Report

NPL REPORT AS 26

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NOT RESTRICTED

June 2008

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Validation of an Alternative Method for the measurement of SO_2 emissions using instrumental methods

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ABSTRACT

This report presents the results of a validation study of Technical Guidance Note M21 “Stationary source emissions — A procedure to use an Alternative Method for measuring emissions of sulphur dioxide, using instrumental techniques”.

TGN M21 was developed by the Environment Agency of England and Wales, for measuring SO_2 in stationary source emissions using instrumental methods. TGN M21 is an Alternative Method (AM) to the European Standard Reference Method (SRM), which uses a wet chemistry method.

Eight instruments were tested against paired SRM measurements in accordance with the European Technical Specification for validating AMs, TS 14793. The study evaluated the procedures in TGN M21 on a test-rig, which simulated stack gas conditions. The results of the study showed that TGN M21 met the requirements for acceptance according to TS 14793.

ISSN 1754-2928

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1. INTRODUCTION

The Environment Agency for England and Wales has issued Technical Guidance Note (TGN) M21 " Stationary Source Emissions - an Alternative Method (AM) for measuring emissions of sulphur dioxide, using instrumental methods". This TGN describes a procedure to use an Alternative Method (AM) for measuring emissions of sulphur dioxide (SO_2) from industrial stacks and flues. The Environment Agency's policy for monitoring is that test laboratories and operators must use European committee standards (CEN), where available. The CEN standard reference method (SRM) for measuring emissions of SO_2 is BS EN 14791. This SRM is a manual method, which employs wet chemistry. However, test laboratories may use other methods instead of SRMs, which are known as Alternative Methods (AM), as long as the test laboratory can demonstrate that the AM produces results of an equivalent quality to the SRM. The Environment Agency recognises that many test laboratories and operators wish to use an AM, which uses instrumental methods for measuring SO_2, instead of using a manual SRM based on wet chemistry and subsequent laboratory analysis.

The scope of TGN 21 provides for the use of instrumental techniques within an AM. The TGN does not specify the exact type of technique, but does specify performance characteristics for the instrumental systems employed within the method. Therefore, to comply with TGN M21 a test laboratory must demonstrate that any instrumental systems used meet these performance characteristics. Instrumental methods can be based on various techniques, such as non-dispersive infrared analysis (NDIR), electrochemical cells, UV-absorption analysis, and Fourier-Transform Infrared (FTIR) analysis.

This report describes the validation study of TGN M21. The validation study followed the procedure within the CEN/TS 14793:2005 "Stationary source emission – Intralaboratory validation procedure for an alternative method compared to a reference method" (referred to as TS 14793 within this report), which provides a methodology for the validation of an AM. The procedure in TS 14793 requires an in-field validation stage. However, Section 4.5.1.2 of TS 14793 allows the user 'to perform the comparison on a test bench recognised by the competent authority to be able to generate the appropriate gas matrix'. This validation study has been carried out using the NPL stack simulator, which is able to reproduce a range of stack gas conditions, and which has been recognised as a suitable test-bench by the Environment Agency. Eight SO_2 instruments were used to carry out the AM measurements in the validation study, and two SRM trains were run. The study has shown that the instruments tests following the procedures specified in TGN M21 gave results that are equivalent to the SRM.

TGN M21 specifies performance characteristics for the monitoring systems used. Meeting these performance characteristics helps to ensure the system meets the uncertainty allowances specified in the Directives for waste incineration (2000/76/EC) and large combustion plant (2001/80/EC). However, this is subject to the caveat that the uncertainty of the monitoring system is sufficient for the intended process application. These performance characteristics were **not** evaluated during this study. However, some of the instruments used in this evaluation had previously been tested and certified against these performance characteristics, others used had not been. In order for TGN M21 to be fully complied with, it is necessary that these performance characteristics are assessed for each instrument. Furthermore, in addition to ensuring the performance characteristics are met the monitoring system must be proven for the intended process application.

2. VALIDATION PROCEDURE

The procedure given in TS 14793 for the validation of an AM consists of a number of items. This study is primarily concerned with the field validation stage. However, this section presents a brief summary of the other requirements in TS 14793, together with full details of the field validation requirements.

The four required items in TS 14793 are (section numbers refer to TS 14793):

1. Description of the alternative method (4.2)
2. Determination of performance characteristics (4.3)
3. Calculation of the overall uncertainty of the method (4.4)
4. In-field validation (4.5)

1) TS 14793 places a requirement that the AM be documented and lists a number of items which the AM method description should address. TGN M21 covers these issues, and has been written within the format of a CEN standard.

2) TS 14793 requires a number of performance characteristics to be determined for the AM. Different characteristics are listed for manual and automatic (instrumental) methods. There is a requirement that these performance characteristics are determined in accordance with test procedures recognized by CEN. The scope of TGN M21 covers any instrumental technique, and therefore these performance requirements must be met by any specific instrument selected by a user to perform the AM. This requirement is addressed in TGN M21 by defining performance criteria and requiring instruments to have demonstrated compliance with them. TS 14793 requires that performance is demonstrated by test methods recognized by CEN. The most straightforward way of demonstrating that an instrument meets the performance requirements is through MCERTS certification. MCERTS test procedures are internationally recognized and are compliant with the recently published CEN performance testing standard, BS EN 15267-3_2007 “Air quality. Certification of automated measuring systems. Performance criteria and test procedures for automated measuring systems for monitoring emissions from stationary sources”.

3) The TGN M21 provides a full procedure for calculating the overall uncertainty, based on the performance characteristics determined for the instrument. An example calculation is also included as an annex to TGN M21. It also includes a requirement that the uncertainty meets a criterion of less than 10% of the daily emission limit value. This requirement explicitly meets the requirements of TS 14793, and therefore any instrument compliant with TGN M21 is also compliant with this item in TS 14793.

Items 1 to 3 above are addressed explicitly by TGN M21, and any instrument which is compliant with TGN M21 will, by definition, be compliant with these requirements of TS 14793.

The fourth item in TS 14793 is a field validation study. This stage is defined to demonstrate, by experimental study, that the AM provides equivalent results to the SRM under field conditions. Items 1-3 demonstrate that the AM is fit for purpose and meets the same performance requirements as the SRM. Item 4 is a demonstration that the results of the methods are equivalent. This is of particular concern in situations such as SO_2 monitoring, where the SRM is actually measuring a different quantity to the AM. The SRM measures total sulphates collected in an impinger, rather than directly measuring gaseous SO_2.

The validation study defined in TS 14793 requires paired measurements using the SRM and the AM, each data point consisting of a pair of SRM and a pair of AM measurements. A range of stack gas concentrations and conditions are required and the validation procedure allows the use of a simulated stack (or ‘test bench’) to generate the test conditions. A statistical assessment of the data is carried out based on the intra-laboratory assessment methodology given in ISO 5725-2. The repeatability of the AM results are determined and required to meet the requirements of the SRM. In addition, repeatability of the SRM results are also checked against the criterion. The next stage of verification is a check of the linear relationship between the AM and the SRM. This is done by using an orthogonal linear regression model, allowing uncertainties in the SRM and AM to be accounted for. Outliers can be checked for by using a Grubbs test. The acceptance test for the AM checks that there is no significant systematic deviation between the AM and SRM; this requires checks on closeness of the slope to unity and the intercept being close to zero. In addition a check is made that the linear fit is good enough for the validation study to be valid, with a requirement that the regression coefficient meets the condition $r > 0.97$. It is recommended in the TS that the total number of tests be of the order of 30 to meet this, which is met by 15 pairs of measurements. For this study a total of 19 tests were carried out, with eight AM instruments (152 individual measurements).

3. REVIEW OF STANDARD REFERENCE METHOD

The standard reference method, against which the AM validation was carried out, is the European standard method, BS EN 14791: 2005 “Stationary source emissions — Determination of mass concentration of sulphur dioxide — Reference method” (referred to in this report as the SRM). This is a manual wet chemistry method, using hydrogen peroxide absorption solutions. Analysis of the collected impinger solutions is by ion chromatography (IC) or the Thorin titration method. For this validation study the analysis laboratories used IC analyses. Two paired sample trains were run, with blanks before and after each set of tests. Full leak tests were carried out, and the criteria given in the SRM were passed.

A test was also made of the absorber efficiency, by analysing the solutions in the two impingers separately. In all cases the first absorber had >97% of the total collected $SO_{2,}$ satisfying the requirements of the SRM (Absorber efficiency > 95%).

4. OVERVIEW OF THE ALTERNATIVE METHOD

The AM procedure being tested in these validation studies has been produced by the Environment Agency, and is titled; Technical Guidance Note M21 - ‘Stationary source emissions – an Alternative Reference Method for measuring emissions of sulphur dioxide, using instrumental methods’ Version 1, January 2008. This provides an alternative method to the existing reference method. The methods covered are extractive instrumental methods.

TGN M21 does not prescribe specific instrumental techniques; rather it provides a set of performance standards for the instrumental techniques. These are based on the MCERTS performance standards and any instrumental method which meets these will also comply with the overall uncertainty requirements of the SRM.

TGN M21 addresses the sampling system, gas conditioning system (where appropriate), and analytical instrument. The following techniques can be used to measure SO_2:

- Electrochemical cells (EC)
- Infrared Gas-Filter Correlation (IRGFC)
- Non-dispersive Infrared (NDIR)
- Ultra-Violet Absorption (UVA)
- Fourier-Transform Infrared (FTIR)

However, these are examples only, and a test laboratory may use any instrumental technique so long as it meets the performance specifications in TGN M21.

The validation study was carried out using the following instruments:

Instrument ID	**Equipment***	**Serial Number**	**Initial range set, ppm**	**Principle**	**Certified**
1	Horiba PG250 (NPL)	7502001 (NPL85349)	0-1000	NDIR	MCERTS 0-460 mg.m^3
2	Gasmet FTIR (Quantitech)	2080218	0-500	FTIR	MCERTS 0-75 mg.m^3
3	Horiba PG250 (Quantitech)	41343020031	0-1000	NDIR	MCERTS 0-460 mg.m^3
4	Servomex 4900 (Servomex)	652979	0-1000	IRGFC	MCERTS 0-572 mg.m^3
5	Servomex 4900 (Servomex)	652978	0-1000	IRGFC	MCERTS 0-572 mg.m^3
6	Testo 350 (Testo)	01491509/802	0-1000	EC	Testo 360 UBA approved
7	ABB 9100 FTIR (NPL)		0-500	FTIR	Not certified
8	ABB AO2000 LIMAS (E-ON)	T1179	0-500	UV-GC	MCERTS 0-75 mg.m^3

* The brackets refer to the companies who provided the instruments

5. DESCRIPTION OF STACK SIMULATOR TEST FACILITY

The NPL stack simulator is able to reproduce a wide range of simulated stack gases under controlled conditions. The simulator is a recirculating system, which recreates a cross section of a 1.5 m duct. Four standard 5 inch ports are available for sampling probes or cross stack instruments to be installed. In addition a number of extractive gas analysers may be connected to gas extraction ports. Figure 1 shows a schematic of the stack simulator.

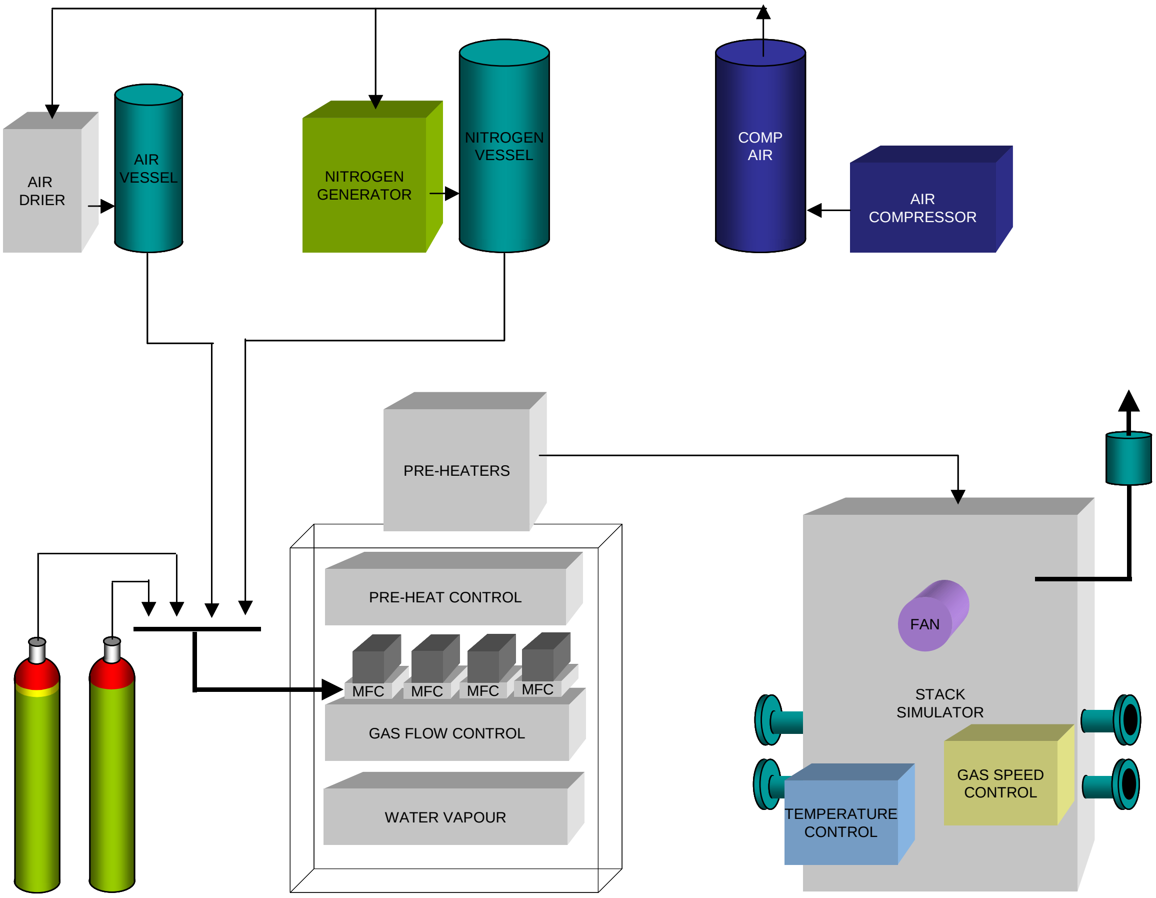

Figure 1. Schematic of outline of stack simulator

The stack simulator is able to generate the conditions in Table 1.

Performance Summary	
Temperature	up to 180°C controlled to ± 2 °C measured to ± 0.5 °C
Gas vertical velocity	up to 12 metres per second
Water vapour	up to 25% by volume
Oxygen content	up to 20% by volume
Input gas flow rate	up to 300 litres per minute

Table 1. Range of stack conditions achievable in the NPL Stack Simulator.

The stack simulator is able to generate a mixture of test gases by blending test gases from cylinders with nitrogen and zero air from reservoirs. The bulk gas delivery is controlled by two 150 l/min mass flow controllers, allowing a blend of nitrogen and zero air. This enables reduced oxygen concentrations to be generated, simulating combustion gas conditions. Two further mass flow controllers allow the introduction of test gases, typically these consist of gas mixtures representative of combustion or waste incineration processes, i.e. SO_2 CO and NO_x. Complex gas mixtures are generated by using source gas cylinders containing a mixture of gases. The stack simulator has two low flow (~1 l/min) mass flow controllers in usual operation, though additional gas generation facilities can be added for more complex matrices.

In the configuration used for the validation studies, a source cylinder of 5% SO_2 was used to provide the range of SO_2 test levels. Other matrix gases were introduced using the second 1 l/min test gas mass flow controller. Additional gases introduced into the matrix to assess interference included CO_2, NO and hydrocarbons. A further key interferent, water vapour, was also generated as a part of the test matrix within the stack simulator. This is produced by vaporising known volumes of water and combining this with the injected test gas. A water concentration of approximately 12% was used for the test programme.

The conditions within the sample region of the stack simulator have been previously verified to be well mixed in both axes. Figure 2 shows an example of the validation of the flow profile across the stack simulator test region.

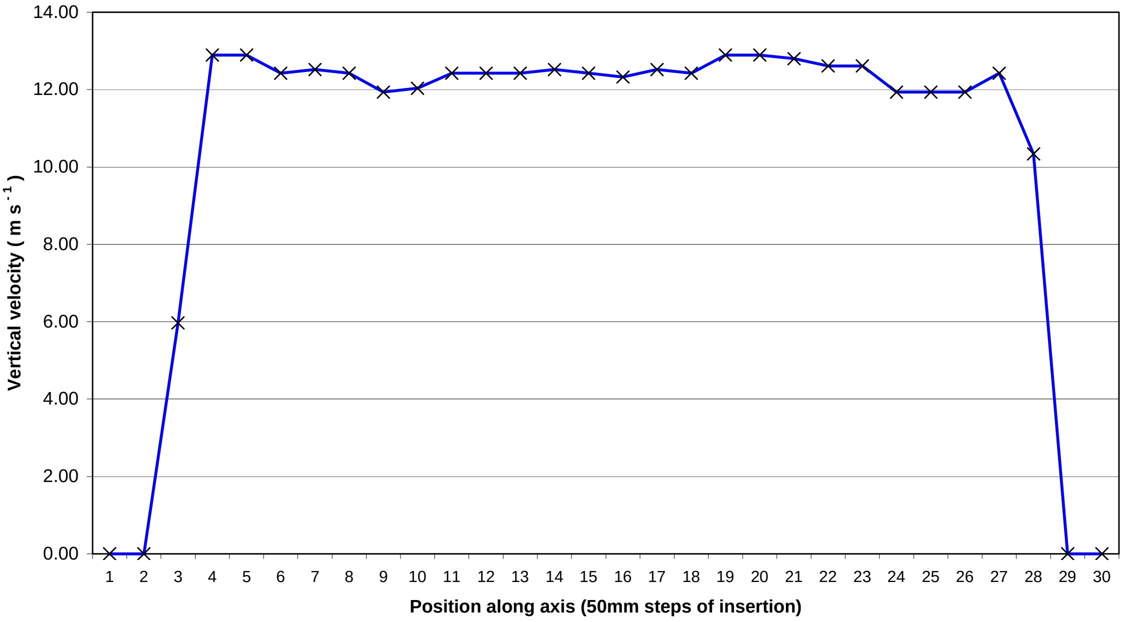

Figure 2. Plot showing flow stability across test region of stack simulator.

6. VALIDATION STUDY WORK PROGRAMME

The work programme was developed to meet the requirements of TS 14793. Nineteen test runs were carried out, with paired SRM tests and eight instruments implementing the AM. The following SO_2 concentrations were used for the tests: 150 ppm, 250 ppm, 3 ppm, 20 ppm and zero. Table 2 lists the tests carried out. The SRM tests highlighted were split and sent to two different analysis laboratories. These tests therefore allowed an assessment of the intralaboratory and interlaboratory repeatabilities of the SRM analysis stage.

SRM Test Number Pair	Date	Start Time	End Time	Conditions plus H_2O ~12%
	18/02/2008	16:49	17:04	Zero + moisture check
Blank 1	19/02/2008			Blank before
P1	19/02/2008	11:40	12:10	Zero
P2	19/02/2008	13:45	14:15	150ppm SO_2
P3	19/02/2008	14:30	15:00	150ppm SO_2
P4	19/02/2008	15:15	15:45	150ppm SO_2
P5	19/02/2008	16:05	16:35	150ppm SO_2
Blank 2	19/02/2008			Blank after
Blank 3	20/02/2008			Blank before
P6	20/02/2008	13:20	13:50	250ppm SO_2
P7	20/02/2008	14:10	14:40	250ppm SO_2
P8	20/02/2008	15:30	16:00	250ppm SO_2 + C_3H_8
P9	20/02/2008	16:15	16:45	250ppm SO_2 + C_3H_8
Blank 4	20/02/2008			Blank after
Blank 5	21/02/2008			Blank before
P10	21/02/2008	12:25	12:55	3ppm SO_2
P11	21/02/2008	13:10	13:40	3ppm SO_2
P12	21/02/2008	14:20	14:50	3ppm SO_2 + 15ppm NO
P13	21/02/2008	15:05	15:35	3ppm SO_2 + 15ppm NO
P14	21/02/2008	16:00	16:30	3ppm SO_2 + CO_2
Blank 6	21/02/2008			Blank after
Blank 7	22/02/2008			Blank before
P15	22/02/2008	10:50	11:20	Zero
P16	22/02/2008	12:25	12:55	20ppm SO_2
P17	22/02/2008	13:05	13:35	20ppm SO_2
P18	22/02/2008	13:50	14:20	20ppm SO_2
P19	22/02/2008	14:35	15:05	20ppm SO_2
Blank 8	22/02/2008			Blank after

Table 2, Test programme for the validation studies.

Calibration Gas ID	Certified traceable gas value	Calibration Concentration
133316	511 ppm	511 ppm
133316 + Gas Dilutor	511 ppm	90 ppm

Table 3, Calibration gas used for AM calibrations.

All analysers where set up and calibrated by the suppliers of the instruments, Quantitech, E-ON, Testo and Servomex. The FTIR analysers directly sampled the wet stack, the other instruments sampled from a single Testers Choice gas conditioning system. Calibrations were performed through the whole sampling manifold using the calibration gases shown in Table 3.

Each morning the follow procedure was carried out:

- The Horiba PG250s, ABB AO2000, Testo 350 and Servomex 4900s were zeroed.
- Span calibration was carried out directly into the analysers. They were then left to settle for a minimum of 10 minutes.
- After the calibration function was completed on each analyser the span gas was applied to the span gas inlet of the sample probe, before the gas conditioner, and allowed to settle for a minimum of 10 minutes.
- The Gasmet FTIR carried out an automatic zero calibration at 06:00 and a span calibration at 22:00 each day. A calibration check was performed on this analyser at the beginning and end of each day, this data was reordered manually and via a data logger program.
- At the end of each day a check calibration was preformed on each analyser following the same procedure as above.

For the low concentration tests (3ppm and 20 ppm) where possible the analysers were adjusted to lower span ranges, given below, and a lower concentration calibration gas was used, as shown in Table 3:

Horiba PG250	0-200
Servomex 4900	0-100
Testo 350	0-1000
ABB AO2000	0-500
Gasmet and ABB FTIR	0-500

A Signal 9000MGA gas divider was used to deliver the calibration gas for the lower calibration ranges.

The two SRM trains were operated in accordance with NPL’s ISO 17025/MCERTS accredited procedure for the SRM. A short probe was used, without a heated line. However, the lagged tubing was monitored using a thermocouple and was always 20ºC above the acid dew point of the test gas. A full leak check was carried out through the complete systems and no leaks were present. Tests were also made of the absorber efficiency, by analysing the solutions in the two first impingers separately. In all cases the first absorber had > 97% of the total collected $SO_{2,}$ satisfying the requirements of the SRM, which states a requirement for the absorber efficiency to be > 95%.

7. RESULTS AND ANALYSIS

The SRM impinger solutions were analysed by external UKAS accredited laboratories. All the solutions were sent to a UKAS laboratory for analysis (Lab 1). The results from this laboratory were used for the AM equivalency assessment. In addition a sub-set of the impinger solutions were split and sent to a second UKAS laboratory (Lab 2) (one pair of solutions at each concentration). This showed some significant systematic differences between the two laboratories. It is recommended that this should be investigated further.

The SRM results are close to the expected concentrations in the stack simulator, based on the dilution settings for the injection of SO_2 into the stack.

	Reference method		SRM		
		Parallel measurements			
Trial No.	Nominal Stack Conc ppm	**Lab 2 S1** **ppm**	**Lab 2 S2** **ppm**	**Lab 1 S1** **ppm**	**Lab 1 S2** **Ppm**
1	0.0			0.03	0.03
2	170.5			142.21	150.55
3	170.5			137.76	140.93
4	170.5	165.9241	173.2606	162.78	149.07
5	170.5			150.42	174.72
6	284.1			248.5	243.6
7	284.1			242.3	234.5
8	284.1	291.6677	306.8719	241.3	251.1
9	284.1			250.1	259.5
10	3.4			3.3	3.3
11	3.4			2.86	12.32
12	3.4	3.42193	3.26884	2.83	2.71
13	3.4			3.40	3.38
14	3.4			3.5	3.0
15	0.0	0.08812	0.051889	0.03	0.03
16	22.7			25.58	24.33
17	22.7			26.06	22.91
18	22.7	27.93293	26.69114	22.38	21.43
19	22.7			26.29	25.97

Table 4 All SRM results from two UKAS laboratories.

The SRM results are plotted in Figure 3, against the nominal stack simulator concentrations. The SRM results agree within 15% to the nominal set concentrations in the stack simulator.

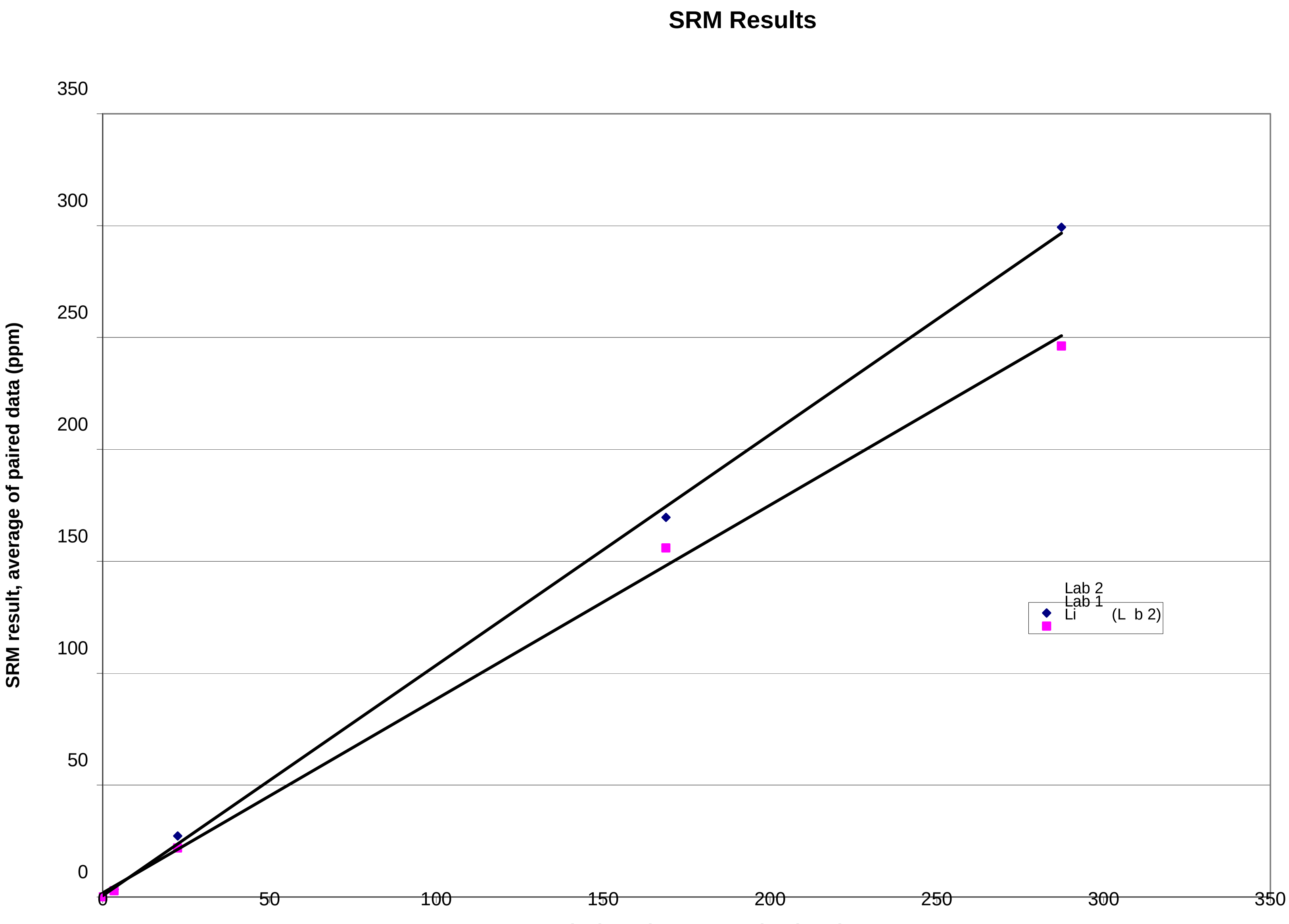

Figure 3, SRM results plotted against nominal stack concentration

The SRM results were tested for outliers by performing a Grubbs test. Table 5 lists the result of the first Grubbs test. For 18 tests the critical value for the Grubb test is 2.651. Test number 11, clearly fails the Grubbs test, with a value of over 4, and is therefore classed as an outlier. The results of Test 11 have been removed from all subsequent analyses. As a further check, the Grubbs test was re-applied to the data set after removing Test 11. No further data sets failed the Grubbs test, the highest value being 2.41 which is less than 2.62, which is the Grubbs outlier criterion for 17 data points.

Test	T1, ppm	T2, ppm	Grubbs
1	0.03	0.03	0.216
2	142.21	150.55	0.022
3	137.76	140.93	0.093
4	162.78	149.07	0.465
5	150.42	174.72	0.333
6	248.5	243.6	0.236
7	242.3	234.5	0.279
8	241.3	251.1	0.036
9	250.1	259.5	0.045
10	3.3	3.3	0.162
11	2.86	12.32	4.024
12	2.83	2.71	0.314
13	3.40	3.38	0.189
14	3.5	3.0	0.687
15	0.03	0.03	0.191
16	25.58	24.33	0.338
17	26.06	22.91	0.602
18	22.38	21.43	0.315
19	26.29	25.97	0.211

Table 5. 1st Grubbs test on the SRM results.

Table 6 presents the AM results, averaged over the same periods as the SRM tests. Initial results showed that the AMs, which were connected to the sample conditioning system (i.e. the Horiba PG250s, Servomex 4900s, Testo 350 and ABB AO2000), gave results that were significantly lower than expected. The sample conditioning system used was a Testers Choice, provided by CES. A series of tests were carried out measuring calibration gas with these AM instruments both through the conditioning unit and directly into the instruments. These tests showed an average loss of 10% due to the conditioning unit. The AM results for these instruments have been corrected for this average loss. One test that was not carried out was to test the residual water collected in the gas conditioning units for the presence of SO_2; this is suggested as a possible future check on whether the conditioning unit is removing SO_2. The reported results have also been corrected for zero and span drifts measured each day, and this is an important requirement in TGN M21.

The FTIR instruments sampled wet gas directly and therefore have required correction for the sample conditioner loss. The FTIR instrument results have been converted to dry conditions, using their own measurement of water vapour concentration to perform the correction. Table 7 presents the results of the SRM and NPL FTIR water vapour results. There is a close agreement between the SRM and FTIR water vapour readings. A further investigation of the results may enable the FTIR to be demonstrated to be equivalent to the SRM for water vapour measurement.

	Alternative Method	AM							
		Parallel measurements Instrument ID							
		1	2	3	4	5	6	7	8
		Horiba	Gasmet	Horiba	Servomex	Servomex	Testo	FTIR	ABB
		PG250	FTIR	PG250	4900	4900	350	ABB	AO2000
Test	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
1	0.0	0.2	-3.1	0.4	-2.3	-1.9	0.1	0.8	-0.3
2	146.4	149.6	152.8	161.3	154.1	157.2	158.1	166.9	143.4
3	139.3	151.7	155.7	155.4	155.8	159.2	159.3	167.2	146.7
4	155.9	152.6	156.9	159.9	156.2	159.6	160.1	167.2	148.3
5	162.6	155.4	160.4	160.1	158.1	161.3	152.6	169.4	151.9
6	246.1	257.1	277.9	269.5	258.6	260.9	266.9	284.3	254.5
7	238.4	259.8	275.8	264.0	261.9	263.8	269.5	280.9	258.2
8	246.2	267.3	287.9	285.7	270.7	272.2	277.6	291.0	265.9
9	254.8	266.7	286.7	289.2	270.7	272.1	277.3	290.6	266.3
10	3.3	1.2	13.1	2.1	2.3	1.9	2.4	3.7	2.6
11	7.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
12	2.8	1.0	11.7	2.1	2.3	1.9	2.4	3.6	1.8
13	3.4	0.9	13.0	1.7	2.3	1.9	2.4	3.7	1.9
14	3.3	1.1	14.9	2.3	2.3	1.9	2.4	2.7	2.1
15	0.0	-0.2	3.1	-0.4	2.3	1.9	-0.1	-0.8	0.3
16	25.0	23.2	30.2	21.1	23.1	23.3	24.3	25.9	23.3
17	24.5	23.3	31.0	22.6	23.1	23.2	24.1	25.9	23.4
18	21.9	23.4	31.2	21.2	23.1	23.4	24.2	25.7	23.5
19	26.1	23.8	31.3	21.3	23.4	23.7	24.2	25.7	23.9
Note. Test 11 removed as an outlier following Grubbs test.									

Table 6, Results of AM tests.

SRM water	NPL FTIR Moisture
%	%
11.0	12.0
10.2	11.2
10.1	11.2
10.2	11.2
10.5	11.3
10.6	11.0
9.2	9.4
13.0	13.0
13.8	14.0
12.6	12.9
12.6	12.9
13.0	13.0
12.9	13.0
13.2	13.3
10.8	11.1
10.9	11.1
10.9	11.0
10.6	10.9
10.6	10.8

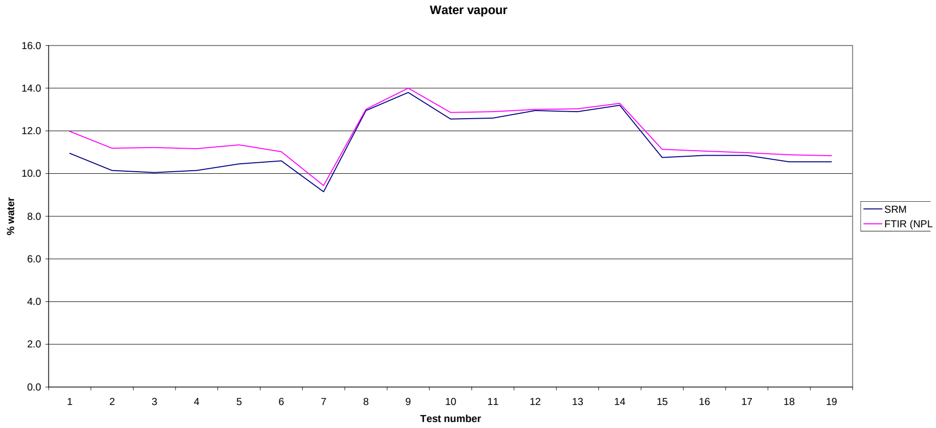

Table 7, Comparison of water vapour measurements.

The following sections present the results of the analyses of the data according to the procedures within TS 14793. These present criteria which the AM must meet. This takes account of the repeatability and reproducibility of the SRM.

Each pair of instruments, FTIR, Servomex AO2000, Horiba PG250 has been assessed. In addition the other instruments have been tested as if they were a pair of implementations of the AM method. Finally, all eight instrument results have been assessed together, treating them all as implementations of the AM method.

These criteria are expressed in mg/m3 and therefore these units have been used in assessing the AM.

a) Verification of repeatabilities.

[TS 14793 Section 4.5.2.2.1 Verification of AM and SRM repeatabilities]

The SRM criterion for the repeatability, given in BS EN 14791, is calculated from 0.051*Conc + 2.3, in mg/m3.

The different techniques, including the SRM, have been compared with the pass criterion. As each pass criterion depends on the average concentration of the test results there is a different criterion for each test. Table 8 presents the results of the repeatability test.

Method	Criterion, mg/m3	Test result, mg/m3
SRM	< 16.08	16.08
Gasmet and ABB FTIR	< 15.64	13.66
Servomex 4900 (IR GFC)	< 15.95	3.40
Horiba PG250 (NDIR)	< 15.96	15.84
Testo 350 (EC) and ABB AO2000 (UVA)	< 15.84	14.49
AM, combined	< 16.18	15.77

Table 8, Repeatability test results.

The Servomex instruments show the best repeatabilities between each other, which may not be surprising as they were identical instrument models supplied directly from the manufacturer's factory. By comparison, the Horiba instruments were both instruments that had been used extensively in the field.

The results show that all methods pass the repeatability test. It is interesting to note that the SRM only just passes the test. This is clear from the graphs of the results, where in general the SRM shows scatter whilst the AMs show greater precision.

b) Orthogonal regression analysis

[TS 14793 Section 4.5.2.2.2 Verification of existence of systematic deviation between the AM and SRM]

Each pair of AMs was tested against the SRM by carrying out an orthogonal regression analysis, as described in TS 14793. The analyses determined the zero crossing C_0 and gradient C_1 for each method. The criteria for C_0 and C_1 are determined from the reproducibility criteria given in BS EN 14791, calculated from 0.0514*Conc + 2 expressed in mg/m3. The criteria calculated for these test data are:

$C_0 < 15.8$ mg/m3
$0.94 < C_1 < 1.06$

The orthogonal regression analyses of the AM implementations against the SRM gave the following fit parameters, listed in Table 9, for each instrument type and for all results treated together.

Method	Parameter	Result
Gasmet and ABB FTIR	C_0	1.86 mg/m3
	C_1	0.96
Servomex 4900 (IRGFC)	C_0	5.92 mg/m3
	C_1	1.01
Horiba PG250 (NDIR)	C_0	8.98 mg/m3
	C_1	1.02
Testo 350 (EC) and ABB AO2000 (UVA)	C_0	6.88 mg/m3
	C_1	1.01
AM, combined	C_0	4.90 mg/m3
	C_1	1.03

Table 9, Results of systematic deviation tests.

The systematic deviation tests are passed for all implementations of the AM.

c) Validity of the test results

A further test required in TS 14793, which must be passed in order for the tests to be accepted, is that the regression fit, r, meets the following requirement, r > 0.97.

Table 10 lists the regression fits for each of the implementations of the AM and the combined AM.

Method	r
Gasmet and ABB FTIR	0.998
Servomex 4900 (IRGFC)	0.999
Horiba PG250 (NDIR)	0.999
Testo 350 (EC) and ABB AO2000 (UVA)	0.998
AM, combined	0.998

Table 10, Regression fit parameter.

The regression fits are all above the criterion of 0.97, and so all the test results are acceptable.

Graphical representation of the AM results are given in the plots presented below. These are presented as standard linear regression fits for illustrative purposes. The NPL FTIR results give the best fit against the SRM results.

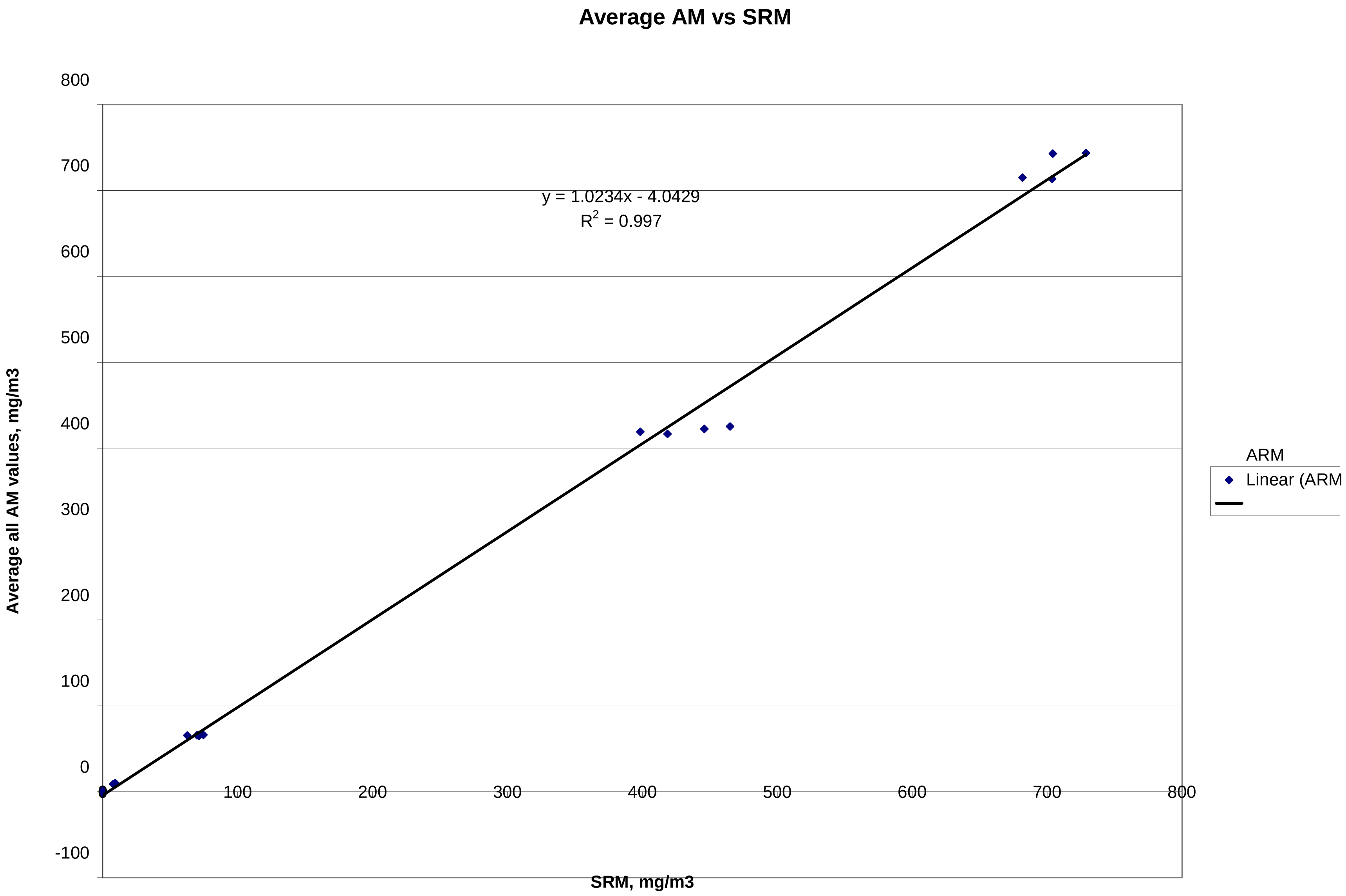

Figure 4, Average AM results plotted against SRM results.

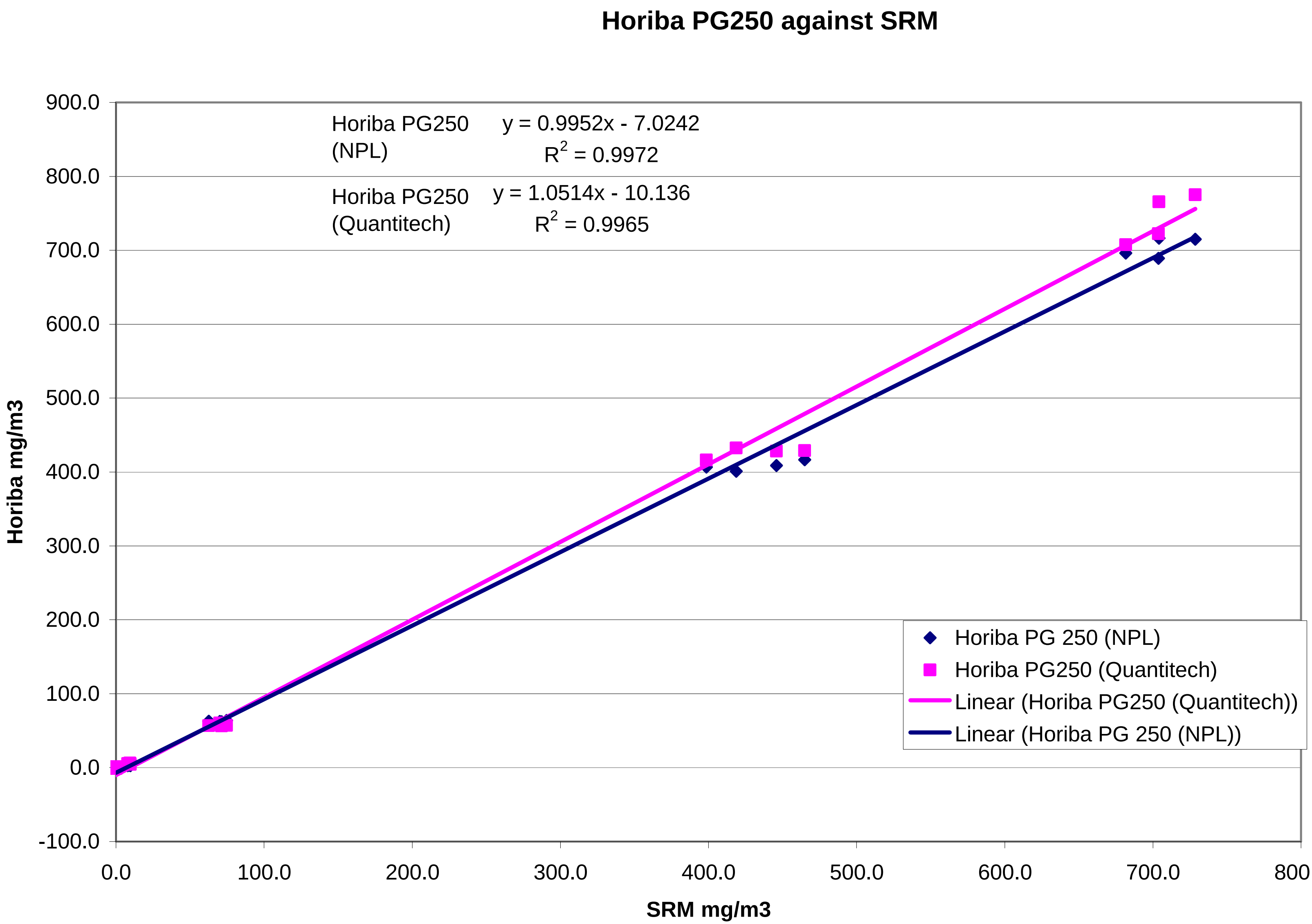

Figure 5, Horiba PG250 AM results plotted against SRM results.

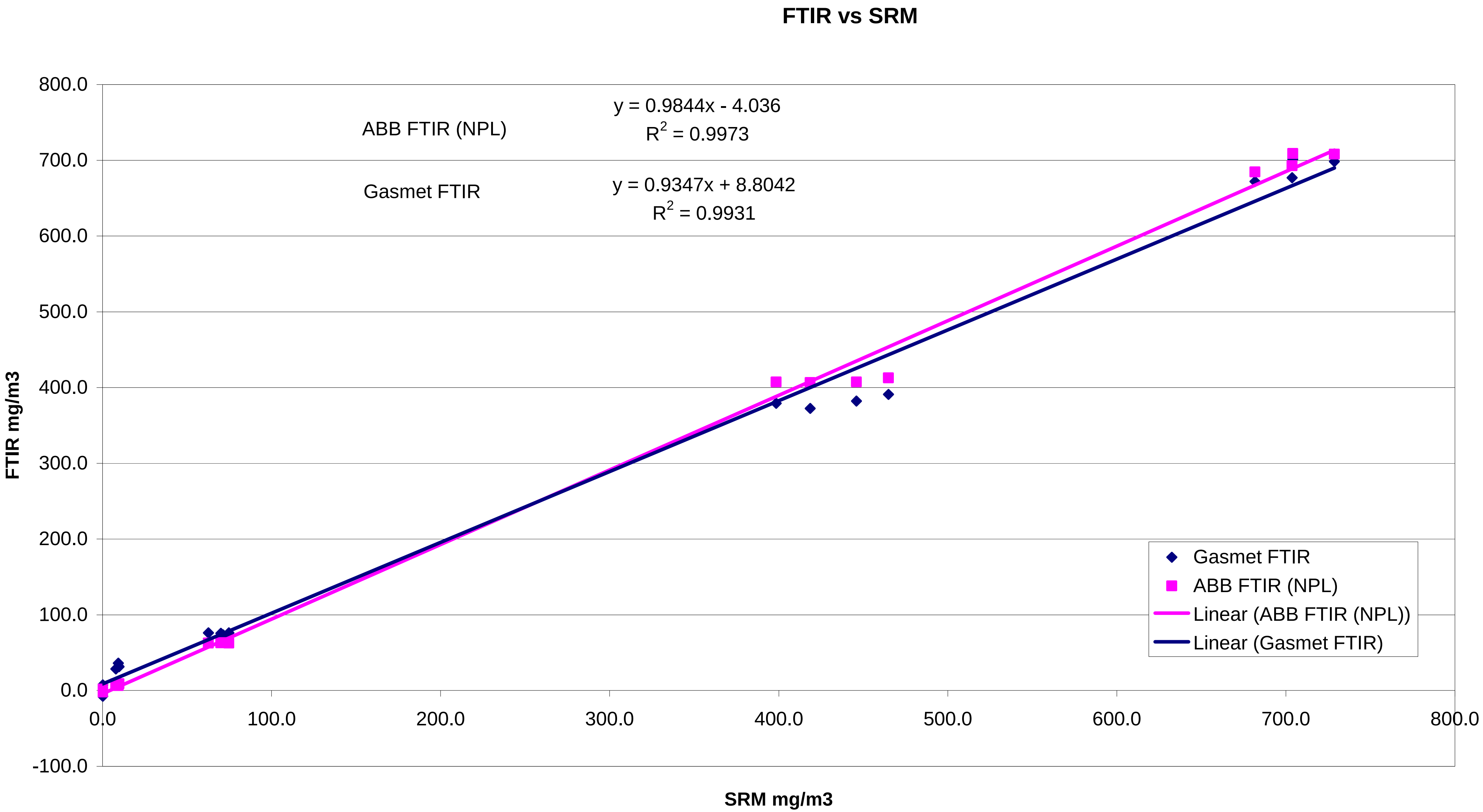

Figure 6, FTIR AM results plotted against SRM results.

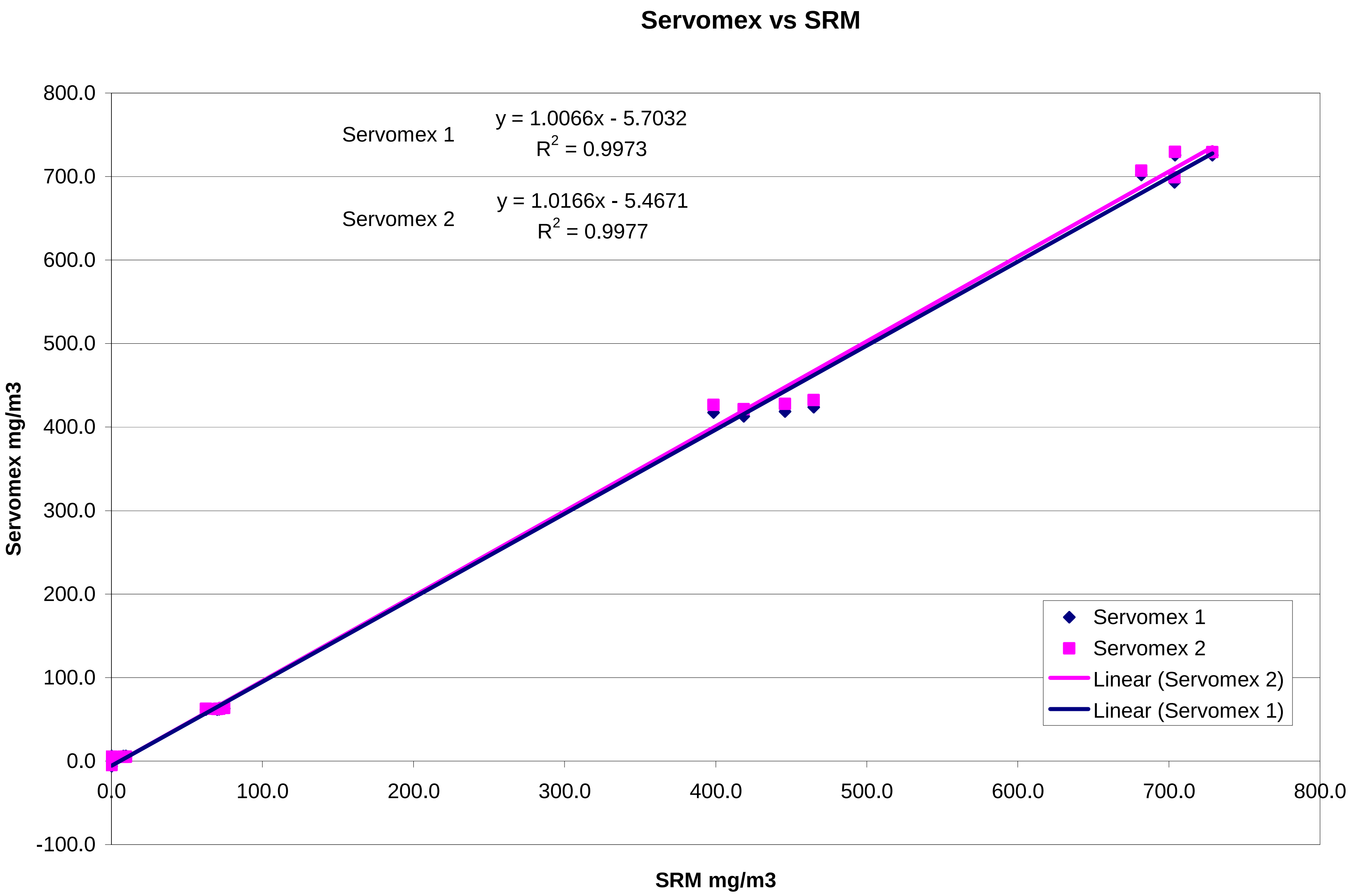

Figure 7, Servomex AM results plotted against SRM results.

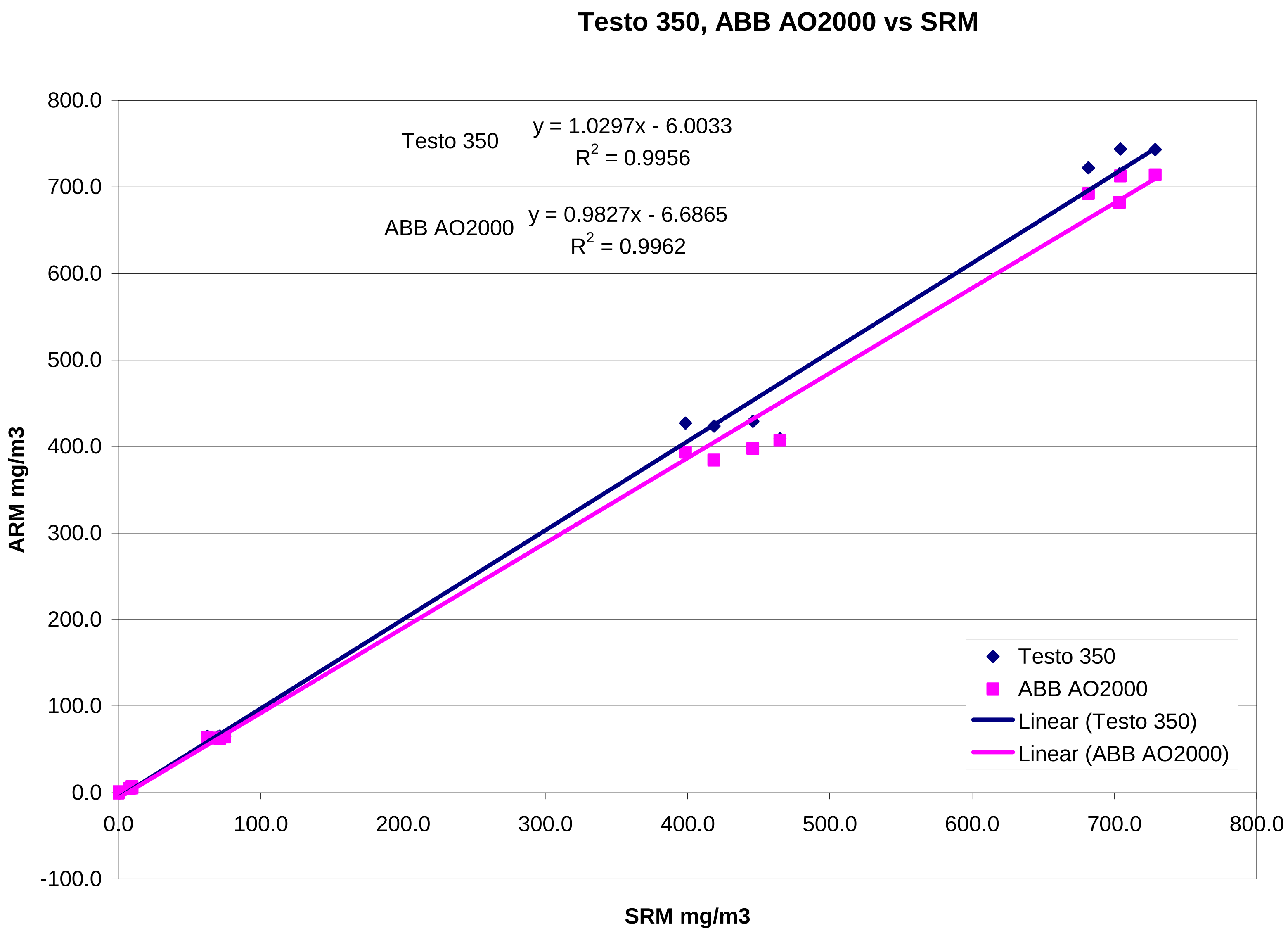

Figure 8, Testo and ABB results plotted against SRM results.

8. CONCLUSIONS

A full set of validation tests compliant with the requirements of CEN/TS 14793:2005 were carried out. The Environment Agency's AM, TGN M21 meets the requirements of the TS, and has been shown to be equivalent to the SRM. All monitoring systems, including FTIR, NDIR, EC and IRGFC were demonstrated to be equivalent, and the ensemble of techniques was also compliant. This demonstrates that TGN M21 is equivalent to the SRM.

Two aspects of the implementation of TGN M21 were identified as requiring specific care:

1) the gas conditioning unit (TGN M21 highlights the requirement to check for potential loss of SO_2 in gas conditioning units).

2) the use of zero and span controls to check for drift

Instruments that have been tested and certified, such as under MCERTS for CEMs, when used within the framework of TGN M21, can be considered to give equivalent results to the SRM. Therefore, the use of an instrument that has been MCERTS certified, as a part of a continuous monitoring (or transportable) system, for the appropriate ranges, is the most straightforward way of demonstrating that an instrument meets the requirements of TGN M21.

Instruments that have not been tested as part of MCERTS certification of CEMs, will require field and performance characteristic tests to demonstrate they comply with TGN M21.

For those monitoring systems, used in the study, that were not certified, the tests carried out in this validation study may be used towards providing evidence of compliance with TGN M21. However, users still need to demonstrate that any instruments used within the AM meet the performance requirements specified in TGN M21. In addition to demonstrating that the performance characteristics are met the monitoring system must be proven on the intended process applications.

Further information on the use of portable instruments for manual stack emissions monitoring is provided in the Environment Agency's MCERTS performance standard for organisations (version 6, June 2008).

9. ACKNOWLEDGEMENTS.

This work was carried out on behalf of the Environment Agency of England and Wales.
The authors acknowledge the support of the following companies who supplied instrumentation for the testing period, and their staff who installed and calibrated the systems.
Instruments were supplied by:
Quantitech,
Testo
E-ON,
Servomex
BV
CES