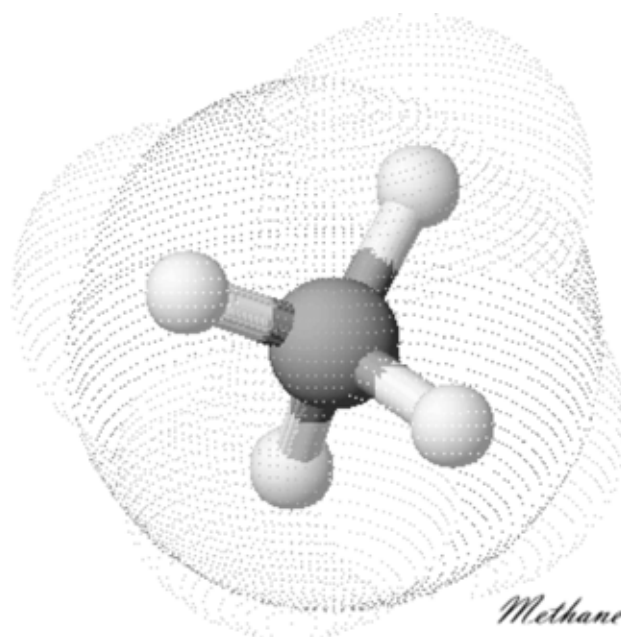


RVF:s UTVECKLINGSSATSNING FÖRBRÄNNING
Rapport nr 4 2005

**Comparison of existing on-line
measurement methods for
determination and monitoring of TOC
emissions from waste incineration**



Svenska Renhållningsverksföreningens Service AB

Prostgatan 2
211 25 Malmö

Tel: 040-35 66 00
Fax: 040-35 66 26

Preface

This project has been financed by the working group Waste incineration at the Swedish Association of Waste Management (RVF), and has been carried out by Jessica Samuelsson and Evalena Wikström at the Energy Technology Department at SP Swedish National Testing and Research Institute in Borås.

The aim of the study was to examine measurements of TOC (Total Organic Carbon) performed by an FTIR instrument and an FID instrument and compare achieved quality and accuracy in relation to demand set in the Waste incineration directive 2000/76/EC.

Thanks are due particularly to staff at Borås Energi and Renova, who made their boilers and instruments available to use for the measurements. And sincere thanks, too, to Hans Schmidt of Sweco International AB, who made many of the measurements at Renova.

The project has had a reference group, consisting of the following persons:

Henrik Lindståhl	Tekniska Verken AB in Linköping
Åse Wosnitza	Högdalenverket, AB Fortum Värme, jointly owned with Stockholm City Council
Lena Blomqvist	Söderenergi in Södertälje
Gunnar Olofsson	Renova AB in Gothenburg

Thanks are also due to the reference group for its help and views during the work of the project.

Malmö December 2005
RVF - the Swedish Association of Waste Management

Weine Wiqvist
Managing Director RVF

Håkan Rylander
Chairman of the working group Waste incineration

Summary

What is needed in order to be able to monitor TOC (Total Organic Carbon) emissions from a waste incineration plant? Is an FID instrument (Flame Ionisation Detector), which measures the sum of all the hydrocarbons, needed, or is it sufficient to use an FTIR instrument (Fourier Transform Infra-Red), which measures only a few? Many incineration plants today already have an FTIR instrument installed, and use it to monitor (for example) CO and NH₃. The extra cost of also measuring a number of specific hydrocarbons with the instrument is therefore low in comparison with the running cost of an FID instrument. As far as the plant owners are concerned, it would therefore be cost-efficient to use an FTIR instrument to monitor TOC as well. This project has therefore investigated whether it is possible to monitor TOC emissions with an FTIR instrument.

However, it must be realised that an FTIR instrument can measure only specific hydrocarbons. It is therefore not possible to measure the total TOC concentration, although a calibration function can be applied to compensate for the hydrocarbons that are not measured. The calibration function that is normally used for a QAL2 procedure is very suitable for use here, as it is regularly checked in connection with the annual surveillance inspection..

As a first stage, the project investigated the hydrocarbon mix in the flue gases, partly by study of the literature and partly by actual measurements on a waste incineration boiler. CH₄ was found to be the hydrocarbon that occurred in the highest concentration, and so a QAL2 procedure was applied (on both a fluidised bed boiler and a grate boiler) to an FTIR instrument that measured only CH₄. The accuracy requirements for QAL2 procedures were fulfilled for both boilers.

A QAL2 procedure was also applied, on the grate boiler, to an FTIR instrument that measured seven hydrocarbons: CH₄, C₂H₂, C₂H₄, C₂H₆, C₃H₈, C₆H₆ and C₆H₁₄. The QAL2 requirements were fulfilled in this case as well, although the margin was less than when measuring CH₄ alone. It is somewhat surprising that the results were poorer when more hydrocarbons were analysed, but this might be due to signal noise increasing when more hydrocarbons at relatively low concentrations are summed to produce a single measured value.

The conclusion from this project is therefore that the use of an FTIR instrument to monitor TOC meets the specified quality requirements, and that the accuracy of measurement is equal to that of an FID instrument. From this, it ought to be possible to use other instruments that can measure CH₄ in flue gases with relatively good accuracy for monitoring TOC. However, no other analysis techniques have been investigated within the framework of this project.

Contents

1. INTRODUCTION AND PROBLEM DESCRIPTION	1
2. THEORY	2
2.1 FID INSTRUMENTS	2
2.2 FTIR INSTRUMENTS	2
2.3 TYPES OF HYDROCARBONS EMITTED FROM COMBUSTION	3
2.4 QUALITY ASSURANCE OF AUTOMATIC INSTRUMENTATION SYSTEMS, QAL2.....	4
3. PLANTS AND INSTRUMENTS.....	6
3.1 THE CHAIN GRATE BOILER.....	6
3.2 THE FLUIDISED BED BOILER	6
3.3 FTIR INSTRUMENTS	6
4. RESULTS AND DISCUSSION	8
4.1 HYDROCARBON COMPOSITION OF FLUE GASES	8
4.2 QAL2 PROCEDURES (MODIFIED).....	9
<i>CH₄ as the monitoring indicator</i>	<i>9</i>
<i>CH₄ + C₂H₂ + C₂H₄ + C₂H₆ + C₃H₈ + C₆H₆ + C₆H₁₄ as the monitoring indicator, grate boiler.....</i>	<i>11</i>
<i>FID as the monitoring instrument.....</i>	<i>11</i>
<i>CO as the monitoring indicator.....</i>	<i>12</i>
<i>Conclusions, QAL2</i>	<i>13</i>
4.3 COMPARISON OF THE ON-LINE SIGNALS FROM FTIR AND FID INSTRUMENTS	14
4.4 ARE INSTRUMENTS CROSS-SENSITIVE FOR CO?.....	16
5. CONCLUSIONS	17
6. REFERENCES.....	18

Appendices

A Measurement pairs, CH₄, grate boiler

B Measurement pairs, CH₄ and FID, fluidised bed boiler

C Measurement pairs, CH₄ + C₂H₂ + C₂H₄ + C₂H₆ + C₃H₈ + C₆H₆ + C₆H₁₄, grate boiler

Nomenclature

Symbols

a	The intersection with the calibration function
b	The slope of the calibration function
S_D	The variability of the difference between measurement pairs.

Abbreviations

AMS	Automatic measurement system installed on a boiler
SRM	Standard reference method
TOC	Total organic carbon
FID	Flame ionisation detector
FTIR	Fourier transformer infra-red
PAH	Poly-aromatic hydrocarbons)

1. Introduction and problem description

When something that is defined as waste is to be burned, it must be burnt in accordance with the requirements and rules in EU Directive 2000/76/EC on the Incineration of Waste [1]. Sweden has incorporated the requirements of the directive in the Ordinance (2002:1060) Concerning the Incineration of Waste [2] and in the Environmental Protection Agency's Regulations no. 2002:28 Concerning the Incineration of Waste [3], which specify that, converted to equivalent TOC values, emissions of organic substances in gas or vapour form^{1,2}, may not exceed 10 mg/m³.

These requirements mean that the plants need to measure TOC emissions. Many plant owners today know from experience that the limit value for TOC is not likely to be exceeded as long as the limit value for carbon monoxide (CO) is not exceeded, i.e. CO concentration is used as the determining limit value indicator. A TOC instrument will therefore show only that TOC emissions are very low, and well below the limit value. The idea of using existing instruments, such as an FTIR³ instrument for monitoring TOC emissions, has therefore been considered. FTIR technology is well proven, and is used by many waste incineration plants to monitor emissions of such substances as HCl, CO and SO₂. In other areas, it is already in use for measuring specific hydrocarbons, such as CH₄ and C₂H₄. However, before it can be used in waste incineration plants, the method needs to be validated - and possibly further developed - for use in the conditions encountered in waste incineration.

The purpose of this investigation is therefore to investigate whether an FTIR instrument can be used for monitoring TOC emissions from a waste incineration plant. The work investigated the calibration range related to the emission limit value. In addition, it should be noted that it was only a method of monitoring TOC emissions in flue gases that was investigated, and not a method intended to measure absolute concentrations.

In response to a request from RVF, we also investigated whether an FID⁴ instrument is cross-sensitive to CO.

¹ TOC, Total Organic Carbon

² Dygnsmedelvärde eller halvtimmesmedelvärde vilket 97 % av mätvärdena ska uppfylla. Enhet omräknat till 11 % O₂, 273 K, 101,3 kPa, torr gas.

³ FTIR, Fourier Transform Infra Red

⁴ FID, Flame Ionisation Detector

2. Theory

2.1 FID instruments

An FID instrument measures the concentration of all specific hydrocarbons simultaneously. Ideally, it functions as a carbon atom counter, the output signal from which is proportional to the concentration of carbon in the hydrocarbons in the analysed gas. However, the strength of the output signal can be affected by many factors, such as the design of the detector, the structure of the molecules under analysis and the composition of the gas, all of which mean that the output signal is not the same as the concentration of carbon in the gas. Consider, for example, an instrument that has been calibrated with 1000 ppm of C_3H_8 , giving an output signal of 3000 ppm C_1 . If it is then later required to analyse 3000 ppm of CH_4 , it should ideally display 3000 ppm C_1 , although in practice the signal is always higher than this. The correct concentration of carbon can therefore be calculated using a conversion factor, which is usually referred to as the response factor. Different hydrocarbons have different response factors.

The composition of hydrocarbons in the flue gases from incineration is unknown, and so response factors cannot be used. Using an FID instrument to measure TOC in flue gases cannot therefore be regarded as providing an exact determination of the concentration, but only an indication of the TOC concentration in the flue gases.

2.2 FTIR instruments

In principle, an FTIR instrument can analyse all substances that absorb light in the infra-red (IR) region, measuring them all simultaneously. A prerequisite for a molecule to absorb IR light is that it can vibrate in such a way that its dipole moment changes during vibration. This means that all molecules, apart from monatomic and biatomic gases such as N_2 , O_2 and H_2 , absorb radiation in the IR range. In principle, therefore, all types of hydrocarbons can be analysed. However, interference from other substances such as water vapour and carbon dioxide can complicate analysis of a specific hydrocarbon, or even render it totally impossible. Nevertheless, there should not be any problems with analysis of hydrocarbons such as CH_4 or C_2H_4 , provided that their concentrations are sufficiently high to ensure that the absorbance exceeds the measurement noise.

Ideally, when using an FTIR instrument for monitoring TOC, all specific hydrocarbons should be analysed. However, this is not possible, as the number of types of specific emitted hydrocarbons runs into the hundreds, or perhaps over a thousand. However, the concentration of many of the hydrocarbons is very low, constituting only a very small proportion of the total hydrocarbon emission. It is therefore sufficient, when using an FTIR instrument to monitor TOC concentration, to measure only those hydrocarbons (or perhaps even only one hydrocarbon) that make(s) up most of the total hydrocarbon concentration. The following questions must therefore be answered:

1. Which hydrocarbons make up most of the total hydrocarbon emission?
2. Which hydrocarbon(s) must be measured if an FTIR instrument is to be used for monitoring TOC emissions?

Summarising, neither an FID instrument nor an FTIR instrument measures the concentration of TOC correctly. The drawback of an FID instrument is that the necessary response factors vary for different hydrocarbons, while that of an FTIR instrument is that it analyses only specific hydrocarbons.

2.3 Types of hydrocarbons emitted from combustion

We have been able to find only a very small number of published works that describe the composition of the gaseous hydrocarbons emitted by combustion. Articles dealing with emissions of hydrocarbons are often concentrated on health-hazardous substances such as PAH⁵ and dioxins, which make up only a very small fraction of the hydrocarbons emitted by combustion. However, three cases that investigated the composition of specific hydrocarbons in flue gases are summarised below. Although none of them was concerned specifically with waste incineration, the formation of various hydrocarbons when incinerating waste is probably not radically different.

Case 1

Schuster [4] measured the concentrations of a range of different substances, including CH₄, C₂H₄ and TOC, produced by CFB combustion of wood fuels and when burning a mix of wood fuels and sorted industrial waste. With CO concentrations below 1250 ppm, the TOC consisted mainly of CH₄, but higher CO concentrations resulted in noticeably higher concentrations of C₂H₄.

Case 2

Persson et al. [5] investigated emissions of a range of substances, including CH₄, C₂H₄ and TOC, resulting from combustion of wood fuels in smaller district heating plants (about 2 MW). The concentrations of TOC, CH₄ and C₂H₄ were often so low that they were not detectable. However, as combustion efficiency deteriorated, e.g. when reducing boiler output or when burning damp fuels, hydrocarbon emissions rose to detectable levels. Figure 1 shows the measured proportion of CH₄ as a function of measured TOC. It can be seen that CH₄ makes up a large proportion of the total hydrocarbon concentration. In this investigation, the concentration of C₂H₄ was considerably lower than the proportion of CH₄.

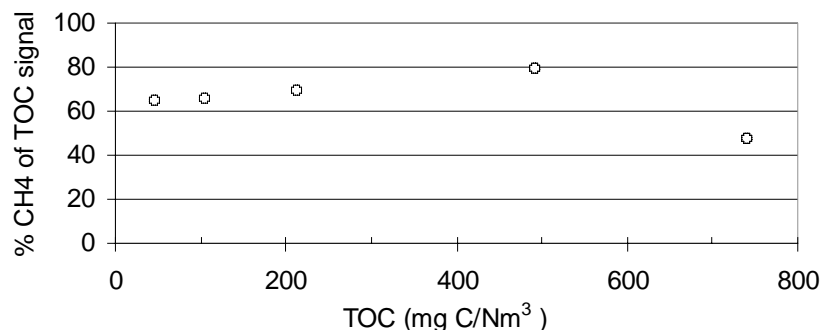


Figure 1. Proportion of TOC consisting of CH₄ at various concentrations of TOC [5].

Case 3

Johansson et al. [6] identified emissions of CO, TOC, NO_x and PAH from small-scale combustion in log-fired and pellets-fired boilers, measuring the concentrations of over about 30 different hydrocarbons. They found that the most prevalent hydrocarbons were CH₄, C₆H₆, C₂H₄ and C₂H₂. Figure 2 shows the proportion by weight of TOC that was measured and expressed as CH₄, C₆H₆, C₂H₄ and C₂H₂. It can be seen that CH₄ is the hydrocarbon that occurs in the highest concentrations in three out of four cases.

⁵ PAH, poly aromatiska hydrocarbons

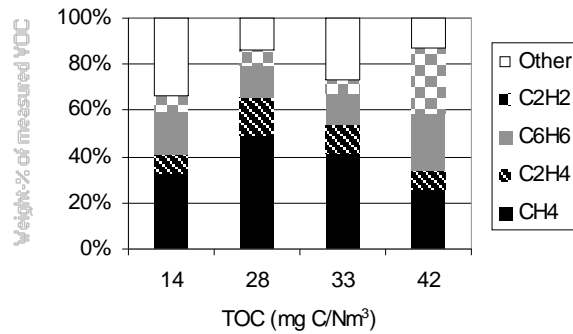


Figure 2. Hydrocarbon composition of flue gases from small-scale biofuel firing [6].

Summarising, these investigations found that CH₄, C₆H₆, C₂H₄ and C₂H₂ made up between 60 % and 85 % of the total measured quantity of TOC in the flue gases, and that CH₄ is the hydrocarbon that occurs in the highest concentrations. The results imply that conditions for TOC monitoring using FTIR instruments should be favourable.

2.4 Quality assurance of automatic instrumentation systems, QAL2

Most combustion plants today are fitted with automatic emission measurement systems (AMS). A quality system has been developed, in order to ensure that the performance of the systems is within the uncertainty requirements specified in legislation. It assures the following quality assurance levels:

- QAL1: Certification of AMS .
- QAL2: Quality assurance of installation of a measurement systems.
- QAL3: Quality assurance during operation.
- AST: Annual surveillance inspection.

Quality Assurance Level 1 (QAL1) is described in Swedish Standard SS-EN ISO 14956 [7], and Quality Assurance Levels QAL2, QAL3 and AST in Swedish Standard SS-EN 14181:2004 [8]. A QAL2 procedure has been used in this project, consisting of:

- Installation of AMS.
- Calibration of AMS using parallel measurements with a standard reference method (SRM). This means that, for example, a calibration function is determined for the measuring system, as well as a validity range for the function.
- Determination of the variability of the AMS, and a check of compliance with the required uncertainty.

For a waste incineration plant, this procedure must be carried out at least once every three years, or whenever any larger changes are made to the plant. In addition, the calibration must be checked as part of the work of the annual surveillance inspection.

It was not possible to comply exactly with the requirements of the QAL2 standard. The procedure had to be modified such that:

- Installation of the AMS was not inspected.
- Instead of calculating half-hourly mean values, they were calculated over shorter time intervals of a few minutes. This was necessary, as the hydrocarbon emissions occur

only in the form of short spikes, which are therefore not correctly represented by half-hourly average values.

- The measured value pairs have not been selected with regular intervals, but have instead been determined by the combustion conditions. During normal operation, the concentration of TOC was hardly measurable, and the frequency of occurrence of TOC spikes was very low. Most of the measurement pairs have therefore been calculated from conditions on those days when the boilers were deliberately operated in a less than optimum manner.
- In none of the QAL2 procedure cases has the calculated calibration function been based on 15 measured value pairs, as prescribed in the standard.

Apart from these points, the QAL2 procedure has been followed, as specified in [8]. A QAL2 procedure includes requirements in respect of the variability of the measured value pairs, S_D :

$$S_D \leq \sigma_0 k_v$$

where σ_0 is the standard deviation that the authority specifies that a measuring instrument must meet, as required (for example) in the Waste Incineration Directive (2000/76/EC) or in the Environmental Protection Agency's regulations no. NFS 2002:28, and where k_v is a test value from an χ^2 test with a β -value of 50 % (Table 1). NFS 2002:28 specifies that 95 % confidence-interval 24-hour average values of the individual measured values of TOC must not exceed 30 % of the emission limit value (10 mg/Nm³). According to [8], σ_0 can then be calculated as:

$$\sigma_0 = \frac{0,3 \cdot 10}{1,96} = 1,53 \text{ mg/m}^3_n$$

Table 1. Values of k_v

No. of measured value pairs	k_v
10	0,9627*
14	0,9743*
15	0,9777
16	0,9791

* Calculated by interpolation.

3. Plants and instruments

In order to investigate possible differences in TOC emissions, measurements were made on two different types of waste incineration plants: one with a grate boiler and one with a fluidised bed boiler.

3.1 The grate boiler

The grate boiler measurements were made on Renova's No. 5 boiler in Gothenburg. This has a power rating of 56 MW, and burns a mixture of domestic waste and business/industrial waste. The measurements were made over a period of ten days, with the boiler being operated normally for most of the time. However, for 2½ hours, the boiler was deliberately operated under non-optimum conditions in order to 'provoke' (see 2.2 above) emissions of TOC. All the measuring instruments were installed downstream of the flue gas cleaning equipment and upstream of the induced draught fan. Hydrocarbons were measured on-line with an FID instrument and with an FTIR instrument that was calibrated for the following seven hydrocarbons: CH₄, C₂H₂, C₂H₄, C₂H₆, C₃H₈, C₆H₆ and C₆H₁₄. In addition to the hydrocarbons, the equipment measured online concentrations of O₂, CO and H₂O in the flue gases. Four bag samples were also taken for analysis of 27 hydrocarbon concentrations in the flue gases. These bag tests collected flue gases in bags over periods of a few minutes, with the contents being analysed by a gas chromatograph later the same day.

3.2 The fluidised bed boiler

The measurements in the fluidised bed boiler were made on Borås Energi's two 20 MW boilers, firing a fuel mixture consisting of domestic and business waste. Five series of measurements were made, each lasting between 75 and 120 minutes. During normal firing, the TOC concentration was very low, and hardly detectable with either an FID or an FTIR instrument, and so the air flow was reduced for two of the measurement sessions in order to 'provoke' TOC emission. The TOC concentration was measured using three different instruments: an FTIR instrument, an FID instrument already fitted to the boiler, and an additional FID instrument, installed for the purposes of the tests. All three extracted gas from the same sampling point, in the chimney after the cleaning equipment but before the ID fan. In addition to TOC analysis, O₂ and H₂O concentrations in the gas were also measured.

3.3 FTIR instruments

Two different types of FTIR instrument were used for the measurements: a GASMET⁶ in the grate boiler, and an MB9100⁷ in the fluidised bed boiler. Table 2 gives more details of the two instruments.

⁶ Från TEMET Instruments Oy

⁷ Från Bomem/Hartmann & Braun

Table 2. FTIR instrument specifications.

	Model 9100	GASMET
Optical wavelength (m)	6,4	5,0
Resolution (cm ⁻¹)	1	8
Working temperature (°C)	174	180
Calibrated hydrocarbons (detection level)	CH ₄ (1,4-2,1 mg/m ³) ^a	CH ₄ (0,3-0,5 mg/m ³) ^b C ₂ H ₂ (0,3-0,5 mg/m ³) ^b C ₂ H ₄ (0,3-0,5 mg/m ³) ^b C ₂ H ₆ (0,3-0,5 mg/m ³) ^b C ₃ H ₈ (0,3-0,5 mg/m ³) ^b C ₆ H ₆ (0,3-0,5 mg/m ³) ^b C ₆ H ₁₄ (0,3-0,5 mg/m ³) ^b

^a Calculated ^b Supplier's information

4. Results and discussion

4.1 Hydrocarbon composition of flue gases

In order to find out which specific hydrocarbons should be analysed with the FTIR instrument, we investigated the hydrocarbon composition in the flue gas by means of bag samples. Four such samples were taken from the grate boiler, and gave the results shown in Table 3. Sample A was taken during normal operation, while samples B, C and D were taken when the boiler was deliberately fired in a sub-optimum manner. During normal operation, CH₄ was the only detectable hydrocarbon. When the boiler was 'provoked' (see 3.2 above), it was still CH₄ that occurred at the highest concentration, although other hydrocarbons, such as C₂H₂, C₂H₄ and C₆H₆, were detected.

Table 3. Analysis of hydrocarbon composition in the bag samples from the grate boiler.

Concentration: mgC/Nm ³	Sample A	Sample B	Sample C	Sample D	Concentration: mgC/Nm ³	Sample A	Sample B	Sample C	Sample D
<u>C1-C6</u>					<u>Aromatics</u>				
Methane	0.16	2.75	26.62	53.27	Benzene	n.d	0.26	0.10	0.88
Ethane	n.d	<0.02	<0.02	0.07	Toluene	n.d	<0.01	<0.01	<0.01
Ethene	n.d	0.05	0.55	1.31	butylacetate	n.d	<0.01	<0.01	<0.01
Propane	n.d	<0.02	<0.02	<0.02	Octane	n.d	<0.01	0.03	0.05
Propene	n.d	<0.02	<0.02	<0.02	ethylbenzene	n.d	0.01	<0.01	0.02
Isobutane	n.d	<0.03	<0.03	<0.03	m+p-xylene	n.d	0.02	0.48	0.48
Butane	n.d	<0.03	0.11	0.18	o-xylene	n.d	<0.01	<0.01	<0.01
Ethyne	n.d	1.28	6.28	11.78	nonane	n.d	0.05	0.03	0.05
t-2-butene	n.d	<0.03	<0.03	<0.03	<u>Total</u>	0.16	4.42	34.25	68.22
1-butene	n.d	<0.03	<0.03	0.03	<p>Figure 3. Graphic illustration of the table values.</p> <p>■ methane, CH₄ ▨ ethyne, C₂H₂ ▩ benzene, C₆H₆ □ Other</p>				
c-2-butene	n.d	<0.03	<0.03	<0.03					
Isopentane	n.d	<0.03	<0.03	<0.03					
Pentane	n.d	<0.03	0.05	0.08					
1,3-butadiene	n.d	<0.03	<0.03	<0.03					
t-2-pentene	n.d	<0.03	<0.03	<0.03					
c-2-pentene	n.d	<0.03	<0.03	<0.03					
1-pentene	n.d	<0.03	<0.03	<0.03					
Hexane	n.d	<0.04	<0.04	0.02					
Isoprene	n.d	<0.03	<0.03	<0.03					

n.d. - not detected.

It is interesting to relate the time when the bag samples were taken to the online measurements. However, this is not easy, as the samples were taken over periods of a few minutes, while the dwell time of the gases in the various sample preparation systems can be up to about a minute. In addition, the on-line instruments take samples at a rate of only once a minute. However, Figure 4 is an attempt to correlate the bag samples with the on-line instruments: the arrows indicate the time during which the flue gas was being pumped to the respective bags.

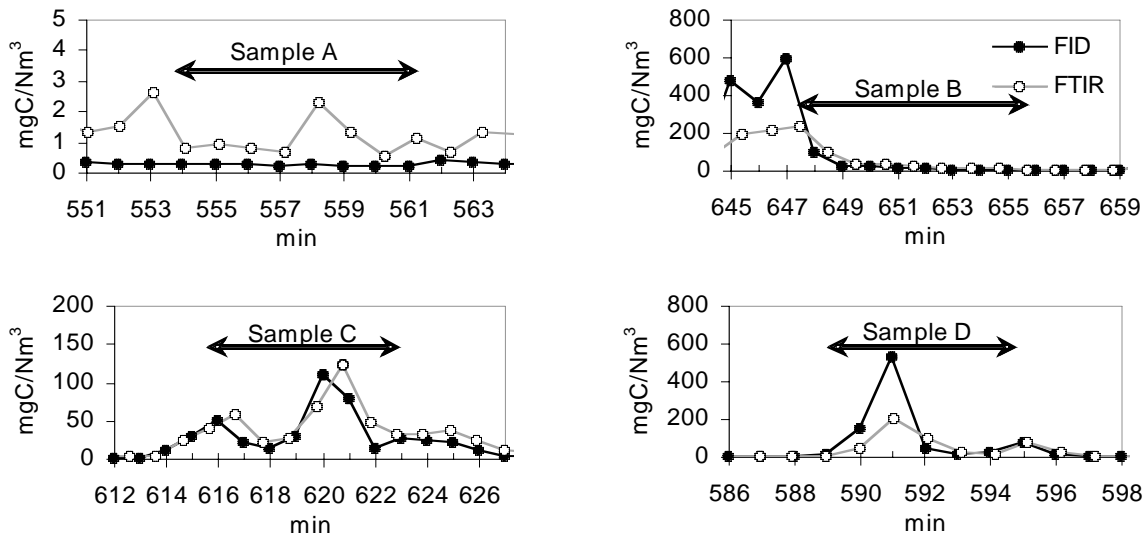


Figure 4. Sampling durations for bag sampling, in relation to FID and FTIR instrument on-line sampling. Note that the exact times of the bag sampling relative to the on-line sampling are uncertain.

4.2 QAL2 procedures (modified)

As described above, an FTIR instrument cannot measure all specific hydrocarbons in the flue gas, i.e. it cannot measure the total TOC concentration. However, a considerable proportion of the hydrocarbons are measurable, and the use of a calibration function compensates for those hydrocarbons that are not measured. The calibration function that is normally calculated for a QAL2 procedure (see 4.2) is very suitable here, as it will be regularly checked by the annual surveillance inspection.

CH₄ as the monitoring indicator

When the hydrocarbon concentration in the flue gas was investigated, it was noted that CH₄ is the hydrocarbon that is present in the highest concentrations (60-100 %). We therefore started by investigating whether it is possible to monitor TOC using an FTIR instrument measuring only CH₄.

The grate boiler

A total of 16 measurement pairs was obtained from the parallel measurements. Appendix A shows the measured data and graphical illustrations of all the measured value pairs. It can be seen from the diagrams in Appendix A that the measured CH₄ concentration tracks the FID signal well for all measured value pairs except for the two extremely high TOC concentrations. This departure at extremely high TOC concentrations is probably due to the fact that, in addition to CH₄, there are also high concentrations of other hydrocarbons [4]. Another possible explanation can be that the FTIR instrument was not calibrated to measure such high concentrations. Figure 5 shows the results of the QAL2 procedure in the form of the calculated calibration function, $S_{D,krav}$ and $S_{D,mätt}$. As $S_{D,mätt}$ is greater than $S_{D,krav}$ the variability requirement included in the QAL2 procedure is not fulfilled.

A correlation model containing extremely high concentrations of TOC is not relevant, as the limit value for CO, and TOC, are both exceeded many times under these conditions. A calibration function is therefore calculated, based on all the measured value pairs having a TOC concentration less than 35 mgC/Nm³. Figure 6 shows the result of this QAL2 evaluation,

and as $S_{D,mätt}$ is significantly less than $S_{D,krav}$, the variability requirement is fulfilled in this case.

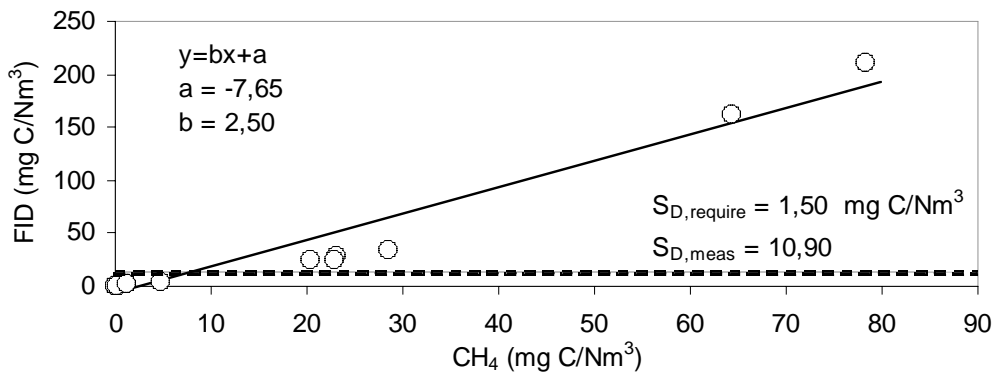


Figure 5. Calibration function for CH₄ for the grate boiler (TOC 0-200 mg C/Nm³). The dotted line shows the emission limit value for TOC.

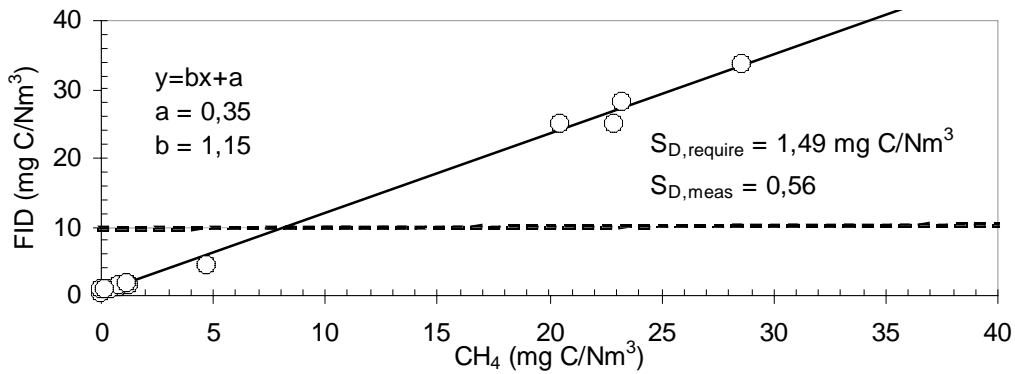


Figure 6. Calibration function for CH₄ measurement on the grate boiler (TOC 0-35 mg C/Nm³). The dotted line shows the emission limit value for TOC.

The fluidised bed boiler

15 measurement pairs were collected from measurements on the fluidised bed boiler: Appendix B shows them as figures and graphically. It can be seen from the diagrams that the measured values of CH₄ concentration track the FID signal relatively well, although the CH₄ concentration is always lower than the FID signal. Figure 7 shows the results of the QAL2 procedure. As $S_{D,mätt}$ is less than $S_{D,krav}$, the variability requirement is fulfilled in this case too.

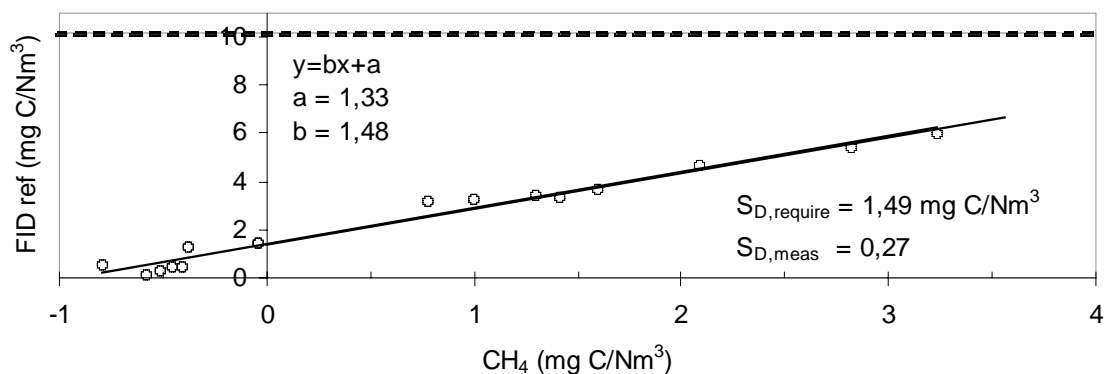


Figure 7. Calibration function for CH₄ on the fluidised bed boiler (TOC 0-6 mg C/Nm³). The dotted line shows the emission limit value for TOC.

CH₄ + C₂H₂ + C₂H₄ + C₂H₆ + C₃H₈ + C₆H₆ + C₆H₁₄ as monitoring parameters

The grate boiler

In addition to CH₄, there are also other hydrocarbons such as C₂H₂, C₂H₄ and C₆H₆ in the flue gas (see 4.1 above, and references [4-6]). Measuring more hydrocarbons than CH₄ alone should therefore give a better picture of the TOC concentration. A QAL2 procedure was therefore run for the grate boiler, analysing seven hydrocarbons (CH₄ + C₂H₂ + C₂H₄ + C₂H₆ + C₃H₈ + C₆H₆ + C₆H₁₄). 16 measurement pairs were then taken from the measurements, shown in Appendix C as measured data and graphically. As can be seen from the diagrams in the appendix, the measured concentration obtained by the FTIR instrument tracks the FID signal well for all measured value pairs, with the exception of two for which the TOC concentration is extremely high. The QAL2 procedure was therefore based on all the measured value pairs having TOC concentrations less than 35 mg/Nm³. Figure 8 shows the results of the QAL2 procedure, and as $S_{D,m\ddot{a}tt}$ is less than $S_{D,krav}$, the variability requirement is fulfilled. However, it is surprising that the variability is somewhat higher when only CH₄ is measured.

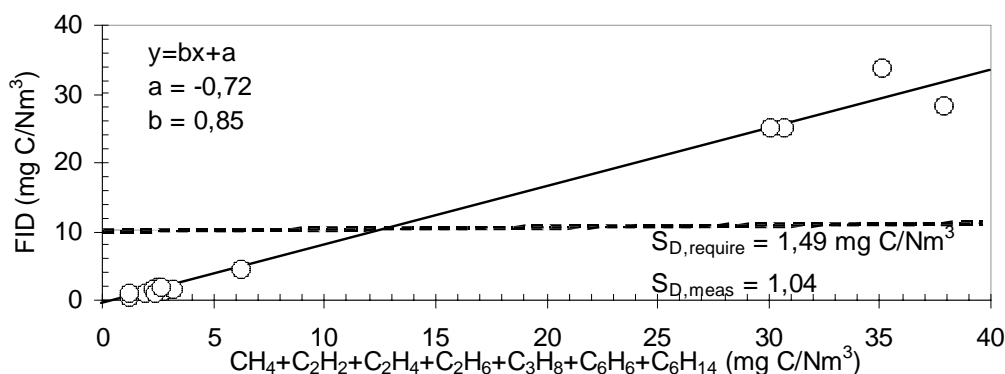


Figure 8. Calibration function for (CH₄ + C₂H₂ + C₂H₄ + C₂H₆ + C₃H₈ + C₆H₆ + C₆H₁₄) on the grate boiler (TOC 0-35 mg C/Nm³). The dotted line shows the emission limit value for TOC.

FID values as the monitoring parameter

A QAL2 procedure was also run on an FID instrument in order to relate its variability to that obtained for the FTIR instrument. The use of FID instruments is already an accepted method of monitoring TOC. 15 measurement pairs were taken from the measurements, and are shown in Appendix B as measured data and graphically. It can be seen from the diagrams in

the appendix that the results from the two FID instruments track each other relatively well. The results of the QAL2 calculations are shown in Figure 9, and it can be seen that the variability requirement is fulfilled ($S_{D,m\ddot{a}tt} < S_{D,krav}$).

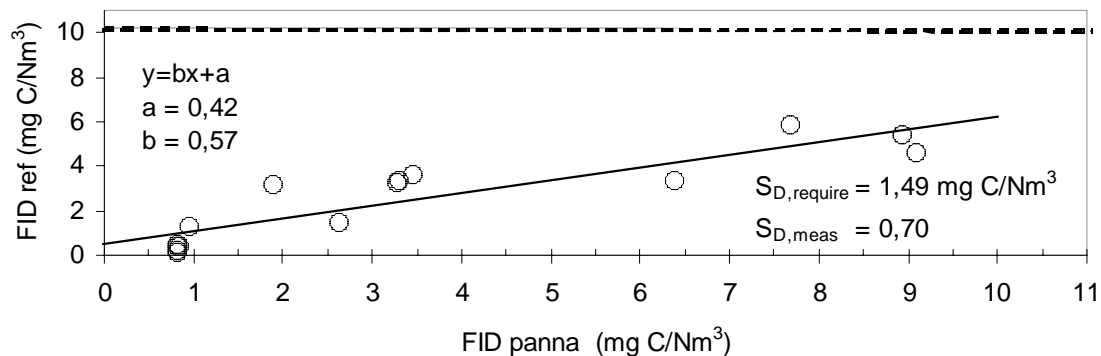


Figure 9. Calibration function for an FID instrument for measurements on the fluidised bed boiler (TOC 0-6 mg C/Nm³). The dotted line shows the TOC emission limit.

CO as the monitoring indicator

Many feel that the limit value for CO⁸ is exceeded long before the TOC emission limit (10 mg/Nm³)⁹ is reached, i.e. that CO should be the determining emission indicator. Figure 10 shows the relationship, for the grate boiler, between measured TOC (FID) and CO. When the highest emission limit value for CO (150 mg/Nm³) is exceeded, the TOC concentration is less than 4 mg/Nm³, which is far below the TOC emission limit. It therefore seems as if CO is the determining emission limit value indicator. It should be noted that these measured values are based on average 60-second values, while the TOC limit value is based on 30-minute average values.

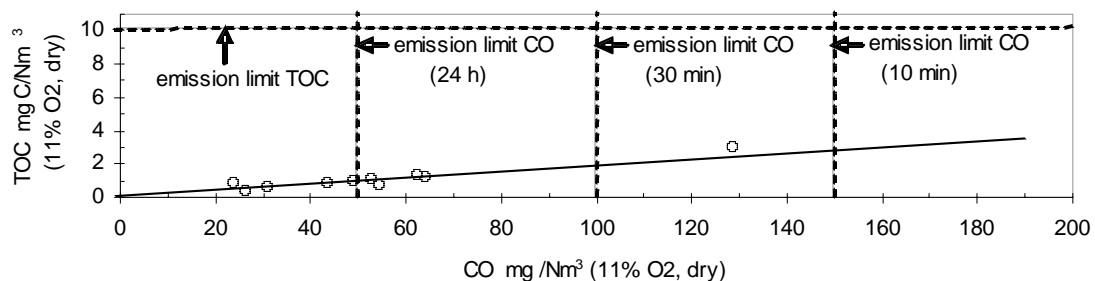


Figure 10. Relationship between measured concentrations of TOC (FID) and CO from the grate boiler. The values are based on 60-second average values¹⁰.

Both TOC and CO are formed as a result of incomplete combustion. As the TOC concentration increases, so also does the CO concentration, which can be clearly seen in Figure 10. This strong connection between TOC and CO raises the question of whether it is possible to monitor TOC by measuring only CO. A modified QAL2 procedure was therefore carried out, with CO used as the AMS. The results of the QAL2 procedure are shown in

⁸ Emissionsgränsvärdet för CO är 150 mg/Nm³ (10 minutersmedelvärde), 100 mg/Nm³ (halvtimmesmedelvärde) resp. 50 mg/Nm³ (dygnsmedelvärde).

⁹ Halvtimmesmedelmedelvärde omräknat till 11 % O₂, 273 K, 101,3 kPa, torr gas

¹⁰ Minutmedelvärde = ett medelvärde baserat på 2-6 minuter

Figure 11, but as $S_{D,m\ddot{a}tt}$ is greater than $S_{D,krav}$, the variability requirement is not fulfilled. However, the relationship seems stronger at low concentrations of CO and TOC. A modified QAL2 procedure was therefore carried out for CO concentrations less than 200 mg/Nm³. The results are shown in Figure 12, from which it can be seen that, as $S_{D,m\ddot{a}tt}$ is less than $S_{D,krav}$, the variability requirement is fulfilled. The relationship between CO and TOC is valid, provided that the combustion process is the only source of TOC emissions. This is not the case, for example, if water containing organic material is injected into the boiler to prevent organic material from burning.

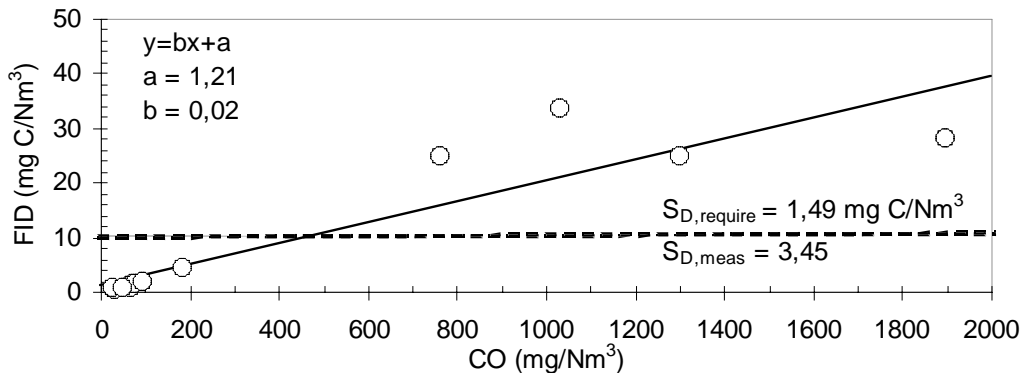


Figure 11. Calibration function for CO for measurements on the fluidised bed boiler (TOC 0-35 mg C/Nm³).

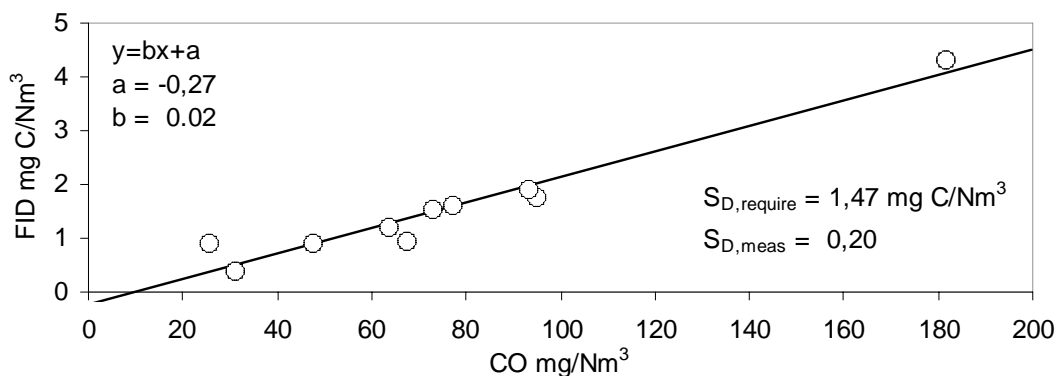


Figure 12. Calibration function for CO for measurements on the fluidised bed boiler (CO 0-200 mg C/Nm³).

Conclusions, QAL2

The following conclusions can be drawn from the modified QAL2 procedures:

- ✓ An FTIR instrument that measures only CH₄ fulfils the variability requirement for a QAL2 procedure, in both the grate and the fluidised bed boiler. However, the variability requirement is not fulfilled at extremely high TOC concentrations, but these concentrations are so extreme that they cannot be regarded as relevant for waste incineration.
- ✓ An FTIR instrument that measures TOC as the sum of seven hydrocarbons also meets the variability requirement, although with a lower margin than when only CH₄ is being analysed. This is surprising, as a greater proportion of the total TOC is being

measured. An explanation for the reduced margin is probably to be found in the increase in instrument noise when several hydrocarbons are being analysed (see Section 4.3).

- ✓ Table 4 shows the variabilities of the QAL2 procedures that were carried out. It is surprising that the variability of the FID instrument, the use of which is already an accepted method of monitoring TOC, is not lower than that of an FTIR instrument. This shows that the uncertainty of measurement of an FTIR instrument is the same as that of an FID instrument.

Table 4. Summary of the variability tests performed, TOC < 35 mg C/Nm³.

	$S_{D,mätt}$ (mg C/Nm ³)	$S_{D,krav}$ (mg C/Nm ³)
FID, fluidised bed boiler	0,7	1,49
FTIR (CH ₄), fluidised bed boiler	0,27	1,49
FTIR (CH ₄), grate boiler	0,56	1,49
FTIR (ΣC _x H _y)*, grate boiler	1,04	1,49

$$* \Sigma C_x H_y = CH_4 + C_2H_2 + C_2H_4 + C_2H_6 + C_3H_8 + C_6H_6 + C_6H_{14}$$

- ✓ It should be realised that TOC emissions occur in the form of short spikes, i.e. that the TOC concentration varies strongly with time. As a result, instantaneous values can at times be considerably higher than the calculated averaged value. The suitability of an FTIR instrument for monitoring TOC depends on the instantaneous concentrations. For concentrations lower than 100 mg C/Nm³, the FTIR signal followed the FID signal well (see the diagrams in Appendices A, B and C).
- ✓ CO seems to be the controlling emission indicator.

4.3 Comparison of the on-line signals from FTIR and FID instruments

Two different types of FTIR instrument were used for the measurements (Table 2): a GASMET in the grate boiler, and an MB9100 in the fluidised bed boiler. The two instruments differ in several ways: a GASMET instrument, for example, has a resolution of 8 cm⁻¹, while an MB9100 has a resolution of 1 cm⁻¹. We therefore decided to compare both FTIR instruments with an FID instrument.

Figure 13 shows the results of comparing the GASMET FTIR instrument with an FID instrument. Graph A shows the results with the boiler being fired normally, while graphs B, C and D show the results with the boiler deliberately being fired in a non-optimum manner. With normal firing (Graph A), the TOC concentration is very low, and hardly detectable by either an FID or an FTIR instrument. At somewhat higher concentrations (Graphs B and C), CH₄ and the seven hydrocarbons all follow the FID signal well, but at very high concentration (Graph D) there is a substantial difference between the FTIR and FID signals, regardless of whether the FTIR instrument is analysing CH₄ alone or the sum of the seven hydrocarbons. The noise level for the FTIR instrument when measuring the sum of the seven hydrocarbon is higher than the noise level of the FID instrument, and is also higher than when it (the FTIR instrument) is measuring CH₄ alone (see Graph A). This can explain why the variability obtained from a QAL2 procedure is higher when seven hydrocarbons are analysed than it is when only CH₄ is being analysed (see 4.2 above).

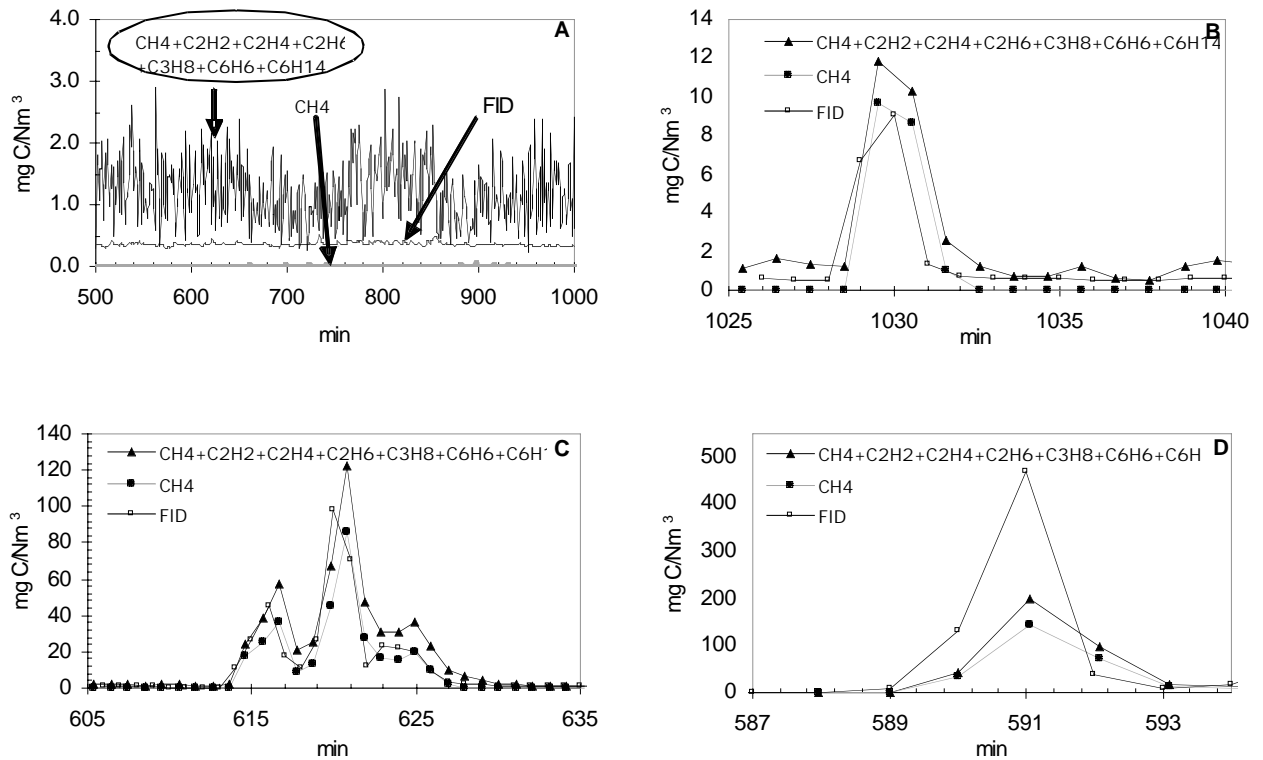


Figure 13. Comparison of an FTIR instrument (GASMET) with an FID instrument on the grate boiler for four different TOC concentrations.

The concentration of TOC in the fluidised bed boiler was also very low during normal firing. Figure 14 shows the TOC concentration as a function of time, both when the boiler is being fired normally (left) and when it is deliberately being fired badly (right). CH₄ could not be detected during normal firing, but the FID instrument detected a low TOC concentration. Somewhat higher TOC concentrations were generated when the boiler was fired badly. The measured CH₄ concentration follows the FID signal well, but the CH₄ concentration is always lower than the FID signal.

This means that, in both the fluidised bed boiler and the grate boiler, the two FTIR instruments follow the FID signal well, regardless of whether CH₄ alone or the seven hydrocarbons are being measured.

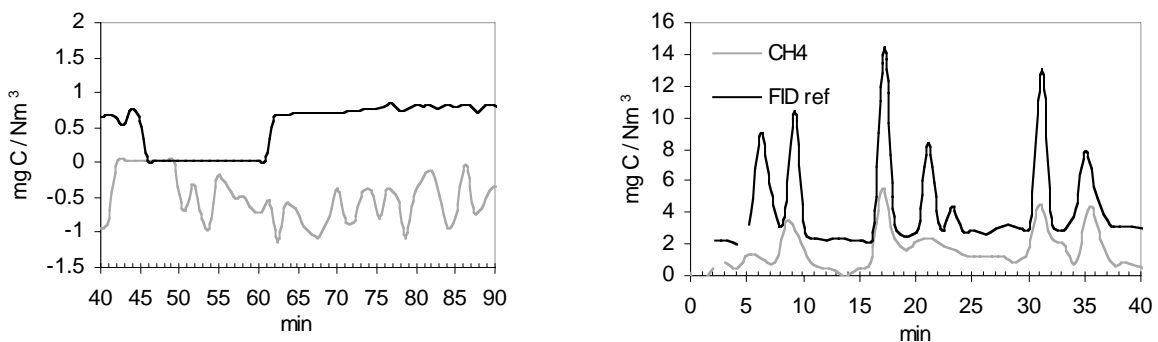


Figure 14. Comparison of an FTIR instrument (MB9100) with an FID instrument in the fluidised bed boiler, with normal firing (left) and deliberate non-optimum firing (right).

4.4 Is the instrument cross-sensitive to CO?

The cross-sensitivity of FID instruments for CO was investigated by mixing CH₄, CO and N₂ gases to known concentrations. Two different CH₄ concentrations, of 4,6 ppm and 69 ppm respectively, were investigated. CO concentrations were varied between 0 and 25 200 ppm for both the CH₄ concentrations. Figure 15 shows the measured concentrations of TOC at different concentrations of CO. No significant difference due to the CO concentration can be seen, which shows that an FID instrument is not cross-sensitive to CO at concentrations below 25 200 ppm. The CO concentration from waste incineration is normally much lower than 25 200 ppm, and so interference by CO when measuring TOC with an FID instrument can be ruled out.

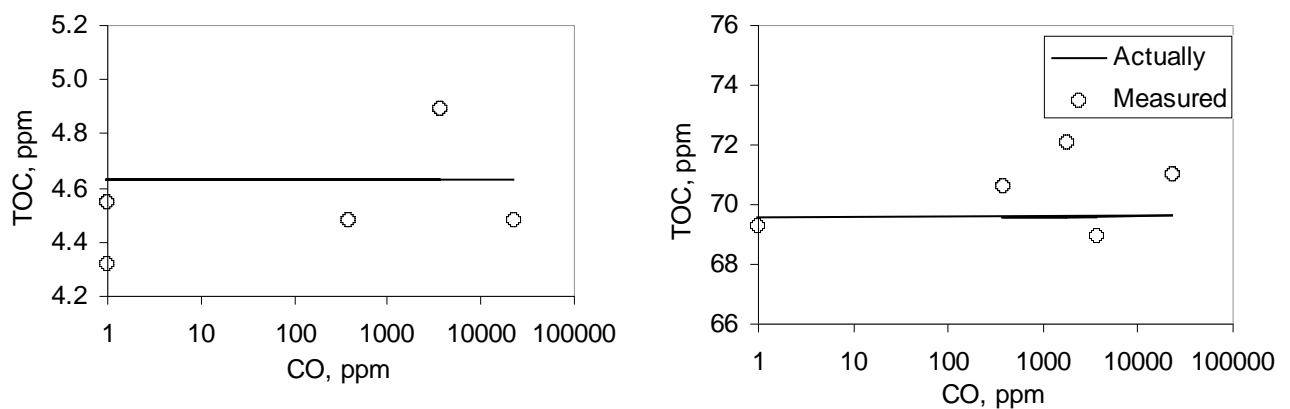


Figure 15. Measuring TOC with an FID instrument at various CO concentrations in a gas mixture containing 4,6 ppm (left) and 69 ppm of CH₄ (right).

5. Conclusions

The following conclusions can be drawn from the investigation:

- ✓ Analysis of four bag samples of flue gas show that CH₄ is the clearly most dominant hydrocarbon in the flue gas (60 -100 %).
- ✓ An FTIR instrument, measuring only CH₄, can be used to monitor TOC emissions from waste incineration in both grate and fluidised bed boilers. From this, it can be expected that other instruments, capable of measuring CH₄ in flue gases with relatively good accuracy, should be suitable for monitoring TOC emissions. However, this has not been investigated in this project.
- ✓ Measuring more hydrocarbons than just CH₄ does not guarantee better performance. The advantage of measuring many hydrocarbons is that this analyses a greater proportion of the hydrocarbons making up TOC, but the drawback is that doing so creates more instrument noise, which reduces the accuracy of measurement at low concentrations.
- ✓ When CO concentrations are around the emission limit value, TOC concentrations are very low, which means that CO seems to be the determining emission indicator.
- ✓ FID instruments do not have a cross-sensitivity for CO.

6. References

1. Directive no. 2000/76/EC of the European Parliament and of the Council of 4th December 2000 on the incineration of waste.
2. Ordinance (2002:1060) concerning waste incineration.
3. Environmental Protection Agency (2002); the Agency's Regulations on Waste Incineration no. 2002:28.
4. Schuster R. (1995), Emissions of hydrocarbons and NO_x with low excess air in CFB, Thermal Engineering Research Association report no. 541 [in Swedish].
5. Persson, H., Johansson, L., Tullin, C., Österberg, S., Johansson, M., and Leckner, B. (2001), Particle emissions from smaller biofuelled district heating boilers, Thermal Engineering Research Association report no. 758. [in Swedish].
6. Johansson, L., Leckner, B., Gustavsson, L., Cooper, D., Tullin, C., and Potter, A. (2004), Emission characteristics of modern and old-type residential boilers fired with wood logs and wood pellets, Atmospheric Environment, 38, pp. 4183-4195.
7. Swedish Standard (2002), Air quality - Determination of the suitability of a measurement procedure by comparison with a required uncertainty of measurement. Swedish Standard no. SS-EN ISO 4956:2002. [in Swedish].
8. Swedish Standard (2004), Emissions and outdoor air - Quality assurance of automatic measurement systems. Swedish Standard no. SS-EN 14181:2004 [in Swedish].

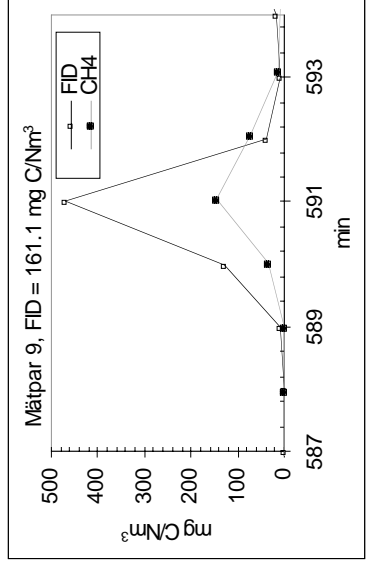
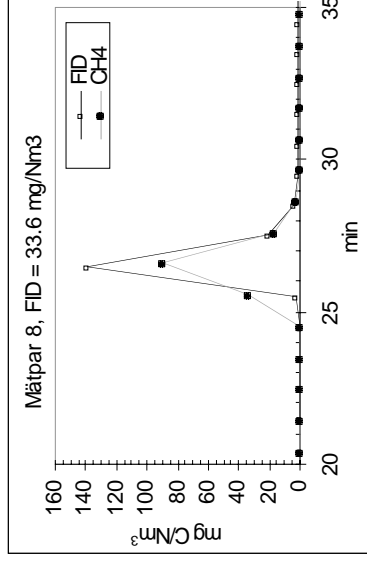
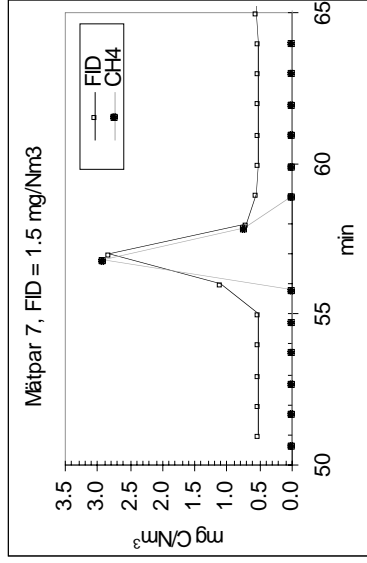
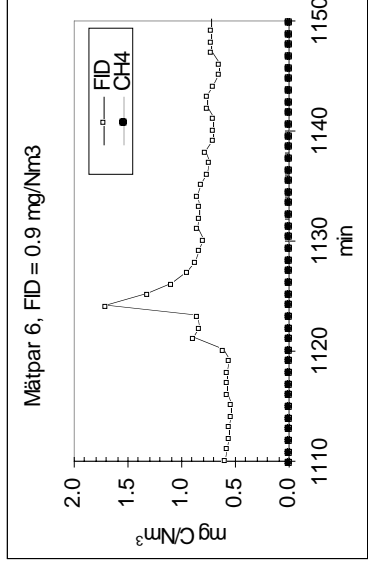
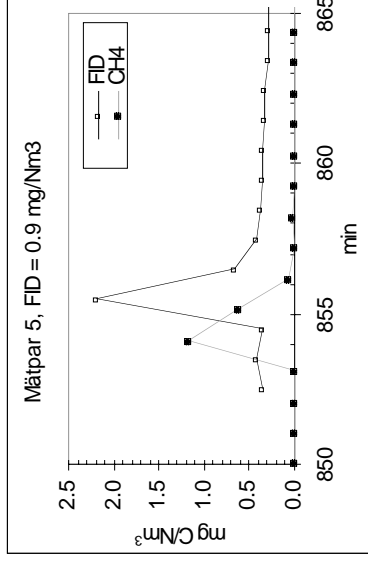
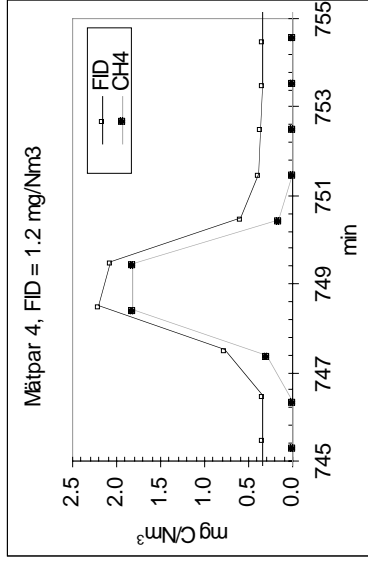
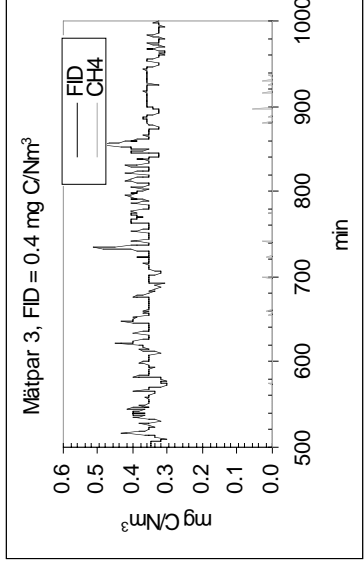
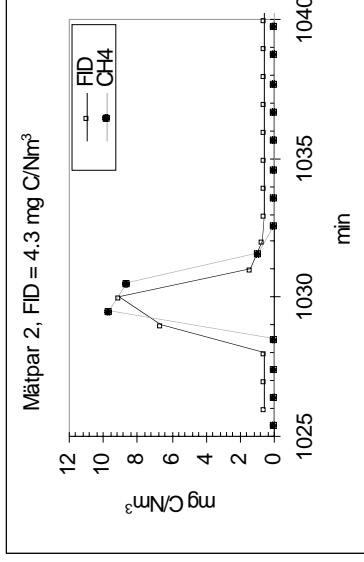
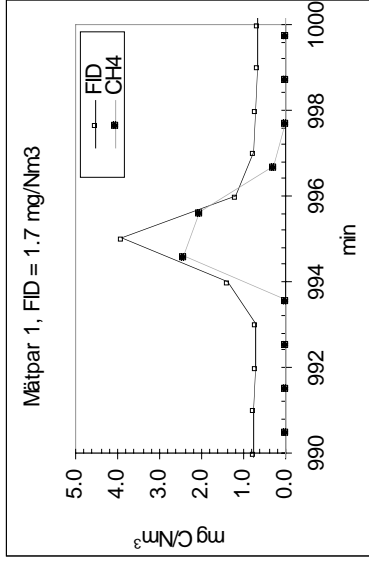
Appendices

A. Measurement pairs, grate boiler, CH₄

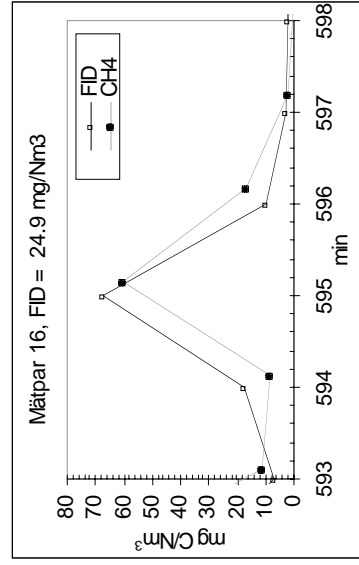
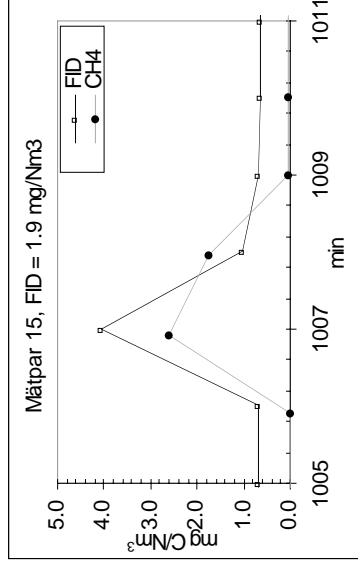
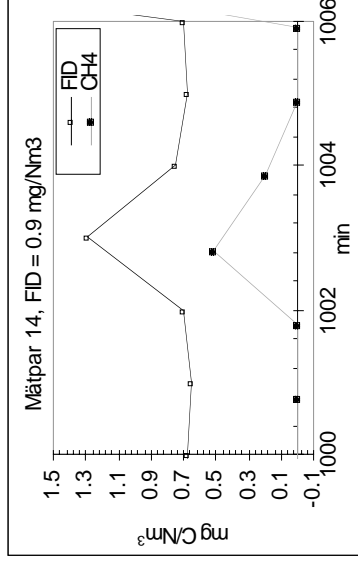
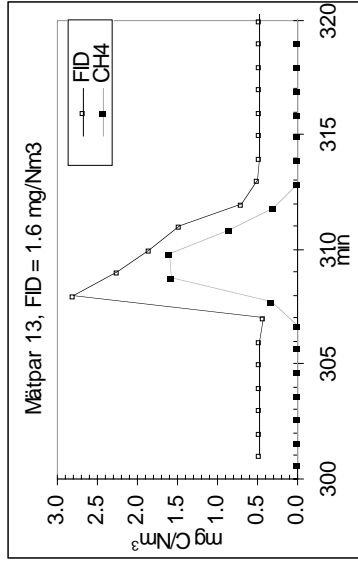
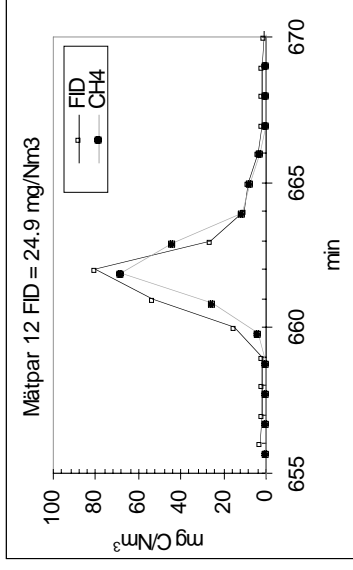
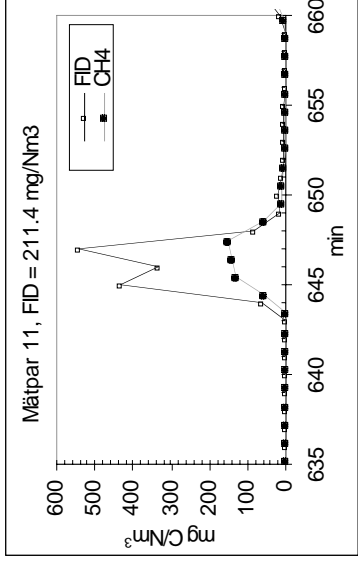
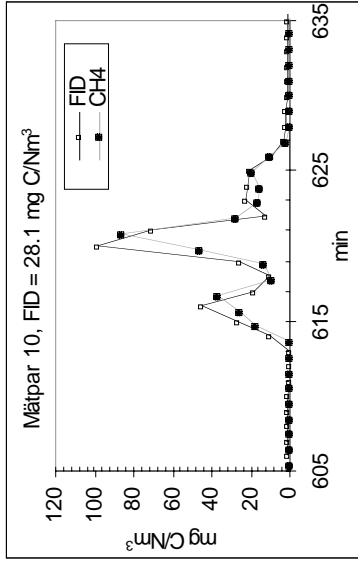
Table 5. All 16 measurement pairs, with O₂ and H₂O.

Measure- ment pair	FID wet <i>mg C/Nm³</i>	CH ₄ wet <i>mg C/Nm³</i>	O ₂ wet <i>v-%</i>	H ₂ O <i>v-%</i>
1	1.7	1.2	4.3	9.1
2	4.3	4.7	5.1	8.4
3	0.4	0.0	7.7	7.1
4	1.2	0.8	4.7	8.1
5	0.9	0.5	7.1	7.4
6	0.9	0.0	8.0	10.5
7	1.5	1.2	4.1	9.7
8	33.6	28.6	4.1	7.4
9	161.1	64.4	2.4	11.5
10	28.1	23.2	2.4	9.2
11	211.4	78.3	1.9	8.1
12	24.9	20.5	2.6	9.1
13	1.6	0.8	4.3	9.7
14	0.9	0.2	3.8	8.8
15	1.9	1.2	4.3	8.4
16	24.9	22.9	3.3	12.0

CH₄



CH₄, continued

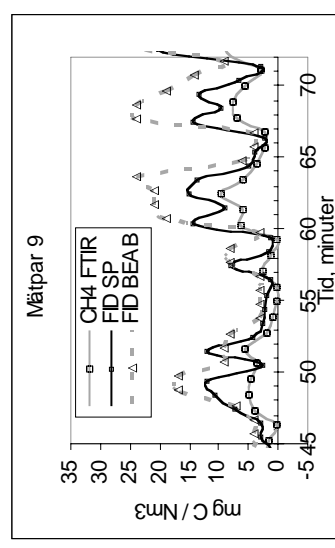
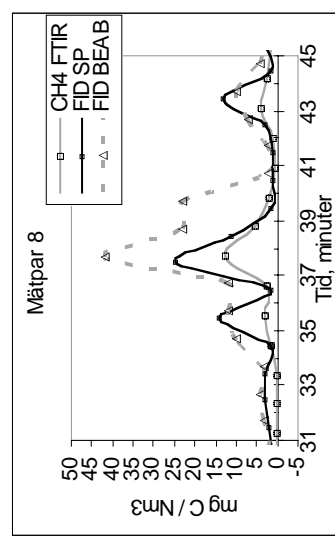
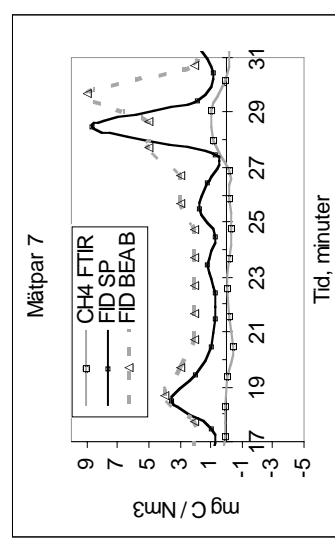
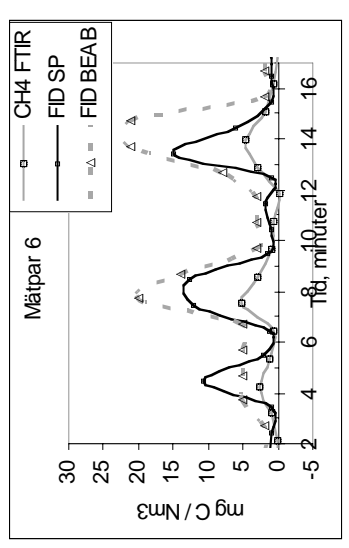
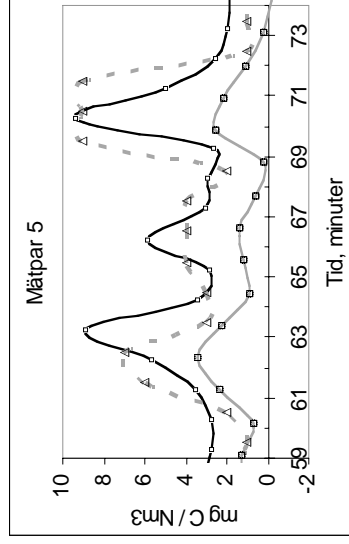
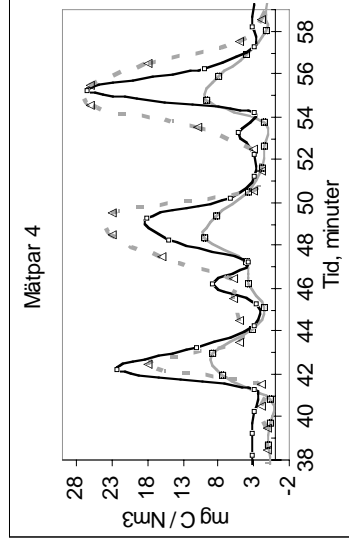
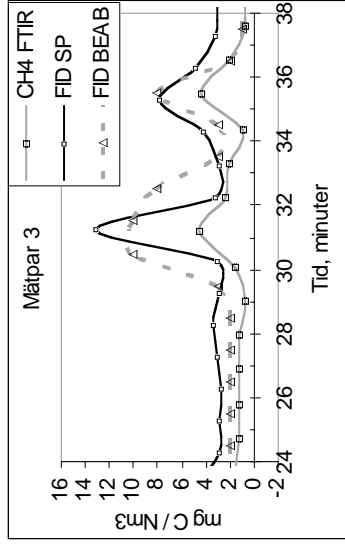
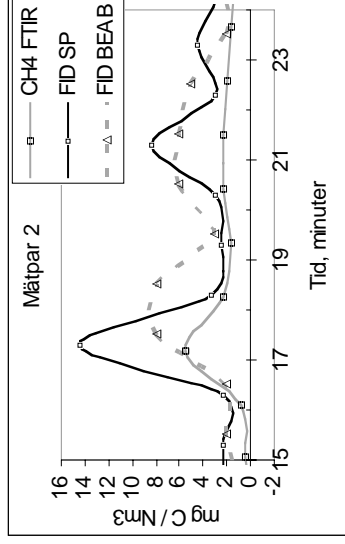
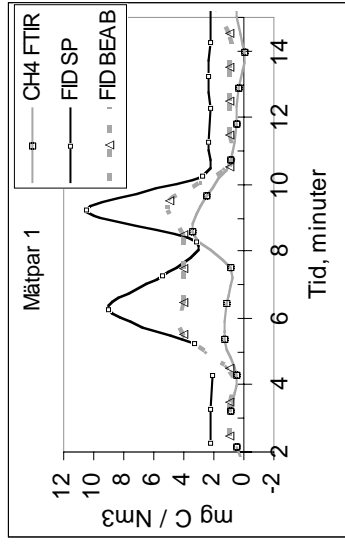


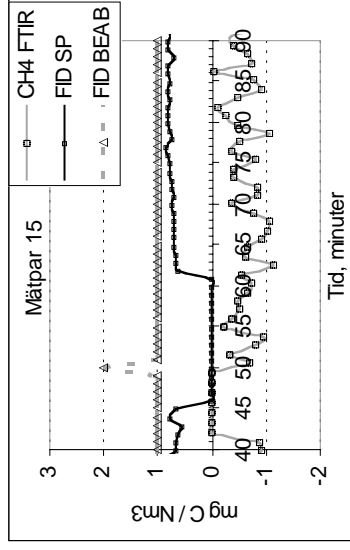
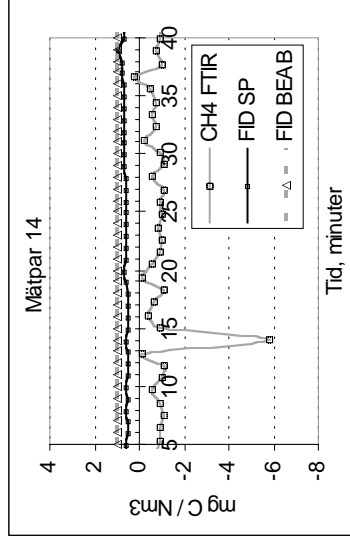
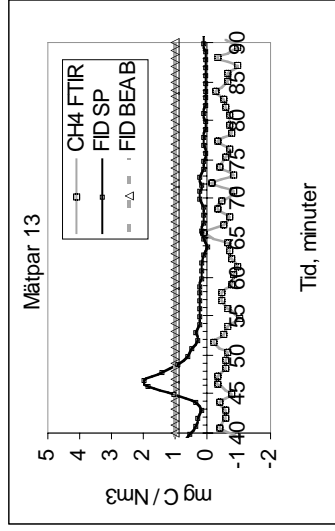
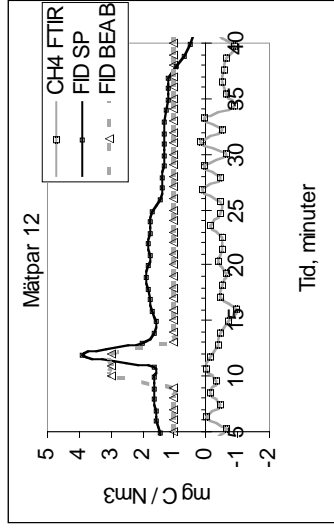
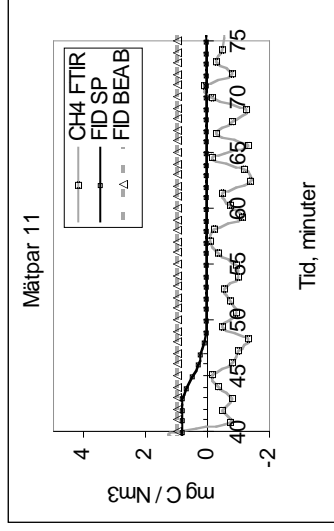
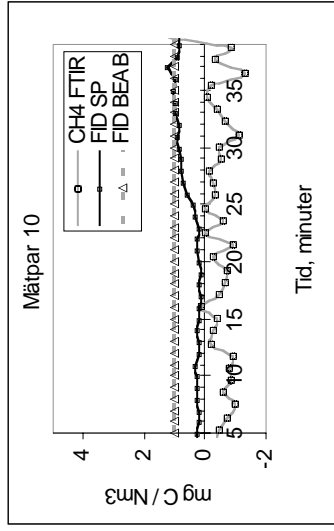
Note that the measurements have been made over a total of ten days, and that the time scale started at 0 each day at midnight. It can therefore seem as if two different measurement pairs have been taken at the same time, but this is never the case.

B. Measurement pairs, fluidised bed boiler CH₄ and FID

Table 6. Measurement pairs for the fluidised bed boiler, with O₂ and H₂O

Measurement pair	AMS FTIR			AMS FID			SRM		
	CH ₄ wet <i>mg C/Nm³</i>	H ₂ O wet <i>v-%</i>	O ₂ dry <i>v-%</i>	TOC boiler wet <i>mg C/Nm³</i>	H ₂ O <i>v-%</i>	O ₂ dry <i>v-%</i>	TOC ref wet <i>mg C/Nm³</i>	H ₂ O <i>v-%</i>	O ₂ wet <i>v-%</i>
1	0,79	18,9	5,73	1,90	18,4	6,12	3,14	18,9	5,73
2	1,60	19,8	4,75	3,46	19,4	5,13	3,60	19,8	4,75
3	1,41	20,3	4,18	3,31	20,0	4,59	3,32	20,3	4,18
4	3,24	20,6	4,33	7,70	20,4	4,69	5,93	20,6	4,33
5	1,01	20,6	4,55	3,29	20,2	5,06	3,24	20,6	4,55
6	1,30	19,2	4,63	6,39	19,3	4,75	3,36	19,2	4,63
7	-0,03	19,2	4,61	2,64	19,3	4,77	1,45	19,2	4,61
8	2,09	19,4	4,40	9,11	19,4	4,49	4,60	19,4	4,40
9	2,82	19,8	3,95	8,95	19,9	4,14	5,41	19,8	3,95
10	-0,40	17,5	6,59	0,82	17,5	6,91	0,38	17,5	6,59
11	-0,57	17,5	6,60	0,82	17,5	6,92	0,11	17,5	6,60
12	-0,37	17,4	6,58	0,97	17,6	6,97	1,28	17,4	6,58
13	-0,51	17,5	6,59	0,82	17,6	6,92	0,22	17,5	6,59
14	-0,79	17,3	7,14	0,83	16,8	9,13	0,46	17,3	7,14
15	-0,45	14,7	4,89	0,85	16,8	9,06	0,42	14,7	4,89





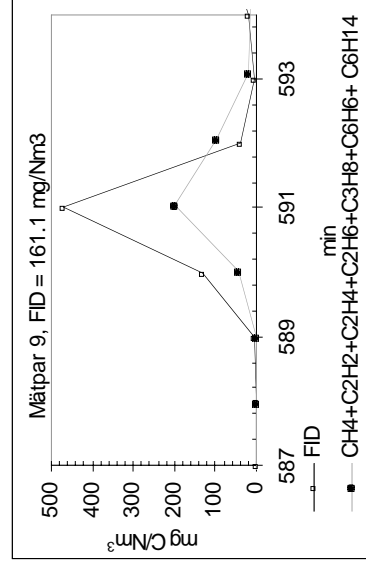
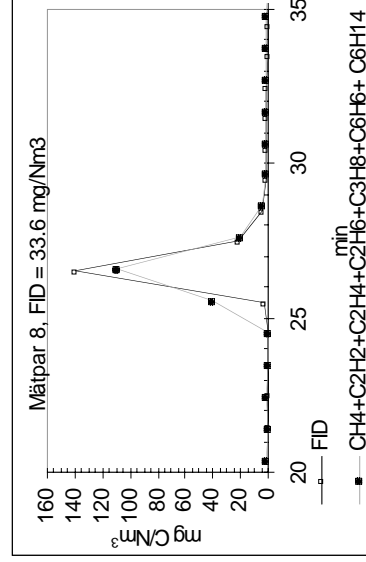
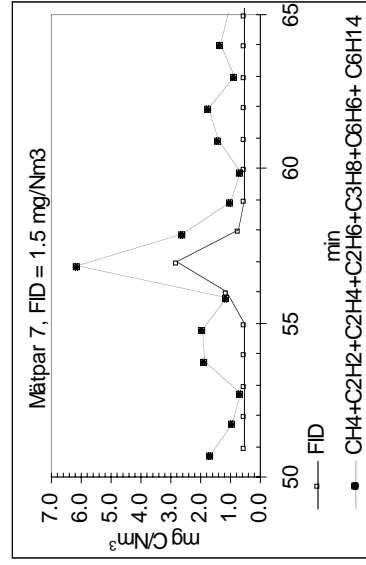
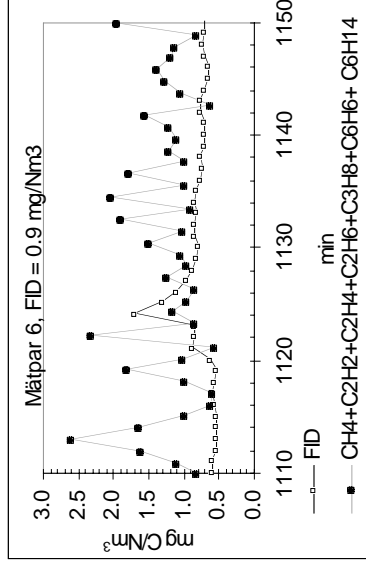
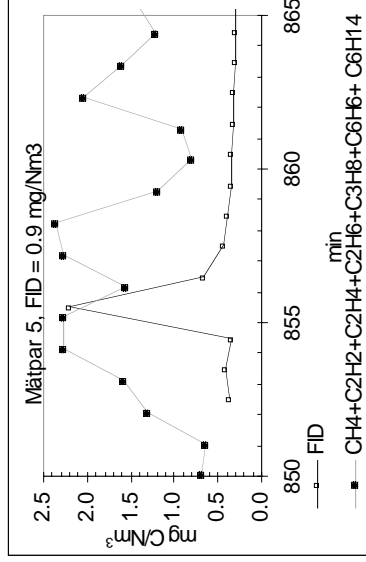
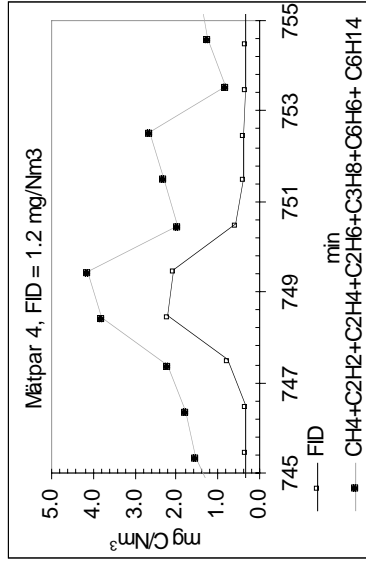
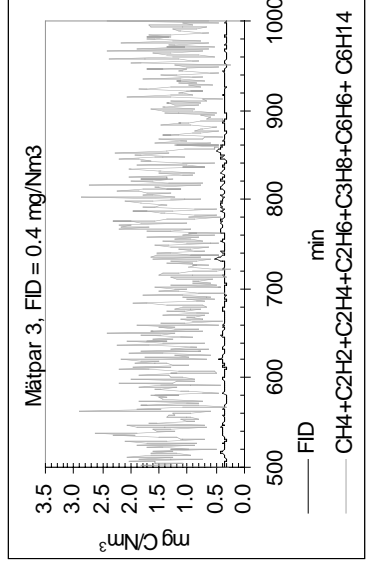
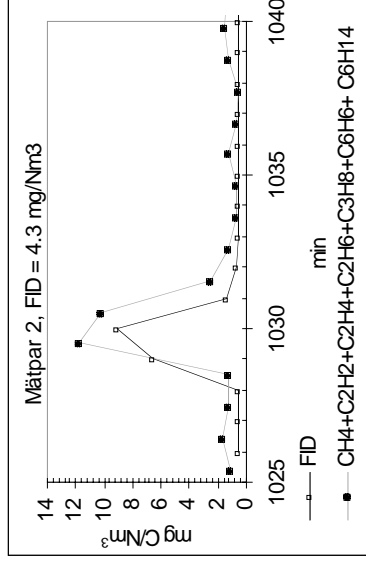
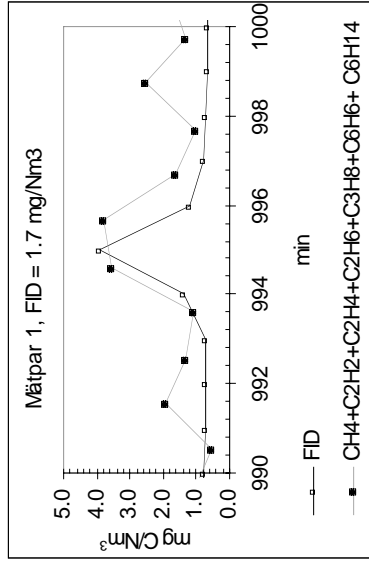
Note that the measurements have been made over a few days, and that the time scale started at 0 each day at midnight. It can therefore seem as if two different measurement pairs have been taken at the same time, but this is never the case.

C. Measurement pairs, grate boiler, CH₄ + C₂H₂ + C₂H₄ + C₂H₆ + C₃H₈ + C₆H₆ + C₆H₁₄

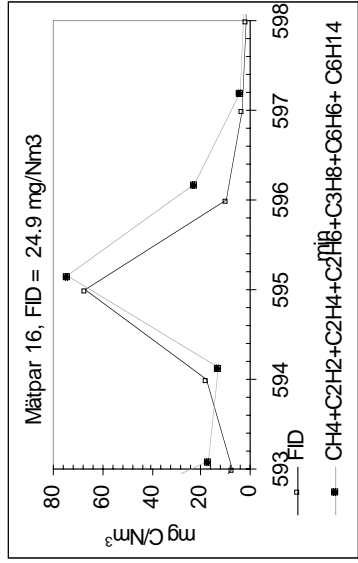
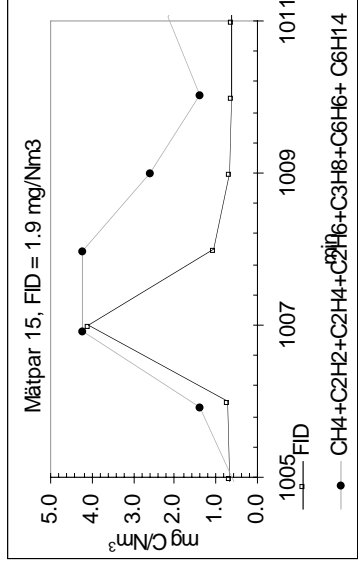
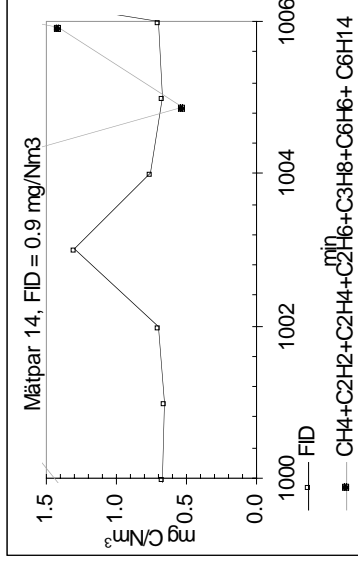
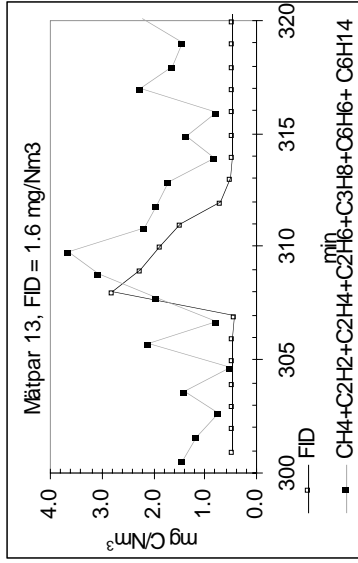
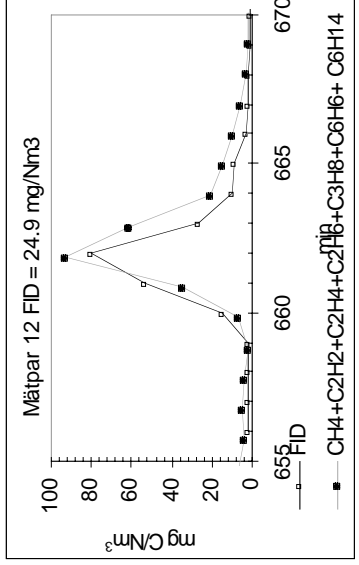
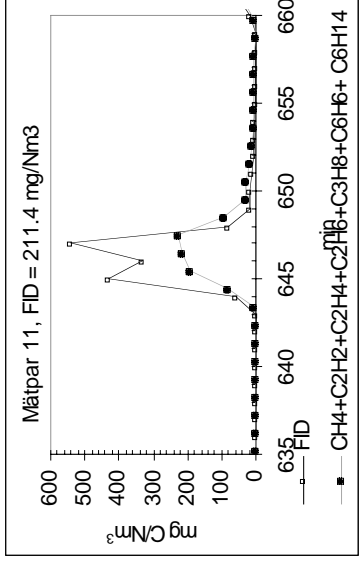
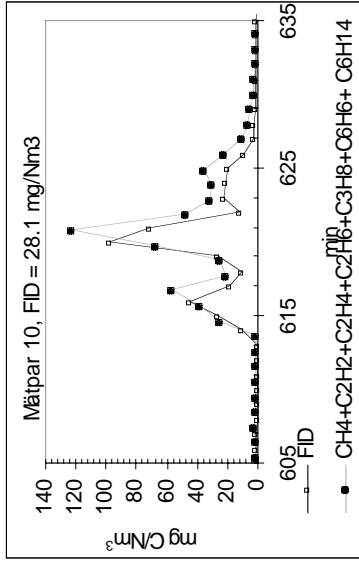
Table 7. All 16 measurement pairs for the grate boiler, with O₂ and H₂O.

Measure- ment pair	FID wet mg C/Nm³	CH₄+C₂H₂+C₂H₄+C₂H₆+ C₃H₈+C₆H₆+C₆H₁₄ wet mg C/Nm³	O₂ wet v-%	H₂O v-%
1	1.7	2.5	4.3	9.1
2	4.3	6.3	5.1	8.4
3	0.4	1.2	7.7	7.1
4	1.2	2.8	4.7	8.1
5	0.9	2.0	7.1	7.4
6	0.9	1.2	8.0	10.5
7	1.5	3.3	4.1	9.7
8	33.6	35.2	4.1	7.4
9	161.1	87.2	2.4	11.5
10	28.1	37.9	2.4	9.2
11	211.4	118.3	1.9	8.1
12	24.9	30.7	2.6	9.1
13	1.6	2.3	4.3	9.7
14	0.9	2.4	3.8	8.8
15	1.9	2.7	4.3	8.4
16	24.9	30.1	3.3	12.0

CH₄+ C₂H₂+ C₂H₄+ C₂H₆+ C₃H₈+ C₆H₆+ C₆H₁₄



CH4+C2H2+ C2H4+C2H6+C3H8+C6H14, continued.



Note that the measurements have been made over a total of ten days, and that the time scale started at 0 each day at midnight. It can therefore seem as if two different measurement pairs have been taken at the same time, but this is never the case.

Rapporter från RVFs utvecklingsinsats för förbränning

Vatten- och kemikalieförbrukning vid svenska avfallsförbränningsanläggningar 1993	1995:01
Restprodukter vid rening av rökgaser från avfallsförbränning. Erfarenheter från svenska undersökningar och anläggningar	1995:02
Prediktionsmodeller för kontinuerlig kvalitetskontroll av process och instrument	1995:03
Tvättning av aska och slagg från avfallsförbränning - en litteraturstudie	1995:04
Underhållskatalog för avfallsvärmeverk	1996:01
Svensk avfallsförbränning 1994-1995. Miljö och ekonomi	1996:02
Nyckeltal 1994. Drift och underhåll. Avfallsförbränning	1996:03
CE-märkning. Nya regler för maskiner 1995	1996:04
Vattenkylda roster för avfallsförbränning	1996:05
Slangfilterproblem i avfallsförbränningsanläggningar. Erfarenhetssammanställning	1996:06
Mätinstrument. Erfarenheter av olika drift- och miljöinstrument på värmekraft- och kraftvärmeverk inom RVF och ADV. 1994/1995 års status	1996:07
Nyckeltal för avfallsförbränning 1995. Drift och underhåll	1997:01
Förbränning av källsorterade förpackningar. Granskning av ÅFs rapport "Energiutvinning ur källsorterade förpackningsfraktioner"	1997:02
Åtgärder för CO-minimering på avfallsförbränningsanläggningar i Sverige. Sammanställning av enkätsvar	1997:03
Rökgasåterföring. Kartläggning av problem vid drift och underhåll	1997:04
Waste incineration in Europe. A study tour to Alkmaar, Bamberg, Vestforbrænding	1997:05
Våt slipfångare av ammoniak. Ny process i pilotskala	1997:06
Rening och återanvändning av rökgaskondensat från avfallsförbränning. Litteraturstudie	1997:07
Drift och underhåll av avfallstraverser. Enkät svar från sex anläggningar	1997:08
Kombination av SNCR och SCR i avfallsförbränningsanläggningar för reduktion av kväveoxider och ammoniakslip	1998:01
Nyckeltal för avfallsförbränning 1996. Drift och underhåll	1998:02
Environmental Optimisation of Waste Combustion	1998:03
Miljöanpassad optimering av avfallsförbränning. Förkortad version på svenska av rapport Environmental Optimisation of Waste Combustion (nr 3 1998)	1998:04
Samförbränning av rötslam	1998:05
Hantering av rökgasreningsprodukter från avfallsförbränning. Tekniska, miljömässiga och ekonomiska aspekter	1998:06
Nyckeltal för avfallsförbränning 1997. Drift och underhåll	1998:07
Eldstadsisolering i avfallseldade pannor i Sverige och Tyskland	1999:01
Lagring av avfall och avfallsbaserat bränsle	2000:01
Dioxiner i rester från förbränning av avfall. Resultat från undersökningar 1999/2000 av svenska avfallsförbränningsanläggningar	2001:01
Dioxiner i rester från förbränning av avfall. En genomgång och redovisning av kunskapsläget beträffande lakning och nedbrytning	2001:02
Hantering av rökgasreningsrest (RGR) från avfallsförbränning. Underlagsrapport	2002:01
Bestämning av vatteninnehåll i bottenaska/aska från avfallsförbränning	2002:02
Rening av rökgaskondensat	2002:03
Utsläpp till vatten från avfallsförbränningsanläggningar. Praktisk hjälpreda för utsläppskontroll	2003:01
Kalibrering av automatiska mätsystem vid Igelstaverket. Praktiskt genomförande av QAL 2 enligt standarden EN 14181	2004:01
Reduktion av svaveldioxidemissioner vid avfallsförbränning med torra rökgasreningsssystem	2004:02
Svavel i avfall	2004:03
Förslag till praktisk tillämpning av standarden "SS-EN 14181, Kvalitetssäkring av automatiska mätsystem"	2004:04
Mätvärdehantering vid avfallsförbränningsanläggningar med anledning av avfallsförbränningsdirektivet	2005:01
Waste turns into heat and electricity	2005:02
Jämförelse av befintlig on-linemetod för bestämning och bevakning av TOC-utsläpp vid avfallsförbränning	2005:03
Comparison of existing on-line measurement methods for determination and monitoring of TOC emissions from waste incineration	2005:04



**RVF – Svenska Renhållningsverksföreningen,
Prostgatan 2, 211 25 Malmö. Tel. 040-35 66 00,
fax 040-35 66 26.**

E-post: office@rvf.se

Hemsida: www.rvf.se