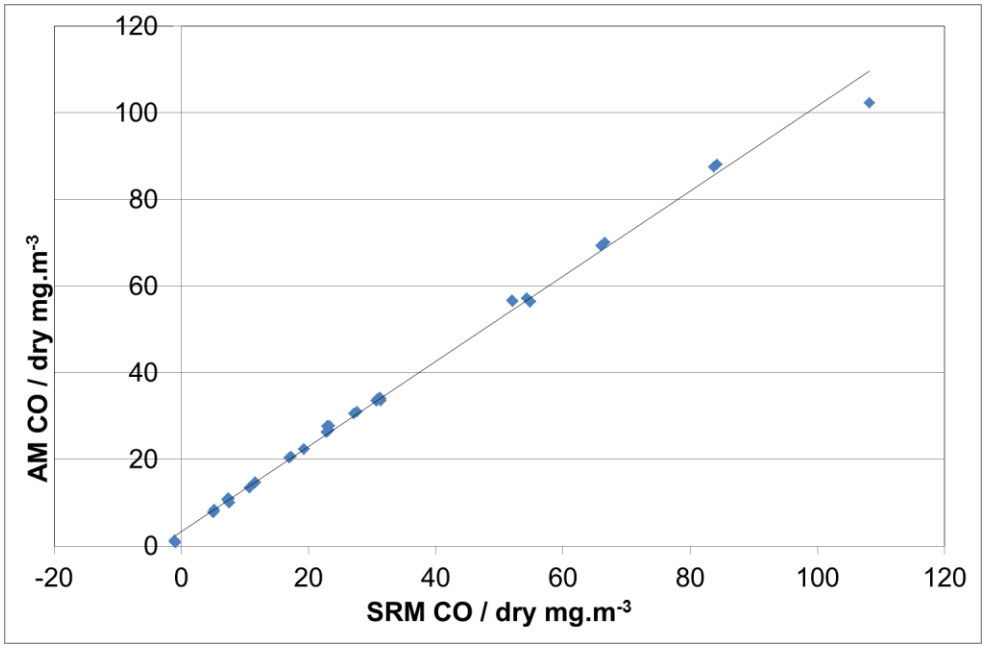

Figure 5 Orthogonal regression of AM vs SRM determinations for CO.

All acceptance criteria for correlation, slope, intercept and repeatability are met, which demonstrates equivalence of TGN M22/FTIR to EN 15058/NDIR for CO monitoring.

9 SO_2 RESULTS & DISCUSSION

All determinations show close agreement (Fig. 6) at low concentrations and for the zero (test 10) and water vapour only (test 9) mixtures (Table 8). Both FTIRs (AM 1 & 2) appear to read high around test 14, however, this observation is not repeated at test 15. Initially it might seem that these observations can be explained by CO_2 being added to the stack simulator for only the former test (i.e. some sort of interferent based effect), however, this is unlikely, as it does not absorb light in the part of the electromagnetic spectrum where the ProtIR analyses for SO_2. Furthermore, CO_2 is not a known interferent for the SRM either, hence, these observation may be just random variation, rather than any bias.

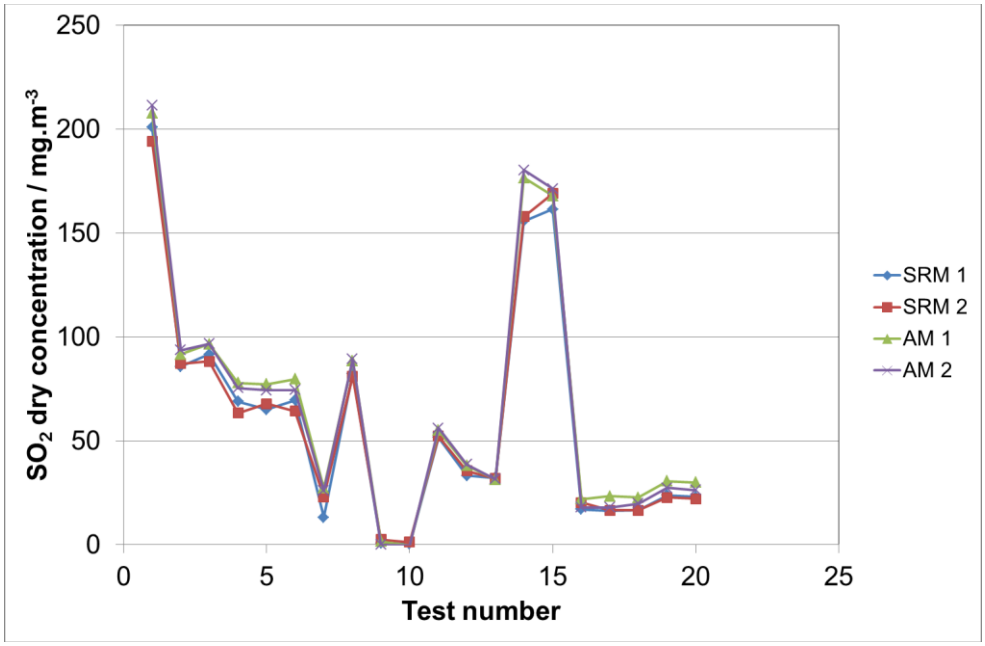

Figure 6 SO_2 determinations as a function of test number.

Table 8 Test mixtures generated in NPL's Stack Simulator Facility to test equivalence of TGN M22/FTIR to EN 14791/ion chromatography for SO_2.

Test	Comment	[CO] / mg.m-3	[SO2] / mg.m-3	[HCl] / mg.m-3	[NO] / mg.m-3	[H2O] / %	[CO2] / %	[NO2] / mg.m-3	[NH3] / mg.m-3	[CH4] / mg.m-3	[C2H6] / mg.m-3	[C3H8] / mg.m-3
1		60	190	15	268	11.2						
2	NH3 interferent	30	95	10	200	11.2			15			
3		30	95	10	200	11.2						
4		21	66	20	41	11.4						
5		21	66	20	41	11.4						
6	NO2 interferent	21	66	20	41	11.4		31				
7		7	22	5	160	9						
8		25	80	20	130	9						
9	H2O only test					9						
10	Zero											
11		16	51	5	70	9						
12		11	35	30	100	9						
13	Dry test	11	35	30	100	0						
14	CO2 interferent	50	159	50	330	11.2	10					
15		50	159	50	330	11.2						
16		5	16	5	30	7						
17		5	16	5	30	7						
18		5	16	5	170	7						
19		7	22	3	170	7						
20	VOC interferent	7	22	3	170	7				9	8	8.5

Compared to CO (Fig. 5) the scatter around the regression (Fig. 7) appears greater for SO_2, which is consistent with the difficulty of measuring a more reactive species. However, all acceptance criteria (repeatability, correlation, slope, intercept – Table 9) are met, thus demonstrating equivalence of TGN M22/FTIR to EN 14791/ion chromatography for SO_2 monitoring.

Table 9 Equivalency tests for SO_2 comparing TGN M22/FTIR to EN 14791/ion chromatography.

Verification tests	Value obtained	Critical value	Conclusion
Non-systematic deviation			
Validation of the test	1.00	=> 0.97	Y
Slope	1.06	0.92 <= & <= 1.08	Y
Intercept	2.74	-5.12 <= & <= 5.12	Y
Repeatability			
Standard uncertainty of the SRM	2.8	<= 5.4	Y
Standard uncertainty of the AM	2.1	<= 5.4	Y

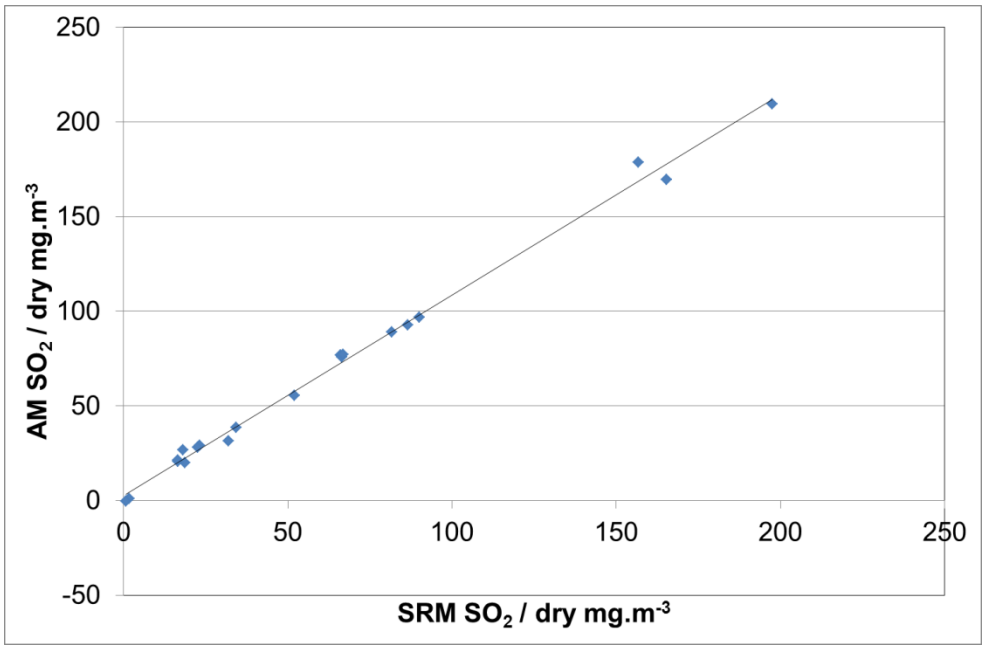

Figure 7 Orthogonal regression of AM vs SRM determinations for SO_2.

10 HCl RESULTS & DISCUSSION

Whilst at some high concentration tests (e.g. test 16, Fig. 8) there is marked deviation between the SRMs and AMs, at others (e.g. test 18) the deviation is no greater than that within the two SRMs. As no interferent species are present for test 16 (Table 10) this deviation cannot be explained by interference and again is likely to be random variation of the AM and / or SRM. It is also seen that there is very close correlation at low concentrations (<20 $mg.m^{-3}$), this is an important observation given that within the stack testing community one of the most challenging measurands is considered to be low concentration HCl.

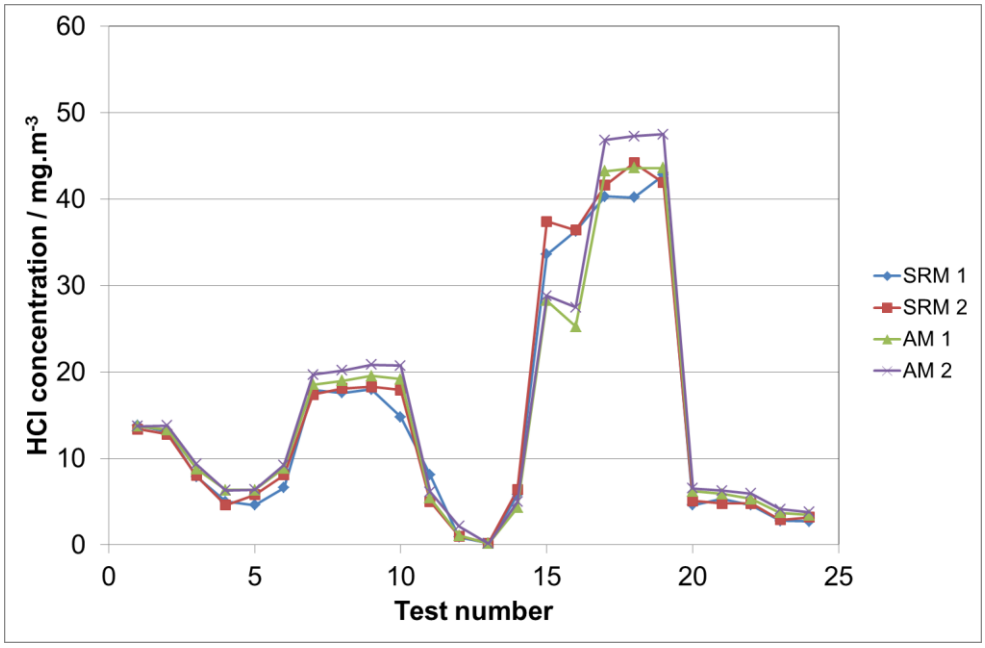

Figure 8 HCl determinations as a function of test number.

Table 10 Test mixtures generated in NPL's Stack Simulator Facility to test equivalence of TGN M22/FTIR to EN 1911/ion chromatography for HCl.

Test	Comment	[CO] / mg.m-3	[SO2] / mg.m-3	[HCl] / mg.m-3	[NO] / mg.m-3	[H2O] / %	[CO2] / %	[NO2] / mg.m-3	[NH3] / mg.m-3	[CH4] / mg.m-3	[C2H6] / mg.m-3	[C3H8] / mg.m-3
1		60	190	15	268	11.2						
2		18	57	15	100	11.2						
3		30	95	10	200	11.2						
4	NH3 interferent	30	95	10	200	11.2			15			
5	NH3 interferent	30	95	10	200	11.2			15			
6		30	95	10	200	11.2						
7		21	66	20	41	11.4						
8		21	66	20	41	11.4						
9	NO2 interferent	21	66	20	41	11.4		31				
10	NO2 interferent	21	66	20	41	11.4		31				
11		7	22	5	160	9						
12	H2O only test					9						
13	Zero											
14		16	51	5	70	9						
15		11	35	30	100	9						
16	Dry test	11	35	30	100	0						
17		50	159	50	330	11.2						
18	CO2 interferent	50	159	50	330	11.2	10					
19	CO2 interferent	80	254	50	330	11.2	10					
20		5	16	5	30	7						
21		5	16	5	30	7						
22		5	16	5	170	7						
23		7	22	3	170	7						
24	VOC interferent	7	22	3	170	7				9	8	8.5

Following on from the observation of marked deviation between the SRMs and AMs at tests 15 and 16 it is seen in the orthogonal regression (Fig. 9) that these data points (the two points sitting below the regression line at an x-axis value of ~35 $mg.m^{-3}$) may be outliers. However, both these points pass a Grubb's test, hence they have not been excluded from the equivalency statistics. The correlation between the methods is 0.972 (Table11), which is relatively close to the acceptance criterion (=> 0.97) and is most likely due to the increased scatter at high concentrations (Fig. 9). However, given the repeatability is the same for both methods (Table 11), the high concentration scatter may be as attributable to the SRM accuracy as to that of the AM. However, all acceptance criteria (repeatability, correlation, slope, intercept) are met, thus demonstrating equivalence of TGN M22/FTIR to EN 1911/ion chromatography for HCl monitoring.

Table 11 Equivalency tests for HCl comparing TGN M22/FTIR to EN 1911/ion chromatography.

Verification tests	Value obtained	Critical value	Conclusion
Non-systematic deviation			
Validation of the test	0.972	=> 0.97	Y
Slope	0.98	0.866 <= & <= 1.134	Y
Intercept	0.78	-1.98 <= & <= 1.98	Y
Repeatability			
Standard uncertainty of the SRM	1.1	<= 1.2	Y
Standard uncertainty of the AM	1.1	<= 1.2	Y

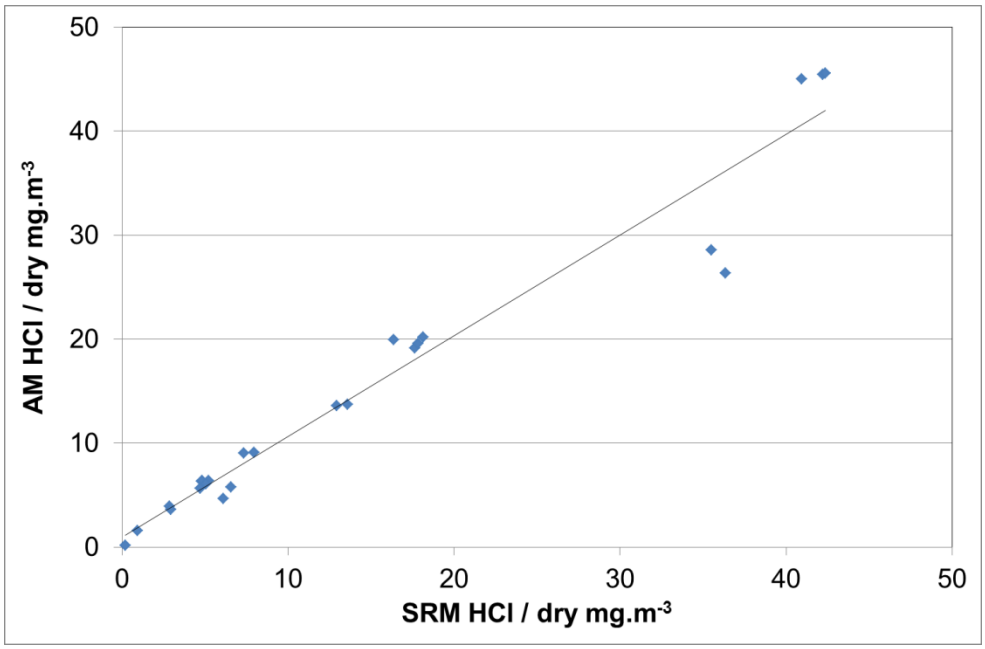

Figure 9 Orthogonal regression of AM vs SRM determinations for HCl.

11 NO RESULTS & DISCUSSION

There appears very close correlation between the SRMs and AMs (Fig. 10) with the only obvious signs of deviation being for AM 2, which appears to over read by a relatively small amount, mainly across tests 49 to 54. VOC interferents are present for tests 53 and 54 but not for 49 to 52, so given no step change is observed this is an unlikely rationale for the deviation.

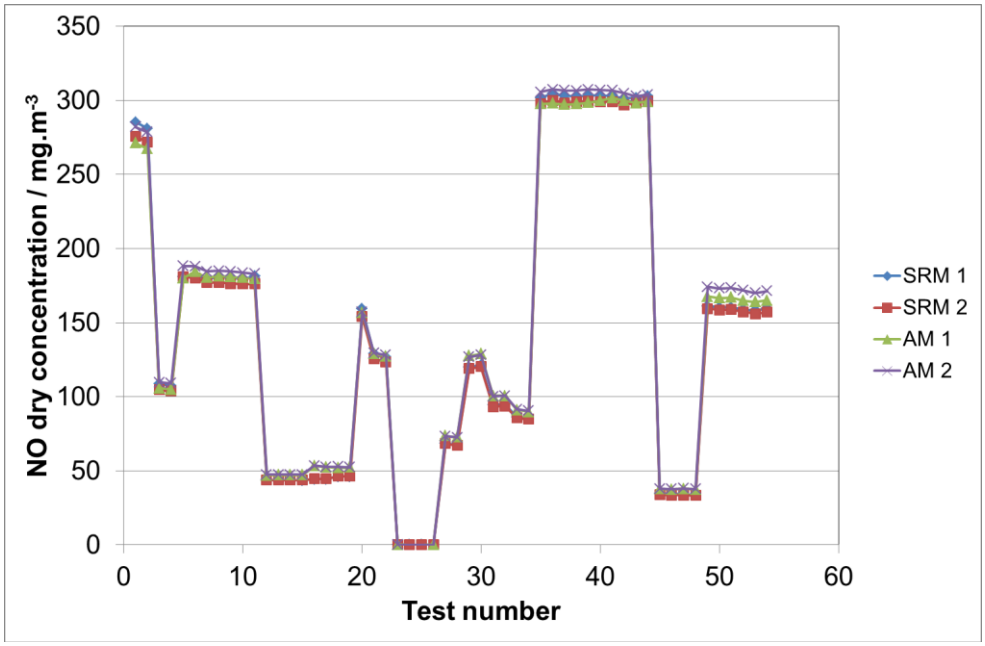

Figure 10 NO determinations as a function of test number.

Table 12 Test mixtures generated in NPL's Stack Simulator Facility to test equivalence of TGN M22/FTIR to EN 14792/chemiluminescence for NO.

Test	Comment	[CO] / mg.m-3	[SO2] / mg.m-3	[HCl] / mg.m-3	[NO] / mg.m-3	[H2O] / %	[CO2] / %	[NO2] / mg.m-3	[NH3] / mg.m-3	[CH4] / mg.m-3	[C2H6] / mg.m-3	[C3H8] / mg.m-3
1		60	190	15	268	11.2						
2		60	190	15	268	11.2						
3		18	57	15	100	11.2						
4		18	57	15	100	11.2						
5		30	95	10	200	11.2						
6	NH3 interferent	30	95	10	200	11.2			15			
7	NH3 interferent	30	95	10	200	11.2			15			
8	NH3 interferent	30	95	10	200	11.2			15			
9	NH3 interferent	30	95	10	200	11.2			15			
10		30	95	10	200	11.2						
11		30	95	10	200	11.2						
12		21	66	20	41	11.4						
13		21	66	20	41	11.4						
14		21	66	20	41	11.4						
15		21	66	20	41	11.4						
16	NO2 interferent	21	66	20	41	11.4		31				
17	NO2 interferent	21	66	20	41	11.4		31				
18	NO2 interferent	21	66	20	41	11.4		31				
19	NO2 interferent	21	66	20	41	11.4		31				
20		7	22	5	160	9						
21		25	80	20	130	9						
22		25	80	20	130	9						
23	H2O only test					9						
24	H2O only test					9						
25	Zero											
26	Zero											
27		16	51	5	70	9						
28		16	51	5	70	9						
29		7	22	50	130	9						
30		7	22	50	130	9						
31		11	35	30	100	9						
32		11	35	30	100	9						
33	Dry test	11	35	30	100	0						
34	Dry test	11	35	30	100	0						
35		100	317	50	330	11.2						
36		100	317	50	330	11.2						
37		50	159	50	330	11.2						
38		50	159	50	330	11.2						
39	CO2 interferent	50	159	50	330	11.2	10					
40	CO2 interferent	50	159	50	330	11.2	10					
41	CO2 interferent	80	254	50	330	11.2	10					
42	CO2 interferent	80	254	50	330	11.2	10					
43		50	159	50	330	11.2						
44		50	159	50	330	11.2						
45		5	16	5	30	7						
46		5	16	5	30	7						
47		5	16	5	30	7						
48		5	16	5	30	7						
49		5	16	5	170	7						
50		5	16	5	170	7						
51		7	22	3	170	7						
52		7	22	3	170	7						
53	VOC interferent	7	22	3	170	7				9	8	8.5
54	VOC interferent	7	22	3	170	7				9	8	8.5

In contrast to the other species the AM does not pass all the equivalency tests because the intercept criterion is failed (Table 13). This is perhaps counter intuitive given the close correlation shown in Table 13 (1.00), and also given that the correlation shown in Figure 10, visually at least, appears no worse (if not in some cases better) than that for the other species. However, as the requirements stand in CEN/TS 14793 equivalence is not demonstrated over this range of concentrations for NO.

Table 13 Equivalency tests for NO comparing TGN M22/FTIR to EN 14792/chemiluminescence.

Verification tests	Value obtained	Critical value	Conclusion
Non-systematic deviation			
Validation of the test	1.00	=> 0.97	Y
Slope	0.99	0.970 <= & <= 1.030	Y
Intercept	4.99	-4.26 <= & <= 4.26	N
Repeatability			
Standard uncertainty of the SRM	2.2	<= 4.3	Y
Standard uncertainty of the AM	3.4	<= 4.3	Y

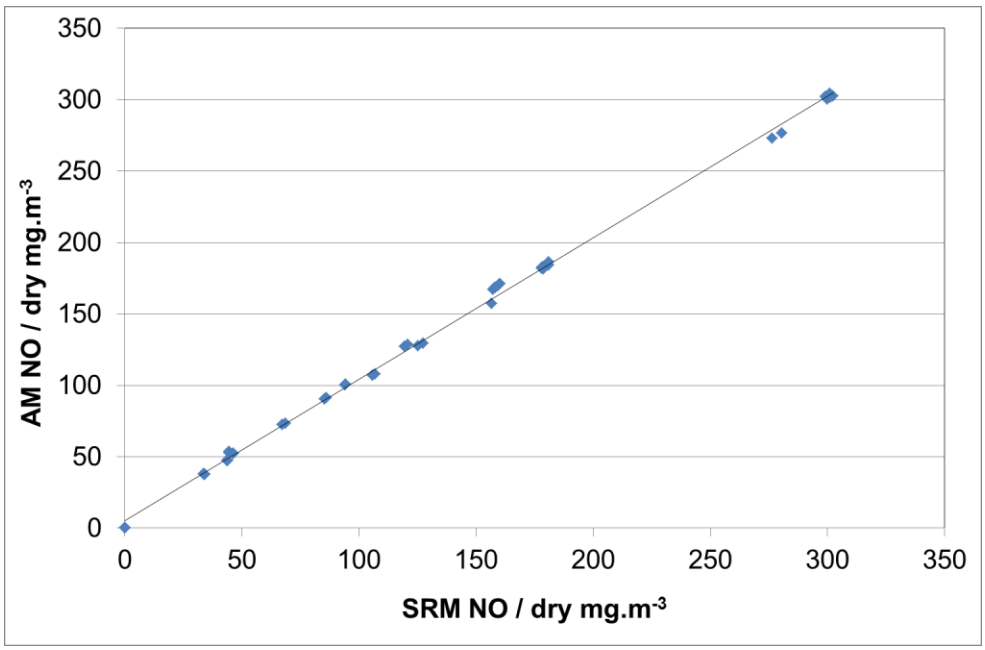

Figure 11 Orthogonal regression of AM vs SRM determinations for NO.

11.1 TESTING NO EQUIVALENCY OVER THE REQUIRED RANGE FOR WASTE INCINERATORS

Repeating the equivalency tests excluding data above 200 mg.m^{-3} (Table 12) shows that across this range the CEN/TS 14793 acceptance criteria are met. Hence, across this range it is possible to demonstrate equivalence of TGN M22/FTIR to EN 14792/chemiluminescence.

Table 14 Equivalency tests for NO across the waste incineration range (200 mg.m^{-3})

Verification tests	Value obtained	Critical value	Conclusion
Non-systematic deviation			
Validation of the test	1.00	=> 0.97	Y
Slope	1.026	0.963 <= & <= 1.037	Y
Intercept	2.37	-3.58 <= & <= 3.58	Y
Repeatability			
Standard uncertainty of the SRM	1.5	<= 3.6	Y
Standard uncertainty of the AM	2.3	<= 3.6	Y

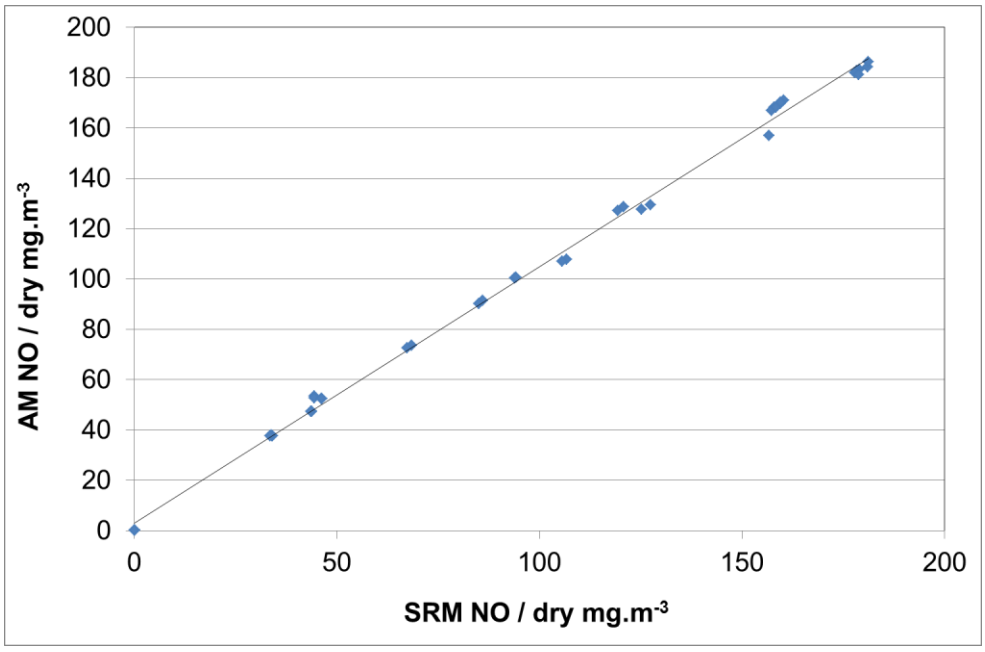

Figure 12 Orthogonal regression of AM vs SRM determinations across the waste incineration range (200 mg.m^{-3}) for NO.

12 CONCLUSIONS

TGN M22/FTIR has been demonstrated as equivalent to EN 14790/gravimetric, EN 15058/NDIR, EN 14791/ion chromatography and EN 1911/ion chromatography for the monitoring of H_2O, CO, SO_2 and HCl, respectively, in accordance with CEN/TS 14793. Furthermore, through analysis against test number (and therefore associated composition) it was shown that any observed deviation was not due to interferences from species commonly found on real stacks. Moreover, this also demonstrated that the AM could meet the acceptance criteria of equivalency in the presence (or absence) of such interferences.

NO was also included throughout the tests with the equivalency of TGN M22/FTIR against EN 14792/chemiluminescence tested in accordance with CEN/TS 14793. It was found that whilst the correlation was very close, equivalency was not demonstrated across a 0-330 $mg.m^{-3}$ range as the intercept acceptance criterion was not met for the orthogonal regression. However, it was shown that across a 0-200 $mg.m^{-3}$ range (required for monitoring waste incinerators), all acceptance criteria were met, hence equivalency was demonstrated.

13 ACKNOWLEDGEMENTS

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