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Use of Continuous Isokinetic Samplers for the Measurement of Dioxins and Furans in Emissions to Atmosphere

April 2006

The Environment Agency is the leading public body protecting and improving the environment in England and Wales.

It's our job to make sure that air, land and water are looked after by everyone in today's society, so that tomorrow's generations inherit a cleaner, healthier world.

Our work includes tackling flooding and pollution incidents, reducing industry's impacts on the environment, cleaning up rivers, coastal waters and contaminated land, and improving wildlife habitats.

This report is the result of research commissioned and funded by the Environment Agency's Science Programme.

Non-Technical Summary by the Environment Agency

This report was commissioned as part of our work programme to review and test the development of new monitoring methods for industrial processes.

Background

Dioxins and furans are a group of chemicals, often referred to simply as dioxins. They are formed by a number of naturally occurring and human activities such as burning fuels like wood, coal or oil, waste incineration and from a number of industrial processes. Forest fires, bonfires and barbecues contain small amounts of dioxins, as does cigarette smoke.

Over two hundred dioxins exist but only 17 are considered to have significant toxicity by the World Health Organisation. These are the ones that are subject to control by regulation. Studies on workers in chemical plants, or people affected following accidental exposure such as Seveso in Italy or Yusho in Taiwan, show that high levels of dioxins can lead to an increased risk of cancer. These people had substantially higher levels of exposure to dioxins than the general public.

The main route by which the general population takes in dioxins is through food. Dioxins in food come from traces present in soils, resulting from processes such as stubble burning, forest fires and industrial emissions. The amount of dioxins in the UK diet has declined substantially over the past 20 years as tighter controls have been placed on industry and stubble burning. In 1997 the average person consumed only one quarter of the amount that an average person consumed in 1982.

It is expected that further environmental controls, for example the European Union Waste Incineration Directive (WID), will continue to reduce levels of dioxins in food. Municipal waste incinerators and cement kilns operate at well below their permitted emission limits and only make a very small contribution to the background level of dioxins in the environment.

We are responsible for regulating a number of industrial processes that generate dioxins. Over the last 15 years, levels of dioxins emitted from these activities have fallen significantly. For example, between 1990 and 2003, the quantity of dioxins released from the industrial sites we regulate fell by 95%.

We grant permits to companies to operate industrial processes provided they can show that the impact of any emissions does not cause harm to people or the environment. Emission limits are set in the permits to protect people and the environment. Operators have to monitor their emissions and report the results to us. We may also carry out our own monitoring to confirm the operators' results.

For many common pollutants we require operators to fit continuous emission monitoring systems. These systems provide the operator with constant feedback on the levels of pollutants being emitted. There is currently no technology available to take, analyse and display instantaneous readings of dioxins levels due to the very low levels that are emitted. These levels are so low that they are at the limits of what can be detected by the most sensitive equipment. Dioxins emitted from waste incinerators must meet the standards of the

WID which has set the emission limit at a tenth of a nanogram (ng), written in scientific writing as 0.1ng I-TEQ/m^3. A nanogram is one billionth of a gram.

As we cannot measure dioxins on a continuous basis because of their very low levels, we use instead a methodology called European Standard BS EN 1948, as do other member states and as is required in the WID. This involves collecting a sample of emissions manually over 6 hours, which is then sent away for laboratory analysis. We also ensure that the formation of dioxins is minimised by controlling other things that can be measured continuously and which we know prevent dioxins formation. These include the combustion temperature, the amount of oxygen present and whether the abatement equipment is operating properly. These are specified in the permit that we issue to operators. If conditions are not correct the operator is required to stop burning waste.

What we tested

As part of our continuous improvement programme we decided to investigate the performance of two commercial systems that sample dioxins continuously. The systems, known as AMESA and DMS are designed to sample emissions continuously over a typical period of 14 to 28 days, producing a single sample which is then analysed. The BS EN 1948 method takes a sample over 6 hours, which is then analysed.

In order to test the AMESA and DMS systems, two operators, one a municipal waste incinerator and the other a cement works, agreed to have these systems installed on their sites. The manufacturers of the continuous systems provided the equipment on loan free of charge. We placed a research contract with Netcen, part of AEA Technology plc. A series of tests were carried out in the laboratory and on the sites to assess the systems' performance. The purpose of tests was twofold, firstly to see how they worked as automatic sampling systems and secondly to assess their performance against measurements made by manual sampling using BS EN 1948. The report gives the detailed technical results of the work.

Conclusions

The extremely low levels of dioxins emissions at both sites meant that the study was working at the limit of what it is possible to measure with any certainty. Although this is good news from an environmental perspective, it presented the researchers with a considerable challenge. Within this constraint some conclusions could be drawn:

- Both continuous systems were able to track the trends in dioxins concentrations as the processes operated. However, differences were observed between the continuous sampling systems and manual sampling and between the two continuous systems.

- The continuous sampling systems did not meet the requirements of BS EN 1948. The emission limit value in the WID applies to the use of BS EN 1948 and this manual sampling method remains the only acceptable way to monitor dioxins for the purpose of regulation.

- The majority of results were well within the 0.1ng I-TEQ/m^3 emission limit value specified by the WID, irrespective of the measurement system and test site. A small number of results at the municipal waste incinerator were higher. Three slightly elevated results were found during plant start-up when the plant is stabilising and

seven elevated results during normal operation which were thought to be due to contamination of the probe.

Follow up Actions

On the basis of this report, we will be undertaking the following:

- We will be commissioning further work to investigate the slightly higher results found at the municipal waste incinerator during start up conditions. These start up periods are specifically excluded from the WID and the research was not designed to investigate start up periods. This new work will look at obtaining samples using BS EN 1948 during start up. We will do this at a number of municipal waste incinerators around the country.

- We will discuss these findings with the Source Testing Association, the principal UK trade association for carrying out emissions monitoring. We want to explore the possibility of sampler contamination, particularly when using titanium probes, and consider options for improved clean up of equipment between sample runs.

- We will make the report available to CEN, the European standards making body, Defra and the European Commission as a contribution to their consideration of developments in sampling and monitoring of dioxins in the future.

Contents

List of abbreviations

AES: Analytical Environmental Services

BREF: Best Available Techniques Reference Document

CEMS: Continuous Emission Monitoring Systems

CEN: European Committee for Standardization

CISD: Continuous Isokinetic Sampling of Dioxins

ELV: Emission Limit Value

EPER: European Pollutant Emission Register

IPPC: Integrated Pollution - Prevention and Control

I-TEQ: International Toxic Equivalent

LAPC: Local Air Pollution Control

LOD: Limit of Detection

MCERTS: Environment Agency's Monitoring and Certification Scheme

MST: Manual Sampling Train

MSW: Municipal Solid Waste

NAEI: National Atmospheric Emissions Inventory

PCDD/Fs: Polychlorinated dibenzo-para-dioxins and polychlorinated dibenzofurans (Dioxins/Furans)

PPC: Pollution Prevention and Control

UKAS: United Kingdom Accreditation Service

USEPA: United States Environmental Protection Agency

WID: Waste Incineration Directive

WHO-TEQ: World Health Organisation-Toxic Equivalent

Glossary of terms

Accuracy: The closeness of agreement between a measured value and the true value (or set value).

Availability: The fraction of the total monitoring time for which data/sample material of acceptable quality has been collected.

Certification range: The determinand values, over which the equipment is tested, bounded by specified upper and lower limits.

Expanded uncertainty: Quantity defining an interval about the result of a measurement that may be expected to encompass a specific fraction of the distribution of values that could reasonably be attributed to a determinand. The confidence interval typically used is 95%.

Isokinetic sampling: Sampling at a rate so that the velocity through the nozzle is the same as that found at the sample point. This ensures that the particle size distribution is unaffected by the sampling process and so represents the particles present in the duct or stack.

Limiting conditions: The extreme conditions, which a CISD can withstand without damage, and any decrease in its abilities to perform reliable sampling, when it is working under its rated operating conditions.

Linearity: Measure of fit of the CISD's performance in achieving a set sampling velocity to a straight line, using a number of approximately equally distributed values of the determinand, and zero.

Maintenance interval: Maximum admissible interval of time for which the performance characteristics will remain within a pre-defined range without servicing, e.g. refill, calibration, or adjustment.

Minimum operational velocity: The minimum operating sampling velocity, below which the CISD fails to respond isokinetically.

Performance characteristic: One of the quantities (described by values, tolerances, range) assigned to the CISD in order to define its performance.

Reference conditions: A specified set of values (including tolerances) of influence variables, delivering representative values of performance characteristics.

Repeatability: The repeatability of the CISD sampling rate in response to a change in the set velocity.

Response time, T_{90}: The time taken for the CISD to reach 90% of the expected sampling rate following introduction of a step change in velocity.

Short-term drift: The observed drift in isokinetic response of the CISD to a set gas velocity over a period of time.

Standard uncertainty: Uncertainty of the result of a measurement expressed as a standard deviation.

Uncertainty: The parameter associated with the result of a measurement that characterises the dispersion of the values that could reasonably be attributed to the determinand.

Use of Continuous Isokinetic Samplers for the Measurement of Dioxins and Furans in Emissions to Atmosphere

1   Introduction

A communication from the Commission to the Council, the European Parliament and the Economic and Social Committee (2001) presented an aim to promote research in the field of continuous measurements of dioxin emissions to air; and to develop guidelines and standards for sampling, data generation and reporting. This project provides part of the Environment Agency's research towards achieving that aim.

The main objective of the project was to perform laboratory and field tests to determine the performance of two commercially available systems, the DMS and AMESA, which are currently being marketed for continuous isokinetic sampling of dioxins (CISD). The laboratory tests were as specified in the MCERTS document "Performance Standards and Test Procedures for Automatic Isokinetic Samplers" developed under this project and published by the Environment Agency. MCERTS is the Monitoring Certification Scheme established by the Environment Agency to provide certification of equipment and personnel for environmental monitoring. The field tests involved operation of the CISD systems at a municipal solid waste (MSW) incinerator, and a cement works, and comparison of results with samples obtained using conventional manual sampling trains (MSTs).

Section 2 of this report provides the findings of a literature search conducted at the start of the project to determine the requirements of European Legislation and Guidance, and experience of CISD performance reported elsewhere. The CISDs under test are described in more detail in Section 3. Section 4 details the laboratory testing undertaken at Sira to determine the operational temperature and vibration performance of the CISDs. Further laboratory tests undertaken by AEA Technology, are described in Section 5, reporting use of a wind tunnel to assess the isokinetic sampling performance of the two CISDs.

Sections 6 and 7 detail the field tests undertaken to assess the use of CISDs in the sampling of dioxins in actual process emissions. Section 8 summarises the tests results in support of MCERTS certification as automatic isokinetic samplers. Conclusions are drawn in Section 9 and recommendations made in Section 10. Finally, Section 11 provides details of all documents referred to in this report.

The first phase of field tests (Section 6) were performed by AES and AEA Technology at Site 1, the MSW incinerator. The second period of field tests (Section 7) were performed by PB Power Ltd and AEA Technology at Site 2, the cement works where particulate emissions were chosen to be significantly higher than at Site 1.

All the testing and analysis procedures described in Sections 4, 5, 6 and 7 were carried out in accordance with the requirements of MCERTS, the United Kingdom Accreditation Service (UKAS), and BS EN ISO 17025.

2   Literature review

2.1   Scope of review

This review aims to put continuous isokinetic sampling of dioxins (CISD) into context with existing and potential regulatory requirements and published experiences. It also identifies a number of issues taken into consideration during drafting of the MCERTS performance standards and test procedures.

2.2   Review of legislation

2.2.1   UK legislation and related guidance

The Waste Incineration Directive (WID) is the main European Union Directive potentially requiring the investigation and possible subsequent use of continuous dioxin samplers, when it is shown that suitable systems are available for this task. According to the WID, the Commission shall decide, as soon as appropriate measurement techniques are available, the date from which continuous measurements of dioxins and heavy metals shall be carried out in accordance with CEN standards. In England and Wales, industrial plants affected by the WID are now regulated either by the Environment Agency or Local Authorities in accordance with the Integrated Pollution Control (IPC) or the Pollution Prevention and Control (PPC) regime. The PPC regime, under the Pollution Prevention and Control Act 1999, and the Pollution Prevention and Control (England and Wales) Regulations 2000 (SI 1973:2000), implements the requirements of the Integrated Pollution Prevention and Control (IPPC) Directive in England and Wales, and also accommodates residual Local Air Pollution Control (LAPC) requirements. Requirements of the WID under PPC are set by a Secretary of State Direction, the Pollution Prevention and Control (Waste Incineration Directive)(England and Wales) Direction 2002. A similar direction exists under IPC. Further review of IPPC and the WID follows in section 2.2.2.

The Environment Agency produces guidance in the form of technical notes to provide operators and its own staff with advice on standards of operation and environmental performance, relevant to given industrial sectors. The technical guidance notes most relevant to WID are reviewed below.

IPPC S5.01 (Incineration of waste and fuel manufactured from or including waste)

Scope of application: This guidance note covers waste incineration where the primary purpose of the installation is the destruction of wastes or the use of waste as fuel in dedicated plant, including:

 ➢   hazardous waste incinerators;

 ➢   certain plants burning solid or liquid hazardous waste as fuel;

 ➢   incinerators (for non-hazardous waste) of capacity > 1 t/hr; and

 ➢   incinerators burning waste excluded from the WID.

Emission limits: Where an installation falls within the scope of a particular Directive, the standards set by that Directive apply *as a minimum*. For dioxin releases to air, benchmark

emission values set by the guidance are the same as the standards set by the Waste Incineration Directive 2000/76/EC (see section 2.2.2 below).

Measurement requirements: For monitoring and reporting of emissions to air, the guidance specifies that the monitoring requirements outlined in the Waste Incineration Directive 2000/76/EC (see section 2.2.2) are considered to represent Best Available Techniques (BAT) for the sector. Amongst other general principles given in the guidance is a clause stating that *"Continuous monitoring shall be used where it is required by legislation, where the releases are significant or where it is needed to maintain process control. In particular, the species required by the WID to be continuously measured are: NO_x, CO, dust, TOC, HCl, HF and SO_2"*.

Implications: The guidance given in IPPC S5.01 does not require use of CISD but repeats the WID requirement of "at least two measurements per year are required for dioxins and furans and heavy metals. In the first year of operation, monitoring is required every 3 months". On the other hand CISD use is not precluded. Indeed the clause concerning continuous monitoring implies that it would be consistent and appropriate to use CISD in those cases where releases are "significant".

IPPC S3.01 (Cement and Lime)

Scope of application: This guidance note covers installations for the production of cement and lime:

a) Producing or grinding cement clinker,

b) Producing lime:

       (i) in kilns or other furnaces with a production capacity exceeding 50 tonnes per day; or

       (ii) where activity is likely to involve the heating in any 12 month period of 5,000 tonnes or more of calcium carbonate or magnesium carbonate or, in aggregate, both.

Emission limits: For dioxins and furans, a benchmark emission value is given for releases to air from kiln exhausts: 0.1 $ng.m^{-3}$ I-TEQ (2,3,7,8-tetrachlorodibenzo-p-dioxin toxic equivalent quantity – defined in Annex A of BS EN 1948-1).

Measurement requirements: The guidance given for dioxin monitoring is to use extractive sampling according to BS EN 1948. As in S5.01, in general terms continuous monitoring is encouraged where emissions are likely to be "significant".

Implications: As in waste incineration, use of CISD could be justified where emissions are considered to be "significant".

2.2.2   Other EU legislation

Integrated Pollution Prevention and Control (IPPC)

EU Member States are required to issue permits to operate certain industrial activities under the IPPC Directive 96/61/EC. These permits must contain conditions based on best available techniques (BAT) with the aim of achieving a high level of protection of the environment. As part of this process the European Commission has organised an exchange of information between Member States and the industries concerned. This information has been produced by

the European IPPC Bureau in the form of BAT reference documents known as BREFs. Final version of the BREF on waste incineration has yet to be issued.

Scope of application: A number of the categories of industrial activities defined in Annex I of the Directive (and Parts A1 and A2 of Schedule 1 of the PPC Regulations) are potential sources of dioxins, most notably energy, refining, metals, cement, lime and incineration.

Emission limits: IPPC Guidance Notes such as IPPC S5.01 and S3.01 have carried forward information from relevant BREFs into domestic guidance, including recommendation on benchmark emission limit values. BREFs and domestic guidance notes usually specify emission limit values (ELV) that are at least as rigorous as those set by the relevant Directives such as the WID. These ELVs are used to define the operation of processes i.e. are a target and have led to plant design achieving lower level of emissions than the ELVs through design and modification of process techniques.

EPER Decision requires Member States to report to the Commission on emissions from all individual facilities listed within Annex I of the Directive. The report must include emissions to air and water for all pollutants for which specified threshold values are exceeded. The threshold for dioxins and furans is 0.001 kg I-TEQ per year.

The EPER guidance document provides an indicative list of measuring methods for relevant air pollutants. For dioxins and furans, the indicated measurement method is BS EN 1948 Parts 1, 2 and 1, 2 and 3.

The draft BREF note on Incineration does refer to continuous dioxin samplers and the experiences of their use in Austria, Belgium and Holland.

The BREF note for cement and lime indicates that regular periodical monitoring is appropriate for dioxins and furans.

The BREF note on monitoring is considered too general to be of direct relevance to the present project.

Implications: CISD is mentioned in the reviewed BREF documents, but they do not describe them as tools for regulatory purposes.

DIRECTIVE 2000/76/EC - The waste incineration directive

Scope of application: It covers incineration and co-incineration plants (with some exclusions). It replaced the three existing Directives: 89/369/EEC, 89/429/EEC, and 94/67/EEC, on the incineration of municipal waste and hazardous waste from 28 December 2005.

Emission limits: Emission limits are set for 17 listed dioxins and furans calculated using the I-TEQ concept of toxicity equivalence. The emission limit is 0.1 ng I-TEQ/m^3 for the sum of the 17 individual I-TEQ concentrations although the standard conditions vary according to situation, shown in Table 2.1. Article 11(10)(c) specifies that the emission limit values for dioxins and furans shall be regarded as being complied with if none of the average values over the specified sampling period exceeds the emission limit values set.

Table 2.1: Standardisation conditions applying to results of measurements made to verify compliance with emission limit values for dioxins and furans laid down in Directive 2000/76/EC

Situation	Standardisation Conditions
Incineration plants; and co-incineration plants not specified separately below	Temperature 273 K, pressure 101.3 kPa, 11 % oxygen, dry gas
Incineration of waste oil	Temperature 273 K, pressure 101.3 kPa, 3 % oxygen, dry gas
Cement kilns co-incinerating waste	Temperature 273 K, pressure 101.3 kPa, 10 % oxygen, dry gas
Combustion plants co-incinerating waste	Temperature 273 K, pressure 101.3 kPa, 6 % oxygen, dry gas
Incineration in an oxygen-rich atmosphere	Standardise to an oxygen content laid down by the competent authority

Measurement requirements: Average values are to be measured over a sample period of a minimum of 6 hours and a maximum of 8 hours, except in the case of cement kilns co-incinerating waste, where the sampling period is not specified.

Article 11(2)(c) states that least two measurements per year of dioxins and furans are required and one measurement at least every three months for the first 12 months of operation of a new plant or after a major modification. The measurement frequency may be reduced to once every two years provided that circumstances identified in Article 11(7) are met i.e. the emissions resulting from co-incineration or incineration are below 50 % of the emission limit values determined according to Annex II (i.e. using the formula to calculate the emission limits during co-incineration) or Annex V respectively.

Article 11(13) of the WID deals with the issue of continuous measurement of dioxins and heavy metals. It suggests that the Commission, assisted by a regulatory committee, will decide, as soon as appropriate measurement techniques are available within the Community, the date from which continuous measurements of the air emission limit values for heavy metals , dioxins and furans shall be carried out in accordance with Annex III. No such decision has yet been made.

Concerning the selection of measurement techniques, paragraph 28 of the preamble to the Directive states that "High-standard measurement techniques are required to monitor emissions to ensure compliance with the emission limit values for the pollutants."

Annex III of the Directive is more specific:

➢ Measurements for the determination of concentrations of air and water polluting substances have to be carried out representatively.

➢ Sampling and analysis of all pollutants including dioxins and furans as well as reference measurement methods to calibrate automated measurement systems shall be carried out as given by CEN-standards. If CEN standards are not available, ISO standards, national or international standards which will ensure the provision of data of an equivalent scientific quality shall apply."

> ➢ Member States are responsible for ensuring that the measurement requirements are complied with, either by specification in the conditions of the permit, or by general binding rules.

Implications: Annex III implies that CEN standards must be followed for compliance monitoring according to the Directive. Therefore the use of a CISD to satisfy directive compliance assessment requirements is only acceptable if it meets EN 1948.

2.2.3   Requirements in Flanders (Belgium)

A limited number of sectors have been set emission limit values for dioxins under the environmental permit laws Vlarem I (procedural) and Vlarem II (specific conditions and objectives) - see Table 2.2. Of these, only the municipal and sewage sludge incinerators are required to install CISD systems with others monitoring dioxins once a year using EN 1948.

Table 2.2: Emission limit values and measurement requirements in Flanders

Sector	Sub-Sector	Emission Limits	Measurement Requirements
Incineration	Municipal waste (> 6 t/hr)	0.1 ng TEQ / m^3 under standard conditions[1] from 1 January 1997	Continuous dioxin sampling and analysis at least every 2 weeks from 1 May 1999
	Municipal waste (< 6 t/hr)	4 ng TEQ / m^3 until 1 January 2001, thence 0.1 ng TEQ / m^3	Continuous dioxin sampling and analysis at least every 2 weeks from 1 May 1999
	Hazardous waste and medical waste	0.1 ng TEQ / m^3 under standard conditions from 1 January 1997	Yearly measurement following EN standards
	Sewage sludge	0.1 ng TEQ / m^3 under standard conditions from 1 January 2000	Continuous dioxin sampling and analysis at least every 2 weeks from 1 May 1999
Sinter plants	Existing plant (authorised before 1 January 1993)	2.5 ng TEQ / m^3 under standard conditions[2]	Yearly measurement following EN standards
	New plant (authorised after 1 January 1993)	0.5 ng TEQ / m^3 under standard conditions	Yearly measurement following EN standards
Primary and secondary production of copper	Existing plant (authorised before 1 January 1993)	1 ng TEQ / m^3 under standard conditions[3]	Yearly measurement following EN standards
	New plant (authorised after 1 January 1993)	0.5 ng TEQ / m^3 under standard conditions	Yearly measurement following EN standards
Production of steel	Same as primary and secondary production of copper		
Smelting plants in the secondary aluminium industry	Same as primary and secondary production of copper		

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[1] 273.15K, 101.3 kPa, dry gas, 11% O_2.
[2] 273.15K, 101.3 kPa, dry gas, 16% O_2.

Sector	Sub-Sector	Emission Limits	Measurement Requirements
Residential, utility and industrial installations for wood combustion	Several sub-sectors, which appear to represent all possibilities burning > 1 t/hr by 1 January 2003	0.1 ng TEQ / m^3 achieved for all sub-sectors by 1 January 2003	Yearly measurement following EN standards

2.2.4   Standards and guidance notes

BS EN 1948

The standard consists of three parts, describing suitable extractive sampling systems and sampling methodologies (part 1), the extraction and clean up of the sample fractions (part 2) and the analysis of the respective fractions (part 3).

For sampling there is a choice between three different systems:

> ➢   filter/condenser method;

> ➢   dilution method; and the

> ➢   cooled probe method.

Isokinetic sampling shall be carried out at representative positions in the duct according to EN 13284-1 Stationary Source Emissions – Determination of low range mass concentration of dust Part 1 Manual gravimetric method. This requires cross-duct sampling. Since cross-duct sampling in accordance with EN 13284-1 is not a standard feature of the CISDs currently available, they are not in strict agreement with BS EN 1948. Furthermore, by implication they are not suitable for use in assessing compliance with the Waste Incineration Directive (see section 2.2.2 above).

The standard has been evaluated at the 0.1 ng/m^3 International Toxic Equivalent (I-TEQ) level of dioxins in the presence of dust concentrations ranging from 1 to 15 mg/m^3. The reported 95% confidence interval for the cooled probe method averaged 0.04 ± 0.06 ng I-TEQ /m^3 and 0.03 ng ± 0.014 ng I-TEQ /m^3 for plant with dust concentrations of 15 mg/m^3 and 3 mg/m^3, respectively. The other sampling systems described in BS EN 1948 (filter/condenser and dilution methods) have comparable performance.

Samples collected by the CISDs currently under consideration were extracted and analysed according to Parts 2 and 3 of the Standard.

Revisions to BS EN 1948

Working Group 1 of CEN Technical Committee 264 has revised BS EN 1948 Parts 1-3 and these have now been published. The revisions to Parts 1 to 3 of the Standard are largely corrections and clarifications of the standard and revisions to incorporate EN 13284 Part 1 for particulate sampling. In addition, the definitions and procedures for the treatment of blanks and labelled standards are clarified. The standard now restricts quantification to the use of high-resolution instruments operating at mass resolutions greater than 10000. Full details of the revisions are given in the Forewords to each part.

The scope of the standard is extended to include determination of dioxin-like PCBs and a Technical Specification is in preparation covering the modifications required for PCB sampling and analysis. The intention of the Working Group is to convert this document into Part 4 if validation work is undertaken. Further work on a further extension (Part 5) to cover CISD systems has not been progressed at this stage.

Monitoring note M2

The Environment Agency's Monitoring Note M2 specifies British Standards and Standards from other relevant committees, which may be suitable for monitoring prescribed substances in releases to air, water and land. The following standards and methods are listed for dioxins:

- BS EN 1948: Parts 1-3: 1997. Stationary source emissions – Determination of mass concentration of PCDDs/PCDFs.

- US EPA Method 23: 1995. Determination of PCDDs and PCDFs from stationary sources

- VDI 3499 Part 1: 2000. Emission measurement of residual materials; Determination of polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) in waste incinerator flue gas – Dilution method.

- VDI 3499 Part 2: 2000. Emission Measurement. Determination of Polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs). Filter/condenser method.

- VDI 3499 Part 3: 2000. Emission Measurement. Determination of Polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs). Cooled Probe Method.

In addition, the use of CISD is mentioned under CEMs with the proviso that although the sample is obtained continuously the results are not instantaneous as analysis of the collected sample is required.

2.3   Experience with CISD

2.3.1   Material from the Becker Messtechnik (AMESA) Website

The scope of application is given as combustion facilities such as refuse incinerators and hazardous material incinerators, with dioxin concentrations up to 10 ng/m^3 TEQ.

The system is based on adsorption using XAD-II (with quartz wool as a pre-filter); dioxins are sampled isokinetically through a cooled ($< 70^{\circ}$C) titanium probe over a period from 6 hours to 4 weeks. Both the air stream and the condensate are drawn through the filter cartridge.

2.3.2   Material from the Dioxin Monitoring System Website

The Dioxin Monitoring System (DMS) was developed at Austrian Energy & Environment GmbH and sold to the manufacturers in 1998.

The system is stated to be applicable to dioxin concentrations in the ranges 0.01 to 100 ng/m^3 TEQ (6 hour sampling) or 0.0001 to 10 ng/m^3 TEQ (6 week sampling).

According to the website, "The accordance of our device to BS EN 1948-1 was certified by the German RWTÜV" and "Our device is a BS EN 1948 reference device. It works completely in

accordance to this standard without any changes of the method. This was certified by the German TUV".

Nine reference installations are listed at the start this project. This number has increased over the intervening period.

2.3.3 Other material from the manufacturers

AMESA POSTER AT CEM 2001

The poster indicates that the AMESA system was approved in 1998 by TÜV Rheinland. Figure 2.1 shows a comparison between dioxin concentrations found by 14-day average samples (AMESA) and 6 hour samples (BS EN 1948). The identity and nature of the plant where the measurements were made is not revealed. . There is no explanation why the dioxin levels dropped by a factor of more than 10 times after the 6th week.
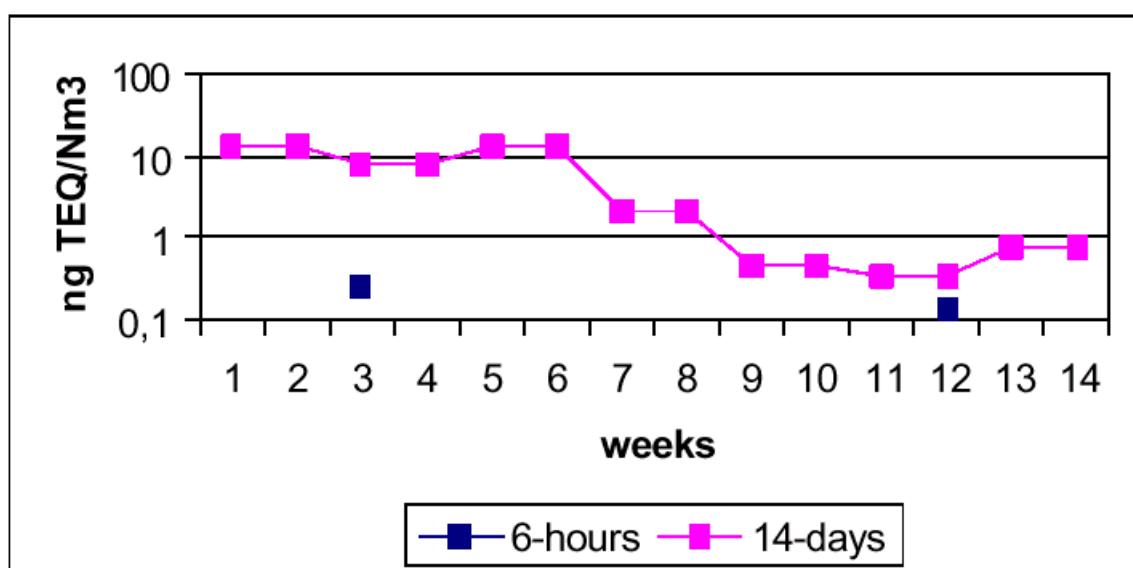
Figure 2.1: TUV Comparison between AMESA system and SRM samples

DMS poster at CEM 2001 (KAHR *et al*., 2001)

The poster presents a schematic diagram of the system and proposes that at stacks with inhomogeneous flue gas concentration, additional sampling units can be installed to ensure representative sampling. Various sources of uncertainty associated with use of the system are described, these are summarised in Table 2.3.

Table 2.3: Summary of uncertainties for the dioxin monitoring systems

Uncertainty	1 Week Monitoring Period	8 Hours Monitoring Period
Application of the standard reference material	5%	5%
Blank values (measurement & laboratory)	1%	10%
Volume measurement	5%	5%
Deviation to representative particle sampling	7%	12%
Probe position in the stack	0%	0%
Defined by the recovery of internal standard	9.2%	3.2%
Inhomogenity of fly ash particles	10%	25%
Total uncertainty	16.9%	30.5%

2.3.4 Experience reported from sources other than manufacturers

De Fré & Wevers (1998)

De Fré & Wevers (1998) postulate that dioxin emissions from Belgian incinerators had hitherto been underestimated by about a factor of four. This conclusion was based on a comparison of dioxin emission concentrations measured in stack versus predicted concentrations derived from dispersion modelling and concentrations found in soils near incinerators.

The paper goes on to describe partial results from a comparison between BS EN 1948 results and results gained with the AMESA continuous sampling system. From January 1997, an emission limit of 0.1 ng TEQ/Nm^3 applied to MSW incinerators in Flanders. In November 1997, five MSW incinerators were ordered to close; three were subsequently allowed to start up again with the condition that a permanent dioxin sampling system would be installed. The paper presents the results from one of the three plants. The AMESA system sampled for periods of about 15 days; analyses were carried out in duplicate by VITO and GfA (the latter being a co-developer of the AMESA system - see GfA Information Note below). Two emission measurements were also made according to the BS EN 1948 method. Table 4 in the paper is reproduced in our Table 2.4 below.

The paper interpreted the results as demonstrating that the BS EN 1948 method underestimates the average emission by a factor of 30 to 50. The reason for the notable differences in the analyses of AMESA samples is not discussed in the paper. It also states that the sampling period by the AMESA system was 15 days, whereas the Table shows that the sampling period varied; the apparent sampling gap during 30 January to 9 February 1998 is not explained.

The paper is clearly a rushed publication of less than ideal results, which nevertheless indicate very significant differences between the concentrations, found using the AMESA sampling system and EN 1948.

Table 2.4: Comparison between continuous (AMESA system) and 6-hour (EN 1948) dioxin samples (De Fré & M. Wevers, 1998)

Period of Measurement (day-month-year)	Measured Dioxin Concentration as ng TEQ/Nm^3 at 11 % O$_2$	
	Continuous Sampling	6-Hour Sample
29-12-97 - 12-01-97 [*sic*]	13.4 (14.3)	
12-01-98 - 26-01-98	8.2 (12.9)	0.25
26-01-98 - 30-01-98	12.6 (10.1)	
09-02-98 - 23-02-98	2.11 (2.12)	
23-02-98 - 09-03-98	0.44	
09-03-98 - 23-3-98	0.33	0.12
23-03-98 - 06-04-98	0.8	

De Fré & Wevers (2001)

The paper gives an update to De Fré & Wevers (1998), with further measurement results from the same Belgian municipal waste incinerator. In Table 2.5, we have juxtaposed those samples, which correspond in date (the paper contains many additional results using the continuous sampler which do not have a corresponding sample taken by the BS EN 1948 method).

The two papers (that is, 1998 and 2001) present conflicting information for the samples taken in March or April 1998 so these results must be considered suspect.

In general, the agreement between the continuous and six hour sampling is much better than was noted in the earlier paper - indeed in some cases the continuous sampler gives a lower value (by a factor of 3) than the EN 1948 method. Clearly, there is variability in the emission; and since the samplers sample over different time periods they inevitably return different results. In the authors' opinion, what has not been adequately addressed by either paper is the apparent variability in the continuous samples - that is, the differences between the paired analyses reported in De Fré & Wevers (1998). In the later paper "For a few cases where more results were available and there was good agreement between labs, the averages are given". Evidently the range of 8.2 to 12.9 observed in January 1998 was considered "good agreement". Regrettably the potential variability in other paired continuous samples is thereby masked. The comparison of 6 hour data with data obtained from the CISD sampling over 14-days does not enable a direct comparison to be undertaken. Hence drawing conclusions about the performance of the CISD from this data is not possible. The data suggests that there could be large differences between the methods. It is not clear whether these differences are due to the methods of sampling, analysis or as a direct result of process operation. There is no evidence that there is a systematic divergence from the "true" concentration in either sampling system.

Table 2.5: Comparison between continuous (AMESA system) and 6-hour (EN 1948) dioxin samples (De Fré & Wevers, 2001)

Period of Continuous Samples	Measured Dioxin Concentration as ng TEQ/Nm^3 at 11 % O$_2$	
	Continuous Sampling	6-Hour Sample (Date)
12/1/98 to 26/1/98	10.5 Note - reported as average; previously reported as duplicate values of 8.2 and 12.9	0.25 (16/1/98)
23/3/98 to 6/4/98	0.5 Note - value for this period previously reported as 0.8; the 0.12 value from BS EN 1948 was previously compared with a continuous value of 0.33	0.12 (1/4/98) Note - previously reported as corresponding with 9/3/98 to 23/3/98 sample
24/4/98 to 27/4/98 but note that a plant shut-down then occurred on 27/4/98	0.55	0.09 (27/4/98)
21/6/98 to 29/6/98	0.082	0.07 (23/6/98)
13/7/98 to 27/7/98	0.073	0.08 (14/7/98)
12/10/98 to 26/10/98	0.092	0.21 (13/10/98) 0.14 (14/10/98) 0.12 (15/10/98)
23/11/98 to 14/12/98	0.12	0.02 (1/12/98)
11/1/99 to 25/1/99	0.11	0.049 (12/1/99)
22/2/99 to 9/3/99	0.12	0.13 (9/3/99)
9/3/99 to 22/3/99	0.14	
12/7/99 to 26/7/99	0.054	0.061 (23/7/99)
20/12/99 to 3/1/00	0.056	0.02 (21/12/99) 0.03 (22/12/99) 0.09 (23/12/99) 0.05 (24/12/99)
17/1/00 to 30/1/00	0.0099	0.029 (19/1/00)
13/7/00 to 27/7/00	0.051	0.060 (20/7/00)

REMEDIA article

Pranghofer G.G., & Fritsky, K.J. (2001) describe measurements made to assess the effectiveness of a catalytic filtration system at three municipal waste incinerators. One of the MSW incinerators at Harelbeke, is situated in the Flanders region of Belgium. The paper reports how MSW incinerators are not allowed to operate in Flanders unless the dioxin limit of 0.1 ng I-TEQ/Nm^3 is met. At Harelbeke continuous sampling (using an AMESA system operating for 2 weeks) and biweekly analysis (6-hour sampling according to EN 1948) are performed. The paper shows a comparison of the AMESA and EN 1948 results, shown in Figure 2.2 below, which the paper concluded showed good agreement. However, there are clearly differences - the data for the period 3/3/00 to 13/3/00 could be interpreted to show the AMESA giving results a factor of 3 higher than the EN 1948 method.
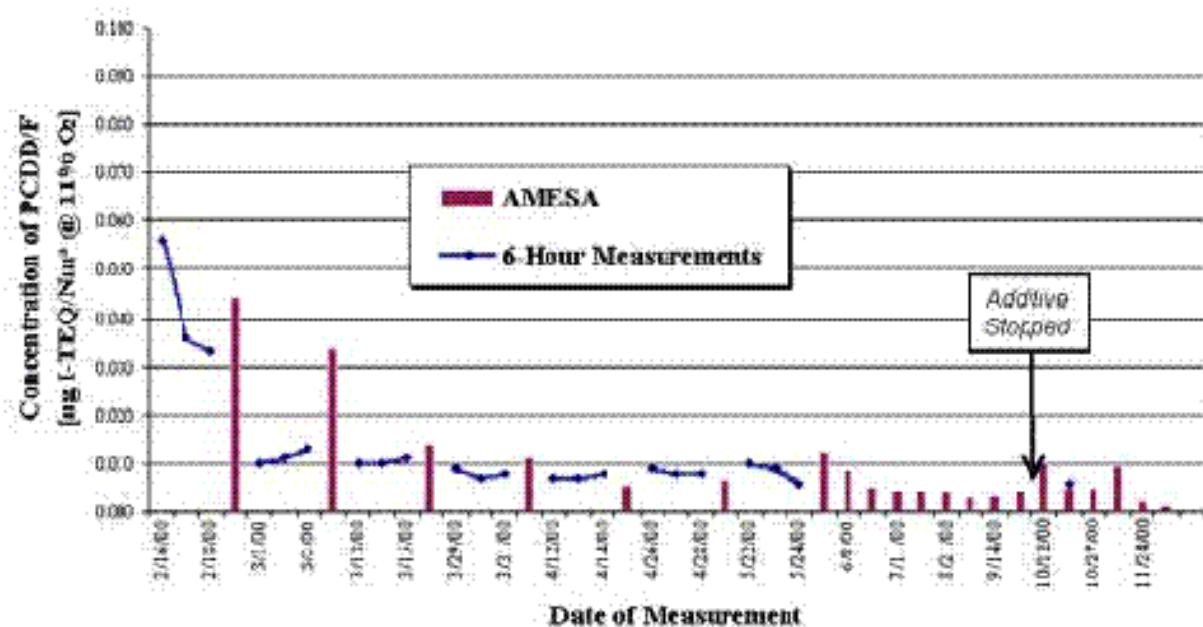
Figure 2.2: Comparison between AMESA and EN 1948 results for dioxins at Harelbeke

GFA information note 01/2000

This article points out that the AMESA system was developed by GfA and Becker Messtechnik, and states that it is certified according to the German environmental regulation 17. BImSch V, citing Mayer *et al*. (1999).

US EPA ABSTRACT (http://www.epa.gov/earlink1/earthlink/00janfeb.htm)

This article states that "AMESA (adsorption method for sampling of dioxins) is a fully automatic system for long term monitoring of dioxin emissions from industrial processes based on the adsorption method. The system has been tested and undergoing a certification procedure according to the German guidelines for certification of systems for continuous monitoring of special substances. The certification covered parameters such as availability of the system, reproducibility of the results and comparability of the sampling method with German and European standard methods. Furthermore, breakthrough, blanks and sample storability were

investigated. The results prove that AMESA is a state of the art sampling system for continuous monitoring of dioxin/furan emissions."

Schepers *et al*., 2001

Schepers *et al*., 2001 report the experiences of Tauw in the use of a cooled probe CISD in the Netherlands and Belgium. The paper lists an inventory of possible problems with continuous sampling of dioxins:

➢ Difficulties with dioxin adsorption due to:

- a limited adsorption capacity of the XAD-2;
- channel forming in the adsorbent due to extended sampling;
- slower mass transfer from liquid phase to resin (since the condensate is passed through the resin rather than being saved and analysed);
- the water washing dioxins away from the adsorbent;

➢ Contamination in the sample carrying parts that are harder to rinse;

➢ A clogging of the continuous rate measuring device (pitot) disturbing the isokinetic control;

➢ Unauthorised manipulation by unauthorised personnel.

Several tests were carried out to characterise the importance of these potential factors. In one set of tests, the adsorption cartridge was split into two parts, the front part being in conformity with EN 1948 and the back part being a cartridge of 5g of XAD-2. It was found that at least 90% of the adsorbed dioxins were in the front part, with an average of 98%. In the second set of tests, two cartridges, both in accordance with EN 1948, were placed in series. This test also showed that at least 90% of the adsorbed dioxins were in the front part, with an average of 98%. As a final test the condensate of 12 different measurements was analysed. The recovered concentrations lay between 0 and 35% of the total content of recovered dioxins, at an average of 20%. The authors presented two potential explanations for this phenomenon:

Channel forming: Long term sampling over one adsorption cartridge creates small channels in the cartridge. Channel forming occurs over the entire length of the cartridge. These channels grow as the sampling continues because the exhaust gases and the condensate prefer these routes as a reaction against the pressure drop in the cartridge. This causes early saturation of the XAD-2 along the channels and adsorption will be minimised.

Particle transfer: There may be insufficient retention of fine particles on the glass wool filter, potentially exacerbated as condensate is washed through the filter over extended periods. Variance analysis between results achieved at a domestic waste incinerator in Belgium using continuous (34 samples) and discontinuous (14 samples) sampling showed that the results were consistent with the hypothesis 'equality of averages for both types of sampling'.

2.3.5 Other sources

Community strategy

A communication from the Commission to the Council, the European Parliament and the Economic and Social Committee (2001) summarises the problem of dioxins and PCBs; describes progress in addressing the problem; assesses the basis for Community action; and presents a strategy to reduce the presence of dioxins and PCBs in the environment. Amongst the short to

medium-term actions (5 years) is an aim to promote research in the field of continuous measurements of dioxin emissions to air; and to develop guidelines and standards for sampling, data generation and reporting.

SRII project

Coggiola *et al.*, 1999 report on a project to develop a real-time CEM for dioxins, apparently funded by the U.S. Department of Energy. The September 1999 progress report points to an imminent project review. The project is not mentioned in subsequent reports and may therefore be assumed to have been cancelled.

BREF note on incineration

This BREF Note points out that there is no continuous measurement system for dioxins, and goes on to briefly describe the use of a continuous sampling system (DMS) at incineration plant in Austria, Belgium and Holland. It describes the CISD as "useful for the assessment of dioxin emissions during unfavorable process conditions". In addition, the system has shown that the emission levels of PCDD/F during the normal process operating are low. This is due to the fact that the CISD enables a larger sample or number of samples to be taken when compared to the routine monitoring. This larger data set allows the effects of changes to the processes to be monitored. Some basic cost data for continuous sampling of dioxins is also given:

> ➢ Investment: EUR 110,000-140,000;

> ➢ Testing of the system: EUR 4,900 (estimation);

> ➢ Analysis (26 samples/year): EUR 20,000/yr; and

> ➢ Maintenance by the supplier (preventive): EUR 2,500/yr.

3   Test systems

3.1   Description of CISDs

3.1.1   AMESA System

The device tested was a Becker Messtechnik (BM) AMESA System utilising a cooled probe condensing system with adsorption of the PCDD/F on to XAD resin. The system comprises of a probe system that mounts to the stack/duct, a mounting box for the resin cartridge, control umbilicals and a control unit that houses the pumps, cooler control systems and gas meters. The AMESA sampling arrangement is shown in Figure 3.1. Becker Messtechnik GmbH is based at Max-Eyth-Strasse 51, Winnenden, Germany.

The probe is of titanium construction with usually a titanium inner liner. Quartz liners are available as an alternative option, but they are considered less durable being more susceptible to accidental breakage. A water-cooled probe is used to cool the sampled gases to a temperature below 50°C. The probe incorporates a Prandtl tube and a thermocouple. These are used to measure the pressure of the gas stream and the static pressure to enable the determination of the stack gas velocity at the point of measurement.

The sample and condensate pass through a brown glass resin trap where the dioxin/furans are absorbed. The resin trap comprises of a quartz wool pre-filter, a bed of XAD-2 resin supported by porous glass frit (porosity grade 0). This resin trap is housed in a weatherproof enclosure, with trace heating to maintain the box temperature at 5°C. The cooled, filtered flue gas sample is then transported via heated PTFE line to an enclosure containing the pump and control systems. The sample is further dried by passage through a Jetstream heat exchanger reducing the temperature to 5°C. Moisture is then collected in a condensate tank.

The system is protected by a filter/liquid sensor combination. The dried gas stream then passes through a mass flow meter used to determine the mass flow of the sampled gas. The output from the mass flow meter controls the sampling rate at the probe and it provides the isokinetic control for the system.

A single tube gas meter measures the integrated volume of gas sampled and the output of the gas meter is recorded by use of an integrated reed contact, which converts each volume of 10 dm^{3} to an electrical signal. The control system converts the measured operating volume into standard volumes. Sample is drawn through the system by a rotary vane pump, which is controlled by a frequency converter via a 4-20mA signal from the control system.

The system operates fully automatically, collecting data relating to both the sampler and other parameters such as plant temperature, duct oxygen and flow. This data is collected via the control system and stored on a 1Mb SRAM card that can be reviewed using programmes such as Microsoft Excel. The rate of data collection can be selected but a normal rate is half-hourly.

The manufacturers claim that dioxin concentrations in the range of 0.0001-10 ng/m^{3} (TEQ NATO) can be measured using their sampling systems.

Table 3.1 lists all the delivered items of equipment, Table 3.2 the supporting hardware and Table 3.3 the documentation.

Figure 3.1: Measuring arrangement of the AMESA system
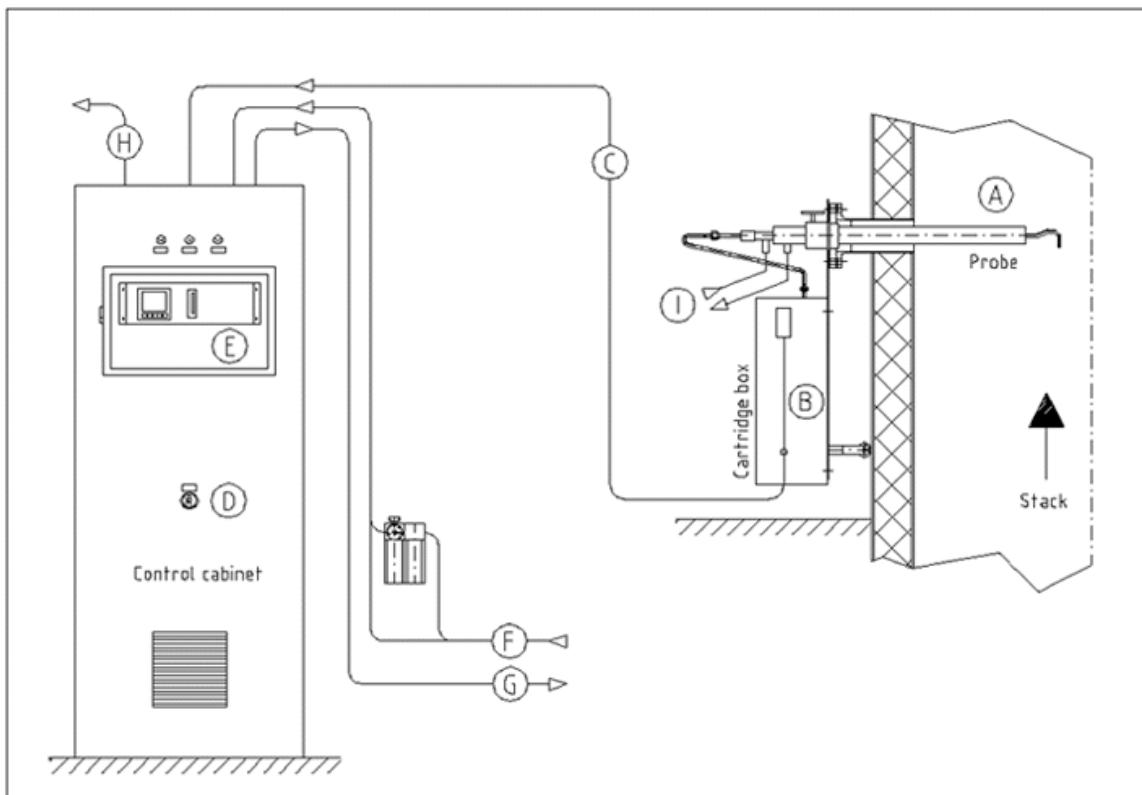
Key

A   Cooled (< 70 °C) titanium probe for isokinetic extraction of a volume stream.

B   Measurement stream and condensate are drawn through the cartridge filled with adsorber resin (quartz wool as a prefilter).

C   Measurement stream and condensate are drawn through the measuring gas line to the control cabinet.

D   Control cabinet with separation of the condensate by cooling (< 5 °C) and infinitely variable control of the isokinetical extraction.

E   User-friendly operation of AMESA by menu dialogue in process controller. Data input for plant specific parameters and operation by means of keyboard and LCD-monitor. Analysis of the emission values by means of SRAM memory chip and analysis results.

F   Compressed air, power supply and input signal conduits.

G   Condensate drain and flue gas recycling.

H   Signal output (optional).

I   Coolant connection (if $T_{Fluegas}$ > 70 °C).

Table 3.1: AMESA instrument information

BM Becker Messtechnik AMESA System				
Type	**Model**	**Manuf. Serial No.**	**Condition**	**Range (Velocity)**
Condensing	AMESA	None	New	0-20 m/s

Table 3.2: AMESA probe information

Item	**Number Delivered**	**Dimensions**	**Condition**
Probe Tip	1	6mm	New
Temperature Sensor	1	n/a	New
Water Cooled Probe	1	1m	New
Union nut	1	n/a	New
Probe Elbow	1	n/a	New
Flange Connection	1	n/a	New
Cartridge Case	1	n/a	New
Ball Valve	1	n/a	New
GL-42 Union	1	n/a	New
Wobble Stick	1	n/a	New
Adsorber Cartridge	1	n/a	New
GL-32 screw union	1	n/a	New
Cartridge Case Heater	1	n/a	New
Umbilical	1	n/a	New
Control Cabinet	1	n/a	New
Analogue output cards	2	n/a	New

Table 3.3: AMESA manual information

Author	**Serial No./Version**	**Condition**
BM Becker	AMESA Version P58.7/ENG/99 Rev 0 12.10.99	New

3.1.2   Dioxin Monitoring System (DMS)

The second system tested was DMS, based on a dilution probe and adsorption on to a filter (see Figure 3.2). Gas is sampled isokinetically from the duct by using two titanium probes at two different fixed points in the duct. Sample is taken alternatively from each probe, each one sampling for a fixed period of time drawing sample into a mixing chamber where it is diluted with cooled dried air. This drops the dew point of the gas mixture to a level avoiding condensation. The sample is then passed through a filter and polyurethane foam (PUF) filter (as used in ambient air monitoring) to capture the sample. An umbilical consisting of a heated sample line, air-lines, control and power cables connects the probe system with the control module. This control module houses the main pumps, gas meters (total and dilution air) and the

data storage unit. The following is a list of all delivered items of equipment (Table 3.4), supporting hardware (Table 3.5) and documentation (Table 3.6).

The DMS system operates fully automatically and has a internal PC based control system that logs data relating sampling (for example volumes, pressures and temperatures) and any error/ alarms. This information is summarised and printed out via an installed printer. However, a more complete data set is stored within the system and can be downloaded via a network connection. The printout provides insufficient resolution of sample volumes.

Figure 3.2: Schematic diagram of the Dioxin Monitoring System
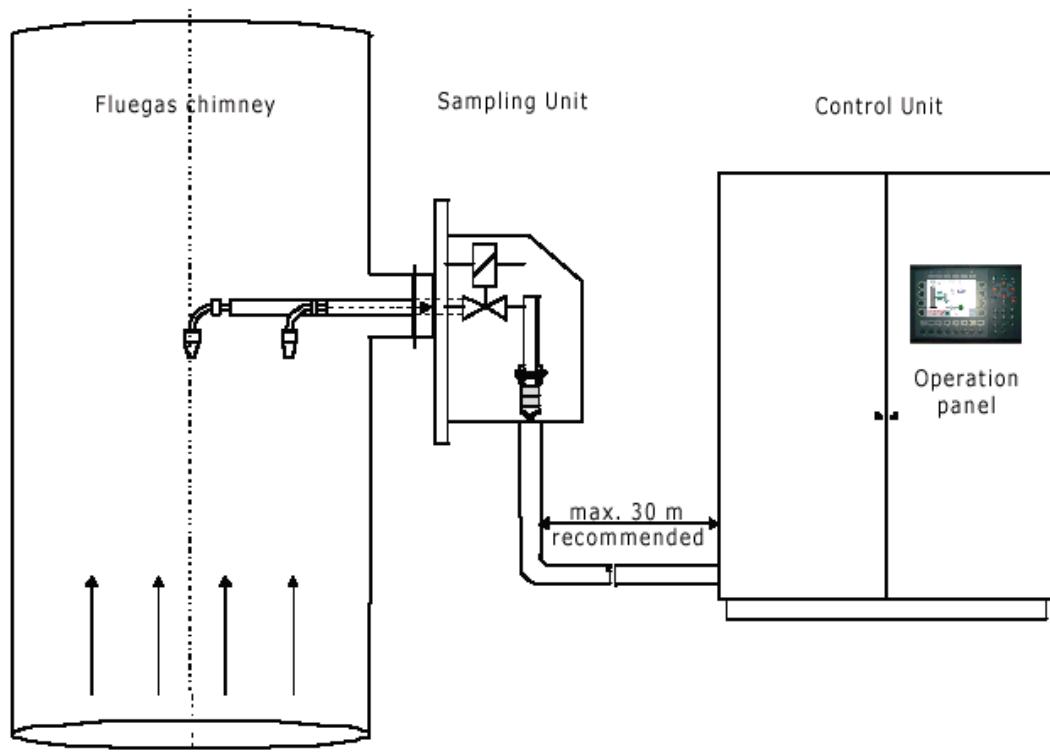
Key
Sampling Unit	This comprises of two sample probes, nozzles, thermocouple, the filter cartridge holder and the system to control the sampling.
Control Cable	A heated line, pressure lines and power cables.
Control unit	Contains the control systems required for sampling and the operator interface.

Table 3.4: DMS instrument information

Dioxin Monitoring System				
Type	**Model**	**Manuf. Serial No.**	**Condition**	**Range (Velocity)**
Dilution	DMS	200574-02	New	0-20 m/s

Table 3.5: DMS probe information

Item	**No Delivered**	**Dimensions**	**Condition**
Probe Tip	2	5.62mm	New
Temperature Sensor	1	n/a	New
Probe	1	1m	New
Union nut	1	n/a	New
Probe Elbow	1	n/a	New
Flange Connection	1	n/a	New
Cartridge Case	1	n/a	New
Ball Valve	1	n/a	New
GL-42 Union	1	n/a	New
Wobble Stick	1	n/a	New
Adsorber Cartridge	1	n/a	New
GL-32 screw union	1	n/a	New
Cartridge Case Heater	1	n/a	New
Umbilical	1	n/a	New
Control Cabinet	1	n/a	New
Analogue output cards	2	n/a	New

Table 3.6: DMS manual information

Author	**Serial No./Version**	**Condition**
Thomas Steiner, Monitoring Systems GmbH, Kottingbrun	M.820496-G19.01, Version: 001, 17/5/2002	New

3.2   Receipt condition report

The DMS and AMESA systems were new when delivered to AEA Technology for functionality tests and installed in the wind tunnel by the suppliers. Following the functionality tests, both CISDs were delivered to Sira for vibration and climate testing.

The CISDs were then moved to the first test site but during movement to Site 1, the AMESA system was damaged in a road traffic accident and returned to Germany for repair. The repaired AMESA system also suffered minor damage during movement back to the UK (glass condenser

units were broken and the data logger housing damaged). However, repairs were undertaken to return the unit to 'as new' condition prior to installation at Site 1. No problems were reported during the movement to, or installation at Site 2.

3.3   Manuals

The manuals gave clear instructions regarding the operation of the systems. Instructions on PCIMA cards formatting used for data storage in the AMESA system were not in the manual. Also, a diagram showing the specification and mounting arrangement of the flange required by the DMS probe system was not present in the manual. Both of these issues were resolved quickly and efficiently by the manufacturers.

4 Operating environmental testing

4.1 Variations in ambient temperature

4.1.1 Scope of testing

Sira undertook test work at their laboratory at Chislehurst to assess the leak-tightness of both CISDs at a range of ambient temperatures. There were no pass/fail criteria set for these tests as they were undertaken to investigate the validity of undertaking such tests.

4.1.2 Test procedures

The CISD was placed in a test chamber with all covers in place and the following temperature profile applied.

Table 4.1: Temperature test conditions

Temperature	Duration
+20ºC	for at least 30 minutes
-25ºC	for at least 30 minutes
+20ºC	for at least 30 minutes (DMS system only)
+50ºC	for at least 30 minutes
+20ºC	for at least 30 minutes

The upper and lower temperatures were the defined certification range for the equipment. Temperature measurements were made using an array of seven platinum resistance thermometers positioned at locations around the equipment.

At each temperature condition, the equipment was subjected to a leak test (note that the leak test was outside the scope of the UKAS accreditation of Sira). The sampling nozzles were sealed; the equipment subjected to a pressure of 31.1 kPa above atmospheric pressure and the pressure change over a period of five minutes was measured and recorded. Note that following initial test work, the pressure applied to the DMS system was 31.1 kPa below atmospheric pressure and the pressure change over a period of five minutes was measured and recorded.

4.1.3 Test results

DMS Sampler: The tests were undertaken as specified but significant pressure change was recorded over five minutes. The equipment incorporates vacuum fittings for joints and these were thought to be leaking at the elevated pressure applied for the leak test. The tests were modified to assess the leak-tightness of the system under a sub-atmospheric pressure. In normal operation the equipment is more likely to be operating below atmospheric pressure. An additional median temperature stage was included in the temperature tests for the DMS system. The results of the measurements are summarised in Table 4.2.

Table 4.2: Temperature test results (DMS System)

Temperature Condition, ºC (Limits)	Time at Condition (hours:mins)	Pressure Fall in 5 minutes (kPa)
+20.1 (± 0.3)	>4:15	1.1
-24.5 (± 0.3)	>3:00	1.8
+20.3 (± 0.5)	>4:30	1.1
+50.3 (± 0.7)	>1:30	1.6
+20.1 (± 0.4)	>5:00	1.3

Sira commented that 1.1 kPa was the minimum pressure rise that could be achieved regardless of the alignment of the internal vacuum fittings. However, it was subsequently discovered that the fittings were faulty and a new set of fittings was provided without repetition of the leak test.

AMESA Sampler: The tests were undertaken as specified. In normal operation, the equipment is more likely to be operating below atmospheric pressure. The results of the measurements are summarised in Table 4.3.

Table 4.3: Temperature test results (AMESA System)

Temperature Condition, ºC (Limits)	Time at Condition (hours:mins)	Pressure Fall in 5 minutes (kPa)
+20.1 (± 0.3)	>0:30	0.1
-24.5 (± 0.3)	>0:45	0.5
+50.2 (± 0.4)	>2:15	0.3
+20.0 (± 0.4)	>2:45	0.1

4.1.4   Conclusions

The leak test was found to be inappropriate for testing the sampling systems but there was no evidence from these tests that the sampling systems could not withstand operating temperatures of –25 to +50°C. Under normal use the sampling systems automatically carry out a leak test of the complete system at the beginning and end of each test. It should be noted however that the system does not carry out a leak test to the end of the sampling probe.

4.2   Vibration testing

4.2.1   Scope of testing

Sira undertook the test work in their laboratory at Chislehurst to assess the leak-tightness of the system following vibration in three perpendicular axes at a range of frequencies based on IEC 68-1/2 recommendations. There were no pass/fail criteria set for these tests as they were undertaken to investigate the validity of undertaking such tests.

4.2.2 Test procedures

The CISD was mounted using a purpose built fixture to a vibration table. Control accelerometers were mounted as close as possible to the mounting points of the equipment with their sensitive axes aligned with the axis of motion. Tests were repeated at three mutually perpendicular axes. Vibration control in all three axes was maintained using the average signal from the accelerometers.

A leak test was undertaken by sealing the equipment and applying a 31.1 kPa over-pressure and monitoring pressure loss over a period of five minutes. The leak test was undertaken before and after the vibration test on each axis.

A resonance sweep was undertaken to find any significant resonant frequencies. A five-sweep cycle endurance test was then undertaken and a further endurance test was undertaken at 50 Hz for two minutes.

Sinusoidal vibration was applied as follows: 10 – 60 Hz at 0.3 mm (peak to peak), 60 Hz – 150 Hz at 19.6 m/s^2 (peak) at a sweep rate of 1 Octave per minute.

Observed resonances were classified as slight, moderate or severe based on comparing the displacement of the vibration table to the resonating component.

4.2.3 Test results

DMS Sampler: The tests were undertaken as specified but significant pressure change was recorded over five minutes for the leak check. The equipment incorporates vacuum fittings for joints and these were thought to be leaking at the elevated pressure applied for the leak test. The tests were modified to assess the leak-tightness of the system under a sub-atmospheric pressure. In normal operation, the equipment is more likely to be operating below atmospheric pressure. Note that the equipment was mounted to the vibration table upside down. The results of the leak check measurements are summarised in Table 4.4.

Table 4.4: Leak check results (DMS System)

Axis	Initial Leak Check Pressure Rise in 5 minutes (kPa)	Post Test Leak Check Pressure Rise in 5 minutes (kPa)
1	0.7	0.9
2	1.0	1.0
3	1.0	1.0

The instrument exhibited some quite severe resonances during testing but did not appear to suffer any mechanical degradation.

AMESA Sampler: The tests were undertaken as specified but the leak tests were modified to assess the leak-tightness of the system under a sub-atmospheric pressure. In normal operation, the equipment is more likely to be operating below atmospheric pressure. The results of the leak check measurements are summarised in Table 4.5.

Table 4.5: Leak check results (AMESA System)

Axis	Initial Leak Check Pressure Rise in 5 minutes (kPa)	Post Test Leak Check Pressure Rise in 5 minutes (kPa)
1	0.2	0.1
2	0.1	0.1
3	0.1	0.2

The instrument exhibited some moderate resonances during testing but did not appear to suffer any mechanical degradation.

4.2.4 Conclusions

The leak test was found to be inappropriate for testing the sampling systems but there was no evidence from these tests that the sampling systems could not withstand the vibration frequencies applied. Under normal use the sampling systems automatically carry out a leak test of the complete system at the beginning and end of each test. It should be noted however that the system does not carry out a leak test to the end of the sampling probe.

5 Functionality tests

5.1 Scope of testing

Sampling of dioxins and furans must be undertaken isokinetically as these species are associated with both the gaseous and particulate phases found in process emissions. Consequently, the sampling performance of a CISD in maintaining isokinetic sampling is fundamental in ensuring accurate determination of dioxins and furans in process emissions. The CISD were therefore subjected to the following tests to assess the sampling performance of the system and the ability to collect a representative sample:

- ➢ Accuracy of isokinetic sampling;

- ➢ Response time;

- ➢ Linearity;

- ➢ Repeatability;

- ➢ Minimum operational velocity; and

- ➢ Short-term drift.

The tests were compatible with the tests described in the MCERTs performance standard for automatic isokinetic samplers.

5.2 Test procedures

5.2.1 Accredited procedures

The tests were conducted between 16-27 September 2003 by AEA Technology using a wind tunnel according to the UKAS-accredited AEA Technology Environment Group Working Instruction AEAT/ENV/EQ/WI/205.

5.2.2 Calibration

The CISDs were calibrated with the manufacturer's representative present and according to the manufacturer's instructions. A stable velocity of 15 m/s was generated in the wind tunnel and the output of the sampling system was then referred to this value. The velocity within the wind tunnel was measured using a reference pitot probe. The wind tunnel was operated continuously for a period of 15 minutes with the instrument manufacturer selecting a period within 15 minutes of operation for correlation.

5.2.3 Accuracy of isokinetic sampling

CISD are designed to operate for long periods. Consequently, the CISD sampling rate was determined by recording the volume sampled over a period of 30mins. The sampled volume was compared over a range of reference volumes calculated from the known velocity, the area of the nozzle, measured pressure and temperature. The isokinetic sampling accuracy of the equipment,

together with the accuracy of the readjustment of the volumetric sampling rate, was then assessed.

5.2.4   Response time

The response time (T_{90}) is defined as the time taken for the CISD to reach 90% of the expected response following introduction of a step change in velocity. The response time was measured with increasing and decreasing velocities over the range 2-20 m/s. The average of the response times provided the response time for the CISD. It was noted that both CISDs responded differently between ascending and descending velocities.

5.2.5   Linearity

The linearity of the isokinetic response of the CISD to changes in the velocity was tested over the full certification range of the CISD using at least five velocities approximately equally spaced across the range. The actual volume sampled by the CISD was compared with the reference volume assuming 100% isokinetic sampling at each velocity. The instrument response was assessed using the correlation coefficient procedure specified in the standard ISO 10155.

5.2.6   Repeatability

The repeatability of the CISD was determined from the measured statistical variation of the isokinetic sampling rate response of the equipment when a set velocity was generated using the wind tunnel. The repeatability is defined as:

$$C_R = t_f(0.95).X_R$$

where:

C_R is the repeatability expressed in volume units;

X_R is the standard deviation of the measurements;

t_f is the student t probability where there are n-1 degrees of freedom at the 95% confidence level;

(0.95) shows that the 95% confidence level is used for the student t-factor.

Sampled gas volume was measured over a period of four times the response time on five occasions at a single velocity. The repeatability value determined by this test using the above equation was expressed as a percentage of the calculated volume at the set velocity.

5.2.7   Minimum operational velocity

The minimum operating flue gas velocity, below which the equipment fails to respond isokinetically, was determined by increasing the velocity of the sample, using the wind tunnel, from zero until the equipment responded with a performance within the linearity criteria. This parameter was also determined starting from an initial velocity of 1.1 m/s and reducing the velocity in stages to 0.1 m/s. However, it should be noted that the system can be set to stop sampling at a given value and provides a means of controlling the sampling of the system relative to the process the unit is monitoring.

5.2.8 Short term drift

The isokinetic response of the CISD to a set gas velocity (10 m/s) was observed over a period of five hours, to check for the presence of drift. The recorded drift of the equipment was the largest deviation of the averaged output values from the set point.

5.3 Functionality test results

5.3.1 AMESA CISD

The results obtained to assess the accuracy of isokinetic sampling for the AMESA system are summarised in Table 5.1 below.

Table 5.1: Sampling accuracy of AMESA

Test No.	CISD Volume (m^3)	Reference Volume (m^3)	Difference (%)
1	0.089	0.089	0.0%
2	0.152	0.154	1.3%
3	0.225	0.229	1.7%
4	0.302	0.307	1.6%
5	0.382	0.389	1.8%
6	0.461	0.460	-0.2%
7	0.544	0.539	-0.9%
8	0.624	0.613	-1.8%
			Max = 1.8

Table 5.2 summarises the recorded response times for the AMESA system.

Table 5.2: Response time of AMESA

Test	Response Time (T_{90})	
	Step Up (s)	**Step Down (s)**
1	68	53
2	67	50
3	50	57
4	53	74
5	48	70
6	52	64
Mean	**56**	**61**

The results obtained in the linearity test for the AMESA System are provided in Table 5.3, together with the parameters of the regression line and in Figure 5.1.

Table 5.3: Linearity of AMESA sampling

Applied Velocity (m/s)	Isokinetic Theoretical Volume (m^3)	AMESA Sampled Volume (m^3)
2.5	0.089	0.089
5.0	0.154	0.152
7.4	0.229	0.225
10.0	0.307	0.302
12.5	0.389	0.382
15.0	0.460	0.461
17.5	0.539	0.544
20.0	0.613	0.624

Regression Parameters	
Slope:	1.012
Intercept:	0.007
Correlation Coefficient:	0.999

The results obtained in the repeatability tests for the AMESA System are provided in Table 5.4

Table 5.4: Repeatability of AMESA

Run	AMESA Sampled Volume (m^3)
1	0.332
2	0.330
3	0.333
4	0.332
5	0.331

Mean sampled volume (m^3)	0.332
Standard deviation (X_R in m^3)	0.0011
Student t factor	2.78
Repeatability (m^3)	0.003
Calculated repeatability (%)	0.9
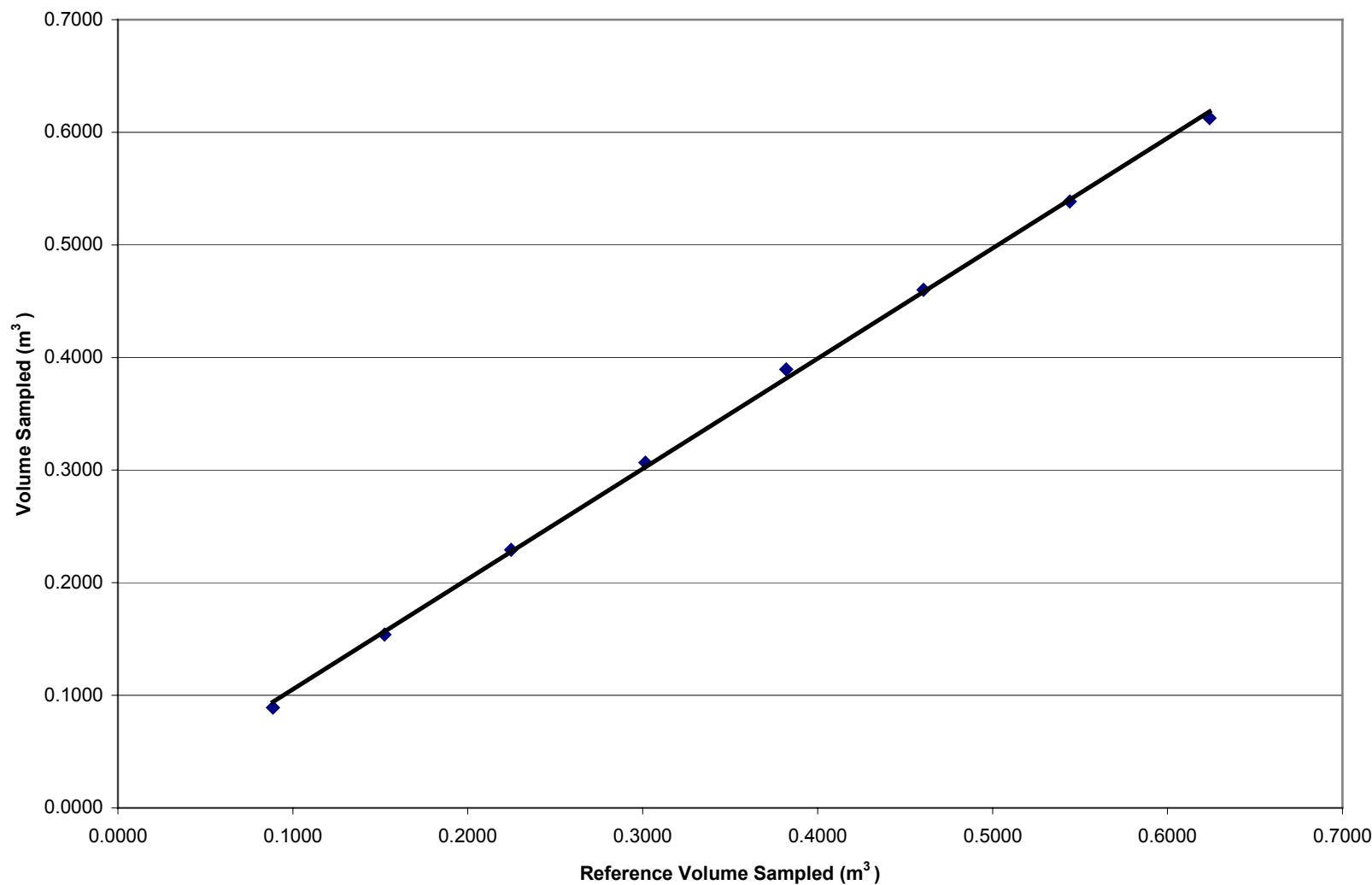
Figure 5.1: Linearity of AMESA Response to Changes in Velocity

The results of the determination of lower operating velocity for the AMESA System are summarised in Table 5.5. The minimum operational velocity for the AMESA System was determined to be 0.5 m. s^{-1}.

Table 5.5: Determination of minimum operating velocity for AMESA system

Decreasing Velocity (m/s)	System Mode	Increasing Velocity (m/s)	System Mode
1.0	Operational	0.1	Shut Down
0.8	Operational	0.2	Shut Down
0.7	Operational	0.3	Shut Down
0.6	Operational	0.4	Shut Down
0.5	Operational	0.5	Operational
0.4	Shut Down	0.6	Operational
		0.7	Operational
		0.8	Operational
		0.9	Operational
		1.0	Operational
		1.1	Operational

The drift of the sampler was assessed by measuring the volume sampled every hour, for a period of five hours at a fixed tunnel wind velocity of 10m/s. An initial measurement of the volume sampled by the system. This was then used as the span point from which deviations were measured. The data is summarised in Table 5.6 showing that the short- term drift for the AMESA system was 0.6%.

Table 5.6: Short-term instrument drift for the AMESA

Elapsed Time (h)	Volume Sampled (m^3)	Drift (%)
1	0.1542	0.1
2	0.1540	-0.1
3	0.1532	-0.6
4	0.1540	-0.1
5	0.1550	0.6
	Set Point = 0.1541	Max = 0.6

5.3.2 DMS system

The results obtained to assess the accuracy of isokinetic sampling for the DMS system are given in Table 5.7 below.

Table 5.7: Sampling accuracy of DMS

Test	CISD Volume (m^3)	Reference Volume (m^3)	Difference (%)
1	0.108	0.107	-0.9%
2	0.235	0.232	-1.3%
3	0.385	0.380	-1.3%
4	0.448	0.447	-0.2%
5	0.559	0.558	-0.2%
6	0.672	0.670	-0.3%
7	0.784	0.782	-0.3%
8	0.897	0.893	-0.4%
		Max =	**1.3**

Note: The volume sampled by the DMS is calculated from gas meter readings.

Table 5.8 summarises the recorded response times for the DMS system.

Table 5.8: Response time of DMS

Test	Response Time (T_{90})	
	Step Up (s)	**Step Up (s)**
1	57	52
2	56	55
3	68	62
4	68	62
5	64	60
6	57	57
Mean	**62**	**58**

The results obtained in the linearity test for the DMS System are provided in Table 5.9, together with the parameters of the regression line and in Figure 5.2.

Table 5.9: Linearity of DMS sampling

| Applied Velocity (m/s)	Isokinetic Theoretical Volume (m^3)	DMS Sampled Volume (m^3)
2.4	0.107	0.108
5.2	0.232	0.235
8.5	0.380	0.385
10.0	0.447	0.448
12.5	0.558	0.559
15.0	0.670	0.672
17.5	0.782	0.785
20.0	0.893	0.897

Regression Parameters	
Slope:	1.002
Intercept:	-0.002
Correlation Coefficient:	1.000

The results obtained in the repeatability tests for the DMS System are provided in Table 5.10.

Table 5.10: Repeatability of DMS

Run	DMS Sampled Volume (m^3)
1	0.293
2	0.294
3	0.293
4	0.296
5	0.296

Mean Sampled Volume (m^3)	0.294
Standard Deviation (X_R in m^3)	0.002
Student t factor	2.78
Repeatability (m^3)	0.004
Calculated Repeatability (%)	1.5%
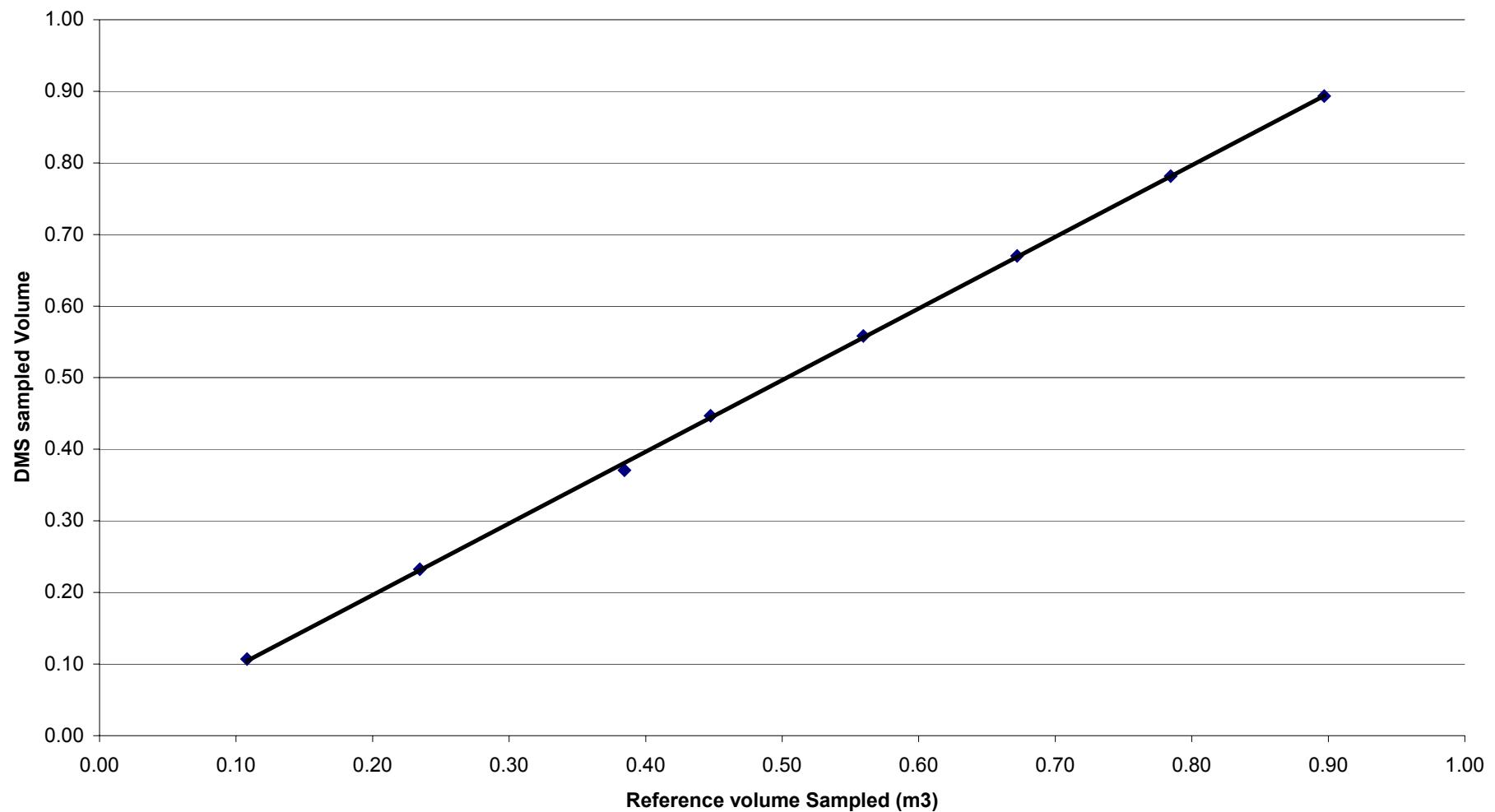
Figure 5.2: Linearity of DMS Response to Changes in Velocity

The results of the determination of lower operating velocity for the DMS System are summarised in Table 5.11. The minimum operational velocity for the DMS System was determined to be 1.0 m. s^{-1}.

Table 5.11: Determination of minimum operating velocity for DMS system

Decreasing Velocity (m/s)	System Mode	Increasing Velocity (m/s)	System Mode
1.0	Operational	0.1	Shut Down
0.8	Shut Down	0.2	Shut Down
0.7	Shut Down	0.3	Shut Down
0.6	Shut Down	0.4	Shut Down
0.5	Shut Down	0.5	Shut Down
0.4	Shut Down	0.6	Shut Down
		0.7	Shut Down
		0.8	Shut Down
		0.9	Shut Down
		1.0	Shut Down
		1.1	Operational

The drift of the CISD was assessed by measuring the volume sampled every hour, for a period of five hours at a fixed tunnel wind velocity of 10 m/s. This was then compared to an initial volume taken at time zero under the same conditions. The data is summarised in Table 5.12 showing that the short-term drift for the DMS system was 0.8%.

Table 5.12: Short -Term instrument drift for the DMS system

Elapsed Time (h)	Volume Sampled (m^3)	Drift (%)
1	0.1476	0.4
2	0.1483	0.9
3	0.1470	0.0
4	0.1478	0.5
5	0.1462	-0.5
	Set Point = 0.1470	**Max = 0.9**

5.4 Conclusions

5.4.1 AMESA

The determined performance characteristics for the AMESA system are compared with the performance requirements in Table 5.13. The AMESA system met the performance requirements of Table 6.1 of the MCERTS Performance Standard.

Table 5.13: Assessment of AMESA system against the performance requirements

Performance Characteristic	Performance Requirement	Performance Result	Decision
Accuracy of isokinetic sampling rate to changes in velocity	$<\pm5.0\%$	1.8%	Pass
Accuracy of determination of volume of gas sampled	$<\pm2.0\%$	1.8%	Pass
Response time, T_{90} (seconds)	<200	56-61	Pass
Linearity of isokinetic sampling rate to changes in velocity	$R^2 => 0.980$	$R^2 = 0.999$	Pass
Repeatability under laboratory conditions	$<5\%$	0.9%	Pass
Minimum operational velocity (m. s^{-1})	<2.0	0.5	Pass
Drift (Short Term)	$<\pm5\%$	0.6	Pass

5.4.2 DMS sampling system

The determined performance characteristics for the DMS system are compared with the performance requirements in Table 5.14.

Table 5.14: Assessment of DMS system against the performance requirements

Performance Characteristic	Performance Requirement	Performance Result	Decision
Accuracy of isokinetic sampling rate to changes in velocity	$<\pm5.0\%$	1.3%	Pass
Accuracy of determination of volume of gas sampled	$<\pm2.0\%$	1.3%	Pass
Response time, T_{90} (seconds)	<200	58-62	Pass
Linearity of isokinetic sampling rate to changes in velocity	$R^2 => 0.980$	$R^2 = 1.000$	Pass
Repeatability under laboratory conditions	$<5\%$	1.5%	Pass
Minimum operational velocity (m/s)	<2.0	1.0	Pass
Drift (Short Term)	$<\pm5\%$	0.9	Pass

The DMS system passed the performance requirements of Table 6.1 of the MCERTS Performance Standard.

6 Field testing (site 1)

6.1 Overview

The two CISDs were subjected to comparative sampling tests at a MSW incinerator, using two manual sampling trains (MSTs) in accordance with BS EN 1948 as specified by the MCERTs project steering body and as detailed in Table 6.1. The achieved sampling plan is shown in Table 6.2.

Table 6.1: Required test details (Site 1)

Weeks	MST Sample Details	CISD Sample Details
Pre-trial	Field Blank x 2 samples	None
1-2	8 x 2 (6-hour samples)	8 x matching 6-hour samples
2	None	1 x 6 day sample
3-4	None	1 x 14 day sample
5-6	7 x 2 (6-hour samples) taken every other day	1 x 14 day sample*
7-10	7 x 2 (6-hour samples) taken every fourth day	1 x 28 day sample*
11	None	1 x 7 day sample
12	7 x 2 (6-hour samples)	7 x matching 6-hour samples
Post-trial	Field Blank x 2 samples	Field Blanks x 2
Total	**62**	**20**

* Some additional samples were taken and analysed to check for breakthrough.

6.2 Test site

6.2.1 Plant description

The MSW incinerator burns municipal waste in two furnace units operated in parallel, with emissions vented to the atmosphere via a single stack. Each line has a separate and independent abatement system. Primary air is supplied at the bottom of each of the two furnace units. The furnaces are fitted with reverse reciprocating grates and with front and rear secondary air injections in the vertical combustion chamber. A dry absorption abatement system is used to abate pollutants in the flue gases. The flue gases are cooled in economisers to produce steam and to reduce the flue gas temperatures to the correct temperature for efficient reaction with the absorbent chemicals.

The gases enter a duct section where sorbents are injected and mixed with the gases. Dry lime (calcium hydroxide) is used to achieve acid gas removal while activated carbon mixed with the lime enhances mercury and dioxin removal. The mixed flue gases and entrained particulate then pass to a fabric filter where the dust is removed together with the absorbed acid gases, mercury and dioxins. The fabric filters are periodically cleaned using reverse air jet pulses. Some of the dust collected in the filter still contains un-reacted lime and a portion of the dust is recycled.

Table 6.2: Sampling details (Site 1)

Start Date	End Date	Test Times	Manual	AMESA	DMS	Comments
			Test Numbers			
01/04/2003	01/04/2003		Field blank 1			
01/04/2003	01/04/2003		Field blank 2			
02/04/2003	02/04/2003	1111-1722	1A	1	1	6hr test
02/04/2003	02/04/2003	1111-1722	1B			
03/04/2003	03/04/2003	0742-1450	2A	2	2	6hr test
03/04/2003	03/04/2003	0742-1450	2B			
03/04/2003	03/04/2003	1514-2130	3A	3	3	6hr test
03/04/2003	03/04/2003	1514-2130	3B			
09/04/2003	09/04/2003	0837-1450	4A	4	4	6hr test
09/04/2003	09/04/2003	1158-1450	4B			
09/04/2003	09/04/2003	1640-2250	5A	5	5	6hr test
09/04/2003	09/04/2003	1640-2250	5B			
10/04/2003	10/04/2003	0827-1443	6A	6	6	6hr test
10/04/2003	10/04/2003	0827-1447	6B			
10/04/2003	10/04/2003	1628-2255	7A	7	7	6hr test
10/04/2003	10/04/2003	1628-2255	7B			
11/04/2003	11/04/2003	0939-1545	8A	8	8	6hr test
11/04/2003	11/04/2003	0938-1545	8B			
11/04/2003	25/04/2003	1725		9	9	14 day test
28/04/2003	12/05/2003			10	10	14 day test
28/04/2003	28/04/2003	1113-1722	10A			
28/04/2003	28/04/2003	1114-1725	10B			
02/05/2003	02/05/2003	0846-1500	10C			
02/05/2003	02/05/2003	0846-1500	10D			
04/05/2003	04/05/2003	0839-1445	10E			
04/05/2003	04/05/2003	0839-1447	10F			
06/05/2003	06/05/2003	0843-1449	10G			
06/05/2003	06/05/2003	0843-1449	10H			
08/05/2003	08/05/2003	0853-1500	10I			
08/05/2003	08/05/2003	0854-1600	10J			
10/05/2003	10/05/2003	0844-1458	10K			
10/05/2003	10/05/2003	0844-1458	10L			

Table 6.2: Sampling details (Site 1) continued

Start Date	End Date	Test Times	Test Numbers Manual	AMESA	DMS	Comments
12/05/2003	08/06/2003			11	11	28 day test
12/05/2003	12/05/2003	1135-1745	11A			
12/05/2003	12/05/2003	1135-1745	11B			
16/05/2001	16/05/2001	0855-1503	11C			
16/05/2003	16/05/2003	0857-1509	11D			
20/05/2003	20/05/2003	0828-1445	11E			
20/05/2003	20/05/2003	0830-1445	11F			
24/05/2003	24/05/2003	0822-1442	11G			
24/05/2003	24/05/2003	0823-1442	11H			
28/05/2003	28/05/2003	0817-1500	11I			
28/05/2003	28/05/2003	0818-1500	11J			
01/06/2003	01/06/2003	0813-1420	11K			
01/06/2003	01/06/2003	0814-1420	11L			
05/06/2003	05/06/2003	0907-1515	11M			
05/06/2003	05/06/2003	0908-1515	11N			
08/06/2003	16/06/2003			12	12	10 day test
16/06/2003	16/06/2003	1026-1637	13A	13	13	6hr test
16/06/2003	16/06/2003	1027-1637	13B			
17/06/2003	17/06/2003	0928-1539	14A	14	14	6hr test
17/06/2003	17/06/2003	0927-1539	14B			
18/06/2003	18/06/2003	0949-1553	15A	15	15	6hr test
18/06/2003	18/06/2003	0950-1553	15B			
19/06/2003	19/06/2003	0655-1301	16A	16	16	6hr test
19/06/2003	19/06/2003	0656-1301	16B			
19/06/2003	19/06/2003	1434-2045	17A	17	17	6hr test
19/06/2003	19/06/2003	1436-2045	17B			
20/06/2003	20/06/2003	0812-1418	18A	18	18	6hr test
20/06/2003	20/06/2003	0813-1418	18B			
20/06/2003	20/06/2003	1531-2140	19A	19	19	6hr test
20/06/2003	20/06/2003	1531-2140	19B			
20/06/2003	20/06/2003		Blank 3			
20/06/2003	20/06/2003		Blank 4			
20/06/2003	26/06/2003			20		6 days
26/06/2003	28/06/2003			21	21	2 days

The remaining part of the dust is discharged to the end product silo into containers for disposal.

Additional ports were installed in the stack to accommodate the test systems and to enable the MST measurements to be made in close proximity to the test system probes.

For reasons of security, the sampler systems were located in a designated cabin measuring 4m x 2m. The cabin was situated in close proximity to the sample plane on the outlet duct from the number 2 unit.

6.2.2 Duct velocity profile

The velocity profile obtained across the sampling plane at Site 1 prior to the trial is summarised in Table 6.3 and Figure 6.1.

Table 6.3: Velocity profile (Site 1)

Distance from wall	Sampling Line (m/s)		
(cm)	A	B	C
7	18.0	18.0	16.8
21	18.0	18.4	18.1
35	17.8	19.0	18.7
49	19.0	19.1	19.0
63	19.0	18.9	19.0
77	19.8	19.4	19.2
91	20.0	19.6	19.2
105	19.8	19.9	19.1
119	20.1	19.8	18.6
133	19.8	20.1	18.9
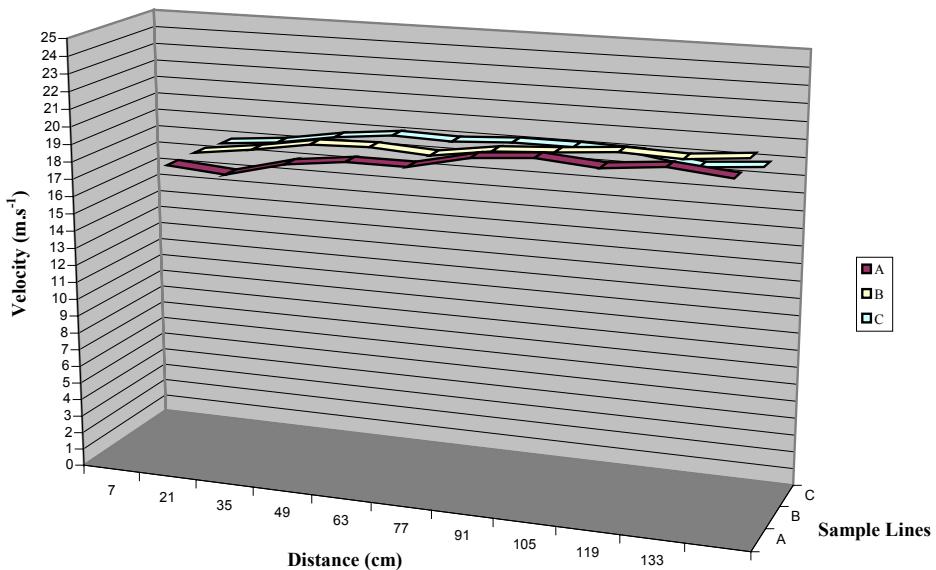
Figure 6.1: Flow profile (Site 1)

Table 6.4 and Figure 6.2 show the temperature profile data across the sampling plane at Site 1.

Table 6.4: Temperature profile at Site 1

Distance from wall (cm)	Sampling Line (°C)		
	A	**B**	**C**
7	136	135	135
21	136	135	135
35	136	135	135
49	136	136	135
63	136	136	135
77	136	136	135
91	137	136	135
105	137	136	136
119	136	136	136
133	136	136	135
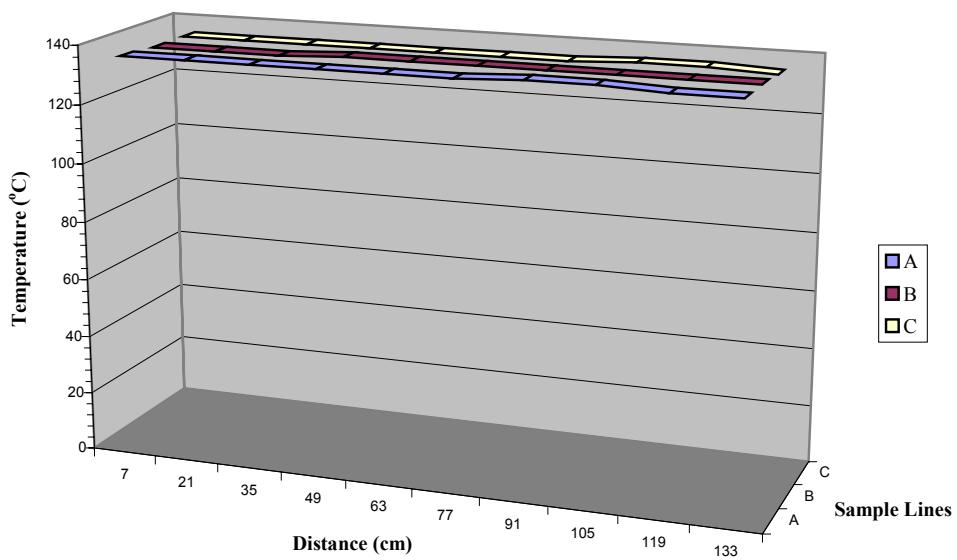
Figure 6.2: Temperature profile at Site 1

Table 6.5 and Figure 6.3 show the oxygen profile across the sampling plane at Site 1.

Table 6.5: Oxygen profile at Site 1

Distance from wall	Sampling Line (%)		
(cm)	A	B	C
7	10.4	10.4	11.5
21	10.0	10.3	10.8
35	9.94	10.4	10.9
49	10.3	11.3	10.1
63	9.66	10.1	10.8
77	9.76	10.3	10.7
91	10.1	10.7	11.0
105	9.74	10.2	11.1
119	9.60	9.85	10.6
133	9.76	10.3	9.60
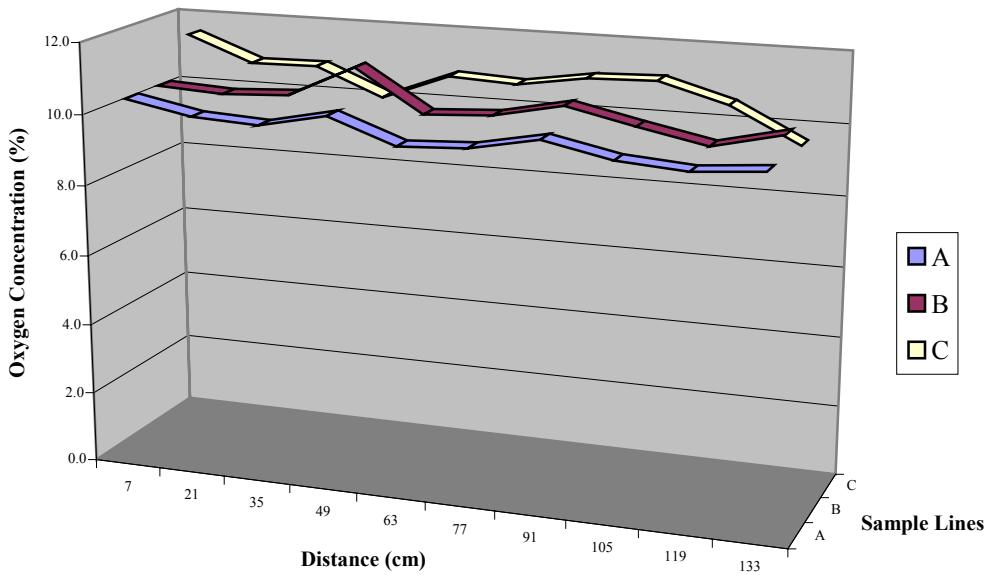
Figure 6.3: Oxygen profile at Site 1

Figure 6.3 shows some variation in oxygen concentration but this is associated with the variation produced by the control system of the plant, which adjusts the amount of air introduced to ensure good combustion is maintained. This results in an observed range of 9 to 12 % in the oxygen concentration with a typical average of 10.0%.

The sample line profile data shows that the sampling position meets the requirements of recognised particulate sampling standards as follows:

> the angle of gas flow is less than 15° with regard to the duct axis (a recommended method for estimation is indicated in section 5.2 a) of BS EN 13284-1:2001 Stationary source emissions – Determination of low range mass concentration of dust – Part 1 Manual gravimetric method ;

> no local negative flow is present;

> the minimum velocity is higher than the detection limit of the method used for the flow rate measurement (for Pitot tubes, a differential pressure larger than 5 Pa);

> the ratio of the highest to lowest local gas velocities is less than 3:1.

6.2.3   Plant operation during evaluation period

The MSW operated at normal load throughout the test programme except during the periods identified in Table 6.6 as boiler tube failure when the unit was shutdown to allow investigation and repair of the fault.

The start-up procedure involves the use of gas burners to raise the temperature of the unit. Waste is then fed in once the furnace temperature has exceeded 850°C. The burners then act as support to maintain the temperature above 850°C until waste has covered the grate and can maintain the unit temperature. It is during this phase (i.e. when the grate is being covered by

waste) that dioxin production is likely to be at its highest as a result of the combustion conditions and since the abatement equipment will not have stabilised. Figure 6.4 shows the start-up temperature profile.

**Table 6.6: Summary of plant shutdowns at Site 1**

Period	Fault Description
16 March 2003	Shut-down
16 March 2003	Plant off-line for tube cleaning
19 March 2003 – 20 March 2003	Start-up
0900 04 April 2003	Shut Down
04 April 2003 - 08 April 2003	Boiler tube failure
18:00 08 April	Start-up
21:40 28 April	Shut Down
29 April 2003 - 01 May 2003	Boiler tube failure
1430 1 May 2003	Start-up
7 May 2003	Feed stopped for 1 hour to clear a grate problem
29 May 2003	Feed stopped to clear a grate problem
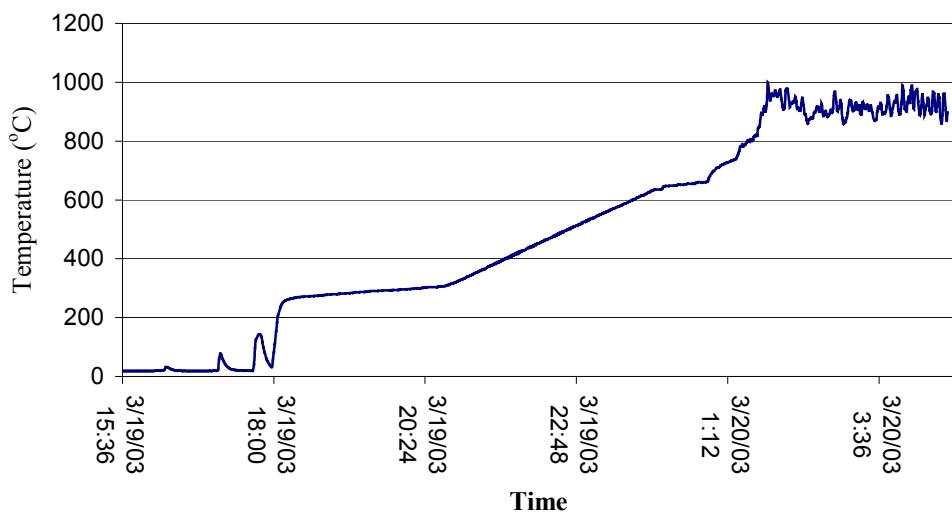
Figure 6.4: Start-up temperature profile at Site 1

6.3   Sampling positions

The sampling plane was in the outlet duct, 3m above the inlet to the ID fan and 3.45m downstream of the nearest bend as shown in Figure 6.5. A plan view of the sampling plan in Figure 6.6 shows the sampling position with the CISD samplers and the two MST probes installed.
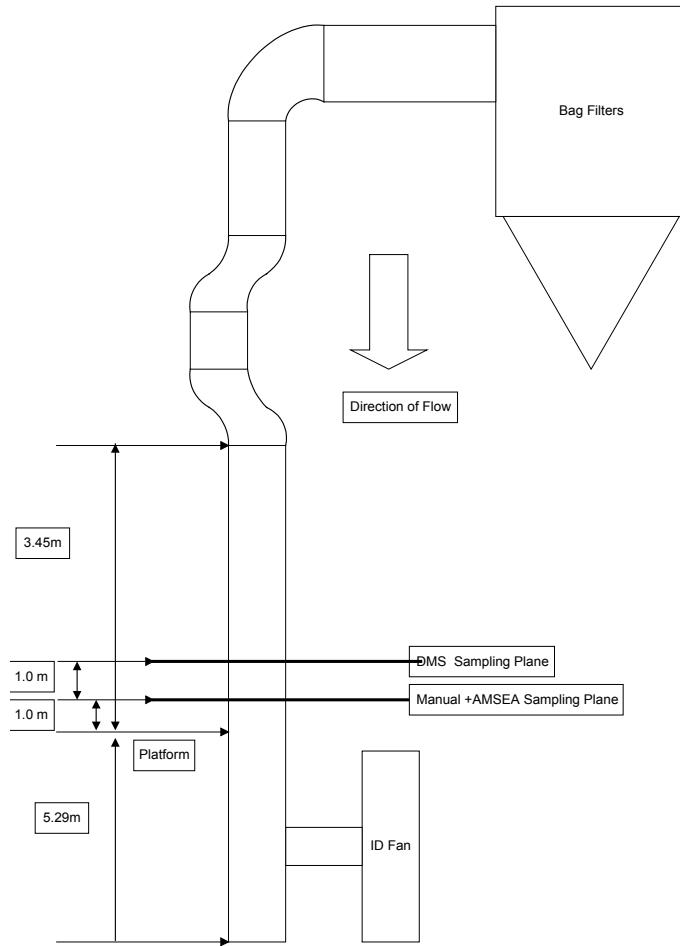
Figure 6.5: Schematic diagram of the sampling plane (Site 1)
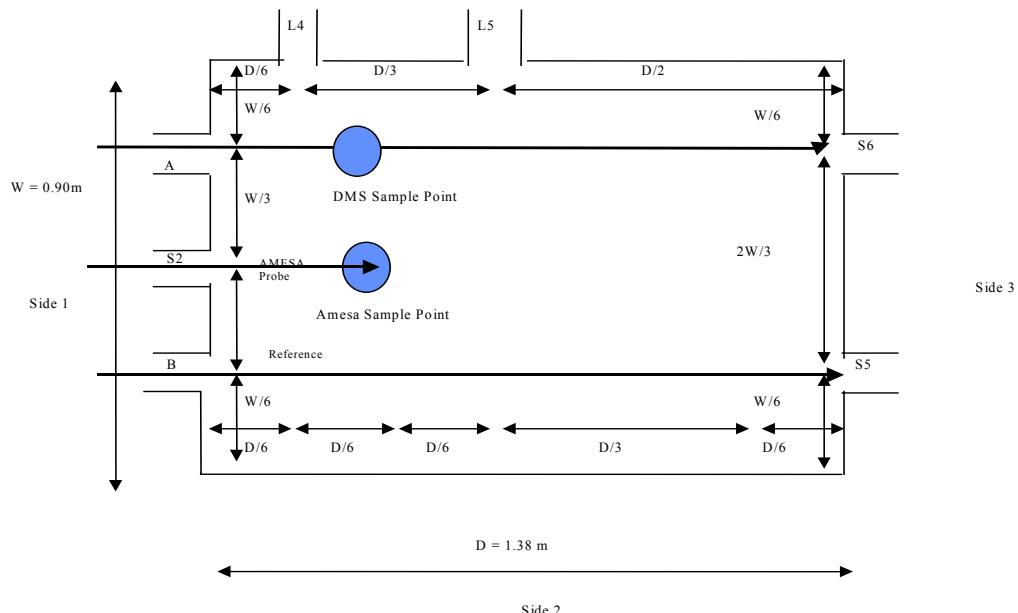
Figure 6.6: Plan view of the sampling plane (Site 1)

6.4   Installation of CISD

The ductwork at the test site was modified to accept the CISD system probes by the installation of the necessary flanges on 23 January 2003. This work had to be undertaken during a plant shut down due to the proximity of an ID fan. In addition to ductwork modifications supplies of air, cooling water and plant operation triggers were installed.

The DMS system was installed over a two-day period (23 and 24 January 2003).

The AMESA system was moved to the test site on Tuesday 28 January 2003, but unfortunately it was damaged in transit. This damage required the unit to be returned to Germany. The repaired system was transported to site 24 February 2003 and installed and commissioned by two AMESA engineers on 3 March 2003.

Each manufacturer's representative installed the test systems accompanied by Alan Leonard of Netcen.

Initially it was proposed to position the CISDs together in one plane and operate the two MSTs in another plane. However, a permanent access platform had been installed close to the required plane between the initial site visit and the installation of the flanges restricting access to these positions. Also the flange initially installed for the DMS system was incorrect as a larger flange was required. This meant that the cartridge holder of the AMESA could not be installed alongside the DMS. Subsequently, the AMESA was installed centrally in the same plane as the MSTs. This is illustrated in Figure 6.7.
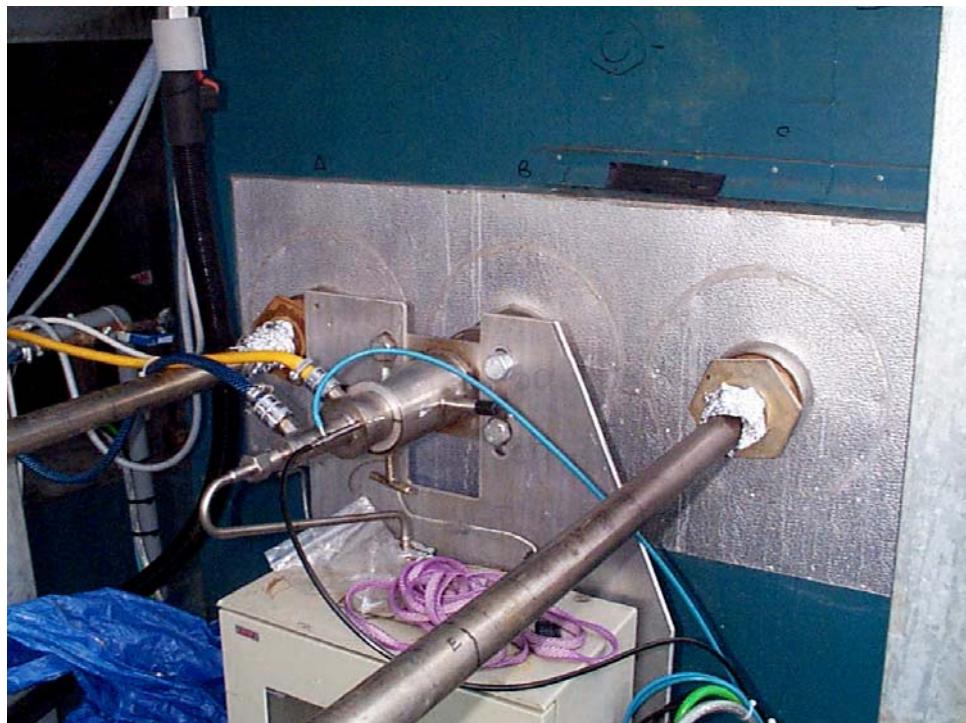
Figure 6.7: Sampling position (Site 1)

6.5   CISD configuration

The following paragraphs describe each of the CISDs as installed at Site 1.

6.5.1   AMESA

The AMESA system installed at Site 1 was configured to utilise a water-cooled probe with the aim of condensing water vapour prior to passage through the resin in the cartridge. The site water supply was used for this purpose. The probe used a nozzle, liner and cartridge box coupling constructed of titanium. The resin cartridge comprised of a brown glass tube with a frit at the base to support the resin. At the top of the resin bed a plug of glass wool was used to filter out particulate material. These cartridges were packed and spiked by the Environment Agency's National Laboratory Service (NLS), Leeds. A trace-heated line was used to transfer the sample from the cartridge holder. The cartridge holder utilises trace heating to ensure that the sample did not freeze during the period of the test. These options were required as the cartridge box and sample transfer line is exposed. The plant oxygen and flow measurement values were configured to enable a plant off trigger to stop and start sampling. The condensate obtained from the sampling system was collected to allow determination of whether there had been any significant break through.

6.5.2   DMS

The DMS system installed at Site 1 was configured in its standard set-up of a twin probe dilution system. Air required for the system was taken from the site's compressed air supply and passed through two coalescence filters to ensure it was dry and particulate free.

A trace-heated line was used to transfer the sample from the probe system to the control unit. The probe system is constructed of titanium and titanium nozzles were installed on to the probes. The filter holder assembly is heated. The cartridges that are installed into the probe assembly are also made of titanium. Within the cartridges, the filter assembly consists of an initial particulate filter followed by two polyurethane foam filters (PUF) to absorb the dioxins. These cartridges were put together and spiked with dioxin labelled standards by NLS. The plant oxygen and flow measurement values were set to enable a plant off trigger to stop and start sampling.

6.6   AES test procedures

The field tests were conducted by Alan Leonard of Netcen and Bill Heslop of AES in accordance with the AES Working Instructions summarised in Table 6.7. AES are accredited by UKAS (UKAS No. 1181) and certified under MCERTS for the sampling of stacks for dioxins, furans, oxygen, flow and moisture. Bill Heslop had achieved MCERTS Level 2 qualification for stack-emission monitoring personnel.

Table 6.7: AES test procedures (Site 1)

Determinant	Test House Document	Reference Method	Description	UKAS Accredited
Dioxins and Furans Flow Moisture	AES A47	BS EN 1948	A representative sample was extracted from the gas stream under isokinetic conditions using a number of sampling points across the duct. The dioxins and furans were collected in an absorbent trap containing XAD-2 resin. To avoid contamination the adsorbent trap and XAD-2 resin were prepared by the AES organic laboratory prior to going to site. This involved, cleaning and drying. The resin traps were spiked by the NLS laboratory prior to sampling.	Yes
Oxygen	AES 32	Instrument Manuals	Direct measurement of the concentration of oxygen in the gas stream using a Servomex Paramagnetic Analyser or Land Combustion Zirconium Probe	Yes

6.7 NLS test procedure

The samples were analysed for tetra through to octa chlorinated dioxins and furans by the Environment Agency's National Laboratory Service (NLS) at Leeds (UKAS Accreditation No 120) using the method detailed in NLS Document HRMS005, in accordance with BS EN 1948.

Method summary: Adsorbent samples are extracted into toluene using a Dionex Accelerated Solvent Extraction (ASE)^{TM} system. Aqueous fractions are extracted with dichloromethane. These two fractions are concentrated and combined along with toluene/acetone washings and concentrated again. The extract is cleaned up to remove fats, sulphur and other interfering compounds. A three-stage clean-up/separation is performed. The sample is first treated with activated, acidic and basic silica gel to remove fats and organic contaminants before being passed through an automated Gel Permeation Chromatography GPC system where contaminants are removed on a size-exclusion basis. The sample is then fractionated using an Alumina LC column to separate the dioxins and furans from the polychlorinated biphenyls (PCBs) before being concentrated to a volume suitable for injection onto a capillary GC system. Analysis is by High-Resolution GC-MS (HR GC-MS) using split-less injection onto a capillary GC column. Quantitation is based upon the isotope dilution method. ^{13}C labelled isotopes of the compounds of interest are added to the sample before extraction and these isotopes are used for quantitation as well as internal standards to correct for losses of each individual isotope of interest in the extraction and clean-up stages. Results are quoted on an individual native isomer basis although total native dioxin and furan isomer results for each level of chlorination can also be quoted along with an International Toxic Equivalent (I-TEQ) value. The NLS procedure performance data is summarised in Table 6.8.

Table 6.8: NLS procedure HRMS005 performance data

Determinant	Standard Solution (unextracted)			
	Concentration ($\mu g\ l^{-1}$)	% RSD	% Bias	L.O.D (ρg)
2, 3, 7, 8 – TCDF	16	10.2	-6.2	1.08
2, 3, 7, 8 – TCDD	16	9.8	6.4	0.35
1, 2, 3, 7, 8 – P_eCDF	32	10.6	-2.9	0.62
2, 3, 4, 7, 8 - P_eCDF	32	4.7	-3.1	1.44
2, 3, 4, 7, 8 - P_eCDD	32	7.6	-3.0	0.39
1, 2, 3, 4, 7, 8 - H_xCDF	32	10.2	3.1	1.04
1, 2, 3, 6, 7, 8 - H_xCDF	32	11.0	3.2	0.45
2, 3, 4, 6, 7, 8 - H_xCDF	32	7.8	3.2	0.96
1, 2, 3, 7, 8, 9 - H_xCDF	32	12.2	3.2	0.70
1, 2, 3, 4, 7, 8 - H_xCDD	32	7.3	3.2	0.64
1, 2, 3, 6, 7, 8 - H_xCDD	32	8.6	-3.0	0.86
1, 2, 3, 7, 8, 9 - H_xCDD	32	10.2	3.2	3.35
1, 2, 3, 4, 6, 7, 8 - H_pCDF	64	8.7	-1.5	1.12
1, 2, 3, 4, 7, 8, 9 - H_pCDF	64	17.2	-1.4	0.88
1, 2, 3, 4, 6, 7, 8 - H_pCDD	64	7.8	1.6	1.44
OCDF	64	7.3	-1.6	4.29
OCDD	64	8.6	-1.5	8.23

6.8   Manual sampling trains

Two manual sampling trains (MSTs) were used to sample simultaneously. The sampling was undertaken in accordance with BS EN 1948. However, as a result of the AMESA system being positioned in the sample line only two of the three sample lines were sampled. Five points were sampled on each sample line. The systems were compliant with the filter/condenser configuration described in BS EN 1948. Both probe liners and nozzles were made of titanium. The systems used 0.39 and 0.45 cm diameter nozzles.

6.9   Test results

The concentrations determined in these tests are reported in ng I-TEQ /m^3 at reference conditions of 11% O_2, dry. These conditions were adopted as this convention is specified in the WID and hence adopted by the Environment Agency for dioxins emission reporting. Table 6.9 summarises the results of the dioxin and furan comparisons. The oxygen concentration measured by the sampling team was used to determine the dioxin and furan concentrations at reference conditions for all the measurement systems. This ensured that no differences were caused by the measurement of oxygen and only related to the volume sampled by each system, which is the parameter that all of the units report.

Table 6.9: Summary of dioxin and furan measurements (Site 1)

Test No.	Total Dioxin and Furan Concentration ng I-TEQ /m³			
	MST 1	MST 2	DMS	AMESA
1	0.020	0.004	0.038	0.104
2	0.006	0.002	0.026	0.103
3	0.006	0.002	0.019	0.068
4	0.042	0.054	0.126	0.201
5	0.031	0.018	0.066	0.096
6	0.020	0.026	0.043	0.062
7	0.009	0.007	0.029	0.038
8	0.037	0.012	0.028	0.046
9			0.008	0.017
10	0.002	0.004	0.252	0.059
	0.057	0.068		
	0.012	0.040		
	0.010	0.021		
	0.006	0.016		
	0.007	0.020		
11	0.007	0.188	0.034	0.022
	0.006	0.035		
	0.005	0.025		
	0.004	0.007		
		0.008		
	0.018	0.034		
	0.005	0.167		
12			0.017	0.011
13	0.003	0.034	0.013	0.035
14	0.004	0.014	0.010	0.023
15	0.002	0.139	0.011	0.019
16	0.005	0.862	0.019	0.016
17	0.004	0.143	0.006	0.018
18	0.007	0.623	0.009	0.012
19	0.004	0.571	0.010	0.012
20				0.009
21			0.005	0.008
	Total I-TEQ ng			
Blank 1	0.001	0.002	0.002	0.004
Blank 2	0.093	0.063	0.002	0.003

6.9.1   MST methods

Figure 6.8 shows the correlation between MSTs 1 and 2 during tests 1-8.
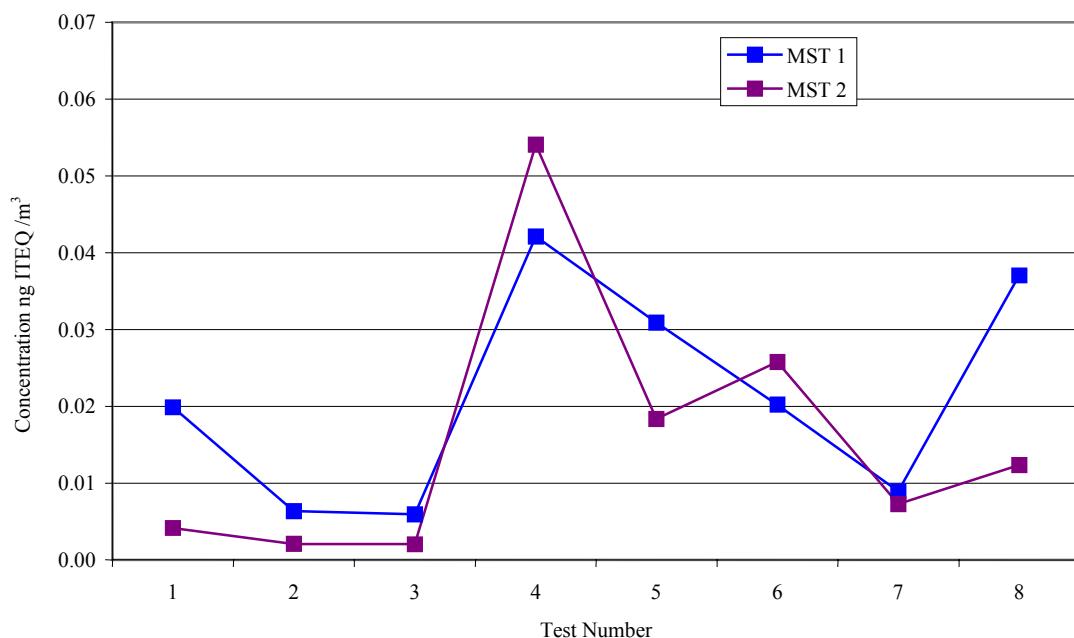
Figure 6.8: MST Determination of dioxins and furans (Site 1: Tests 1 to 8)

The results obtained during the second phase of comparative six-hour tests i.e. tests 13-19 are illustrated in Figure 6.9.
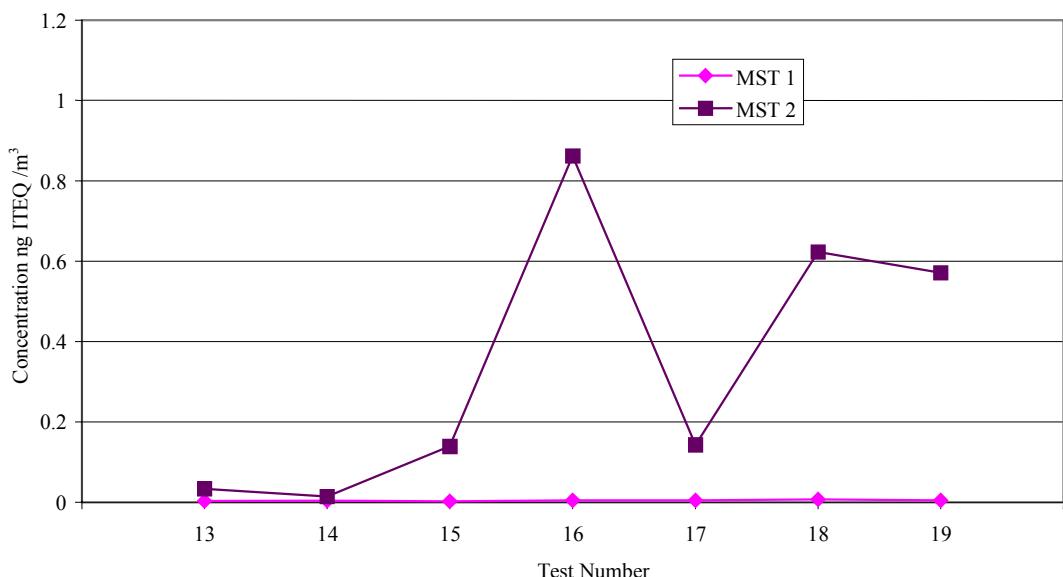

Figure 6.9: MST determination of dioxins and furans (Site 1: Tests 13 to 19)

The results obtained during for all tests at Site 1 are shown in Figures 6.10 and 6.11.

Figure 6.10 includes the outlier tests 11-19 obtained with MST 2 whereas Figure 6.11 shows a comparison of the two CISDs against MST 1 only.
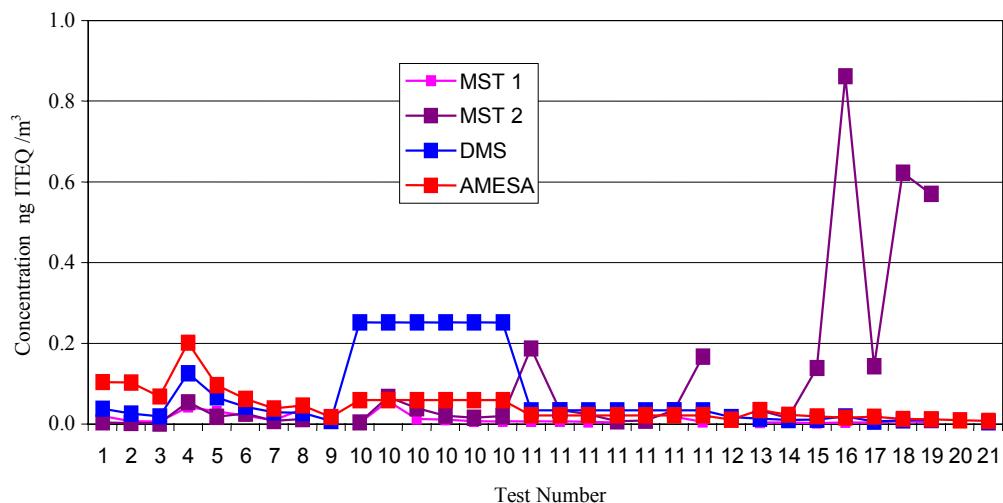
Figure 6.10: Determination of dioxins and furans (Site 1: Tests 1 to 21)
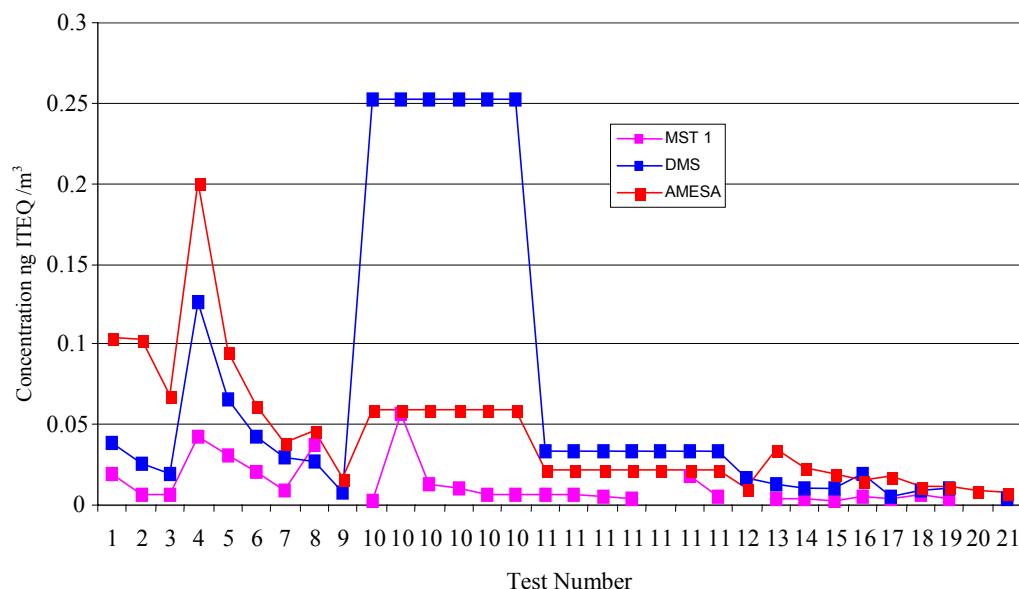
Figure 6.11: Determination of dioxins and furans (Site 1: Tests 1 to 21 excluding MST 2)

6.9.2 AMESA and MST comparative data

Figure 6.12 shows the comparative measurement data between the AMESA and the two MSTs during tests 1-8 at Site 1.
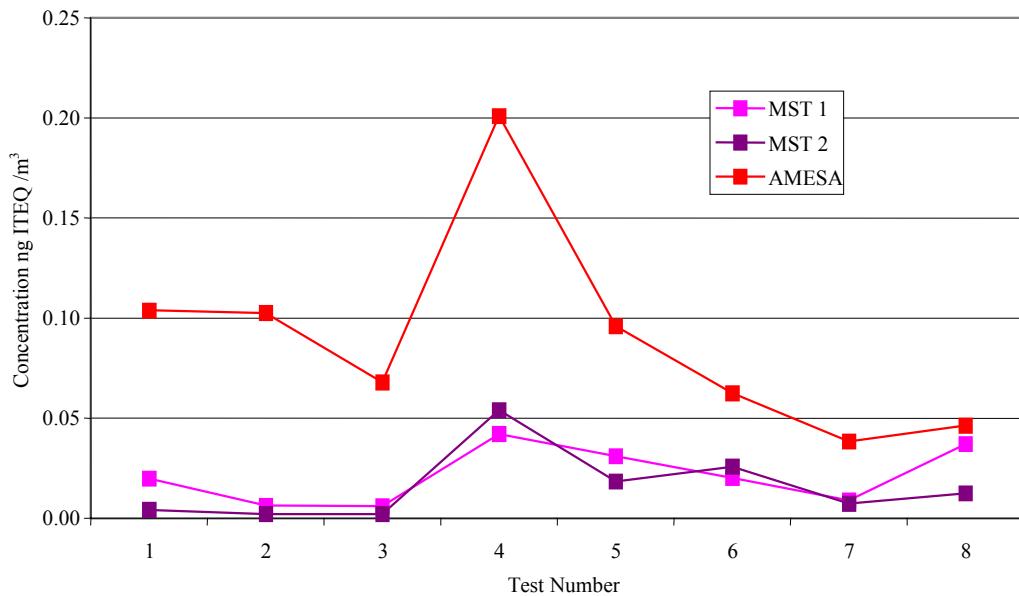
**Figure 6.12: MST and AMESA dioxins and furan results (Site 1: Tests 1 to 8)**

Figure 6.13 shows the comparative measurement data between the AMESA and the two MSTs during test 10 over a 14-day period testing with MST tests every other day at Site 1. It should be noted that the AMESA data correspond to a single analysis of the 14-day sample.
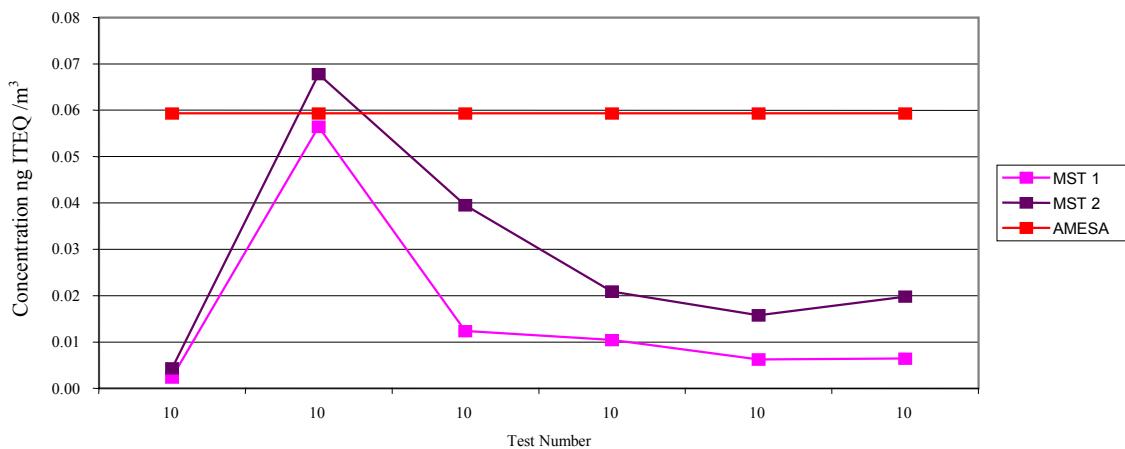
Figure 6.13: MST and AMESA dioxins and furan results (Site 1: Test 10)

Figure 6.14 shows the comparative measurement data between the AMESA, DMS and two MSTs during test 11 over a 28-day period testing with MST tests every fourth day at Site 1.

It should be noted that the AMESA and DMS data correspond to a single analyses of 28-day samples.
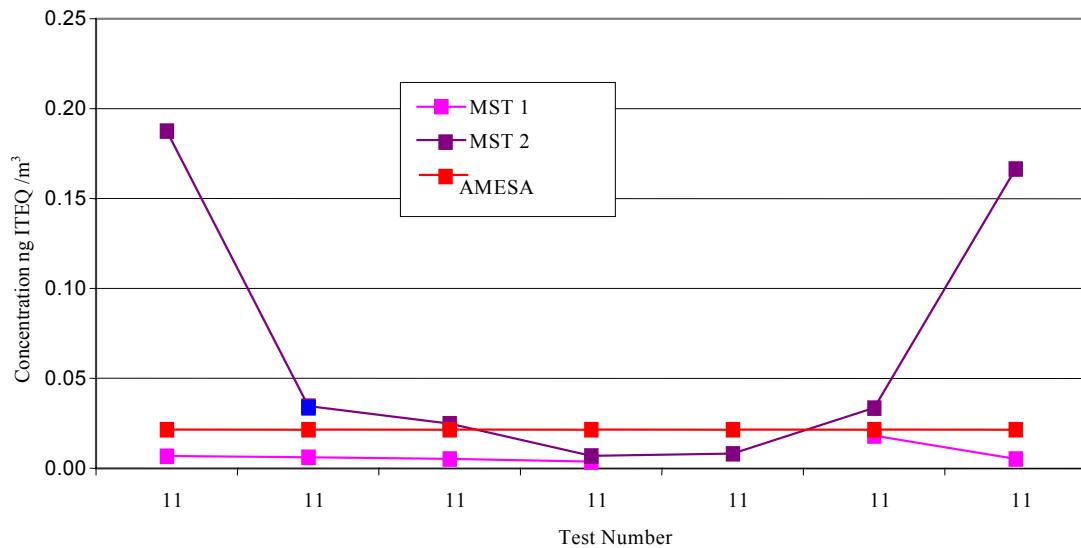
Figure 6.14: MST and AMESA dioxins and furan results (Site 1: Test 11)

Figure 6.15 shows the comparative measurement data between the AMESA and MST1 during tests 13-19 over a 7-day period with MST tests each day at Site 1.
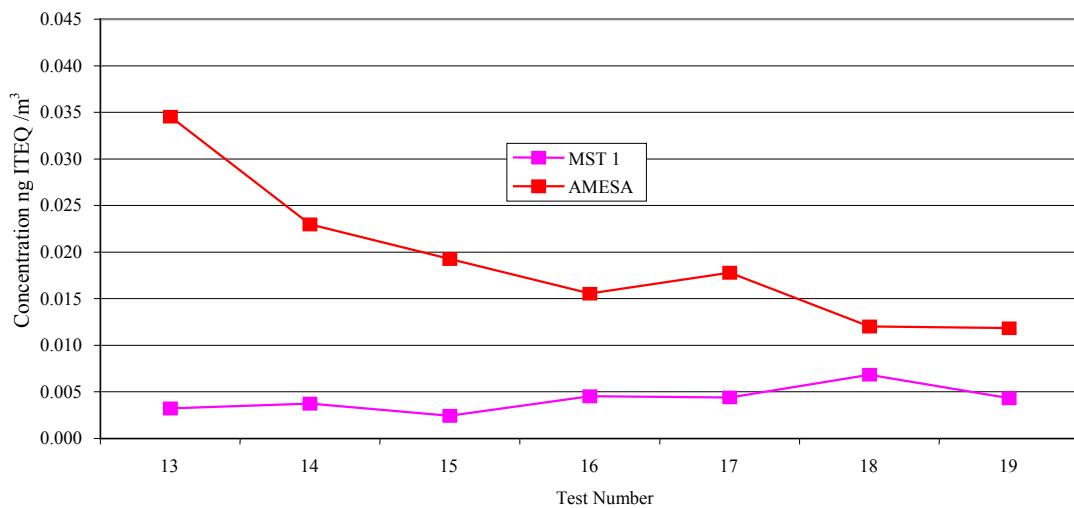

Figure 6.15: MST and AMESA dioxins and furan results (Site 1: Tests 13-19)

6.9.3 DMS and MST comparative data

Figure 6.16 shows the comparative measurement data between the DMS and the two MSTs during tests 1-8 at Site 1.
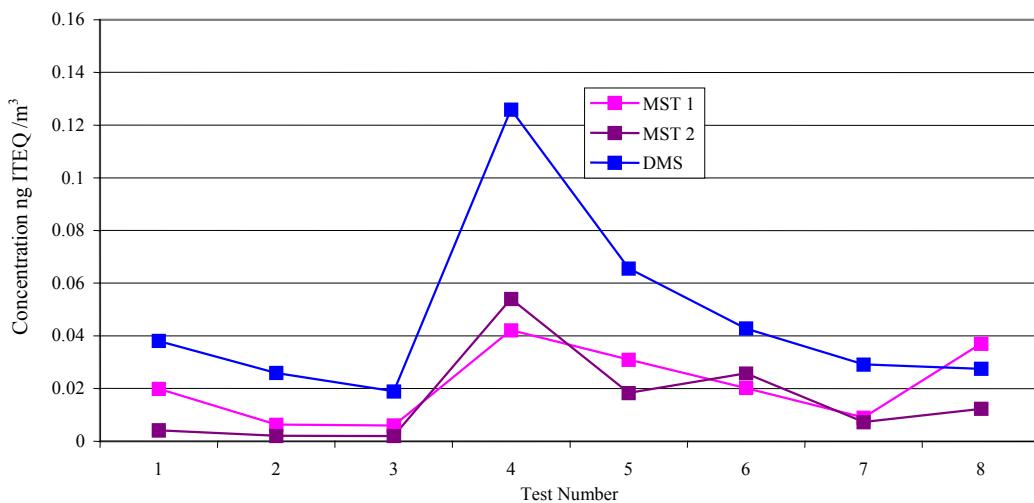
Figure 6.16: MST and DMS dioxins and furan results (Site 1: Tests 1 to 8)

Figure 6.17 shows the comparative measurement data between the DMS and the two MSTs during test 10 over a 14-day period testing with MST tests every other day at Site 1. It should be noted that the DMS data corresponds to a single analysis of the 14-day sample.
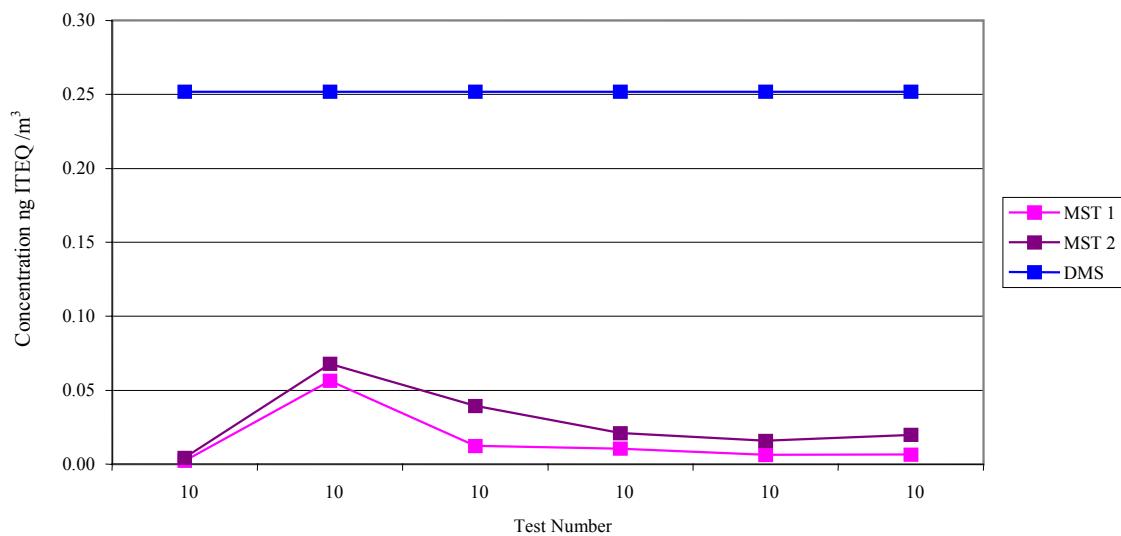

Figure 6.17: MST and DMS dioxins and furan results (Site 1: Test 10)

Figure 6.18 shows the comparative measurement data between the DMS and the two MSTs during test 11over a 28-day period testing with MST tests every fourth day at Site 1. It should be noted that the DMS data corresponds to a single analysis of the 28-day sample.
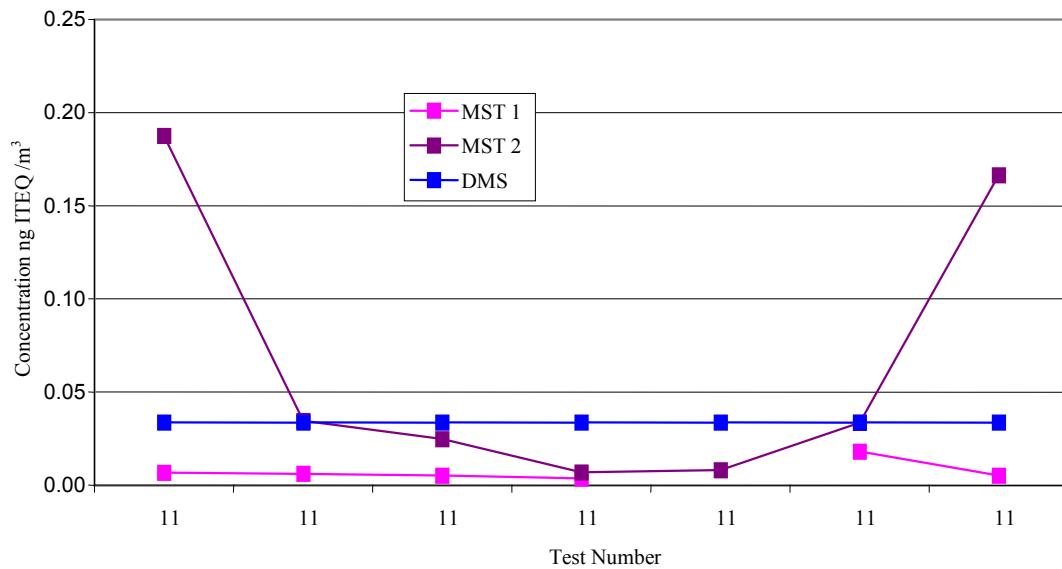
**Figure 6.18: MST and DMS dioxins and furan results (Site 1: Test 11)**

Figure 6.19 shows the comparative measurement data between the DMS and MST1 during tests 13-19 over a 7-day period with MST tests each day at Site 1.
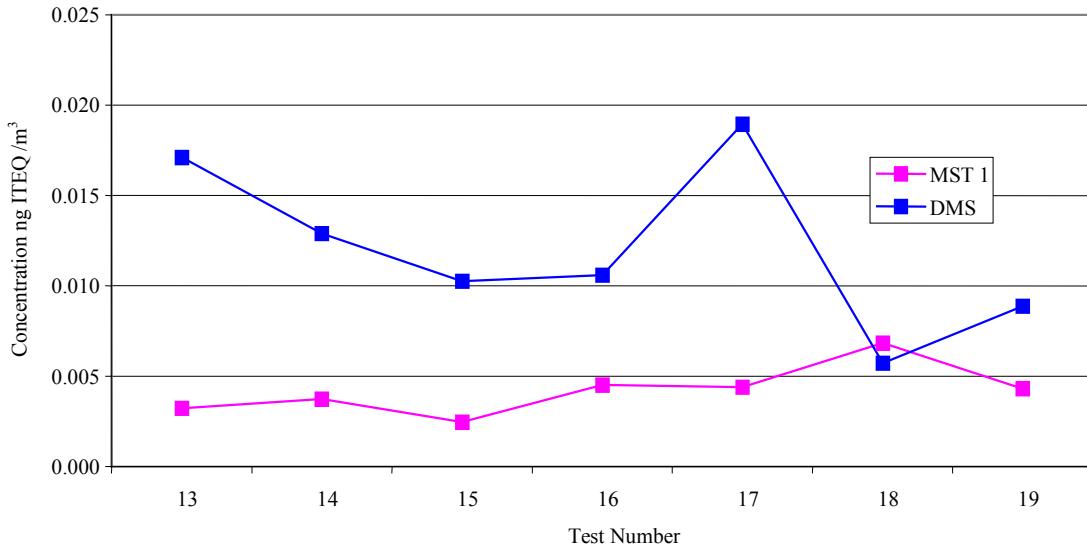
Figure 6.19: MST1 and DMS dioxins and furan results (Site 1: Tests 13-19)

6.9.4   AMESA and DMS comparative data

Figure 6.20 shows the comparative measurement data between the DMS and the AMESA during all tests at Site 1.
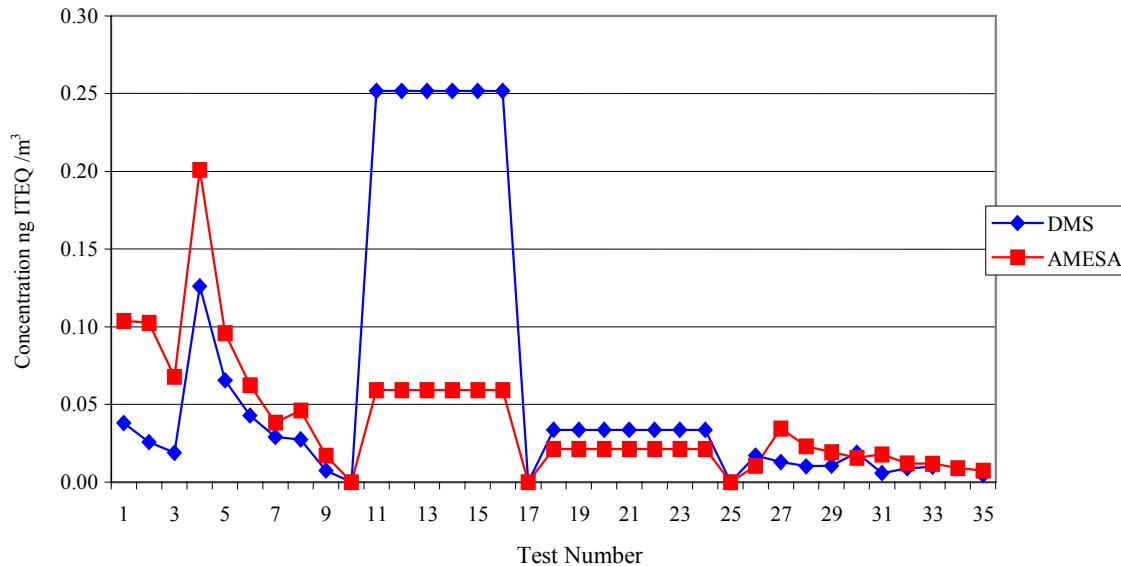
Figure 6.20: DMS and AMESA dioxins and furan results (Site 1: All tests)

6.9.5   Measurement Uncertainties

It is important to take measurement uncertainties into account in any performance assessment. Annex B of the CEN standard being updated for dioxins (prEN1948-2004) contains detailed analysis of the measurement uncertainty associated with dioxin determinations. The concentration levels to which the analysis applies is not absolutely clear, but it can be assumed that it is valid around the regulatory limit of 0.1 ng I-TEQ/m^3 and does not apply to concentrations close to the detection limit of the method (LOD).
The method of estimation is based on the approach outlined in the ISO-GUM document (Guide to the Expression of Uncertainty in Measurement, ISBN 92-67-10188-9). The following contributing parameters are identified and taken into account:

  ➢ Unrepresentative sampling

  ➢ Sample inhomogenties

  ➢ Sampler contamination

  ➢ Extraction losses

  ➢ Column chromatography

> - Loss during sample concentration

> - Certified value of standard

> - Dilution

> - Matrix effects

> - Signal integration

> - Interferences.

The total measurement uncertainty is estimated to be in the region of 20-30% (at the ELV). The uncertainty is likely to increase by an order of magnitude when the concentrations approach the limit of detection.

6.10   Instrument faults during site trial 1

During the field tests at Site 1 the DMS system failed a number of leak tests. On the majority of occasions this was caused by a leaking seal between the two halves of the cartridge holder. Great care is required as the seal seats on the outer edge of the join and can become pinched by the clamp that holds the two halves together. Tables 6.10 and 6.11 provide a summary of instrument faults/error messages during site trial 1 for the DMS and AMESA systems, respectively.

Table 6.10: Summary of DMS instrument faults/error messages during site Trial 1

Date	Fault Description	Remedy	Comments
12 May 2003	The DMS system failed an automatic leak test at midnight on day one of the 28-day test period. It restarted on the fourth day of the 28-day test period.	The system was reset to leak test at the start and end of each test period rather than at each probe change. No reason for the failure could be found. The system was secured and the internal password protected.	Comment from Mr T Steiner: There are only two possible reasons for this: change of internal device or parameter manipulation.
3 June 2003	Probe 1 Blocked Sim error. The system showed a blocked No.1 probe alarm but restarted after acknowledgement of the alarm without problems.	System re-started without further problems.	Comment from T Steiner: If there was a blocked probe this is properly cleaned when starting up by the blow back purging of the probe.

Table 6.11: Summary of AMESA instrument faults/error messages during site Trial 1

Date	Fault Description	Remedy	Comments
Off 28 April 2003 On 1 May 2003	$O_2 > O_2$ Max	Plant shut down	Not included in availability calculation
Off 6 May 2003 14:58 On 6 May 2003 15:30	$O_2 > O_2$ Max	Plant shut down	Not included in availability calculation
Off 28 May 2003 21:40 On 29 May 2003 22:31	$O_2 > O_2$ Max	Plant shut down	Not included in availability calculation

6.11   System availability

The CSID availability is defined as the fraction of the total time for which usable measurement data was available during the field tests. The period of testing was from 1 April 2003 until 29 June 2003 giving a total test time of 2160 hours (90 days).

6.11.1 AMESA availability

No time was lost due to the CISD system unavailability. The only lost time was due to plant shutdowns and the corresponding programmed response from the system. Therefore, availability for the AMESA system during trial 1 can be calculated as follows:

$$Availability = 100 - \left(\frac{0}{2160} \times 100 \right) = 100.0\%$$

6.11.2 DMS availability

Only 30 minutes were lost other than through system shut downs associated with plant shut downs. These occurred when setting up the system for a test during the leak-check phase. As such this loss of data is outside the availability assessment. Therefore, availability for the DMS system during trial 1 can be calculated as follows:

$$Availability = 100 - \left(\frac{1}{2160} \times 100 \right) = 100\%$$

6.12   Calibration checks

Both CISDs use devices that measure temperature, volume, pressure and velocity. All such devices were calibrated to traceable German national standards. It should be noted that recalibration of these components should be part of the servicing of the CISD.

6.13   Maintenance interval

The definition of maintenance interval for continuous emission monitoring systems is defined as the time in the operating environment over which the instruments zero and span drift remain within the limits specified. However, as span and zero points cannot be defined for the CISDs the maintenance interval was not determined.

6.14 End of trial condition

The condition of the CISD at the conclusion of testing at Site 1 is described in the following sections.

6.14.1 DMS

The following photographs illustrate the condition of the system at the conclusion of testing at Site 1.
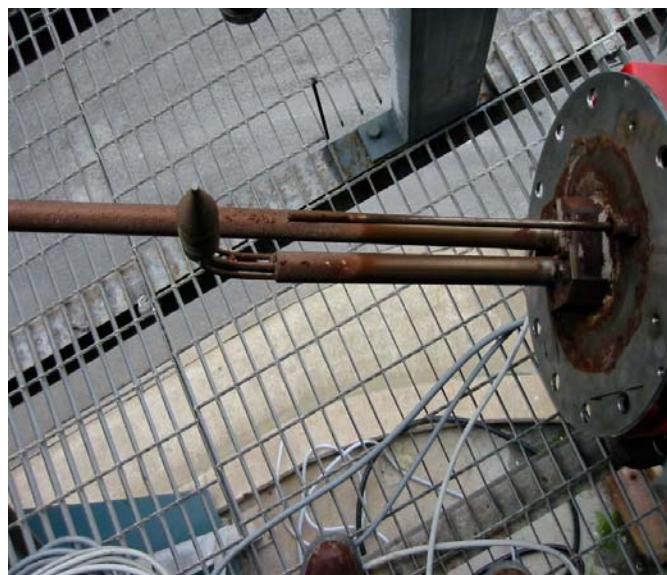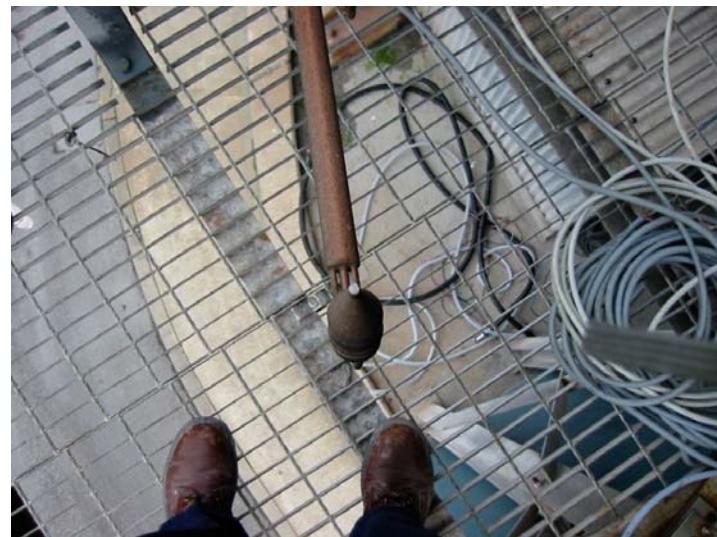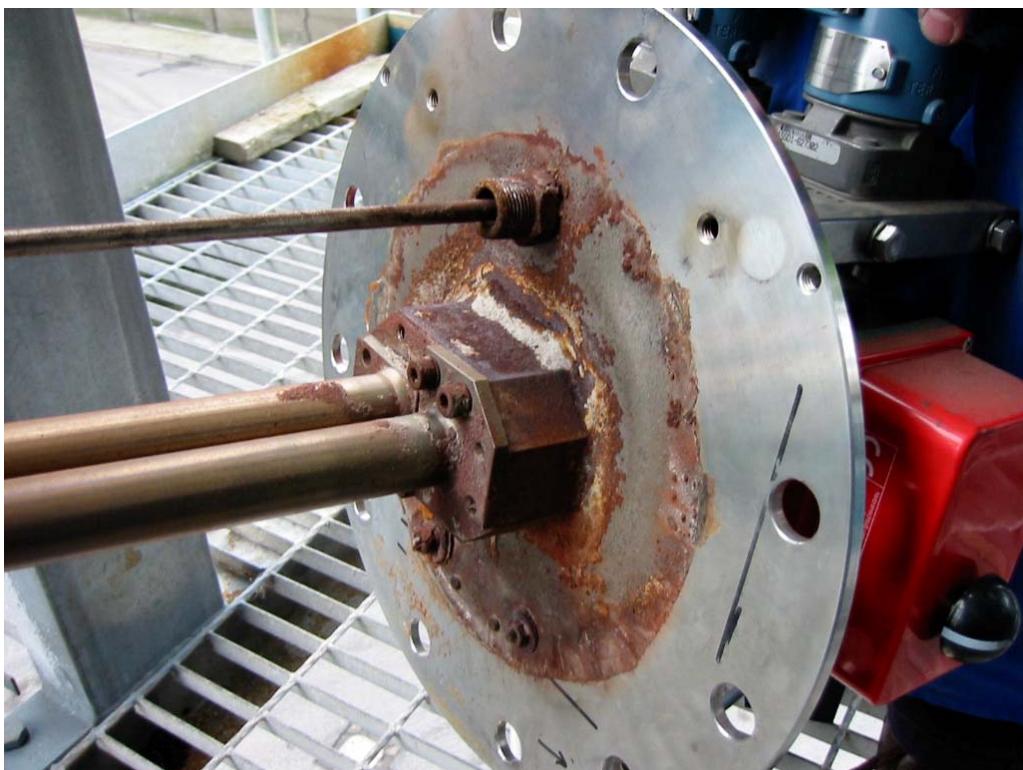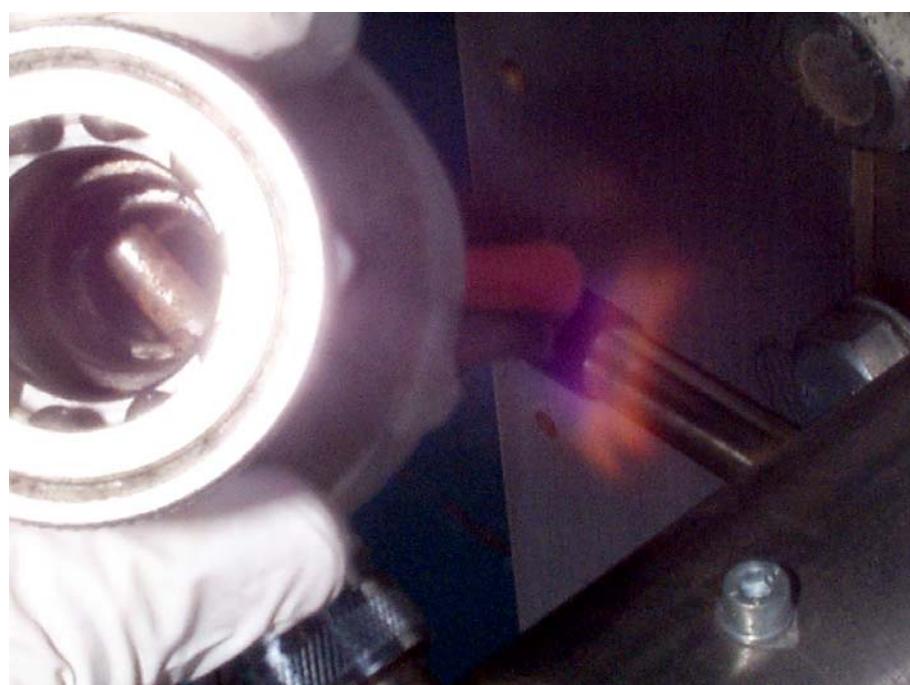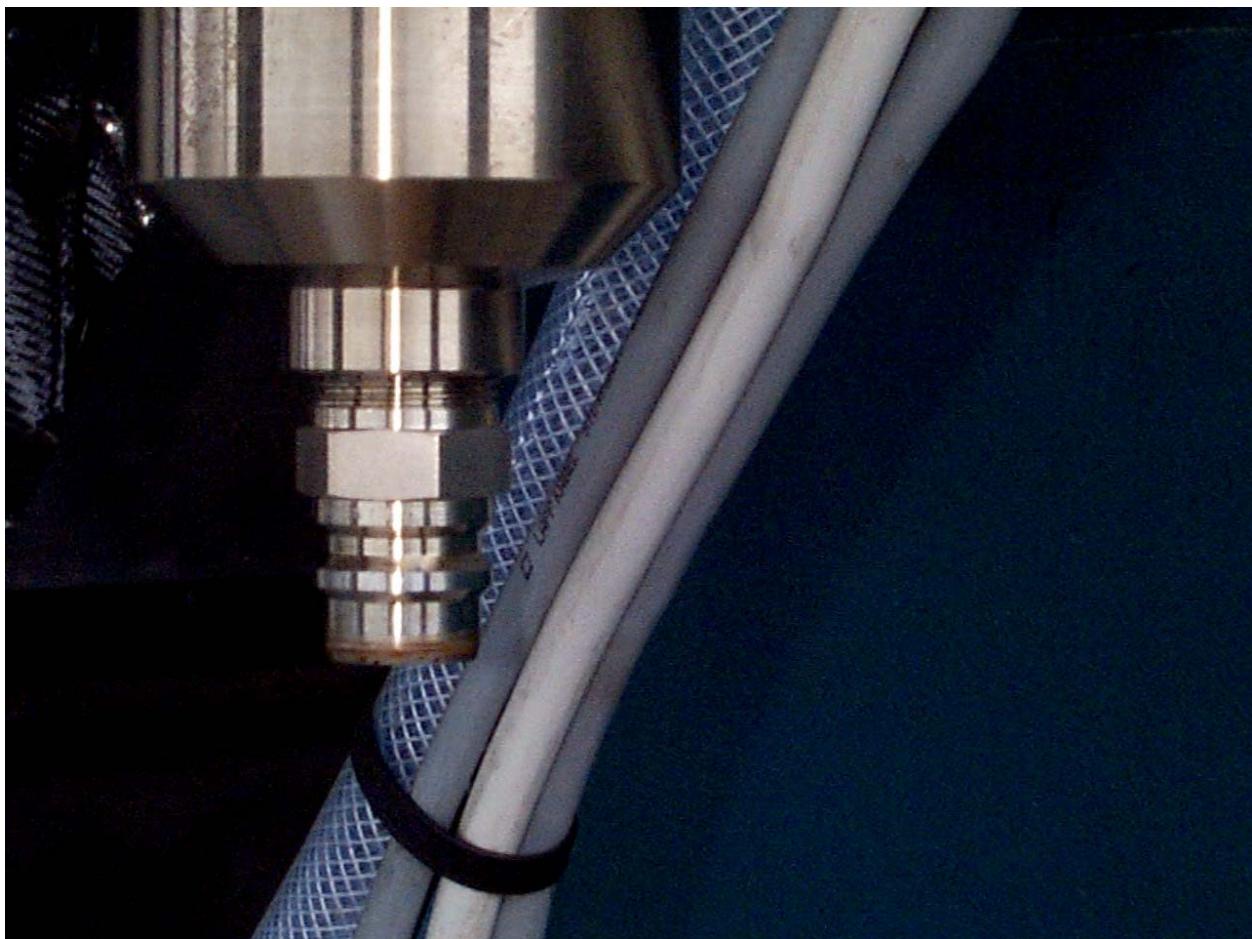
It can be seen from these photographs that the DMS system showed discolouration of the section of the probe system that was inside the duct during testing. In addition there was a brown (rust) coloured material on the coupling inside the heated line and base of the filter holder. The number 1 probe was also blocked with particulate material. Whilst the probe system required servicing before the system could be put back into normal use the control systems were all operational. It should also be pointed out that the CISD was in the duct for an additional four months prior to dismantling, servicing and transportation on to the next site.

The presence of hydrogen chloride in the gas stream and the fact that the gas stream was so close to the dew point is likely to have caused the surface corrosion observed. However, DMS were happy that the system was unaffected as this appeared after filtration and therefore would not affect the sample or the device function.

The function of control via the Internet was not operational for the period of the test. It is possible that the telephone line installed at the site was operating at reduced voltage and as such the unit could not communicate via the system installed.

6.14.2 AMESA

The AMESA probe showed the same discolouration as described above for the DMS sampling probe. There was also a dark coloration of the glass wool plugs in the resin traps.

6.15   Discussion of data

6.15.1 MST comparative data

The data for the first phase of 6hour comparative tests (tests 1 to 8) show good agreement between the two manual sampling trains, with both following the same trend and generally within expected variation between duplicate samples at such low levels of dioxins. However, the results for the second intensive phase of 6hour comparative tests (i.e. tests 13 to 19) showed significant differences in the concentrations measured by the two MSTs. The following steps were undertaken to establish possible causes:

➢ revision of the analysis of the samples;

➢ investigation of possible contamination of the resin;

➢ assessment of the plant performance during the tests; and

➢ tracing of the usage of the sampling equipment.

A review of the analysis procedures indicated that no contamination occurred during the analysis process. The analysis spectra obtained were also reviewed, these showed that peak selection and the subsequent integration to give peak areas was undertaken correctly. However, it was observed that there were differences in the congener profiles of the MST determinations; this is illustrated by two profiles shown in Figure 6.21 and Figure 6.22. Figure 6.21 shows the analysis profile of a suspected contaminated sample obtained from MST 2 and Figure 6.22 shows the typical analysis profile of a non-contaminated sample obtained from MST 1.
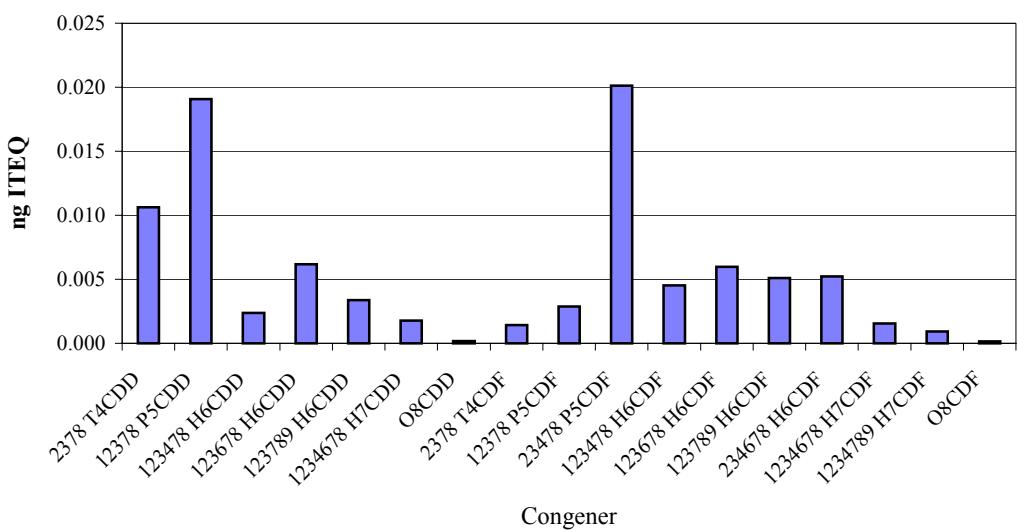
Figure 6.21: Typical analysis profile for suspected contaminated sample from MST 2 (Test 15B)
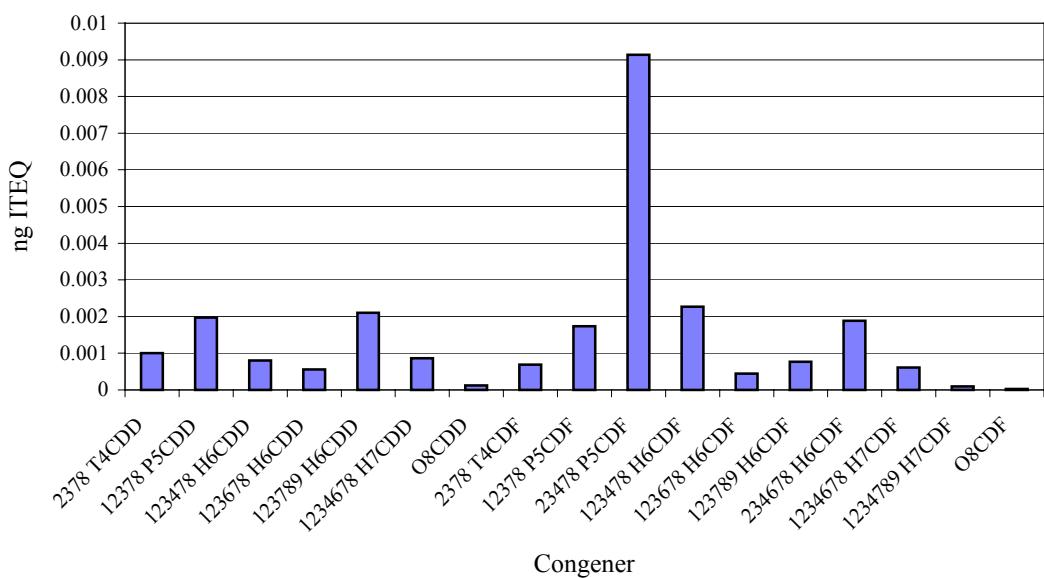
Figure 6.22: Typical analysis profile for sample obtained from MST 1(Test 3A)

The resin batch numbers were checked and it was found that both systems used the same resin so this was discounted as a cause.

The plant was operating normally throughout the period of these six hour tests and as both MSTs sampled from the same points within the duct, but not at the same time this seemed an unlikely cause for the observed change in concentration.

The probe of MST 2 had to be changed after test 10A due to a heater failure. Unfortunately, the replacement probe had been used previously on an application with higher dioxin levels. Limitations in the clean up of the titanium probe (titanium cannot be subjected to the rigorous cleaning procedures used for glass sampling probes) may have resulted in residual contamination being present. This could then have become dislodged during the sample clean up stages of the MST2 probe during subsequent use at Site 1 (Samples 10B-19). The results obtained from Samples 10B-19 at Site 1 were therefore discounted from any inter-comparison studies. Furthermore, it was decided that glass liners and nozzles would be used at Site 2 as these could be removed, cleaned and visually checked between tests.

6.15.2 AMESA and MST comparative data

The results of tests 1-8 (Figure 6.12) and 13-19 (Figure 6.15) should be used for comparison, as these represent comparable 6 hour tests. These comparative tests showed that the two measurement systems followed the same trend in dioxin concentration. Overall, the AMESA produced results five times higher than the MST but with some variation within expected experimental error.

6.15.3 DMS and MST comparative data

As above, the results of tests 1-8 (Figure 6.16) and 13-19 (Figure 6.19) should be used for comparison, as these represent comparable 6hour tests. These comparative tests showed that the two measurement systems followed the same trend in dioxin concentration. Overall, the DMS produced results three times higher than the MST but with some variation within expected experimental error.

6.15.4 AMESA and DMS comparative data

Figure 6.20 demonstrates a trend in the comparative tests between the DMS and AMESA systems at Site 1. During the 6 hour comparative tests the AMESA produced results two times higher than the DMS overall but with some variation within expected experimental error. Conversely, over the extended tests (tests 10 and 11) the DMS produced higher results than the AMESA system and this is probably due to differences in the on/off triggers of oxygen and flow set to control sampling for both systems. During test 10, it was observed that the DMS system started up sooner than the AMESA and as a result may have sampled a higher concentration of dioxins resulting from a plant start-up after a boiler clean-up and tube failure on the incinerator unit being sampled. However, it should be noted that these triggers are adjustable for each CISD and should be determined for each process. Other triggers can also be used by both systems to stop/start sampling. It is recognised that the on/off triggers used for site 1 may not have been the optimum ones for this process.

7 Field testing (site 2)

7.1 Overview

The two CISDs were subjected to further comparative sampling tests at a second test site using two manual sampling trains (MSTs) as detailed in Table 7.1. The sampling plan is summarised in Table 7.2.

Table 7.1: Required test details (Site 2)

Weeks	MST Sampling Details	CISD Sampling Details
Pre-trial	Field Blanks	Field Blanks
1-2	3 x 2 (6-hour samples)	3 x matching 6-hour samples
2	None	1 x 10 Day sample
3-4	4 x 2 (6 hour samples)	4 x matching 6-hour samples
5-6	None	1 x 14 day samples
7-10	None	1 x 28 day samples
11 - 12	3 x 2 (6-hour samples)	3 x matching 6-hours samples
13-14	4 x 2 (6- hour samples)	4 x matching 6-hours samples
Post-trial	Field Blanks	Field Blanks

7.2 Test Site 2

7.2.1 Plant description

Site 2 is a cement works comprising of a single 58 metre long rotary kiln into which raw meal enters after passing down a pre-heater tower. In the pre-heater tower the previously prepared powder is heated by hot exhaust gases, which rise up the tower via a series of cyclones. The final stage of the pre-heater is a calciner that burns chipped tyres and powdered coal to raise the temperature to above 850°C. The kiln is fired by pulverised coal; this raises the temperature in the chamber to above 1400°C. In addition to coal, chipped tyres and palletised sewage sludge are used to supplement coal usage. At this stage the material hydraulic calcium silicates known as clinker is passed over cooling grates reducing its temperature to 100°C. This product is then stored.

The main kiln exhaust is treated by electrostatic precipitator. There are other process emissions which are discharged from the main stack and these have fabric filters for particulate abatement. The stack temperature at the sampling point location is about 100-110°C. Dust loading is stated as a maximum of 20-30 mg/m^3. Flow was reported to be about 105 m^3/s. No flow, temperature or oxygen profiles were undertaken in this site trial as MST sampling was undertaken at just two specific points within the duct (see sections 7.3 and 7.6).

Table 7.2: Site 2 Sampling Details

Date	Activity	MST Sampling Details	CISD Sampling Details
04/06/2004	Start 3 Month Test Period		
16/06/2004	Field Blank	Field blank/MST	CISD field blank
17/06/2004	Test 1	Duplicate 6h samples	Matching 6h sample
18/06/2004	Test 2	Duplicate 6h samples	Matching 6h sample
18/06/2004	Test 3.	Duplicate 6h samples	Matching 6h sample
18/06/2004	Test 4		10-day CISD Test
29/06/2004	Test 5	Duplicate 6h samples	Matching 6h sample
30/06/2004	Test 6	Duplicate 6h samples	Matching 6h sample
30/06/2004	Test 7	Duplicate 6h samples	Matching 6h sample
01/07/2004	Test 8	Duplicate 6h samples	Matching 6h sample
01/07/2004 to 16/7/2004	Test 9		14-day CISD Test
16/07/2004 to 14/08/2004	Test 10		28-day CISD Test
18/08/2004	Test 11 (no DMS cartridges available)	Duplicate 6h samples	No matching CISD samples
19/08/2004	Test 12 (no DMS cartridges available)	Duplicate 6h samples	No matching CISD samples
19/08/2004	Test 13 (no DMS cartridges available)	Duplicate 6h samples	No matching CISD samples
01/09/2004	Test 14	Duplicate 6h samples	Matching 6h sample
02/09/2004	Test 15	Duplicate 6h samples	Matching 6h sample
03/09/2004	Test 16	Duplicate 6h samples	Matching 6h sample
04/09/2004	Test 17	Duplicate 6h samples	Matching 6h sample
04/09/2004	Field blank	Field blank/MST	CISD field blank

### 7.2.2 Plant operation during site trial

The plant operated at normal load throughout the trial at Site 2 except during the periods identified in Table 7.3 when the unit was shutdown to allow investigation of the fault.

**Table 7.3: Summary of Plant Shutdowns at Site 2**

Period	Fault Description	Test Affected
06 July 2004 – 07 July 2004	External power failure	9
07 July 2004 – 08 July 2004	Cooler breakers overload	9
22 July 2004 – 24 July 2004	Electrostatic precipitators	10
25 July 2004 – 25 July 2004	Cooler breakers overload	10
5 August 2004 – 6 August 2004	External power failure	10
7 August 2004 – 8 August 2004	Temp of cooler exhaust fan	10
16 August 2004	Electrostatic precipitators	None: delay only
17 August 2004	External power failure	None: delay only

7.3   Sampling positions

The sampling plane was at the 58 metre level of the vertical main stack, 10 metres above the final input where the coal mill-exhaust enters the stack. It has been observed previously that there is no noticeable distortion of flow and temperature profiles. Two sampling positions were chosen that gave access to the CISDs and enabled one of the two MSTs to reach a point within 30cm of a CISD. The duct diameter is 2.77m. The DMS system was paired with MST 1 and the AMESA system paired with MST 2 as shown in Figure 7.1. The connection of the required services is shown in the Figure 7.2.
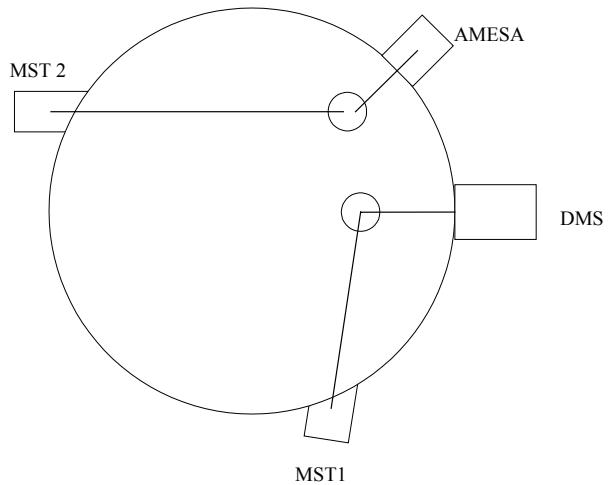
Figure 7.1: Plan View of the Sampling Plane (Site 2)
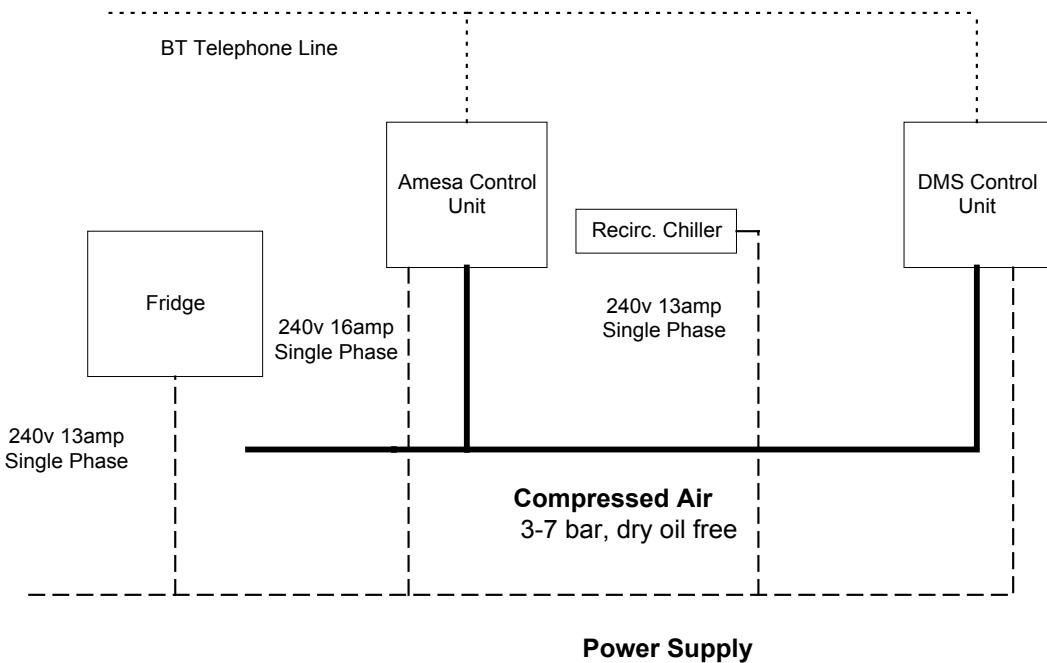
Figure 7.2: Schematic Description of Services (Site 2)

7.4　Installation

The UK distributor/agent of each CISD moved the systems from Site 1 to Site 2. The distributor/agent undertook the connection and commissioning of their respective CISD.

7.5　CISD configuration

The following paragraphs describe each of the systems as installed at Site 2.

7.5.1　AMESA

The AMESA system installed at Site 2 was configured to utilise a water-cooled probe with the aim of condensing water vapour prior to passage through the resin in the sampling cartridge. A cooled water supply was provided by a sealed water chiller and recirculating pump. The sampling probe was modified to allow the liners to be changed between tests. The probes and nozzles were made of titanium (4mm in diameter). The plant oxygen values were set to enable a plant-off trigger to stop and start sampling in case of breakdown. The condensate obtained from the sample system was collected to determine break through.

7.5.2　DMS

The DMS system installed at Site 2 was configured as for Site 1 although an updated version of the operating software was installed prior to the tests at Site 2. The air for the system was taken from the plant's compressed air supply and passed through two coalescence filters to ensure that the air was dry and particulate free. The plant oxygen and flow measurement values were set to enable a plant-off trigger to stop and start sampling.

7.6　MST configuration

Two MSTs were used to sample simultaneously. The MSTs were positioned to ensure sampling within 30 cm of each of the systems under test in accordance with ISO 7935. Positioning the systems in this way ensured that one MST sampled in close proximity to one of the CISDs and the other MST with the other CISD. Apart from sampling at only one position the MST sampling followed the procedures outlined in BS EN 1948. The probe liners and nozzles for both MST systems were made of glass (5.0mm glass nozzles were used on both MSTs).

7.7　PB Power test procedures

Alan Leonard of Netcen conducted the field tests with John Green and Malcolm Lee of PB Power in accordance with the PB Power Instructions summarised in Table 7.4. PB Power has UKAS accreditation (UKAS No.2065) and MCERTS certification for the sampling of stacks for dioxins, furans, oxygen, flow and moisture.

Table 7.4: PB Power test procedures (Site 2)

Determinant	Test House Document	Reference Method	Description	UKAS Accredited
Dioxins and Furans	KP-TP-12	BS EN 1948	A representative sample was extracted from the gas stream at a single point under isokinetic conditions. The dioxins and furans were collected in an absorbent trap containing XAD-2 resin. To avoid contamination the glassware, filters and adsorbent traps were prepared by AEA Technology prior to going to site. This involved, ashing where possible at 550°C, soaking and rinsing in solvents, and drying as described in KP-TP-12. The NLS laboratory spiked the resin traps with the required sampling standards prior to sampling.	Yes
Moisture	KP-TP-11	USEPA 4	Representative sample withdrawn from the duct and absorbed onto silica gel. The mass of water determined gravimetrically and its associated volume measured using a calibrated gas meter.	Yes
Oxygen	KP-TP-10	ISO 12039	Direct measurement of the concentration of oxygen in the gas stream using a Servomex Paramagnetic Analyser or Land Combustion Zirconium Probe.	Yes

7.8   NLS test procedure

As described in section 6.7 of this report.

7.9   Test results

The concentrations determined in these tests are reported in ng I-TEQ /m^3 at reference conditions of 11% O_2, dry. These conditions were adopted as this convention is specified in WID and hence adopted by the Environment Agency for reporting dioxins emission. Table 7.5 summarises the results of the dioxin and furan comparison tests at Site 2.

The oxygen concentration measured by the sampling team was used to determine the dioxin and furan concentrations at reference conditions for all the measurement systems. This ensured that no differences were caused by the measurement of oxygen and only related to the volume sampled by each system, which is the parameter that all of the units report.

7.5: Summary of dioxin and furan measurements (Site 2)

Test	Total Dioxin and Furan Concentration ng I-TEQ /m^3			
Number	MST 1	DMS	MST	AMESA
1	0.0013	0.0079	0.0014	0.0144
2	0.0004	0.0024	0.0004	0.0079
3	0.0003	0.0016	0.0009	0.0092
4		0.0007		0.0005
5	0.0011	0.0062	0.0008	0.0312
6	0.0005	0.0018	0.0007	0.0253
7	0.0050	0.0027	0.0004	0.0272
8	0.0003	0.0009	0.0004	0.0083
9		0.0003		0.0014
10		0.0006		0.0015
11	0.005			
12			0.0005	
13	0.0004			
14	0.0007	0.0061	0.0010	0.0050
15	0.0030	0.0014	0.0005	0.0031
16	0.0007	0.0025	0.0009	0.0023
17	0.0005	0.0030	0.0004	0.0023
	Total I-TEQ ng			
Blank 1	0.001	0.002	0.002	0.004
Blank 2	0.093	0.063	0.002	0.003

These results are graphically shown in the following sub-sections. It should be noted that all the MST results obtained at Site 2 were at or below the reportable method detection limit and therefore have a high level of uncertainty.

7.9.1 MST comparative results

The comparative results obtained from the two MSTs at Site 2 are illustrated in Figure 7.3
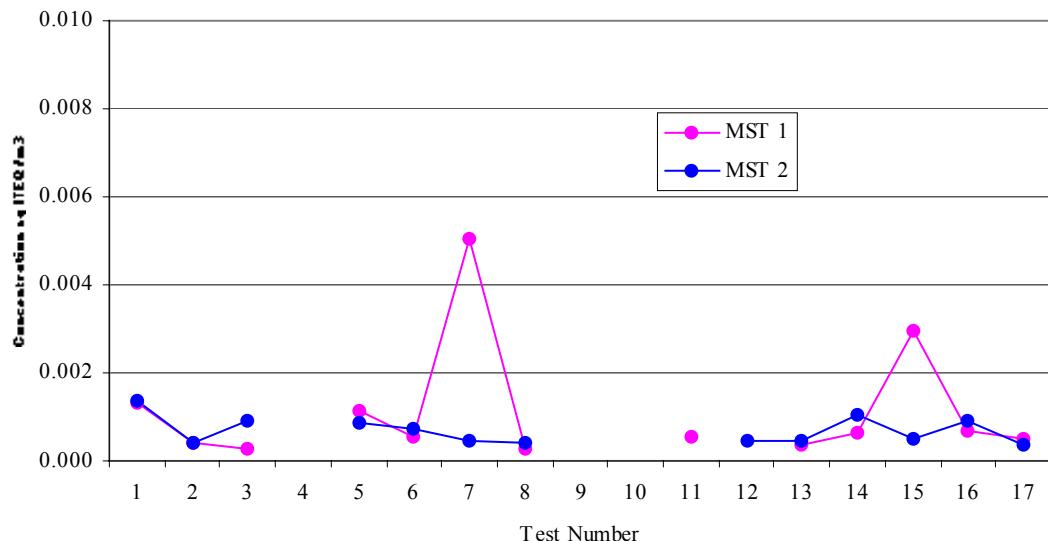

Figure 7.3: MST determination of dioxins and furans (Site 2: Tests 1 to 17)

7.9.2 AMESA and MST comparative data

The comparative results obtained from MST 2 and the AMESA at Site 2 are illustrated in Figure 7.4.
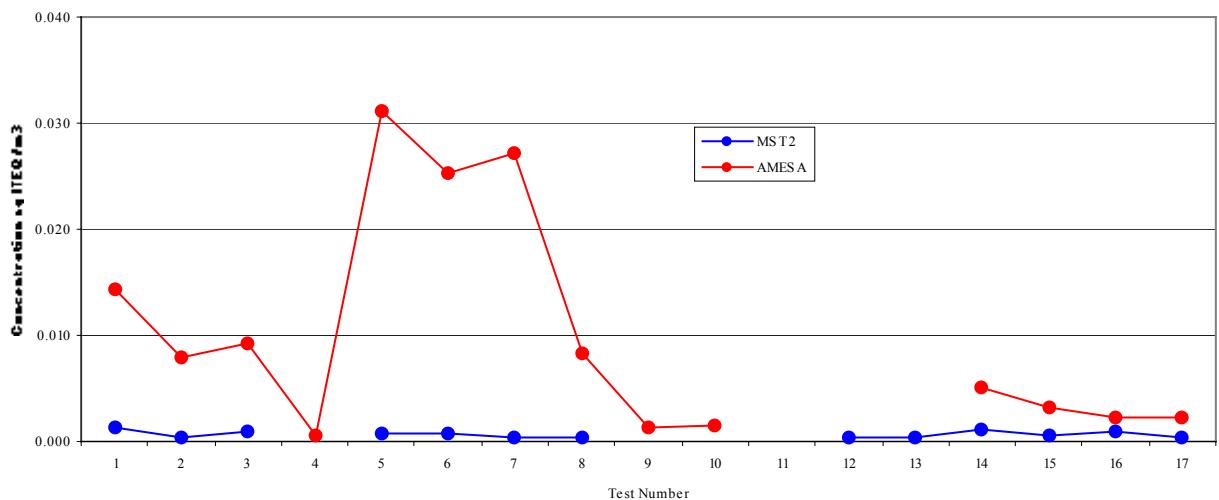

Figure 7.4: MST 2 and AMESA determination of dioxins and furans (Site 2: Tests 1 to 17)

7.9.3 DMS and MST comparative data

The comparative results obtained from MST 1 and the DMS at Site 2 are illustrated in Figure 7.5.
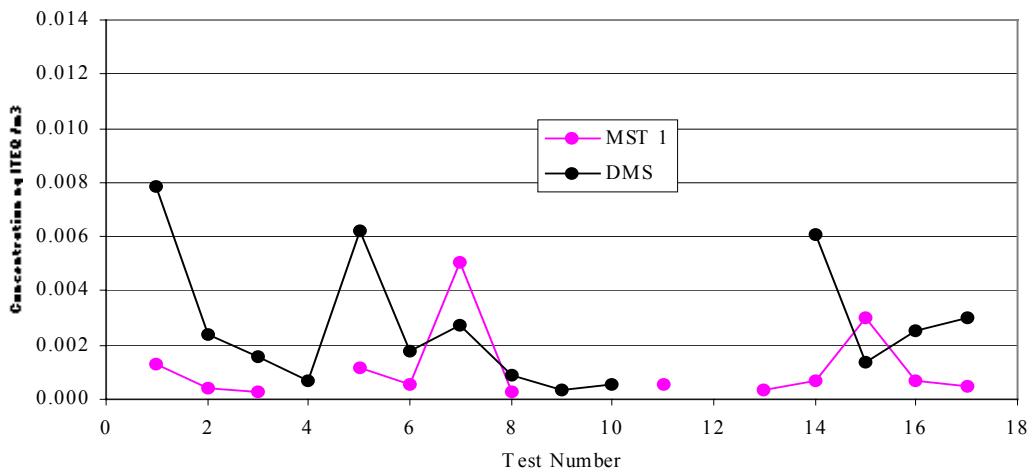
Figure 7.5: MST 1 and DMS determination of dioxins and furans (Site 2: Tests 1 to 17)

The samples for DMS tests 16 and 17 were diluted due to matrix issues. Hence, the above graph represents the worst case-scenario as the quoted detection limit was used to calculate the measured dioxin concentration.

7.9.4 AMESA and DMS comparative data

The comparative results obtained from the two CISDs at Site 2 are illustrated in Figure 7.6.
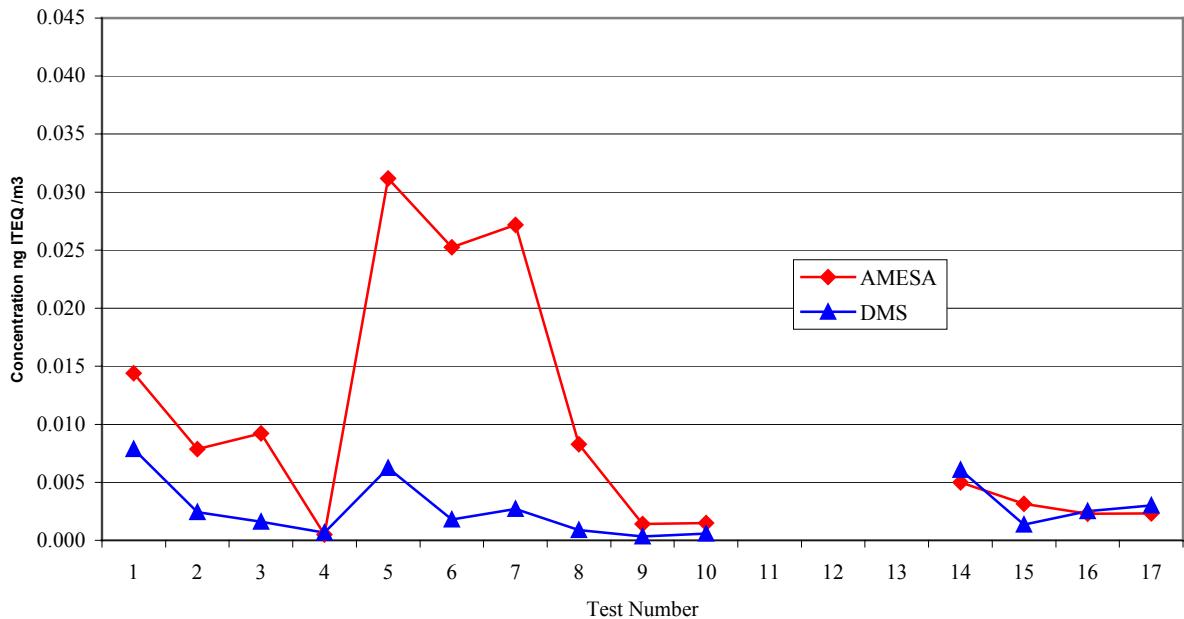
Figure 7.6: AMESA and DMS determination of dioxins and furans (Site 2: Tests 1 to 17)

7.9.5 Measurement uncertainties

The total measurement uncertainty is estimated to be in the region of 30-35% (at the ELV). The uncertainty is likely to increase by an order of magnitude when the concentrations approach the limit of detection. See section 6.9.5 for more details.

7.10 Instrument faults during site trial 2

During the field tests at site 2 the DMS system failed a number of leak tests. On the majority of occasions this was caused by a leaking seal between the two halves of the cartridge holder. Great care is required as the seal seats on the outer edge of the joint and can become pinched by the clamp that holds the two halves together. Tables 7.6 and 7.7 provide a summary of instrument faults/error messages during site trial 2 for the DMS and AMESA systems. It should be noted that the majority of the observed alarms and subsequent actions were normal responses of the CISDs to the condition of the stack or surrounding environment. As described for site 1, the setting of the on/off triggers can affect the overall concentration of dioxins reported due to differences in the parameters set by the two systems.

Table 7.6: Summary of DMS instrument faults during evaluation at Site 2

Date	Fault Description	Remedy	Comments
17 June 2004	Maximum filter temperature exceeded	System started once temperatures met specified values.	The positioning of the sample platform is inside a building, above the kiln and beside the calciners resulting in very high ambient temperatures that can be in excess of 40 ^{o}C. Also the mounting point for the system is away from air-flow which would help alleviate the problem.
18–21 June 2004	Problems with mixed gas values being exceeded.	The Manufacturer's Agent adjusted the control parameters.	The on/off control triggers were adjusted by the Manufacturer's Agent.
27 June 2004	O_2 value exceeded system stopped.		Normal response to plant shutdown affecting the 14-day test (Test 5).
29 June 2004	Maximum filter temperature exceeded for 6 mins.	System automatically restarted when temperature fell to acceptable limits.	Normal response to ambient environment exceeding control limit of filter temperature affecting Test 5.
30 June 2004	Maximum filter temperature exceeded for 30 mins.	System automatically restarted when temperature fell to acceptable limits.	Normal response to ambient environment exceeding control limit of filter temperature affecting Test 6.
19 July 2004 to 16 August 2004	Oxygen signal out of range.	System automatically restarted when oxygen fell to acceptable limits.	Normal response to plant shutdown affecting the 28-day test (Test 10).
04 Sept 2004	Maximum filter temperature exceeded for 52 mins.	Roof space vent opened to reduce ambient temperature.	Normal response to ambient environment exceeding control limit of filter temperature affecting Test 17.

Table 7.7: Summary of AMESA instrument faults during evaluation at Site 2

Date	Fault Description	Remedy	Comments
18/06/2004	Mixed gas value greater than 100%.	Air added to control temperature during a phase of kiln problems.	Normal response affecting Test 4.
29/06/2004	The system stopped 4 hrs into test 5. It was found that the coupling between the probe and the cartridge holder had blocked.	The coupling was cleaned and the washings collected. The material appeared to be grit size.	The test was re-started and the 6 hr period was completed without a problem. After this, the procedure was modified to include cleaning of the coupling after each test.
06/07	The plant power tripped and this resulted in the chiller tripping out plus a high O_2 alarm was observed.	This resulted in the CISD closing down due to a gas cooler high alarm. The CISD also stopped for a period due to a high O_2 reading.	Normal response to plant shut-down affecting Test 9.
07/08/2004	Gas cooler alarm (high ambient temperatures of $>40^{\circ}C$.	Reduced the effectiveness of the chiller.	Normal response affecting Test 10.

7.11   System availability

Both of the CISD systems suffered a few problems when sampling as detailed in section 6.2.17. However, these periods of stopped sampling related to plant operation i.e. increases in flow rate that pushed the systems outside the operational parameters defined at the start of the evaluation. Therefore, these periods have not been included in the evaluation of availability.

7.11.1 AMESA system availability

The CSID availability is defined as the fraction of the total time for which usable measurement data was available during the field tests. The period of testing was from 4 June 2004 until 4 September 2004 giving a total test time of 2208 hrs (92 Days) with no loss of system availability. Therefore, availability for the AMESA System was:

$$Availability = 100 - \left(\frac{0}{2208} \times 100 \right) = 100\%$$

7.11.2 DMS System availability

The CSID availability is defined as the fraction of the total time for which usable measurement data was available during the field tests. The period of testing was from 4 June 2004 until 4 September 2004 giving a total time of testing of 2208 hrs (92 Days) with no loss of system availability. Therefore, availability for the DMS System was:

$$Availability = 100 - \left(\frac{0}{2208} \times 100 \right) = 100.0\%$$

7.12   Calibration checks

The CISD systems use devices that measure temperature, volume, pressure and velocity. These measurements are calibrated to traceable German national standards. Recalibration of these components should be part of the servicing of the units when in normal use.

7.13   Maintenance interval

The definition of maintenance interval for continuous emission monitoring systems is defined as the time in the operating environment over which the zero and span drift remains within the limits specified. However, as span and zero points cannot be defined for the CISDs the maintenance interval was not determined.

7.14   End of trial condition

The condition of the CISDs at the conclusion of testing at Site 2 is described in the following sections.

7.14.1 DMS

The DMS system was operational at the end of the field evaluation. There was a build up of particulate material on the top edge of the probes and in stack thermocouple. The outer casing of the control unit was covered by cement dust. The internals were protected by the control enclosure.

7.14.2 AMESA

The AMESA system was operational at the end of the field evaluation. There was a build up of particulate material on the top edge of the probe. Whilst the probes and flow measurement tubes remained unblocked throughout the tests, the coupling between the probe and the cartridge box blocked during one of the 6-hour tests. Cleaning between tests prevented blocking of the coupling. For processes such as this where the particulate material is hydrophilic an increase in diameter of this coupling may resolve this issue. The outer casing of the control unit was covered by cement dust but the internals were protected by the control enclosure.

7.15   Discussion of data

7.15.1 MST Comparative Data

When comparing the MST results with each other it is important to remember that they were both sampling from a single point but in different areas of the stack. In addition, all the MST results obtained at Site 2 were at or below the method detection limit and therefore have a high level of uncertainty. Given the very low levels measured the results showed good agreement. In fact, a 1:1 relationship was observed overall when a few outlier tests were removed.

7.15.2 AMESA and MST comparative data

As stated in section 7.17.1 the MST results were very low and as a result the errors in measurement play a significant role and make it difficult to produce a direct relationship between the MST and the AMESA system. The AMESA system produced values that were consistently above those reported by the corresponding manual system. As reported in Table

7.7, a blockage was observed in the AMESA coupling after test 5. The coupling was subsequently cleaned between tests after test 5. However, it seems likely that this blockage and subsequent cleaning during tests 5-8 produced erroneously high dioxin concentrations and hence this comparative data should be ignored. It is possible that the build up of material evident in the coupling after test 5 was not removed during the first cleaning. Alternatively, material may have built up in the coupling but prior to the resin trap i.e. in a section that was not possible to clean. The blocking of the coupling would have reduced the flow rate through the system and may have left material in this section that once the system was restored to normal operation then contributed to the next sample.

If we therefore ignore the earlier tests where contamination seems possible a similar trend was observed between the results obtained with the AMESA and MST 2. However, the AMESA produced results 5-8 times higher than the comparative MST between tests 1-3 and 14 and 17.

7.15.3 DMS and MST comparative data

As stated in section 7.17.1 the MST results were very low and as a result the errors in measurement play a significant role and make it difficult to produce a direct relationship between the MST and the DMS system. In fact, the majority of the DMS results obtained at Site 2 were at or below the reportable method detection limit for the MST method. A similar trend was observed between the results obtained with the DMS and MST 1 although the DMS produced results five times higher than the comparative MST overall.

7.15.4 AMESA and DMS comparative data

When comparing the results obtained with the two CISDs it is important to remember that they were both sampling from a single point but in different areas of the stack. However, a similar trend was generally observed between the two CISD systems. If we accept that there was a problem with contamination of the AMESA system in tests 5-8, and we examine the other comparative tests then the AMESA produced similar results to the DMS.

8 Comparison of test results with MCERTS performance specifications

8.1 Environmental chamber testing

The leak test used in this study was found to be inappropriate for testing the CISDs against temperature and vibration conditions. However, there was no evidence from these tests that the systems tested could not withstand operating temperatures of –25 to +50°C or the vibration frequencies applied. Under normal use the sampling systems automatically carry out a leak test of the complete system at the beginning and end of each test. It should be noted however that the CISD does not carry out a leak test to the end of the sampling probe.

8.2 Functionality tests

Sampling of dioxins and furans must be undertaken isokinetically as these species are associated with both the gaseous and particulate phases found in process emissions. Consequently, the isokinetic sampling performance of a CISD is fundamental in ensuring accurate determination of dioxins and furans in process emissions. The CISD were therefore subjected to a number of tests to assess the sampling performance of the system and the ability to collect a representative sample. The results are summarised in Tables 8.1 and 8.2 below.

It can be seen from Tables 8.1 and 8.2 that both the DMS and AMESA systems passed the performance requirements of the MCERTS performance standard for automatic isokinetic samplers.

Table 8.1: Assessment of AMESA system against the MCERTS performance standard

Performance Characteristic	Performance Requirement	Performance Result	Decision
Accuracy of isokinetic sampling rate to changes in velocity	$<\pm5.0\%$	1.8%	Pass
Accuracy of determination of volume of gas sampled	$<\pm2.0\%$	1.8%	Pass
Response time, T_{90} (seconds)	<200	56-61	Pass
Linearity of isokinetic sampling rate to changes in velocity	$R^2 =>0.980$	$R^2 = 0.999$	Pass
Repeatability under laboratory conditions	<5%	0.9%	Pass
Minimum operational velocity (m. s^{-1})	<2.0	0.5	Pass
Drift (Short Term)	$<\pm5\ \%$	0.6	Pass

Table 8.2: Assessment of DMS system against the MCERTS performance standard

Performance Characteristic	Performance Requirement	Performance Result	Decision
Accuracy of isokinetic sampling rate to changes in velocity	$<\pm5.0\%$	1.3%	Pass
Accuracy of determination of volume of gas sampled	$<\pm2.0\%$	1.3%	Pass
Response time, T_{90} (seconds)	<200	58-62	Pass
Linearity of isokinetic sampling rate to changes in velocity	$R^2 =>0.980$	$R^2 = 1.000$	Pass
Repeatability under laboratory conditions	<5%	1.5%	Pass
Minimum operational velocity (m.s^{-1})	<2.0	1.0	Pass
Drift (Short Term)	$<\pm5\ \%$	0.9	Pass

9   Conclusions

Despite good ability to track the same trends in changing dioxin concentrations, systematic differences were observed between the CISD and MST measurements as well as between the two CISD systems themselves.

MSTs conforming to BS EN 1948 remain the only acceptable method for dioxin monitoring against the emission limit value in the WID. Although CISD systems comply with BS EN 1948 in most respects, they are currently designed for operation at a fixed sampling point (or two fixed points in the case of the DMS) within the duct, and traverses are not carried out automatically. BS EN 1948 requires traverses of the duct to be carried out in accordance with EN 13284-1 (Stationary Source Emissions – Determination of Low Range Mass Concentration of Dust Part 1 - Manual Gravimetric Method) to ensure a representative dust (and hence dioxin) sample is collected.

The dioxin concentrations in the field trials were extremely low. The majority of results were well within the 0.1ng I-TEQ/m^3 emission limit value specified by the WID, irrespective of the measurement system and test site. However, a small number of results were higher.

The results appear to show that dioxin releases were higher during start up especially at the municipal waste incinerator. A 14 day test including a process start up showed an average dioxin level of 0.25 ng I-TEQ /m^3 with the DMS but 0.059 ng I-TEQ /m^3 with the AMESA. The two 6-hour MST results following start up were 0.057 and 0.068 ng I-TEQ /m^3 respectively, but ranged between 0.002 – 0.012 and 0.004 – 0.040 ng I-TEQ /m^3 at other times during the 14 day test. CISDs and MSTs started sampling at different times. However, sampling start time is just one variable which may or may not account for the 0.25 ng I-TEQ /m^3 and other readings. Further work on measuring dioxin levels during start up is required.

There were some indications of probe contamination for some of the higher results but the study did not provide conclusive evidence of this. Further work on investigating possible contamination effects and options for improved clean up of equipment is required.

Both the DMS and the AMESA systems have been awarded certificates confirming that they pass the MCERTS performance requirements for "automated isokinetic samplers". This certificate does not convey MCERTS approval as continuous dioxin monitors.

10 Recommendations

The Environment Agency should continue to require operators to measure dioxins using the CEN standard, BS EN 1948, for regulatory controls.

The Environment Agency should carry out further work to confirm that the high results found at the municipal waste incinerator following start-up were due to start up conditions. Samples should be obtained using BS EN 1948 at the point waste feed commences following a process start up.

The Environment Agency should initiate discussions with the Source Testing Association on the possibilities of probe contamination, particularly when using titanium probes, and explore options for improved clean up of equipment between sample runs.

The R&D report should be made available to CEN, Defra and the European Commission for their consideration in the development of continuous monitors for dioxins in the future.

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