



TAMPERE UNIVERSITY OF TECHNOLOGY

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**CO<sub>2</sub> EMISSION MONITORING AND MEASUREMENT QUALITY CONTROL**

Master of Science Thesis

Examiner: Professor Matti Vilkkö  
Examiner and topic approved in  
the Faculty of Computing and  
Electrical Engineering Council  
meeting on 07 November 2012

## **ABSTRACT**

TAMPERE UNIVERSITY OF TECHNOLOGY

Master's Degree Programme in Electrical Engineering

**UOTILA, TURKKA:** CO<sub>2</sub> emission monitoring and measurement quality control

Master of Science Thesis, 48 pages, 1 Appendix page

May 2013

Major: Process Automation

Examiner: Professor Matti Vilkkö

Keywords: Monitoring, flue gas, carbon dioxide (CO<sub>2</sub>), emission trading system (ETS), quality control

This thesis was carried out as part of the Measurement, Monitoring and Environmental Assessment (MMEA) program, which is one of the research programs managed by the CLEEN Ltd. The Program concentrates on developing environmental monitoring technologies and tools for measurement quality control. The project was primarily financed by the Finnish Funding Agency for Technology and Innovation (Tekes). Work was developed in co-operation with Helsingin Energia and IndMeas Oy.

European Commission set new regulations for third Emission Trading System period (2013-2020), that increase requirements for risk assessment, uncertainty estimation and continuous accuracy surveillance for CO<sub>2</sub> monitoring system. The main objectives of this thesis were to research methods and requirements of CO<sub>2</sub> emission monitoring and quality control. To meet these objectives three independent methods are described and discussed to determine CO<sub>2</sub> emissions in power plants that fulfil the set requirements. The presented methods were standard method, direct measurement method and energy balance method, which was developed during the research work.

The results of the thesis indicate that all methods have their own strengths and weaknesses and applicability of these three CO<sub>2</sub> monitoring methods are case specific. The standard method almost always provides the best accuracy, but its weakness is not to provide good real-time information in typical installations. Instead, the direct measurement provides good real-time information with reasonable accuracy. The greatest interest focused on the energy balance method, which was developed to enhance quality monitoring and provide redundant information for both the standard method and direct measurement.

The energy balance calculation method can be used as emissions trading observation method or in combination with approved methods within certain limits. If more than one fuel is used in the boiler, it is also good to use other monitoring method as addition

assurance. In order to meet the accuracy requirements of emissions trading system when using energy balance method, the most important energy flow measurements must be calibrated.

Primary monitoring method and the authentication method should be selected so that they are not based on the same measurements. In this way dependence on individual measurements can be avoided. Also possible problems are detected quickly and they can be addressed with determination.

The thesis includes the principles of energy balance calculations of CO<sub>2</sub> emissions. To facilitate the deployment of the energy balance method the calculation has been conducted thoroughly in the thesis. All the presented methods are then applied in Salmisaari coal-fired power plant.

## TIIVISTELMÄ

TAMPEREEN TEKNILLINEN YLIOPISTO

Sähkötekniikan koulutusohjelma

**UOTILA, TURKKA:** CO<sub>2</sub> päästöjen seuranta ja mittausten laadunvarmennus

Diplomityö, 48 sivua, 1 liitesivu

Toukokuu 2013

Pääaine: Prosessiautomaatio

Tarkastaja: Professori Matti Vilkkö

Avainsanat: Monitorointi, savukaasut, hiilidioksidi (CO<sub>2</sub>), päästökauppa laadunvarmennus

Diplomityö tehtiin osana TEKESin rahoittamaa ja energia- ja ympäristötekniikan tutkimusyhtiö CLEEN Oy:n koordinoimaa Mittaus, Monitorointi ja Ympäristötehokkuus (MMEA) -tutkimusohjelmaa. Työn tavoitteena oli kehittää uusia teknologioita ja työkaluja teollisuusprosessien mittausten laadunvarmennukseen. Työ tehtiin yhteistyössä Helsingin Energian ja IndMeas Oy:n kanssa.

Euroopan komissio asetti uusia säännöksiä kolmannelle päästökauppakaudelle (2013–2020), jotka lisäävät vaatimuksia riskinarviointiin, epävarmuuden arvioimiseen ja jatkuva-aikaiseen mittaamiseen CO<sub>2</sub>-päästöjen osalta. Työn päätavoitteena oli tutkia menetelmiä ja vaatimuksia liittyen CO<sub>2</sub>-päästöjen monitorointiin ja laadunvarmennukseen. Kyseiset tavoitteet saavuttaakseen työssä otettiin tarkastelukohteeksi kolme itsenäistä tapaa määrittellä CO<sub>2</sub>-päästöt voimalaitoksissa, jotka täyttävät asetetut vaatimukset lainsäädännön osalta. Työssä käsitellyt menetelmät ovat ns. standardimenetelmä, suora mittaus ja energiatasemenetelmä, jota kehitettiin diplomityön aikana.

Työn tulokset osoittavat, että riippuen kohteena olevan voimalaitoksen ominaisuuksista ja käytetystä polttoaineesta, jokaisella tässä työssä esitellyllä menetelmällä löytyy omat vahvuutensa ja heikkoutensa CO<sub>2</sub>-päästömittausten suhteen. Pääsääntöisesti standardimenetelmä tarjoaa parhaimman tarkkuuden pitkällä aikavälillä. Johtuen toimintaympäristöstä ja tyypillisestä mittausjärjestelystä kyseisen menetelmän heikkoutena tätä vastoin voidaan usein pitää heikkoa mahdollisuutta tarjota reaaliaikaista tietoa prosessista. Sen sijaan suora mittaus tarjoaa monesti parhaan mahdollisuuden reaaliaikaiseen tietoon ja tarkkailuun kohtuullisen hyvällä tarkkuudella. Suurin mielenkiinto työssä kohdistui energiatasemenetelmään, joka kehitettiin parantamaan mittausten laadunseurantaa ja luotettavuutta tarjoamalla redundantista tietoa sekä standardimenetelmälle että suoraan mittaukseen.

Energiatasemenetelmää voidaan käyttää jossain määrin päästökaupassa päästöjen tarkkailuun yksin tai yhdessä muiden hyväksytyjen menetelmien kanssa. Jos voimalaitoskattilassa käytetään useampaa erilaista polttoainetta, niin tällöin tarvitaan toinen tarkkailumenetelmä luotettavan monitoroinnin aikaansaamiseksi. Käytettäessä energiatasemenetelmää kaikki keskeisimmät energiavirrat ovat kalibroitava, jotta saavutetaan päästökaupassa asetetut tarkkuusvaatimukset.

Päätarkkailumenetelmä ja mahdollinen todennusmenetelmä on syytä valita siten, että ne eivät perustu samoihin mittauksiin. Tällä tavoin voidaan välttää yksittäisten mittausten riippuvuutta toisistaan, jolloin mahdolliset ongelmat voidaan tunnistaa nopeammin ja korjata ne.

Työ sisältää pääperiaatteet hiilidioksidipäästöjen laskentaan eri menetelmien avulla. Helpottaakseen energiatasemenetelmän käyttöönottoa työssä esitellään yksityiskohtaisemmin energiatasteiden laskenta ja hiilidioksidipäästöjen määrittäminen. Kaikki työssä esiteltyjä menetelmiä on testattu pääpolttoaineenaan hiiltä käyttävässä Salmisaaren voimalaitoksessa.

## PREFACE

This Master of Science thesis work was carried out as part of Measurement, Monitoring and Environmental Assessment (MMEA) program, which is one of the research programs managed by the CLEEN Ltd. The main component of the program is environmental information systems which monitor, evaluate and disseminate certified information concerning the environmental efficiency of various processes. The work was done mainly in Tampere University of Technology at the Department of Automation Science and Engineering.

The case process was coal-fired Salmisaari power plant of Helsingin Energia. The project was primarily financed by the Finnish Funding Agency for Technology and Innovation (Tekes). The applications were developed in co-operation with Helsingin Energia and IndMeas Oy. The financiers and co-operators are gratefully acknowledged.

During the process of this thesis conference paper “Monitoring of CO<sub>2</sub> emissions in coal fired power plants” was published in AutomaatioXX 2013 seminar. The paper concentrated on the same research which was conducted in this thesis.

I would like to thank my supervisors Researcher M.Sc. Timo Korpela and Project Manager M.Sc. Yrjö Majanne for their invaluable advice and support during the work and Professor Matti Vilkkö who examined this thesis.

Thanks belong to Process Master Olli Salminen and Process Technician Leif Lindfors from Helsingin Energia, who were always ready to consult me with their expertise in Salmisaari power plant. I would like to thank also Development Manager Ville Laukkanen from Indmeas Oy with his business enthusiastic approach to the subject and Product Manager Kari Karhula from Sick Oy for his helpful advices to clarify complexity of emission monitoring.

Sincere thanks go to my parents Erkki and Tuija for encouraging me in life and studies. My greatest and dearest gratitude is dedicated to Heidi for her endless support.

In Tampere on May 20<sup>th</sup> 2013

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## ABBREVIATIONS, NOTATIONS AND SYMBOLS

### Abbreviations

AD	Activity data means the data on the amount of fuels or materials consumed or produced by a process as relevant for the calculation-based monitoring method i.e. standard method
AMS	Automated Measuring System. Measuring system permanently installed on site for continuous monitoring of emissions
AST	Annual Surveillance Test. A procedure to evaluate the CEM to show that it continues to function correctly and the calibration procedure determined in the QAL 2 is still valid.
AVR	Accreditation and Verification Regulation (A&V Regulation) for the verification of emission reports produced by companies and the accreditation and supervision of qualified verifiers
CEM/CEMS	Continuous Emission Monitoring System
DAU	Data Acquisition Unit
ELV	Emission Limit Values
EMV	Energy Market Authority
ETS	EU Emission Trading System
IED	Industrial Emission Directive
MRG	Monitoring and Reporting Guidelines
MRR	Monitoring and Reporting Regulation (M&R Regulation) for monitoring and reporting of emissions
NTP	Normal Temperature and Pressure

ppm	Parts per million
QAL	Quality Assurance Levels
SRM	Standard Reference Method
Tier	Tier means sets of requirements used for determination of activity data, calculation factors, annual emission and annual averaged hourly emission

### Chemical abbreviations

C	Carbon
CO	Carbon monoxide
CO <sub>2</sub>	Carbon dioxide
H <sub>2</sub>	Hydrogen
H <sub>2</sub> O	Water
N <sub>2</sub>	Nitrogen
NO	Nitrogen oxide
NO <sub>2</sub>	Nitrogen dioxide
O <sub>2</sub>	Oxygen
S	Sulphur
SO <sub>2</sub>	Sulphur dioxide

### Notations by MRR

<i>EF</i>	Emission Factor
<i>Em</i>	Emissions
<i>FQ</i>	Fuel Quantity
<i>NCV</i>	Net Calorific Value
<i>OF</i>	Oxidation Factor

### Symbols

<i>A</i>	Area [m <sup>2</sup> ]
<i>C</i>	Specific heat capacity [J/(kg·K)]
<i>h</i>	Specific enthalpy [J/kg]
<i>H</i>	Calorific value [J/kg]
<i>M</i>	Molecular weight
<i>m, <math>\dot{m}</math></i>	Mass [kg], mass flow [kg/s]
<i>n</i>	Amount of substance
<i>p</i>	Pressure [Pa]

$Q, \dot{Q}$	Heat [W], Heat flow [W/s]
$T$	Temperature [K]
$u$	Ratio
$v$	Velocity [m/s]
$V, \dot{V}$	Volume [m <sup>3</sup> ], Volume flow [m <sup>3</sup> /s]
$x$	Percentage ratio of component in chemical composition
$\eta$	Efficiency

### Subscripts

A	Air
B	Boiler
BD	Blowdown
CA	Combustion air
F	Fuel
FA	Fly ash
FG	Flue Gas
FW	Feed water
m	Molar
meas	Measured
N	Net
norm	Normalisation
RD	Radiation and convection
SL	Bottom ash
ST	Steam
stoich	Stoichiometric
UC	Unburned combustibles

# 1 INTRODUCTION

There is a growing need to control emissions and to monitor the environment and industrial processes. European Commission set new regulations for the third Emission Trading System (ETS) period (2013-2020), that increase requirements for risk assessment, uncertainty estimation and continuous accuracy surveillance for CO<sub>2</sub> monitoring system. Gradually stringent restrictions on greenhouse gas emissions are expanding the need for and raising the performance requirements of CO<sub>2</sub> measurements and monitoring.

Increasing power of scientific computing, sensor and monitoring technologies provide new opportunities to measurement quality control. Combining these techniques it is possible to create new ways to enhance data reliability.

## 1.1 Thesis objectives

The thesis concentrates on CO<sub>2</sub> emission measurement related to the energy and industrial sector. The objective is to study and develop new methods to CO<sub>2</sub> emission monitoring and quality control. Potentially inaccurate measurements can generally affect to the control of emissions and hence ETS. By improving quality of emission monitoring it is also possible to enhance efficiency of industrial processes and economic efficiencies. The second objective is to provide an overview of typical measurements used in power plants together with an assessment of current technologies and the potential for improving them.

Set objectives were met by testing and discussing about three independent methods to determine CO<sub>2</sub> emissions in power plants. The principals of the methods are intended to be fuel generic, but the discussion in this thesis is focused on combustion systems having coal as their primary fuel. The monitoring task is essentially more demanding with solid fuel than with combustion systems having natural gas or oil as the primary fuel. In discussion, the methods themselves and the required measurements and their properties are considered. The methods are applied in Salmisaari B power plant of Helsingin Energia and the results are compared and discussed.

## 1.2 Quality control definitions and requirements

When determining the quality of measurements, international standards usually refer to the quantity of “uncertainty” but there are also two different terms, accuracy and

precision, frequently used in a similar way as uncertainty. However, these are not synonyms, but have their own defined meanings.

Accuracy refers to how closely the measured value of a quantity corresponds to its “true” value. It should be stressed that this true value is a conceptual term, which can never be exactly determined. If a measurement is not accurate, this can sometimes be due to a systematic error. Often this can be overcome by calibration and adjustment of instruments. (ISO 5725-1, 1994; MRR, 2012)

Precision instead describes the closeness of the measurement results of the same measured quantity under the same conditions. It is often quantified as the standard deviation of the values around the average. It reflects the fact that all measurements include a random error, which can be reduced, but not completely eliminated. (ISO 5725-1, 1994; MRR, 2012)

All measurements have associated with uncertainty. The goal is to quantify this uncertainty, so that the results can be properly interpreted. Uncertainty as a term characterizes the range within which the true value is expected to lie with a specified level of confidence. It is the overarching concept which combines precision and assumed accuracy. Hence measurements can be accurate but not precise, precise but not accurate, both or neither. The ideal situation is precise and accurate. In the case of many stack measurements, it is also necessary to show that the measurement is fit for purpose, by demonstrating that the uncertainty of the measurements is within certain criteria. (ISO 5725-1, 1994; MRR, 2012)

Reliable process measurements are the basis for efficient process operation and control. Sensor faults are almost inevitable even with the most advanced design of instruments especially in harsh industrial environments. In real environments, sensor noise, deterioration, system dynamics, and changing conditions bring challenges to detection of sensor faults. Quality Control (QC) is a system of routine technical activities, to measure and control the quality of the measurements. The QC system is designed to provide routine and consistent checks to ensure data integrity, correctness, and completeness. It eases to identify and address errors and omissions. It is important to distinguish sensor faults from process changes, because process changes can interfere with sensor fault detection. (Penman *et al.*, 2000; Nikula *et al.*, 2012)

QC activities include general methods such as accuracy checks on data acquisition and calculations and the use of approved standardised procedures for emission calculations and measurements, uncertainty estimation, information archiving and reporting. (Penman *et al.*, 2000)

Quality Assurance (QA) activities include a planned system of review procedures conducted by personnel not directly involved in the inventory compilation/development process. Reviews, preferably by independent third parties, should be performed upon a finalised inventory following the implementation of QC procedures. Reviews verify that data quality objectives are met and ensure that the inventory represents the best possible estimates of emissions given the current state of scientific knowledge and data available, and support the effectiveness of the QC programme. (Penman *et al.*, 2000)

Before implementing QA and QC activities, it is necessary to determine which techniques should be used, and where and when they will be applied. There are technical and practical considerations in making these decisions. The practical considerations involve assessing local circumstances such as available resources and expertise and the particular characteristics of the database. The level of QA and QC activities should be compatible with the methods or level used to estimate emissions. List of general QC procedures are listed in APPENDIX I. (Penman *et al.*, 2000)

### **1.3 Fault detection and diagnostics**

Model-based fault detection and diagnosis methods utilize an explicit mathematical model of the monitored plant. The engineering systems (production facilities, processes, etc.) are dynamic systems characterized by continuous-time operation. Their natural mathematical description is in the form of differential equations, or equivalent transformed representations. However, the monitoring computers operate using sampled data. Therefore it is customary and practical to describe the monitored plants in discrete time, in the form of difference equations or their transformed equivalents. (Gertler, 1998) This is the main approach followed in this thesis as well.

Most of the model-based fault detection and diagnosis methods rely on the concept of analytical redundancy. In contrast to physical redundancy, when measurements from parallel sensors are compared to each other, now sensory measurements are compared to analytically computed values of the respective variable. Such computations use present and/or previous measurements of other variables, and the mathematical plant model describing their nominal relationship to the measured variable. The idea can be extended to comparison of two analytically generated quantities, obtained from different sets of variables. In either case, the resulting differences, called residuals, indicate the presence of faults in the system. (Gertler, 1998)

Redundant information can be used as decision-making support in process monitoring and fault diagnostics. A proper detector is sensitive to change, but does not induce false alarms. In physical redundancy multiple sensors are installed to measure the same physical quantity. Any serious difference between the measurements can indicate a sensor fault. With only two parallel sensors, fault isolation is not possible. With three

sensors, a voting scheme can be formed which isolates the faulty sensor. (Gertler, 1998) Physical redundancy involves usually extra hardware cost. Software based virtual sensors or models can partially replace some of the sensor hardware, thus reducing the cost and space requirement. E.g. using different kind of techniques and calculation methods together for emission monitoring, they provide redundant information for data assurance and sensor failure detection. In case of sensor failure, the virtual sensors can provide estimated measurements so that other system components requiring this measurement as input can function smoothly.

Limit checking is also widely used method for fault detection. Setting limits to measurements are used to detect possible faulty measurement. Measurement above the upper limit or below the lower limit may indicate about problems in the process. A method, such as this, may give rough prediction of faulty measurements.

Cumulative sum of measurements difference are used to evaluate the reliability of measurement values. When the cumulative sum exceeds the set limit, measurement can be considered to be false. It may also be useful to observe differences in balance calculations.

## **1.4 Methodology**

The core of the study was to build models to produce additional information of the emission status of the monitored systems. The tools were implemented in Matlab environment. The purpose was to develop a system that is able to model emissions of the process and to provide reference information, which was compared with the measurements in operation.

## **1.5 References and sources**

The EU ETS legislation and set requirements are used as ground information in this work. Studies of combustion models and boiler efficiency standards have been used as main sources to develop monitoring model and energy balance method. There are many standards used for definition of boiler efficiency. Of those, the German DIN 1942 is widely used in Europe. The American equivalent is an American Society of Mechanical Engineers (ASME) standard: PTC 4-2008 Fired Steam Generators – Performance Test Codes. In this thesis the efficiency is mainly calculated according to widely approved European standard EN 12952-15: Water-tube boilers and auxiliary installations – Part 15: Acceptance tests. One of the most interesting studies related to efficiency of boiler and its accuracy is Accuracy Improvement Analysis of the Standard Indirect Method for Determining a Steam Boiler's Efficiency by Andrej Senegacnik, Igor Kuštrin and Mihael Sekavcnik. In research project Validated methods for flue gas flow rate calculation with reference to EN 12952-15 by David Graham, Henrik Harnevie, Rob

van Beek and Frans Blank is compared very broadly stoichiometric calculations against empirical calculation which are mainly used in standards.

## **1.6 Structure of the thesis**

The structure of this thesis is organized as follows: Chapter 2 introduces legislation issues associated with CO<sub>2</sub> emissions monitoring in addition to measurement requirements for ETS. Also concepts of three different methods of monitoring CO<sub>2</sub> are presented. Chapter 3 concentrates on measurements and analysers related to combustion emission control. Chapter 4 presents the energy balance method principle in detail. Chapter 5 describes the data collection and experiments at the case plant. Chapter 6 consists of results, where methods themselves and the required measurements and their properties are evaluated and discussed. Chapter 7 consists of the summary and the conclusion.

## **2 LEGISLATION, REQUIREMENTS AND STANDARDS OF CO<sub>2</sub> EMISSION CONTROL**

This Chapter concentrates mainly on legislation associated with CO<sub>2</sub> emissions of power plants. The Chapter gives an overview of the Emission Trading System (ETS) and issues related to that. Especially, the most important changes in the monitoring and reporting requirements that came into force with the new EU Monitoring and Reporting Regulation (MRR), compared to the 2007 Monitoring and Reporting Guidelines (MRG) that were in force during the second trading period are presented. Compared to the MRG, the MRR emphasizes the quality of the measuring systems and their correct use in the practical determination of activity data.

### **2.1 The EU Emissions Trading System**

European Commission launched in 2005 Emission Trading System (ETS) in order to reduce greenhouse gas emissions in energy and industry sector (MRR, 2012). The main emission in ETS is carbon dioxide (CO<sub>2</sub>). After two periods, the third ETS period (2013-2020) involves several modifications and updates compared to previous ones. In order to clarify these changes and to make the monitoring and reporting of greenhouse gas emissions more complete, accurate and transparent, the Commission has adopted two new rules, Monitoring and Reporting Regulation (MRR) on monitoring and reporting of greenhouse gas emissions and Accreditation and Verification Regulation (AVR) on verification and accreditation of verifiers under the ETS (MRR, 2012). The most important updates from power plants (Class A2, B and C; Table 1) point of view are requirements for risk assessment, uncertainty estimation and continuous accuracy surveillance for CO<sub>2</sub> monitoring system. The Energy Market Authority (EMV) is the supervisory authority of ETS issues in Finland. EMV states, that each power plant involving ETS must guarantee that the CO<sub>2</sub> emissions are monitored constantly at specified accuracies. This requirement is also valid at times when the primary CO<sub>2</sub> monitoring method is malfunctioning. Therefore, additional independent methods to CO<sub>2</sub> monitoring must be provided in order to meet the new requirements.

The ETS is a cornerstone of the EU's policy to combat climate change and its key tool for reducing industrial greenhouse gas emissions cost-effectively. The ETS is a market-based method used to control pollution by providing economic incentives for achieving reductions in the emissions of pollutants. The main mechanism for doing this is through the allocation and trading of greenhouse gas emissions allowances (one allowance

equals one tonne of CO<sub>2</sub> emissions) throughout the EU. (EMVI, 2012) The MRR and AVR have direct legal effect in the Member States. This means that the regulations do not require transposition and implementation in national legislation. (AVR, 2012)

EU ETS system for monitoring and reporting provides a building block system of monitoring methodologies. Each parameter needed for the determination of emissions can be determined by different data quality levels. These data quality levels are called “tiers”. Table 1 presents definitions of the tiers on maximum permissible uncertainty for the method. It can be seen that there are uneven acceptable uncertainty levels for different CO<sub>2</sub> monitoring methods within the tiers. The tiers with lower numbers represent methods with lower requirements and being less accurate than higher tiers. (MRR, 2012; MRRGD4, 2012)

**Table 1.** Definitions of tiers on maximum permissible uncertainty (MRRGD4, 2012).

<b>Tier No.</b>	<b>Power plant category</b>	<b>Annual emissions [tCO<sub>2</sub>]</b>	<b>Standard method / activity data [%]</b>	<b>Measurement method / CEMS [%]</b>	<b>Energy balance method [%]</b>
<b>1</b>	A1	< 25 000	± 7,5	± 10,0	± 7,5
<b>2</b>	A2	25 000 – 50 000	± 5,0	± 7,5	± 7,5
<b>3</b>	B	50 000 – 500 000	± 2,5	± 5,0	± 5,0
<b>4</b>	C	> 500 000	± 1,5	± 2,5	± 2,5

## 2.2 Monitoring and Reporting Regulation

The MRR, like the MRG, allows the user to choose CO<sub>2</sub> monitoring methodologies from different monitoring methods. However, the MRR is significantly more flexible than the prior MRG, as now all types of combinations of these methods are allowed, if only required quality standards are met and there will not occur any double counting or data gaps during the measurement process. In particular, measurement-based methods have been put on equal footing with calculation-based methods including minimum tier requirements (MRR, 2012)

The traditional way to determine the CO<sub>2</sub> emissions is so called standard method, in which CO<sub>2</sub> emissions are determined by fuel feed flow measurement and an emission factor. Secondly, the CO<sub>2</sub> emissions can be measured from stack by means of CO<sub>2</sub> and flue gas flow measurements in addition to required auxiliary measurements by using Continuous Emission Measurement Systems (CEMS). Thirdly, the CO<sub>2</sub> emissions can be evaluated by balance calculations. (MRR, 2012) All these methods have different and complementary features and they fulfil the requirements of EMV for third ETS period. Using two independent CO<sub>2</sub> monitoring methods they provide redundancy and enable attractive monitoring prospects for sensors and processes.

It is worth noting that the standard or the energy balance calculation methods also require measurements. However, the measurements here are usually applied to parameters such as the fuel consumption, which can be related to the emissions by calculation, while the measurement based method always includes measurement of the greenhouse gas itself.

### 2.2.1 Standard method

The standard method is based on calculation of emissions by means of activity, e.g. amount of fuel or process input material multiplied by calculation factors. The calculation factors may include e.g. emission factor, net calorific heat value, oxidation factor or conversion factor. These factors are determined by default or they are based on fuel analysis made by operators. These factors are also used for correcting the emissions in case of incomplete chemical reactions. The standard method is straightforward to apply in cases where a fuel or material is directly related to the emissions. The precision scales are typically verified by physical redundancy and located prior to intermediate fuel silos, so in practise the standard method provide accurate but off-line indication of CO<sub>2</sub> emissions.

Under this methodology, the equations for calculating power plant CO<sub>2</sub> emissions are by the notation used by the MRR:

$$Em[\text{t CO}_2] = AD \cdot EF \cdot OF \cdot (1 - BF), \quad (1)$$

where  $Em$  stands for emissions [t CO<sub>2</sub>],  $AD$  for activity data [TJ, t or Nm<sup>3</sup>],  $EF$  for emission factor [t CO<sub>2</sub>/TJ, t CO<sub>2</sub>/t or CO<sub>2</sub>/Nm<sup>3</sup>],  $OF$  for oxidation factor [-] and  $BF$  for biomass fraction [-]

The activity data may refer to either an input material or the resulting output of the process. In both cases the activity data is used with positive values due to the direct correlation with the emission value. Activity data of fuels (including if fuels are used as process input) has to be expressed as net calorific value (MRR, 2012):

$$AD = FQ \cdot NVC, \quad (2)$$

where  $FQ$  stands for fuel quantity [t] and  $NVC$  for net calorific value [TJ/t or TJ/Nm<sup>3</sup>].

### 2.2.2 Measurement based method

Flue gas measurements in the stack provide an attractive online method for CO<sub>2</sub> monitoring. In contrast to the first and second trading periods, the measurement-based method is now recognised as equivalent to calculation-based methods for the determination of CO<sub>2</sub> emission sources. There, the CO<sub>2</sub> emissions are measured from

chimney by means of CO<sub>2</sub> concentration and flue gas flow measurements in addition to required auxiliary measurements. This method utilizes sensors that primarily exist in power plants, but the accuracy and therefore calibration requirement might be further increased. Direct measurement is well suited for processes with changing fuels and mixed fuels, if all the used fuels are included in ETS.

Compared to the MRG, the regulations for measurement based methodologies have been significantly updated. In contrast to the calculation based methods, the greenhouse gases are themselves the object of the measurement in the measurement based methods. This may be difficult in installations with many emission sources. On the other hand, the strength of the measurement based methodologies is the independence of the number of different fuels and materials applied e.g. where many different waste types are combusted. Also stoichiometric relationships are irrelevant when using the measurement based method. (MRR, 2012) Often a part of the used fuels are bio-based which are not included in the ETS. In practise, this complicates the use of direct measurement.

For quality assurance purposes, installation operators must establish a procedure that ensures the calibration, adjustment and checking of measuring equipment at regular intervals. All the measurements shall be carried out based on international standards (MRR, 2012):

- EN 14181 Stationary source emissions – Quality assurance of automated measuring systems
- EN 15259 Air quality – Measurement of stationary source emissions – Requirements for measurement sections and sites and for the measurement objective, plan and report.
- EN ISO 14956 Air quality - Evaluation of the suitability of a measurement procedure by comparison with a required measurement uncertainty

### **2.2.3 Energy balance method**

Similar to the measurement based method, energy balance method provides real-time information about CO<sub>2</sub> emissions. Monitoring of CO<sub>2</sub> emissions by energy balance method is based on calculation of fuel flow rate by formulating an energy balance for the boiler. Additionally, the flue gas composition is calculated based on fuel ultimate analysis. Finally, the estimated CO<sub>2</sub> flow rate can be calculated by multiplying the fuel flow rate and the flue gas CO<sub>2</sub> content. The method is described in more detail in Chapter 4.

In MRR energy balance method is categorized as “fall-back approach” according to EMV (Ilme, 2012). Term fall-back approach is used for approaches where measured variable which does not have direct contact with emissions is benchmarked. This means that also an approach in which e.g. heat or electricity are benchmarked is referred to as a

fall-back approach. MRR notes that an industrial site may use the fall-back method to determine the uncertainty of its CO<sub>2</sub> monitoring system if it can demonstrate that achieving tier 1 for a source stream would result in technically infeasible or unreasonable costs. This could mean e.g. a case where components of the measuring systems cannot be calibrated or costs of the system would be much higher than achieved benefits. The fall-back method does not demand an uncertainty requirement for each source stream and requires a 'typical total uncertainty' to be calculated and used for the whole CO<sub>2</sub> installation. This enables an industrial site to consider the impact of a stream on the total CO<sub>2</sub> emissions of the installation. (MRR, 2012)

Using the fall-back method user determines the data, where available, or the best estimates of the activity data, net calorific values, emission factors, oxidation factors and other parameters, where appropriate using laboratory analyses, and reports these in the annual emission report.

#### **2.2.4 Combinations of methods**

MRR allows the user to combine seamlessly the different methods presented above, on the condition that no data gaps or double counting occur. Where different methods would lead to similar tier levels, the user may use other criteria for choosing the methodology. Methods can be evaluated for example on the basis of which method gives the more reliable results, i.e. where are the more robust measurement instruments used or fewer observations needed. One reason to use a particular method can simply be its easier control and usability. (MRR, 2012)

### **2.3 Accreditation and Verification Regulation**

AVR defines harmonised requirements concerning the verification of emission reports for operators. Verification involves an independent assessment of the way the monitoring plan (MP) has been implemented and of the data sources that have been used to collect and collate the data in the emission report. Verification is an essential instrument in providing confidence to competent authorities and other relevant parties that the report submitted to authorities represents a true and fair account of the emissions. (AVR, 2012)

To achieve the objective of verification and ensure that the verification is sufficiently robust and of high quality, the verifier has to check that a number of fundamental principles of the MRR and the AVR have been met, i.e. the principles of reliability and faithfulness, completeness, consistency, comparability, accuracy, integrity of the method and continuous improvement. The fundamental principle is the requirement that a verified report of operator is reliable for its users, which may include Competent Authorities (CAs), operators, verifiers, accreditation bodies, the general public or other

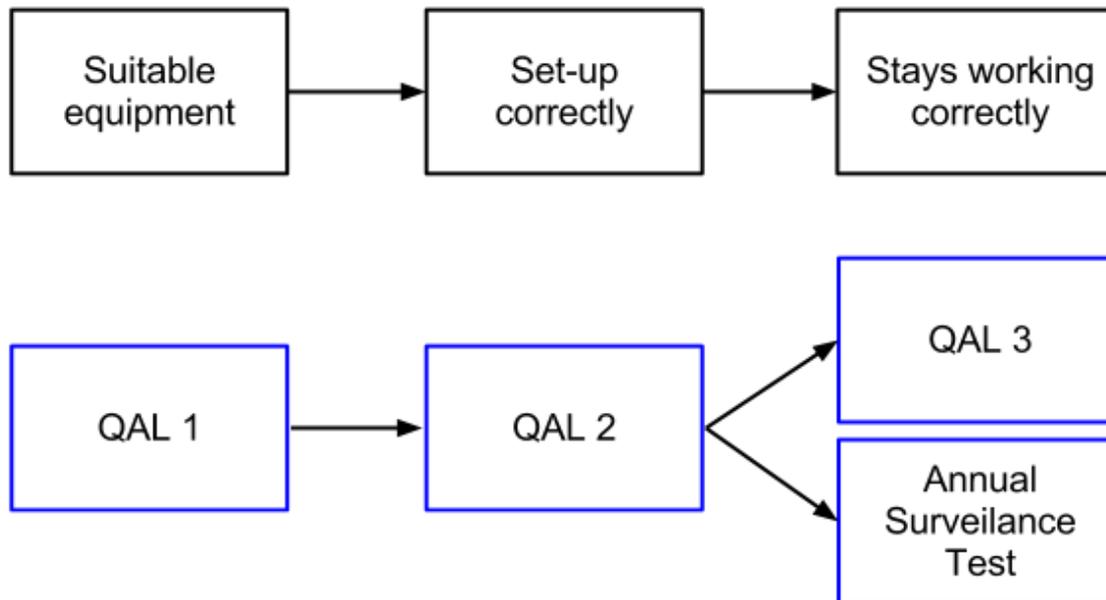
parties. (AVR, 2012) The role of verification is fundamental for creating assurance on the accuracy of the data in the operator's report.

Verifiers should check that the data management system of operator enables transparent reporting and ensures ease of verification. Effective data management with accessible data and records will streamline the process, reduce verification time and minimise costs. Good data management means that verifiers can be more confident in the quality of the data being checked, and this may influence the data sampling strategies and the verification plan.

## 2.4 Quality assurance of automated measuring systems

Standard EN 14181 (Stationary source emissions – Quality assurance of automated measuring systems) is one of the main standards that details quality assurance procedures required to assure that the CEMS can meet the measurement uncertainty requirements of legislation.

Three different Quality Assurance Levels (QAL 1, QAL 2, and QAL 3) are defined to achieve this objective. The basic structure of the QA process is shown in the flow diagram presented in Figure 1.



**Figure 1.** Basic structure of QA process of AMS (VGB, 2006)

QAL 1 requires that instruments are shown to be suitable for purpose based upon a set of laboratory and field procedures that test the performance of the system against predefined limits. (SFS-EN 14181, 2004; VTT, 2004b)

QAL 2 specifies testing procedures to verify that each CEMS will meet the accuracy requirements laid down by EN 14181 standard. The performance of the complete installation is monitored and compared against a series of measurements made with approved Standard Reference Method (SRM). (SFS-EN 14181, 2004; VTT, 2004b)

QAL 2 procedures must be carried out after installation and commissioning of the CEMS and subsequent to a significant change in plant operation which changes the emission levels, a failure of the CEM equipment or an upgrade or other significant change to the CEMS that affects its calibration. Also QAL 2 must be performed after corrective action following a failure of the CEMS in either the QAL 3 or AST procedures. (SFS-EN 14181, 2004; SFS-EN 13284-2, 2004)

QAL 2 requires operators to ensure that the CEM is installed in the correct location for a representative measurement of emissions and that there is sufficient safe access to maintain and control it. Operators must also to ensure that CEMS is calibrated and operating correctly. (SFS-EN 14181, 2004)

QAL 2 testing contains two parts. In the first part there is a set of functional tests and checks to ensure that the CEMS has been installed correctly and is performing within the required performance levels. The second part comprises a calibration and validation exercise consisting of parallel measurements using statistical operations and tests. QAL 2 testing must be conducted by an approved independent test house or laboratory. (SFS-EN 14181, 2004)

QAL 3 is a procedure to maintain on-going quality. This is accomplished by detecting and recording drift or changes in precision in the CEMS through regular checks of the zero and span readings against reference materials (such as bottled protocol gases or optical filters in the case of opacity/dust monitors). Such testing may be either automatic or manual, but the results must be collected and presented on control charts, one for span and one for zero, that clearly identify any characteristic drifts in calibration. (SFS-EN 14181, 2004; VTT, 2004c)

The implementation and performance of the QAL 3 procedure is the responsibility of the plant operator. QAL 3 is a procedure to maintain and demonstrate the required quality of the CEM during its normal operation by checking the zero and span readings. Drift and precision is required to be measured frequently and regularly to check whether the instrument remains within the required specification. The data collected is plotted using control charts which are used to determine whether the instruments require maintenance. QAL 3 also requires that details of CEMS to be recorded e.g. monitoring technique, operating range and model. (SFS-EN 14181, 2004; VTT, 2004c)

Annual Surveillance Test (AST) is a procedure which is performed annually to verify the continuing validity of the calibration function. The requirements and responsibilities for carrying out the AST tests are the same as for QAL 2. If the calibration function remains good then no further action is required. If it does not then a full QAL 2 is required. Responsibility for the tests must be with an approved test house or laboratory, although either the operator or the CEM supplier may perform the tests. In such cases these tests should be verified by audit by the accredited laboratory and included in their report. (SFS-EN, 14181 2004; VTT, 2004b)

### **3 BOILERS AND FLUE GAS MEASUREMENTS**

Combustion boilers are widely used to generate steam for industrial applications and power generation. The scope of this thesis is limited to steam boilers using fossil fuels, particularly coal, while all kinds of energy sources – biomass, nuclear and solar energy – can be used to generate heat and steam.

A boiler can be described as an enclosed vessel in which water is heated and circulated, either as hot water, steam, or superheated steam for the purpose of heating and/or producing electricity. The furnace of the boiler is where the fuel and air are introduced to combust. Fuel and air mixtures are normally introduced into the furnace by using burners, where the flames are formed. The resulting hot gases travel through a series of heat exchangers, where heat is transferred to the water flowing through them. The combustion gases are finally released to the atmosphere via stack of exhaust section of the boiler. (Ibrahim, 2010)

Flue gas consists of a mixture of toxic and non-toxic gases in different concentration. Stoichiometric or theoretical combustion is the ideal combustion process where fuel is burned completely with stoichiometric amount of air. A complete combustion is a process burning all the carbon (C) to carbon dioxide (CO<sub>2</sub>), all the hydrogen (H) to water (H<sub>2</sub>O) and all the sulphur (S) to sulphur dioxide (SO<sub>2</sub>). With unburned components in the exhaust gas, such as C, H<sub>2</sub>, CO, the combustion process is uncompleted and not stoichiometric. In addition to SO<sub>2</sub>, flue gas also contains a small percentage of pollutants such as particulate matter, nitrogen oxides (NO<sub>x</sub>) and sulphur trioxides (SO<sub>3</sub>). (Moran & Shpiro, 1995)

#### **3.1 Emission measurement systems and techniques**

The measurement systems used for measuring the properties of flue gas are known as continuous emission monitoring systems (CEMS) and are equipped with an analyser that has been approved by authorities. CEMS are usually provided with functions for measuring the concentration, temperature, pressure and flow rate of regulated substances. Therefore, CEMS are significant in environmental supervision and pollutant control in thermal power plants. Real-time information on the composition of combustion gases is important for improving efficiency and reducing emissions. It provides the operators of power plant with real time information about current emission levels and this way enables a proactive reaction on potential problems on time. Also the

storage of history values enables long term reporting and trending of emission parameters and this way helps to follow up environmental performance and continuous improvement.

### 3.1.1 Determination of CO<sub>2</sub> emissions

The application of CEMS always requires two elements: Measurement of concentration and volumetric flow of the gas stream where the measurement takes place. The choice of methods to be used to estimate CO<sub>2</sub> emission depends on how the estimates will be used and the degree of accuracy required.

Normalized CO<sub>2</sub> concentration  $x_{\text{CO}_2,\text{norm}}$  [%] and flue gas flow  $\dot{V}_{\text{FG},\text{norm}}$  [Nm<sup>3</sup>/s] are calculated using the equations

$$x_{\text{CO}_2,\text{norm}} = x_{\text{CO}_2,\text{meas}} \cdot \frac{100}{100 - x_{\text{H}_2\text{O},\text{FG}}} \cdot \frac{20.9 - x_{\text{O}_2,\text{ref}}}{20.9 - x_{\text{O}_2,\text{dry}}} \quad (3)$$

$$\dot{V}_{\text{FG},\text{norm}} = v_{\text{meas}} \cdot \frac{100 - x_{\text{H}_2\text{O},\text{FG}}}{100} \cdot \frac{20.9 - x_{\text{O}_2,\text{dry}}}{20.9 - x_{\text{O}_2,\text{ref}}} \cdot \frac{T_{\text{ref}}}{T_{\text{FG}}} \cdot \frac{p_{\text{FG}}}{p_{\text{NTP}}} \cdot A_{\text{stack}}, \quad (4)$$

where  $x_{\text{CO}_2,\text{meas}}$  stands for measured CO<sub>2</sub> concentration,  $x_{\text{H}_2\text{O},\text{FG}}$  for flue gas moisture concentration in stack [%],  $x_{\text{O}_2,\text{ref}}$  for reference O<sub>2</sub> concentration [%],  $x_{\text{O}_2,\text{dry}}$  for dry flue gas O<sub>2</sub> concentration in stack [%],  $T_{\text{ref}}$  for reference temperature [273 K],  $T_{\text{FG}}$  for flue gas temperature [K],  $p_{\text{FG}}$  for flue gas pressure in stack [Pa],  $p_{\text{NTP}}$  for the standard atmosphere pressure,  $v_{\text{meas}}$  for measured flue gas velocity [m/s] and  $A_{\text{stack}}$  for flue gas stack area [m<sup>2</sup>]. (VTT, 2004a)

Total CO<sub>2</sub> emissions is calculated using the equation

$$m_{\text{CO}_2}[t] = \int_{t_1}^{t_2} \rho_{\text{CO}_2} \cdot x_{\text{CO}_2,\text{norm}} \cdot \dot{V}_{\text{FG},\text{norm}} \cdot 10^{-2} \left[ \frac{1}{\%} \right] \cdot 10^{-3} \left[ \frac{t}{\text{kg}} \right] dt, \quad (5)$$

where  $\rho_{\text{CO}_2}$  stands for density of carbon dioxide [kg/m<sup>3</sup>],  $x_{\text{CO}_2,\text{norm}}$  for corrected CO<sub>2</sub> concentrations [%] in the flue gas,  $\dot{V}_{\text{FG},\text{norm}}$  for flue gas flow [Nm<sup>3</sup>/s] and  $t$  for time.

As the final CO<sub>2</sub> value is calculated according to information obtained from several sensors, special attention to validity of each measurement, including the auxiliary measurements, should be paid.

### 3.1.2 Gas analysers

There is a wide spectrum of different sampling and analytical techniques used for combustion control and combustion emissions monitoring. One approach to monitor gas

composition is to collect a sample gas, which can then be analysed either by spectroscopic techniques or by room temperature gas sensors. However, there are many sources of errors related to the extraction and preconditioning of the sample gas. In particular, when the main fuel is coal, it must be taken care to remove sulphuric acid mist and dust, which cause pipe blockages and contamination, from the flue gas. These kinds of measurements are usually also time-consuming. Due to low concentrations the gas has to be extracted for a long time before an amount sufficient for reliable measurement is obtained. (Linnerud *et al.*, 1998) The gas composition could change during cooling to room temperature, so analysis of the gas at high temperatures is preferred.

Optical spectroscopic techniques based on infrared radiation or laser spectroscopy can work well without preconditioning of the gas. They therefore have the potential to be used in in-situ measurements with fast response and are ideally suited for industrial applications provided they can measure with sufficient sensitivity. (Linnerud *et al.*, 1998; Chao *et al.*, 2012) Optical measurements do not require contact with the high temperature gas, but do require line-of-sight measurement. Absorption or scattering in the optical path can affect the received signal. Placement of a sensor directly in the high temperature gas would avoid such interferences, so sensors for in-situ monitoring of combustion gas components at the high temperatures of combustion processes have been developed. (Kohse-Höinghaus *et al.*, 2005)

The traditional technique has been Non-Dispersive Infrared (NDIR) where the transmission has been measured at two wavelength regions, one at absorbing and the other at non-absorbing wavelengths. This technique is suited for gases with broad absorption bands but it has the disadvantage of being fairly slow and insensitive because it is easily influenced by the variation of light source intensity and requiring frequent calibration. (Acha *et al.*, 2000) More advanced techniques include Fourier Transform Infrared Spectrometry (FTIR), Laser-Induced Fluorescence (LIF) (Matsumoto and Kajii, 2003), Differential Optical Absorption Spectroscopy (DOAS), and Tuneable Diode Laser Absorption Spectroscopy (TDLAS) (Chao *et al.*, 2012). These techniques can achieve high measurement precision and accuracy, but require relatively complex optical systems and expensive equipment. This adds considerable operational complexity and cost (Matsumi *et al.*, 2005; Nakamura *et al.*, 2010). The method of infrared technology is most commonly used in the commercial CO<sub>2</sub> analysers (Marzouk & Al-Marzouqi, 2010).

### **3.1.3 Flue gas flow measurements**

Operators of combustion plant need to know the flue gas flow rate to calculate the mass release of pollutant emissions. Flue gas flows of boilers are very difficult to measure accurately and they are usually estimated by calculation. The minimum requirement is

that the boiler measurement data on which the calculations are based must be quality assured. Flow measurement accuracy can be affected by many factors. The most significant factor is usually instrument itself and its measuring technique. Also compensation measurements like temperature and pressure are needed at determination of correct flow rate. (Kuoppamäki, 2003; Laukkanen, 2012)

There are a number of ways to determine the velocity and volume flow rate of gas streams in ducts, stacks and chimneys. They vary by cost and accuracy. Most traditional and inexpensive methods include pitot tubes and hot wire anemometers. Pitot tubes and hot wire anemometers kind of solutions will not provide an accurate reading if the stack flow profile changes. There are a number of common furnace adjustments that can affect the flow profile, e.g. changes in draught. These methods are also prone to fouling from the particulate in the stack. (Drummond III, 2012)

Different kind of approach to measure flue gas flow is to calibrate the stack gas fan to serve as a flow meter. In this so called fan method the flue gas flow is continuously calculated from the measured values for differential pressure over the flue gas fan and for its control quantity. The mathematical form of the calculation equation is derived from the fan physics. The values for the constants in the equation are determined from in-situ calibration measurements. The method works well both for blade angle and revolution speed controlled fans. (Juuti & Kuoppamäki, 1994)

More technically advanced methods include ultrasonic and optical scintillation. In ultrasonic pulse detection volumetric flow rate of flue gas is measured by transmitting ultrasonic pulses at an angle across the stack in both directions. The flow causes the ultrasonic pulse to move faster going up the stack (with the flow), and slower going down the stack (against the flow). These time differences are measured and used to calculate gas velocity. The two heads of the flow monitor must not be perpendicular to gas flow to create the time differences described above. Optical scintillation monitors are based on the principle that temperature causes turbulence in gases which affects light transmission. This turbulence can be measured and used to determine air velocity. Both methods are less sensitive to changes in flow profile since they measure the flow across the entire width of the flow. (Drummond III, 2012)

#### **3.1.4 Normalization of results to standard conditions**

Concentration and flow measurements must be reported to a standard set of conditions so that comparisons can be made with Emission Limit Values (ELVs), emission concentrations measured at different times on the same site and emission concentrations at different sites. The applicable reference conditions are usually specified in the environmental permit. Reference conditions are specified for temperature and pressure, and may also be set for moisture and oxygen content. Concentration measurements are

usually reported at Normal Temperature and Pressure (NTP). Notion of NTP may vary between countries but e.g. in Europe it stands for 273 Kelvin (K) and 101.3 kilopascals (kPa). (VTT, 2004a)

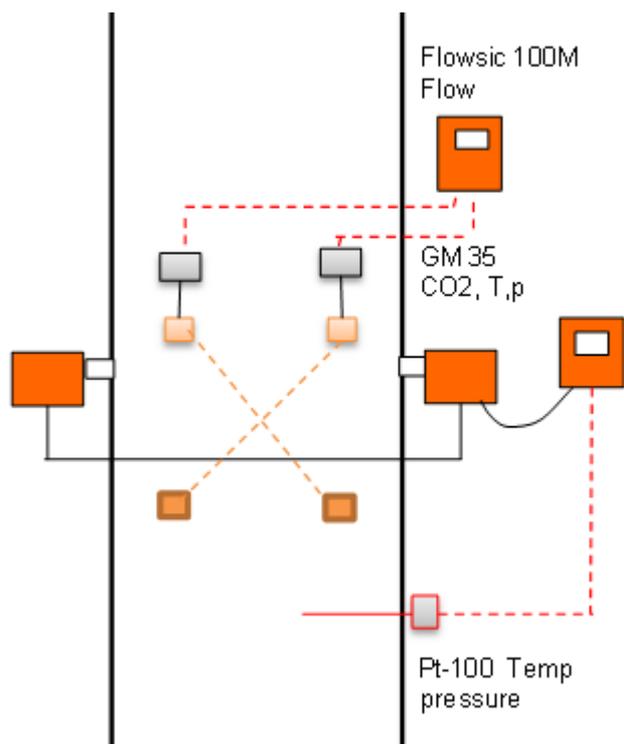
Concentration measurements expressed as mass per unit volume, e.g.  $\text{mg/m}^3$ , are affected by temperature, pressure, moisture, and oxygen concentration. Concentrations expressed as volume per unit volume, e.g. ppm, are unaffected by temperature and pressure, but affected by moisture and oxygen. Mass emissions results, e.g. kg/h, are unaffected by temperature, pressure, oxygen and moisture levels. (VTT, 2004a)

The concentration of water vapour and oxygen affects the measured concentration of a substance by adding to the volume of measured gas. This is particularly relevant for processes involving combustion, where oxygen will be consumed and water vapour produced during the combustion process. The oxygen level can cause significant changes in measured concentrations. Many emission permits therefore require the concentration results to be expressed at a standard oxygen reference level. It is important that an oxygen reference level is set that is appropriate for the process. It should be based on the typical oxygen level of the process when it is running at normal conditions and the fuel type used. Different oxygen reference values are used for different fuels, e.g. 3 % for gas or liquid fuels, 6 % for solid fuels and 11 % for most incineration processes. (European Commission, 2010) Emissions of flue gases are often expressed on a dry gas basis, so that variation in the moisture of flue gas does not affect the assessment of the emissions.

### **3.1.5 Case example: SICK solution for monitoring of CO<sub>2</sub> emission**

Sick AG provides in-situ solution called GHG-Control that allows monitoring of greenhouse gas emissions in real state directly from stack. The GHG-Control records the CO<sub>2</sub> gas concentration and flue gas volume flow and determines the total quantity in real time. (Sick AG, 2012)

Continuous CO<sub>2</sub>-emission monitoring is carried out using the in-situ method in which CO<sub>2</sub>-concentration and gas flow rate are measured directly in the flue gas duct and in that state as it is in the duct (measurements at real-state) in order to avoid using compensator factors. Also, the response times of the measurements are the same. This solution allows for the concentration and flow measurement results multiplied with each other, so that the uncertainty required by MRR is less than 2.5%. The measurement arrangement is shown in Figure 2.



**Figure 2.** CO<sub>2</sub> measuring system of SICK Oy (Sick AG, 2012)

The Sick GHG-Control measures the CO<sub>2</sub> with the GM35 “Cross Duct” gas analyser which is based on NDIR in-situ technology. The transmitter/receiver and the reflector are fitted opposite each other on the exhaust duct. The light beam passes through the entire duct cross-section twice to increase measuring accuracy. The volume flow measurement system Flowsic 100 measures the total flue gas flow based on ultrasonic measurement. The duct average diameter is determined within  $\pm 1$  mm accuracy, so that the volume flow measurement fulfils accuracy requirements by MRR. The volume flow measurement may be configured as either a single- or multi-path measurement. (Sick AG, 2012)

Measuring signals are collected at least once per minute. The signals are so called raw values, which mean that measurements are taken under real process conditions in moist exhaust gas without converting from the moist to dry state. Therefore there is no need for additional conversions. This minimizes the number of influencing variables and their impact on measurement accuracy, but at the same time it degrades the possibility to comparable monitoring with other emissions and plants. For the ETS only total emissions are important, but from quality control point of view it would be important that all the measurements would be at the same reference state.

The collected signals for Sick GHG-Control are the concentration of CO<sub>2</sub> [g/m<sup>3</sup>] and volume flow [m<sup>3</sup>/s]. Measurement results tend to show lower values than standard method because “the safety margin” derived from used coefficients of standard method

is removed. Measuring accuracy uncertainty is promised to be under 2 %. (Sick AG, 2012)

### **3.2 Estimation of uncertainties**

For a measurement-based method the MRR requires a list of all relevant equipment, indicating its measurement frequency, operating range and uncertainty. All measurements shall be carried out based on the standards:

- EN 14181 Stationary source emissions – Quality assurance of automated measuring systems,
- EN 15259 Air quality – Measurement of stationary source emissions - Requirements for measurement sections and sites and for the measurement objective, plan and report
- And other corresponding EN standards.

EN 14181 e.g. contains information about quality assurance procedures (QAL 2 and 3) to minimise the uncertainty as well as guidelines on how to determine the uncertainty itself. For QAL 1 guidance can be found in EN ISO 14956 Air quality - Evaluation of the suitability of a measurement procedure. MRR states that in a case where such standards are not available, the methods should be based on suitable ISO standards, standards published by the Commission or national standards. In addition operators are obliged to consider all relevant aspects of the continuous measurement system, including the location of the equipment, calibration, measurement, quality assurance and quality control.

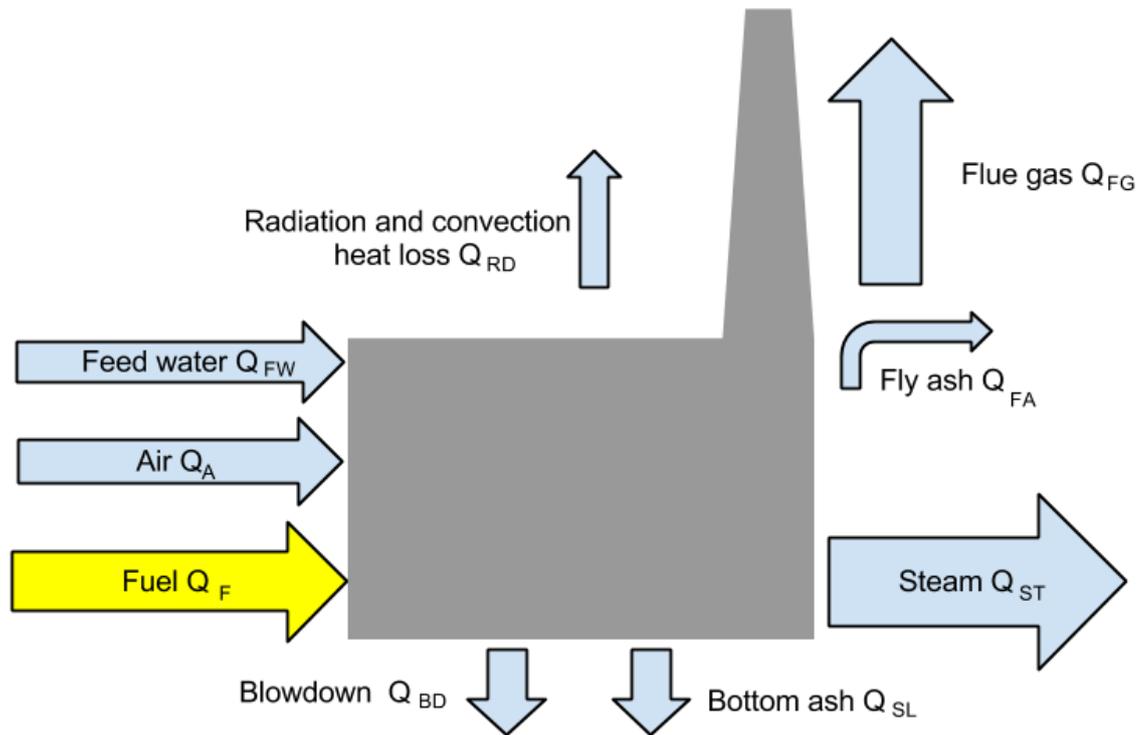
## 4 MASS AND ENERGY BALANCE

As mentioned in Chapter 2, the traditional way to calculate CO<sub>2</sub> emissions is the so called standard method. The principle of this method is the calculation of emissions by means of activity, e.g. amount of fuel or process input material consumed multiplied by an emission factor.

In the mass balance method, material quantities, as they pass through processing operations, can be described by mass balances. Such balances are statements on the conservation of mass. Similarly, energy quantities can be described by energy balances, which are statements on the conservation of energy. These balances are used widely in engineering and environmental analyses.

Energy takes many forms, such as heat, kinetic energy, chemical energy, potential energy but because of internal conversions it is not always easy to isolate separate constituents of energy. However, under some circumstances certain aspects dominate while other forms of energy are insignificant. E.g. in some chemical situations mechanical energy is insignificant and in some mechanical energy situations, as in the flow of fluids in pipes, the frictional losses appear as heat but the details of the heating need not be considered. (BEE, 2005)

Like the standard method, the energy balance method is a calculation based method for determining the emissions of the process. The standard method is straightforward to apply in cases where a fuel or material is directly related to the emissions, but it is often difficult to relate the emissions directly to individual input materials, because the products and wastes might contain significant amounts of carbon. Thus, it is not enough to account for the amount of non-emitted carbon by means of an oxidation factor or conversion factor. More realistic and real-time information is possible to achieve using energy balance method (Figure 3). Utilizing energy streams entering and leaving the process it is possible to solve energy balance of the process and to determine used fuel quantity.



**Figure 3.** Boiler energy flows.

The energy balance calculation can be used e.g. to determine the energy content of fuel, on the basis of how much heat the boiler is releasing from burning process. The balance calculations takes into account all known energy flows, which are measured (e.g., flows), or estimated by calculation (e.g. the boiler heat losses). As a result of calculations the fuel power is obtained. Based on information of the fuel ultimate analysis and fuel flow it is possible to calculate  $\text{CO}_2$  emissions. The results can be compared with other measurements and data, e.g. fuel flow by precision scales before boiler and stack emissions after the process.

Almost all of the power plants have a system to store all the main measurement information. Most power plants also have some kind of management or energy balance calculation system to calculate monthly energy report. If the power plant has the balance accounting system, it is generally in accordance with the standard European Standard EN 12952-15 - Water-tube boilers and auxiliary installations – Part 15: Acceptance tests. The standard describes the basic principles for boiler efficiency calculation and defines empirical formulas for flue gas calculation.

The amount of heat generated by the boiler and the efficiency of that system can be used as additional information to monitor combustion performance and to estimate the expected emissions. When using energy balance method for emissions calculation it is possible to decrease uncertainty of fuel moisture fluctuations. (Pöyry, 2007)

## 4.1 Determination of energy balance and CO<sub>2</sub> emissions

Combustion is complete when all the carbon in the fuel is burned to carbon dioxide, all the hydrogen is burned to water and all the sulphur is burned to sulphur dioxide. When these conditions are not fulfilled, combustion is incomplete. (Moran & Shpiro, 1995)

Coal is a familiar solid fuel. Its composition varies considerably with the location from where it is mined. For combustion calculations, the composition of coal is usually expressed as a result of ultimate analysis. The ultimate analysis gives the composition on a mass basis in terms of the relative amounts of chemical elements (carbon, sulphur, hydrogen, nitrogen, and oxygen) and ash. (Moran & Shpiro, 1995)

Oxygen is required in every combustion reaction. Typically in most combustion applications, air provides the needed oxygen. The composition of a typical sample of dry air is given in **Table 2**.

**Table 2.** Approximate composition of dry air (MAOL, 2001)

Component	Concentration (volume-%)
Nitrogen N <sub>2</sub>	78.08
Oxygen O <sub>2</sub>	20.95
Argon Ar	0.934
Carbon dioxide CO <sub>2</sub>	0.033
Neon, helium, methane, and others	0.003

In calculation applications, all components of air other than oxygen are collected together with nitrogen. Accordingly, air is considered to contain 21% oxygen and 79% nitrogen on a molar basis. With this idealization the molar ratio of the nitrogen to the oxygen is  $0.79/0.21 = 3.76$ . When air supplies the oxygen in a combustion reaction, therefore, every mole of oxygen is accompanied by 3.76 moles of nitrogen. (Moran & Shpiro, 1995)

Theoretical amount of air is the minimum amount of air that supplies sufficient oxygen for the complete combustion of all the carbon, hydrogen, and sulphur present in the fuel. For complete combustion with the theoretical amount of air, the products consist of carbon dioxide, water, sulphur dioxide, the nitrogen accompanying the oxygen in the air, and any nitrogen contained in the fuel, and no free oxygen appear in the products. (Moran & Shpiro, 1995; Sulkala, 2005)

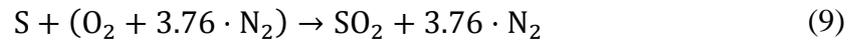
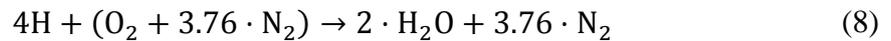
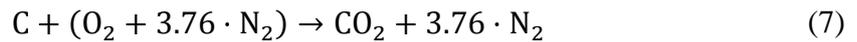
The air–fuel ratio describes the ratio of the amount of air in a reaction to the amount of fuel. The ratio can be written on a molar basis (moles of air in a reaction to the mole amount of fuel) or on a mass basis (mass of air divided by mass of fuel). Conversion

between these values is accomplished using the molecular weights of the air,  $M_{\text{air}}$  and fuel,  $M_{\text{fuel}}$ . (Moran & Shpiro, 1995)

$$\frac{m_{\text{air}}}{m_{\text{fuel}}} = \frac{n_{\text{air}} \cdot M_{\text{air}}}{n_{\text{fuel}} \cdot M_{\text{fuel}}} \quad (6)$$

#### 4.1.1 Chemical equations

When the composition of fuel is known by ultimate analysis and the combustion is complete, the respective amounts of the products can be determined by applying the principle of the conservation of mass using the chemical combustion equations  $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$ ,  $4\text{H} + \text{O}_2 \rightarrow 2 \cdot \text{H}_2\text{O}$  and  $\text{S} + \text{O}_2 \rightarrow \text{SO}_2$  (SFS-5625, 1990). Air and flue gas volumes calculated on the basis of the reaction equations do not apply due to the fact that combustion does not occur in pure oxygen. There is nitrogen of 3.76 times the amount of oxygen. When this is taken into account theoretical combustion reaction for carbon, hydrogen and sulphur is given in the following equations. (Moran & Shpiro, 1995)



When the composition of the fuel is known, it can be calculated how many grams of each element is, for example, per kilogram of fuel. These results of each element are divided by their molar masses to define the amount of substance. From the reactions it can be seen the needed theoretical amount of oxygen. Each component of oxygen is summed up to find out the total oxygen requirement. Potential oxygen already in fuel reduces the needed oxygen for the combustion. (Moran & Shpiro, 1995; Sulkala, 2005) Molar oxygen demand  $n_{\text{O}_2, \text{stoich}}$  for the ideal combustion can be calculated by

$$n_{\text{O}_2, \text{stoich}} = \sum \frac{m_i}{M_i} = \frac{1}{1} \frac{m_{\text{C}}}{M_{\text{C}}} + \frac{1}{4} \frac{m_{\text{H}}}{M_{\text{H}}} + \frac{1}{1} \frac{m_{\text{S}}}{M_{\text{S}}} - \frac{1}{2} \frac{m_{\text{O}}}{M_{\text{O}}} \quad (10)$$

Molar oxygen demand can be transformed to volume unit  $V_{\text{O}_2, \text{stoich}}$  by multiplying by the standard molar volume  $V_{\text{m}}$  which is  $22.39 \text{ m}^3/\text{kmol}$ .

The ratio of the theoretical amount of combustion air  $n_{\text{CA}, \text{stoich}}$  and theoretical amount of oxygen according to Table 2 is

$$V_{\text{CA}, \text{stoich}} = n_{\text{CA}, \text{stoich}} \cdot V_{\text{m}} = \frac{100}{20.95} n_{\text{O}_2} \cdot V_{\text{m}} = 4.76 \cdot n_{\text{O}_2} \cdot V_{\text{m}} \quad (11)$$

Theoretical combustion air requirement as moles is 4.76-times compared to the oxygen demand. Since the combustion air is not practically dry, the humidity causes an increase to the theoretical air demand. This increase must be taken into account, if the humidity is significant. Knowing the water and dry air ratio of air it is possible to determine theoretical volume increase caused by humidity. Since the density of dry air is  $\rho = 1.29 \text{ kg/m}^3$ , it is known that the volume of one kilogram of dry air is

$$V_{A,dry} = \frac{1 \text{ kg}}{1.29 \text{ kg/m}^3} = 0.775 \text{ m}^3 \quad (12)$$

Water vapour density is  $\rho = 0.803 \text{ kg/m}^3$ , and when it is known how many grams of water vapour is per kilogram, the volume of water vapour  $V_{A,H2O}$  can be calculated by dividing the mass of water with density. Using the proportion

$$\frac{V_{A,dry}}{V_{A,H2O}} = \frac{V_{CA,stoich}}{V_{CA,H2O}}, \quad (13)$$

and on the basis of equation (11), it is possible to determine water vapour amount  $V_{CA,H2O}$ .

Thus the actual stoichiometric combustion air requirement is sum of the dry air and the moisture of the air.

$$V_{CA,tot} = V_{CA,H2O} + V_{CA,stoich} \quad (14)$$

Moisture in the air increases the amount of water vapour in combustion, but since the calculation is performed on a dry fuel, flue gas increase caused by the moisture can be taken into account later.

Carbon dioxide, sulphur and nitrogen quantities can be calculated with sufficient accuracy using reactions (7), (8) and (9). By adding these components together and taking into account additional nitrogen it is possible to calculate theoretical dry flue gas molar amount  $n_{FG,stoich}$ . Flue gas amount can be converted to cubic meters by multiplying each component equivalent molar volume  $V_m$  (Moran & Shpiro, 1995; Coskun *et al.*, 2009)

$$V_{FG,stoich} = V_{m,CO2} \cdot \frac{1}{1} n_C + V_{m,N} \cdot \frac{1}{2} n_N + V_{m,SO2} \cdot \frac{1}{1} n_S + V_{m,N} \cdot 3.76 n_{O2}. \quad (15)$$

The theoretical amount of air is not really enough to perfect combustion. This is due to the fact that all the oxygen present in the air does not react with combustible material.

For this reason, excess combustion air is needed. Air factor lambda  $\lambda$  is the ratio of actual and the theoretical air. The actual amount of combustion air is therefore

$$V_{CA} = \lambda \cdot V_{CA,stoich} \quad (16)$$

The increase of flue gas volume caused by excess air must be added when calculating the actual dry flue gas volume  $V_{FG,dry}$ . (Moran & Shpiro, 1995)

$$V_{FG,dry} = V_{FG,stoich} + (\lambda - 1) \cdot V_{O_2} + 3.76 \cdot (\lambda - 1)V_{O_2} \quad (17)$$

The mass balance equation can be expressed in the rate form as,

$$\Sigma \dot{m}_{in} = \Sigma \dot{m}_{out},$$

where  $\dot{m}$  stands for the mass flow rate, and the subscript in stands for inlet and out for outlet. Simplified mass balance for combustion is

$$\dot{m}_F + \dot{m}_{CA} = \dot{m}_{FG} + \dot{m}_{ash} \quad (18)$$

$$\dot{m}_{FG} = \dot{m}_F + \dot{m}_{CA} - \dot{m}_{ash}, \quad (19)$$

where  $\dot{m}_F$  stands for fuel mass flow,  $\dot{m}_{CA}$  for combustion air mass flow,  $\dot{m}_{FG}$  for flue gas mass flow and  $\dot{m}_{ash}$  for ash mass flow.

Required combustion air mass flow  $\dot{m}_{CA}$  can be calculated by equation depending on excess air ratio and chemical composition of wet fuel. (EN 12952-15, 2003; Coskun *et al.*, 2009)

$$\dot{m}_{CA} = (x_C + 2.9792 \cdot x_H + 0.3746 \cdot x_S - 0.3754 \cdot x_O) \cdot (11.5122 \cdot \lambda) \cdot \dot{m}_F \quad (20)$$

At stoichiometric point the air amount is  $\lambda = 1$ .

$$\dot{m}_{CA,stoich} = (11.5122 \cdot x_C + 34.2974 \cdot x_H + 4.3129 \cdot x_S - 4.3212 \cdot x_O) \cdot \dot{m}_F \quad (21)$$

Equations (20) and (21) are obtained by solving combustion mass balance equations and can be found in standard EN 12952-15. Here  $x$  denotes the percentage ratio of the element in wet fuel chemical composition with ash included. Flue gas amount can be determined the same way using equation

$$\begin{aligned} \dot{m}_{FG} = & (x_C + 2.9792 \cdot x_H + 0.3746 \cdot x_S - 0.3754 \cdot x_O) \cdot (11.445 \cdot \lambda) \\ & + (\dot{m}_F - x_{ash}) \end{aligned} \quad (22)$$

When calculations are done for fuel flow of 1 kg/s, the equation can be expressed as follows:

$$\dot{m}_{FG} = (x_C + 2.9792 \cdot x_H + 0.3746 \cdot x_S - 0.3754 \cdot x_O) \cdot (11.445 \cdot \lambda) + (1 - x_{ash}) \quad (23)$$

When  $\lambda = 1$ , flue gas amount can be given by the equation:

$$\dot{m}_{FG,stoich} = \dot{m}_{CA,stoich} + (1 - x_{ash}) \quad (24)$$

For solid fuels these empirical relations provided in EN 12952-15 are a good approximation for a wide range of solid fuels. Flue gas volume can be solved the same way using equation (EN 12952-15, 2003; Blank *et al.*, 2013)

$$\dot{V}_{FG} = 8.8930 \cdot x_C + 20.9724 \cdot x_H + 3.3190 \cdot x_S - 2.6424 \cdot x_O + 0.7997 \cdot x_N \quad (25)$$

The fuel-specific CO<sub>2</sub> amount per kilogram of fuel is determined in standard EN 12952-15 as

$$u_{CO_2} = u_{CO_2,stoich} + \rho_{A,dry} \cdot V_{FG,dry} \cdot (\lambda - 1) \cdot x_{CO_2,A,dry}, \quad (26)$$

where  $u_{CO_2,stoich}$  stands for stoichiometric ratio of flue gas and fuel [kg/kg],  $\rho_{A,dry}$  for dry air normal density (1,239 kg/Nm<sup>3</sup>) and  $x_{CO_2,A,dry}$  for mass fraction of CO<sub>2</sub> at dry air [kg/kg]. Total mass of CO<sub>2</sub> in the flue gas over is then determined by

$$m_{CO_2}[t] = \int_{t_1}^{t_2} \dot{m}_F \cdot u_{CO_2} \cdot 10^{-3} \left[ \frac{t}{kg} \right] dt, \quad (27)$$

where  $\dot{m}_F$  stands for flue gas flow [kg/s] and  $t$  for time.

#### 4.1.2 Determination of boiler energy flows

The energy content of fuel is determined by the energy balance. The fuel energy divided by the fuel calorific value of gives the mass of fuel. At the energy balance all the input energy into the boiler, produced energy and losses are calculated (e.g., boiler heat losses) or measured (e.g., steam flow). (EN 12952-15, 2003)

The steam energy produced by the boiler is calculated by

$$\dot{Q}_{ST} = \dot{m}_{ST} \cdot h_{ST}(T_{ST}, p_{ST}), \quad (28)$$

where  $T_{ST}$  stands for steam temperature [K],  $p_{ST}$  for steam pressure [Pa] and  $\dot{m}_{ST}$  for steam mass flow [kg/s]. Enthalpy of steam  $h_{ST}$  [J/kg] is defined as a function of temperature and pressure. (EN 12952-15, 2003)

Flue gases leave the boiler in high temperature and thus they carry significant amount of energy away from boiler process. The flue gas heat loss  $\dot{Q}_{FG}$  is usually the largest loss in a fuel fired boiler. (Coskun *et al.*, 2009). To decrease flue gas losses, flue gas exit temperature should be decreased. However, the acid dew point of flue gases restricts the flue gas temperature to about 130-150 °C for sulphur containing fuels. (Teir & Kulla, 2002) Flue gas analysis and flue gas temperature can be used to calculate the loss.

$$\dot{Q}_{FG} = \dot{m}_{FG} \cdot c_{FG} \cdot (T_{FG} - T_{ref}), \quad (29)$$

where  $\dot{m}_{FG}$  stands for flue gas mass flow [kg/s],  $c_{FG}$  for specific heat capacity of flue gas [J/(kg·K)],  $T_{FG}$  for flue gas temperature and  $T_{ref}$  for reference temperature [K] (in standard EN 12952-15  $T_{ref}$  is 298 K).

Boiler blowdown is steam intentionally wasted from a boiler to avoid concentration of impurities during continuing evaporation of steam. As the blowdown steam is saturated only pressure  $P_{BD}$  or temperature  $T_{BD}$  is needed to specify the steam enthalpy. Then the boiler blowdown loss  $\dot{Q}_{BD}$  can be calculated as the amount of steam and steam enthalpy

$$\dot{Q}_{BD} = \dot{m}_{BD} \cdot h(P_{BD} \text{ or } T_{BD}).$$

Normally the mass flow rate of blowdown is 1-3 % of the mass flow rate of feed water coming into steam drum (Teir & Kulla, 2002).

Ash can exit the furnace either as bottom ash from bottom of the furnace or as fly ash with flue gases. The bottom ash loss can be calculated as the amount of bottom ash mass flow and the temperature of the bottom ash. If the bottom ash mass flow  $\dot{m}_{SL}$  [kg/s] and the fly ash mass flow  $\dot{m}_{FA}$  [kg/s] are not measured, they can be determined from ash balance and estimated ash collection efficiency. In these calculations it is made an assumption that from the overall ash content bottom ash is 10%, and the remaining is fly ash. Boiler bottom ash loss  $\dot{Q}_{SL}$  is

$$\dot{Q}_{SL} = \dot{m}_{SL} \cdot ((c_{ash} \cdot (T_{SL} - T_{ref}) + x_{SL,u} \cdot H_{UC}), \quad (30)$$

where  $c_{ash}$  stands for specific heat of ash [J/K·kg],  $T_{SL}$  for temperature of bottom ash [K],  $x_{SL,u}$  for unburned proportion of bottom ash [-] and  $H_{UC}$  is the lower heating value of unburned combustibles [J/kg].

Respectively fly ash loss  $\dot{Q}_{FA}$  is determined by

$$\dot{Q}_{FA} = \dot{m}_{FA} \cdot (c_{ash} \cdot (T_{FA} - T_{ref}) + x_{FA,u} \cdot H_{UC}), \quad (31)$$

where  $T_{FA}$  stands for temperature of fly ash and  $x_{FA,u}$  for unburned carbon proportion of fly ash [-].

Boiler radiation and convection losses  $\dot{Q}_{RD}$  can be estimated using EN 12952-15 by standard formula

$$\dot{Q}_{RD} = C \cdot \dot{Q}_{\max}, \quad (32)$$

where  $C$  stands for standard coefficient (for coal boilers = 0.0220) and  $\dot{Q}_{\max}$  for maximum heat power of a boiler.

#### 4.1.3 Efficiency and determination of fuel flow

In order to determine the efficiency of the boiler and the amount of fuel flow it is important to take into account all known energy flows to get as good and accurate estimate as possible.

The efficiency of the boiler  $\eta_B$  is determined by the equation

$$\eta_B = \frac{\dot{Q}_N}{\dot{Q}_N + \dot{Q}_{L,tot}}, \quad (33)$$

where  $\dot{Q}_N$  stands for the net thermal power of the boiler and  $\dot{Q}_{L,tot}$  for total losses of boiler.

Net thermal power  $\dot{Q}_N$  is determined by equation

$$\begin{aligned} \dot{Q}_N = & \dot{m}_{ST}(h_{ST} - h_{FW}) + \dot{m}_{SW1}(h_{FW} - h_{SW}) + \dot{m}_{SW2}(h_{FW} - h_{SW}) \\ & + \dot{m}_{BD}(h_{BD} - h_{FW}), \end{aligned} \quad (34)$$

where  $\dot{m}_{ST}$  stands for steam mass flow [kg/s],  $h_{ST}$  for enthalpy of live steam [J/kg],  $h_{FW}$  for enthalpy feed water [J/kg],  $\dot{m}_{SW1}$  for spray water 1 mass flow [kg/s],  $h_{SW}$  for enthalpy of spray water [J/kg],  $\dot{m}_{SW2}$  for spray water 2 mass flow [kg/s],  $\dot{m}_{BD}$  for mass flow of blowdown water and  $h_{BD}$  for enthalpy of blowdown water. (EN 12952-15, 2003; Senegacnik *et al.*, 2008)

Total losses  $\dot{Q}_{L,tot}$  is calculated by

$$\dot{Q}_{L,tot} = \dot{Q}_{FG} + \dot{Q}_{SL} + \dot{Q}_{BD} + Q_{RD} \quad (35)$$

From all the previous calculation, the fuel flow of the boiler can be formulated as

$$\dot{m}_F[\text{kg/s}] = \frac{\frac{\dot{Q}_N}{\eta_B} - \dot{Q}_Z}{H_{N,\text{tot}} \cdot (1 - u_{UC})}, \quad (36)$$

where  $\dot{Q}_Z$  stands for heat credits, i.e. amounts of heat other than chemical heat caused by pulverisers, recirculating gas fans, circulating pumps and any other drive motors etc. E.g. flue gas fan can raise the flue gas temperature by 2-3 °C.  $H_{N,\text{tot}}$  stands for fuel net calorific value [kJ/kg] and  $u_{UC}$  for ratio of unburned combustibles. Iterative calculation is needed to solve the equation so that factors  $\eta_B$  and  $\dot{m}_F$  are in equilibrium with each other. (EN 12952-15, 2003; Senegacnik *et al.*, 2008)

## 4.2 Estimation of uncertainties and accuracy of the model

The accurate determination of heat input and heat output requires the use of sensitive flow meters and analysers which are not always found on boilers in the industrial installations. Use of inaccurate instruments affects significantly to final results.

Precision of measuring device does not mean the precision of measurement. Measuring instruments are today, typically very accurate according to measuring device manufacturers. Even  $\pm 0.1$  % errors in accuracy are not uncommon. These errors may be quite true figures when sources of measurement error have been eliminated under laboratory conditions, but in industrial conditions it is difficult to achieve such precisions. (Pöyry, 2007)

Estimation of uncertainties typically includes a description of calculation method, used calculations, the results of the calculations and assessment of the results. As the basis information to calculate accuracy of the energy balance method, estimated errors of used variables and individual measurements can be used. There is also need to assess the significance of different variables to the overall accuracy. (AVR, 2012)

The determination of total error can be made in stages from single measurement accuracies, proceeding heat flows to determine the accuracy of the balance method and continues to the total error determination. If accuracies specified by sensor manufacturer are used in balance calculations, accuracies of  $\pm 1.5$  % can be achieved. If the measurements of the power plant have been poorly executed and only fresh steam flow rate, which has the biggest influence, is measured incorrectly, balance calculation error can easily be  $\pm 10$  % or more. (Pöyry, 2007)

### 4.2.1 Uncertainty calculations

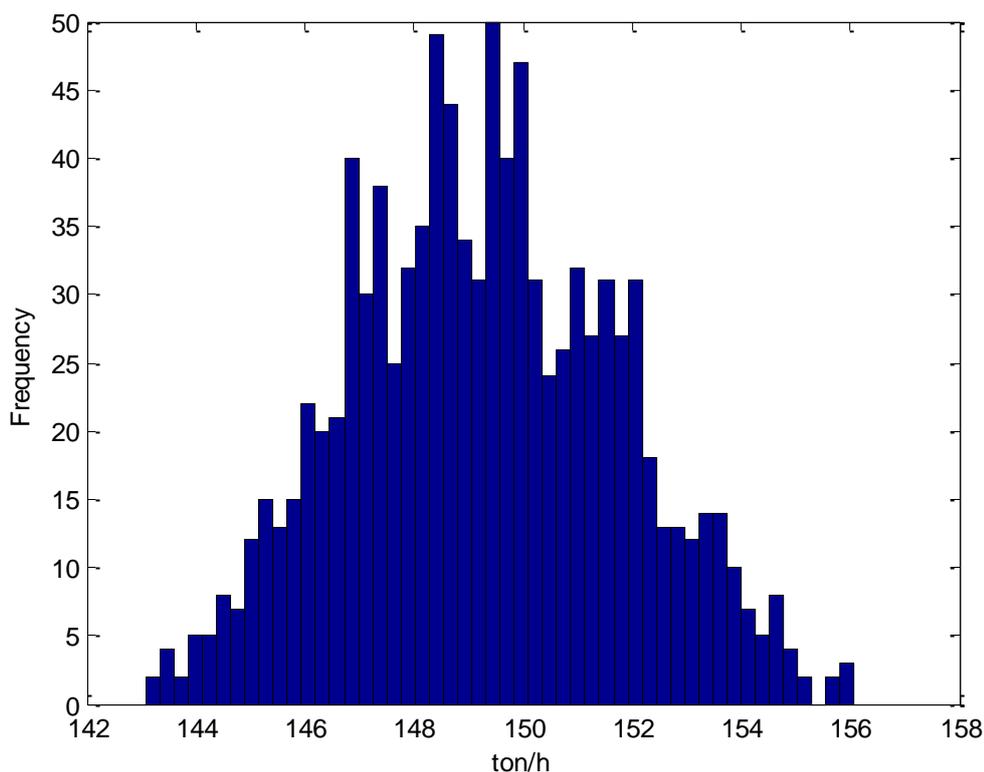
The tiers for activity data of a source stream are defined using maximum uncertainty allowed for the determination of the quantity of fuel or material over a reporting period. It must be demonstrated by submitting an uncertainty assessment to the competent authority together with the monitoring plan that these requirements are met.

Traditional methods for determining uncertainty of energy balance method are difficult because the use of iterative means in calculations. In this case, the Monte Carlo method is the best alternative for the calculating uncertainty of energy balance method.

In general terms, the Monte Carlo method (or Monte Carlo simulation) can be used to describe any technique that approximates solutions to quantitative problems through statistical sampling (Binder & Heermann, 2010). In this thesis, Monte Carlo simulation is used to calculate how measurements uncertainties affect as model inputs into uncertainties in model outputs, in this case CO<sub>2</sub> emissions.

In Monte Carlo simulation, the simulation test run is carried out many times (e.g. 1000) and all of the uncertain parameters are sampled (i.e., a single random value is selected from the specified distribution describing each parameter). Each simulation run is equally likely and the result is a large number of separate and independent results, each representing a possible solution for the calculus.

Monte Carlo simulation is perhaps the most common technique for propagating the uncertainty in various aspects of a system to predict overall uncertainty. The accuracy of a Monte Carlo simulation is a function of the number of test runs. The confidence bounds on the results can be readily computed based on the number of runs. (Binder & Heermann, 2010) As an example in Figure 4 is uncertainty histogram of CO<sub>2</sub> mass flow one hour average. Result in this example is  $150 \pm 6$  ton/h with a 95 % confidence level.



**Figure 4.** Histogram of CO<sub>2</sub> mass flow calculated with Monte Carlo simulation with 1000 rounds.

#### 4.2.2 Fault detection and diagnostics

The most significant advantage using energy and emission balances is to detect possible non-consistency between the measurements. The main idea is to form an observation balance for measurements before and after the process and compare the balances to detect differences in the process. This so called residual information can indicate possible fault in the emission monitoring system. Therefore this information can be used as decision-making support in process monitoring and fault diagnostics.

The energy balance method can provide redundant CO<sub>2</sub> measurement for sensor failure detection or even work as a virtual sensor when e.g. CEMS is out of operation. It may also be useful to observe difference of the mass balance method with the standard method in the long-term.

## 5 CASE SALMISAARI

The methods presented in previous Chapters were tested in Salmisaari power plant of Helsingin Energia. The Salmisaari power plant is a coal fired combined heat and power (CHP) plant. In addition to CHP, Helsingin Energia also uses trigeneration in its Salmisaari power plant, which means that district cooling is also produced in the same process with heat and electricity.

The benefits of coal as a fuel include its good availability and its reasonable and stable costs. Coal is also easy to store for emergency situations. The bulk of coal is imported by ship from Russia and Poland. The coal used by the plant has been stored in an underground rock cavern since 2004. (Helsingin Energia, 2012)

Salmisaari power plant constitutes from two units, A and B. The heat production unit A is taken into use according to the heat load. The main production unit is the Salmisaari B power plant. The output of the plants is 160 MW of electricity, and the corresponding output of district heat is 480 MW. The flue gases of boilers K1 and K7 are cleaned using electrostatic precipitators and after that directed to desulphurisation plant, where flue gases of boiler K7 are mixed with K1 flue gas flow. After that mixed flue gas flow is directed to 153-meter high stack of boiler B. (Häyriinen *et al.*, 2010)

The international environmental certificate ISO 14001 was granted to the Salmisaari power plant in 2000. (Helsingin Energia, 2012) This study concentrates on CO<sub>2</sub> emission monitoring at the Salmisaari B power plant.

### 5.1 Data collection

Calculation of presented CO<sub>2</sub> monitoring methods requires process data. Energy balance calculation utilizes ca. 20 different process measurements. In addition to that fuel analysis information is used to calculate the composition of the flue gas flow and hence the CO<sub>2</sub> emission. Operation and precision scale measurement data are used to calculate the CO<sub>2</sub> emissions with standard method. Emission measurements and compensation measurements from the stack are needed in direct measurement and online observation. Data from the power plant were chosen so that the emissions of the process could be studied at different operation states of the plant.

The choice of a suitable averaging period is strongly influenced by the expected short-term variability in emission levels and whether such peaks are important. Also, the averaging period must be consistent with the averaging period of the relevant emission limit specified in the authorisation or permit, with which the data will be compared. For CEMS, the averaging time may be specified in legislation, such as International Emission Directive (IED) or Directive 2003/87/EC.

Process data for the test purpose were extracted from a database with the time resolution of 60 min. The sizes of the data matrices used as an example were approximately 40 times 700 (40 variables in rows, 700 time steps in columns), covering ca. 30 days of operation. As it is typical for large-scale processes that there are several measurements for some parameters, some variables used here were averages calculated from several different measurements. Spray water flow, for instance, is measured in two parts and it is the calculated average of these measurements that is used in the present analysis. Table 3 presents the main measurements used for calculating the energy balance.

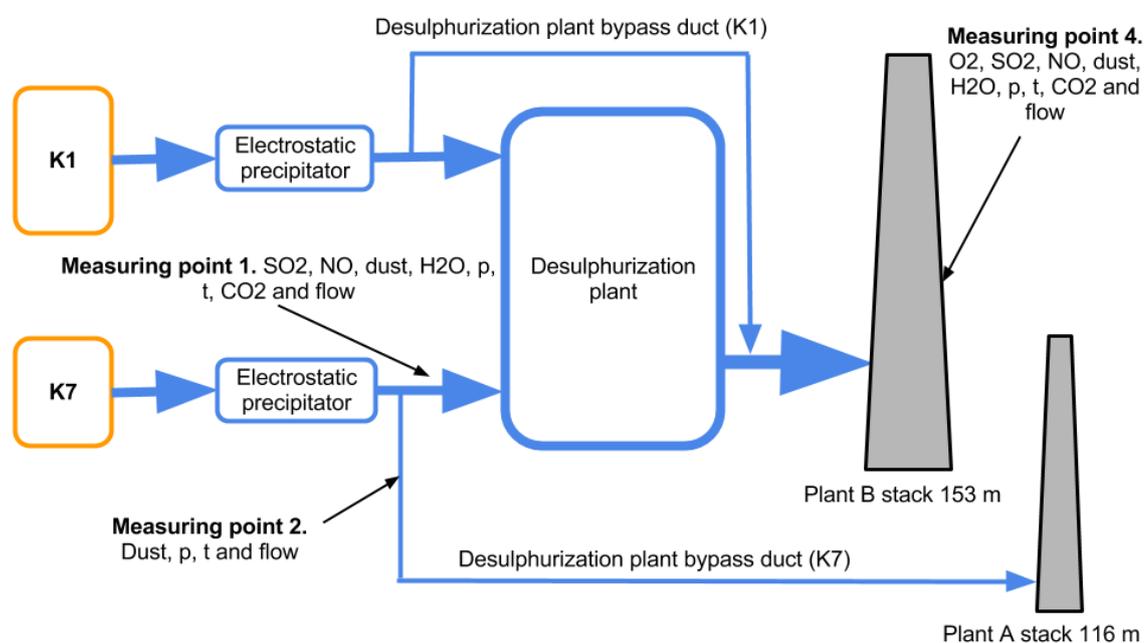
**Table 3.** The main measurement for boiler K1 (Häyrinen *et al.*, 2010)

Tag	Name	Unit	Range	Type	Rel. error %
1RA00T001	Steam temp.	°C	0-550	NiCrNi	0.5
1RA00F903	Steam flow	t/h	0-750	Orifice plate	1.0
1RA00P001	Steam pressure	bar	0-160	Pressure transmitter	0.5
1RA10F001	Internal consumption	t/h	0-110	Orifice plate	1.0
1RS23F001	Spray 11	t/h	0-15	Orifice plate	1.0
1RS24F001	Spray 12	t/h	0-15	Orifice plate	1.0
1RS25F001	Spray 21	t/h	0-30	Orifice plate	1.0
1RS26F001	Spray 22	t/h	0-30	Orifice plate	1.0
1RL00T002	Spray water temp.	°C	100-200	PT100	0.5
1RL00P002	Spray water pressure	bar	0-210	Pressure transmitter	0.5
1RL00T007	Feed water temp.	°C	0-1000	NiCrNi	0.5
1RL00F001	Feed water flow	t/h	0-750	Orifice plate	1.0
1RL00P002	Feed water pressure	bar	0-210	Pressure transmitter	0.5
1NR00T033	Flue gas temp.	°C	0-200	PT100	0.5
1NB10P103	Drum pressure	bar	0-210	Pressure transmitter	0.5
1NC10F001	Blowdown steam	t/h	0-25	Orifice plate	1.0
1NG00T999	Combustion air temp.	°C	0-50	PT100	0.5
1NG00F001	Combustion air flow	knm <sup>3</sup> /h	0-1000	Orifice plate	1.0
1NR00A017	Flue gas O <sub>2</sub>	%	0-21	Oxygen analyser	1.0
0ML01M002	Outdoor air humidity	%	0-100	Weather station	1.0
0ML01P001	Outdoor air pressure	mbar	750-1200	Weather station	0.5

The energy balance method constantly uses large amounts of process data which can be a problem for the information system if the time resolution is increased considerably. On each execution cycle the energy balance method needs a data set determined by the corresponding process state.

## 5.2 Current state analysis of CO<sub>2</sub> emission monitoring

Flue gases of the boilers K1 and K7 are mixed before semi-dry desulphurization process (**Figure 5**). Therefore measured emissions must be divided by calculation when both boilers are in use. (Häyrinen *et al.* 2010) For simplicity, it is possible to concentrate on cases where the heating boiler K7 is not in operation, which is the case in results presented in Chapter 6.



**Figure 5.** Measuring points. (Häyrinen *et al.*, 2010)

Standard method is used in Salmisaari to estimate the amount of CO<sub>2</sub> emissions in ETS system, so it can be considered as a reference value for the other two methods. As the new EMV regulations were not yet in action at time of the test period, some of the calibrations of the measurements used when calculating results of direct measurement and energy balance method were outdated.

### 5.2.1 Emission data evaluation system

For collecting data and calculating emissions, Salmisaari power plant is equipped with Sick Meac 2000 emission data acquisition and evaluation system. The Data Acquisition Unit (DAU) collects the measuring data of the connected analysers, preprocesses and

transmits data to the Emission PC (EPC). There, the raw measurement data is processed and normalized using the MEAC2000 software. All of the evaluation results are stored in the databases and are readily available. The calculation can take place e.g. once a minute, but the reporting is done based on one hour averages. (Häyrinen *et al.*, 2010; Sick AG 2012)

## 5.2.2 Analysers for flue gas monitoring

GM 35 analyser provides measurements of CO, CO<sub>2</sub> and humidity. Sick Flowsic 100 measuring system is used for flow measurement. The most important measurement points and analysers for CO<sub>2</sub> emission control are shown in Table 4. The measuring points in the table refer to Figure 5.

**Table 4.** Flue gas measurement devices and techniques. (Häyrinen *et al.*, 2010)

Measuring device	Measuring point	Measuring components	Principle	Measuring ranges	Accuracy
Sick GM 31	1, 4	SO <sub>2</sub> , NO, Temperature	In-situ, DOAS	T: 0-200 °C SO <sub>2</sub> :0-2100 ppm NO:0-600 ppm	± 2%
Sick GM 35	1, 4	CO <sub>2</sub> , H <sub>2</sub> O	In-situ, IR filter, and/or gas correlation	CO <sub>2</sub> : 0-20 % H <sub>2</sub> O: 0-30 %	± 2%
Sick GM 302	1, 4	O <sub>2</sub>	Zirconium dioxide current probe	0-21 %	± 0.2 %
Foxboro	1, 2, 4	Pressure	Absolute pressure measurement	800–1200 mbar (abs.)	
Sick Flowsic 100	1, 2, 4	Flow	Transmitting and receiving ultrasonic pulses	0-40 m/s	± 0.1 m/s
SKS	2	Temperature	PT100	0-250 °C	

Nitrogen monoxide, sulphur dioxide, carbon dioxide and dust as well as pressure, temperature, humidity and flow rate of the flue gas are measured continuously at the measuring point 1 of Figure 5. The measuring point is located in rectangular shape duct, dimensions 2 x 3.2 m, right after the electrostatic precipitator and before the desulphurisation plant. This duct is used for K7 boiler flue gases before desulphurization plant. (Häyrinen *et al.*, 2010)

Nitrogen monoxide, sulphur dioxide, carbon dioxide and dust as well as oxygen, pressure, temperature, humidity and flow rate of the flue gas is also measured continuously at the measuring point 4, which is located in the stack B. This duct is used for both K1 and K7 boiler flue gases. The measuring point is located after the desulphurisation plant in the round duct, diameter of 3.58 m. (Häyrinen *et al.*, 2010)

Flow rate of the flue gas, particle concentration, pressure and temperature are measured continuously at measuring point 2. It is located after the electrostatic precipitator in a channel which used for flue gas of the boiler 7 to bypass desulphurisation plant, if needed. ((Häyriinen *et al.*, 2010)

### **5.2.3 Flue gas volume and flow rate**

The flue gas volume can be calculated from fuel data. In addition that the flue gas volume flows are also measured by flow monitors. When using the measured values in the calculation it must be taken into account that gases are in the same state, i.e. same temperature, pressure, oxygen and level. (Häyriinen *et al.*, 2010)

## **5.3 Fuel analysis**

The uncertainties of the fuel ultimate analysis are fundamental to the accuracy of the standard and energy balance calculations. The uncertainties associated with fuel analysis cover determination methods for C, H, N, O, S, moisture, ash and heating value. The uncertainties reported by the laboratory are for C  $\pm 1$  %, H for  $\pm 3$  %, N for  $\pm 9$  %, S for  $\pm 8$  %, moisture for  $\pm 7$  % and for heating value  $\pm 1.5$  %. (Häyriinen *et al.* 2010)

## **5.4 Implementation**

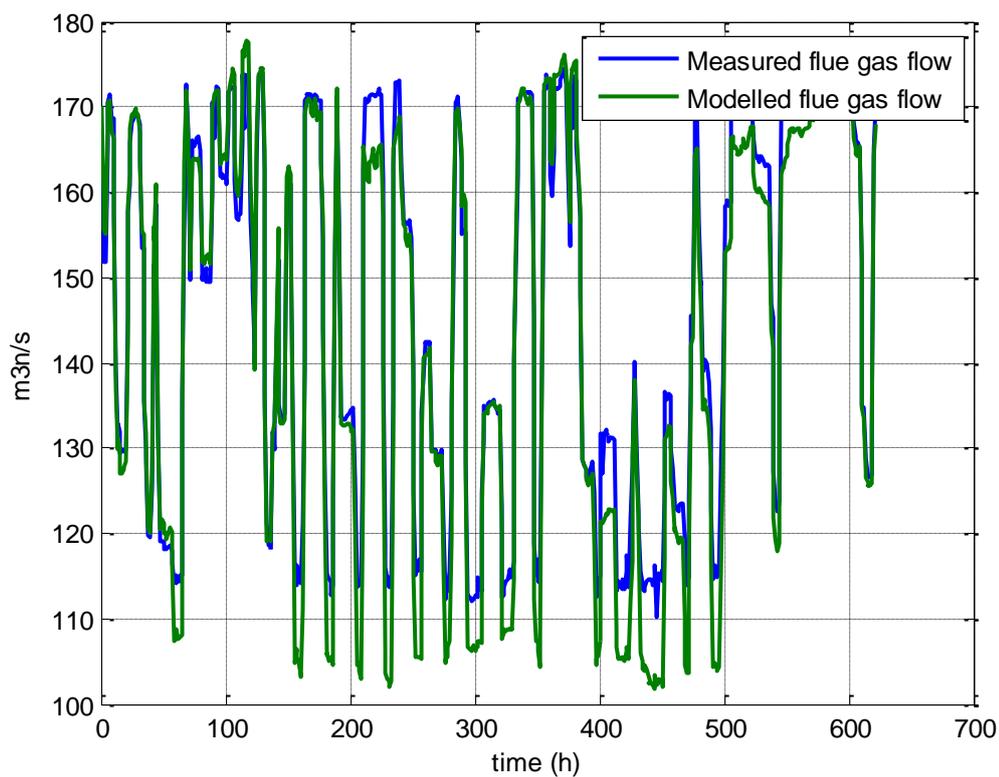
The methods were tested during normal operation of the plant, with both boilers in use and also only with boiler K1 in operation to test how well different methods work in these situations. Advantage to test methods while both boilers were in use, was that then boiler K1 worked mainly to generate base load and primarily all the power fluctuation were handled using boiler K7. This means that the fuel flow, the flue gas flow and the CO<sub>2</sub> emissions for boiler K1 were more static. However uncertainties of individual boilers' flue gas flow measurements increased, because of the shared stack and additional calculation to separate flows. In these situations it was only reasonable to compare the differences between the standard and the energy balance method, which were not affected by these situations. The presented results in Chapter 6 are from the period where only boiler K1 was in use and all the methods are comparable. Also during a one observation period, an abnormal freeze emerged in the CO<sub>2</sub> analyser. Although this measurement was not currently used for ETS it works as a good example of why there is need for extra observation methods.

## 6 RESULTS

Desired objective was to find a way to improve the quality of emission measurements. The study concentrated on CO<sub>2</sub> emissions in large coal-fired power plants, but used methods can be in some extent exploited in different kind of power plants. In this Chapter three separate observation methods are unified where possible to allow for a meaningful comparison.

### 6.1 Flue gas flow

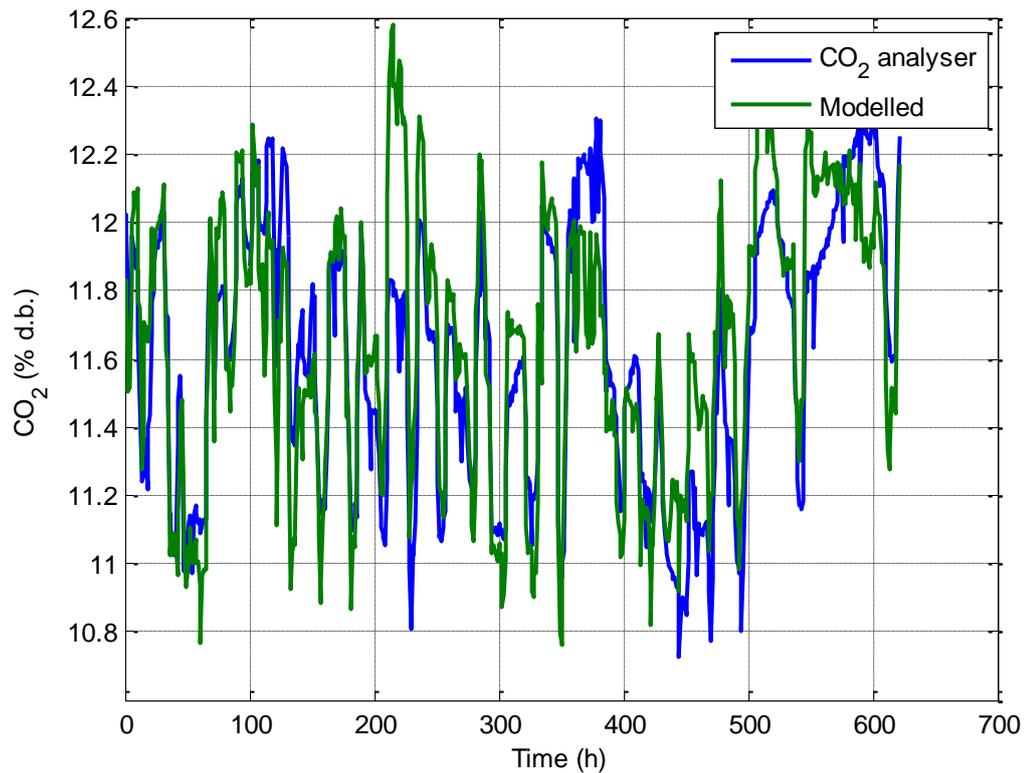
Calculated flue gas flow is obtained from the model which is obtained using results from equations of (25) and (36). As seen in Figure 6, the flue gas flow modelled by energy balance method performs reasonably well against measured value. When there are no significant power level fluctuations, the difference is ca.  $\pm 2\%$  at high power levels, but at lower power levels difference grows to ca.  $\pm 10\%$ . Direct flue gas measurements are usually very difficult to get accurate, so also in this case, comparison is made mainly to show how good online approximation it is possible to get using energy balance method. Even when significant fluctuations occurs energy balance method reacts considerably fast to these changes.



**Figure 6.** Measured and modelled dry flue gas flow

## 6.2 Online CO<sub>2</sub> emissions

CO<sub>2</sub> direct measurement values are reported as percentage (%) of dry flue gas flow. To compare this measurement with energy balance method, there is a need to use modelled CO<sub>2</sub> mass flow and divide it with modelled dry flue gas flow. As can be seen in Figure 7, the estimate obtained by energy balance method gives a relatively good approximation in the relation to measurement results. Some over- and under-estimation of CO<sub>2</sub> emission can be attributed to uncertainty of measurements.



**Figure 7.** Comparison of the CO<sub>2</sub> concentration in dry flue gas measured and calculated result

### 6.3 Comparison of the methods

Table 5 presents the absolute CO<sub>2</sub> emissions and their uncertainties in the case example in addition to relative uncertainty and the ETS requirements applied in Salmisaari power plant. For standard method, the standard deviation of the estimate is derived from uncertainty assessment reports of Salmisaari, which are based on scale calibration reports and evaluation of uncertainties due to handling of coal. For direct measurement based method and for energy balance method, the standard deviations were calculated by Monte Carlo simulation by varying all the measurement values with evenly distributed white noise at their uncertainty ranges. Using these simulation rounds results were calculated the 95 % confidence interval for the uncertainty result. It should be noted that these are the uncertainties for an hourly average. Increasing the frequency of sampling time would eventually affect that the dynamics of the system would begin to affect and degrade the accuracy of the method. In all the cases, type A (statistically estimated standard deviation) measurement uncertainties were only considered. Therefore, validity and correctness of measurements must be verified by calibrations and online monitoring to avoid increased uncertainties.

**Table 5.** Absolute CO<sub>2</sub> emissions and their uncertainties in a case example in addition to relative uncertainty and the ETS requirement applied in Salmisaari power plant.

	<b>CO<sub>2</sub> emissions</b> [tCO <sub>2</sub> ]	<b>Absolute uncertainty</b> [tCO <sub>2</sub> ]	<b>Relative uncertainty</b> [%]	<b>Tier 4 requirements</b> [%]
<b>Standard method</b>	85 000	± 1100	± 1,2	± <b>1,5</b>
<b>Direct measurement method</b>	91 000	± 2 600	± 2,8	± <b>2,5</b>
<b>Energy balance method</b>	84 000	± 2 900	± 3,4	± <b>2,5</b>

According to Table 5, the measurement based method provides some 7 % higher values than the standard method. The obvious reason for this variation is outdated calibration of CO<sub>2</sub> measurement during the run. Instead, the relative uncertainty just exceeds the tier 4 requirement, as the uncertainty is dominated by the uncertainty of the flue gas flow measurement. On the other hand, the energy balance method manages to provide about the same amount of CO<sub>2</sub> emissions compared to the standard method. However, the relative uncertainty exceeds the tier 4 requirement. Still, the method is able to provide on-line redundancy for direct CO<sub>2</sub> measurement, whose reliability, unfortunately, was not further verified.

### 6.3.1 Evaluation of the methods

The validity and significance of a method is determined to a large extent by its suitability for general use. Although with the standard method or the direct measurement it is usually possible to obtain a better approximation of CO<sub>2</sub> emissions, energy balance method can be useful as a simplified model for an overall evaluation and real-time observation. In online detection, it is desirable to detect the change in real-time as soon as it occurs. However, the modelling involves the use of numerical methods and simplifying assumptions which may lead to errors if not approached with care.

Direct measurement measuring the flue gas flow from the stack has some drawbacks when compared to standard or energy balance method. In some plants, the flue gas flow velocity profile can be very asymmetric and fluctuating and there is, of course, an uncertainty related to both the continuous monitoring and the manual methods used for calibration of the monitoring equipment. Also the costs relating to maintenance, quality assurance and calibration of a continuous monitoring can be high. Since plants usually report concentration on a dry basis, it may be therefore simpler to calculate an annual mass emission if the flue gas flow is also available on a dry basis. In any case, the moisture content in the flue gas must also be measured continuously and this can lead to

higher uncertainties and the addition of a relatively expensive instrument that is difficult to calibrate. (Hermansson *et al.*, 2011)

The uncertainty assessment of direct measurement provides a perspective on the significance of a single measurement to total uncertainty. Relative effect of each calculation element is calculated using reported uncertainties of measurements and results are shown in Table 6.

**Table 6.** Effect of the individual measurements at direct measurement

Name	Uncertainty %
CO <sub>2</sub> concentration	1.00
Flue gas flow	2.00
Oxygen	0.50
Moisture	0.22

Direct measurement relies primarily on two pieces of input data, stack concentration and stack flow rate. According to Table 6 a good stack flow measurement is essential to obtaining accurate mass data. It is therefore important to pay particular attention to probe calibration accuracy and the geometric shape of stack in order to achieve acceptable accuracy. In addition, if moisture and oxygen corrections are needed to use, the overall uncertainty is greatly reduced.

In general, the findings indicate that using energy balance method it is possible obtain more redundant information for emission monitoring. The energy balance method is particularly useful for comparing real-time measurements of the stack but it can be also used as well in long-term monitoring e.g. ETS.

From the perspective of utilization the strength of calculation based methods depends significantly on knowing the process stoichiometric relationships. Hence, using these kinds of methods for modelling with mixture of different fuels and NO<sub>x</sub> emissions may be very difficult. Despite the challenges, it is probable that interest to develop and use qualitative models of processes will increase in the future as a result of increasing power of scientific computing, sensor and monitoring technologies.

Properly executed real-time CO<sub>2</sub> emission modelling requires reliability estimates of each individual measurement, which are used to calculate emission values. The uncertainties of the fuel ultimate analysis and flow measurements are fundamental to the accuracy of the energy balance method.

Table 7 shows the most important individual measurement effects on overall uncertainty when the relative errors of Table 3 and fuel analysis uncertainties reported by laboratory are used.

**Table 7.** Effect of the most important individual measurements on overall uncertainty at energy balance method.

Measurement	Uncertainty %
Heating value	1.45
Carbon	1.06
Steam flow	0.92
Steam temperature	0.27
Feed water temperature	0.20
H <sub>2</sub> O	0.07
Flue gas O <sub>2</sub>	0.04
Flue gas temperature	0.04
Hydrogen	0.03
Ash	0.03
Steam pressure	0.03
Combustion air temperature	0.01

As can be seen in Table 7, the dominating uncertainty factors to uncertainties for energy balance method are the carbon content in the fuel, heating value of the fuel and the steam flow. Special attention should also be paid to hydrogen, water and ash content in the fuel, and steam, feed water and flue gas temperature measurements as well as the oxygen content in the flue gas.

### 6.3.2 Usability of energy balance method at ETS

Due to nature of the energy balance method its use at ETS needs to be considered case by case. Energy balance method is best suited for the use of installations with the use of one fuel and one fuel supplier. Compared to traditional method, energy balance method, in which fuel use is determined by balance calculations, fuel heating value and fuel analysis, can take more accurately into account humidity, unburned materials and other fluctuations in fuel. This way energy balance method may provide more realistic results, which is desirable feature e.g., for annual mass emission reporting.

The usability of energy balance method becomes more difficult when there are several different sources of fuel. In such a case all but one of fuel sources should be estimated with an assistant observation method, because the consumption separation of various fuel flows (e.g. bio, peat, coal) is otherwise impossible.

## 6.4 Discussion

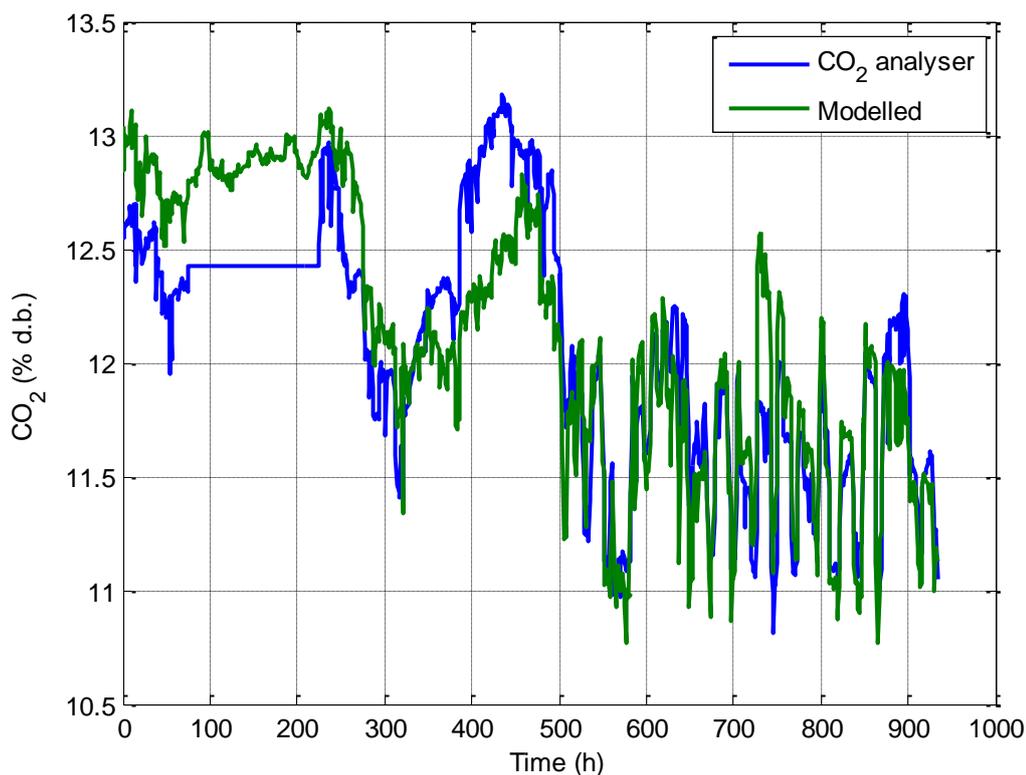
One method is not inherently superior to the others. All methods have their own strengths and weaknesses depending on the purpose and applicability of presented CO<sub>2</sub>

monitoring methods. In general, it can be noted that direct measurement and energy balance method provide more information for both regulatory purposes and process control in a form of on-line measurement.

The standard method is suitable for coal combustion even in co-combustion, if the fuels are not mixed before the rate measurements. Due to intermediate silos, standard method typically provides only off-line information of the produced CO<sub>2</sub> emissions. Then, the direct measurement method is suitable for applications where only fuels considered in ETS are used, as all the CO<sub>2</sub> emissions are measured despite of the fuel source. The analysis is more complex in cases when there are flue gases from several boilers to one stack, as it is the case in Salmisaari power plant with boilers K1 and K7.

The energy balance method is especially suitable for boilers having one main fuel. Otherwise, the other fuel flows must be estimated to be considered in the calculation. Disadvantage of energy balance method is that the creation of the balance equations requires some work and process knowledge. Using energy balance method it is important as completely as possible to utilize monitoring data, i.e. all input materials and fuels must be taken into account. However, in some cases it may be difficult to determine smaller amounts of carbon precisely. Assuming the amount of carbon leaving the process in bottom ash or wastes as zero may be considered an appropriate estimation. This would be then similar assuming a conversion factor of 100% in case of the standard method.

Although the methods were tested in normal operation of the plant, during a one observation period, an abnormal freeze emerged in the CO<sub>2</sub> analyser which is seen in Figure 8.



**Figure 8.** Measured and Modelled CO<sub>2</sub> concentration with abnormal freeze

This incident shows why it is useful to have redundant data of the measurements. If the CO<sub>2</sub> analyser would have been used as part of ETS during that period, this data gap would have to be verified in some way, e.g. using energy balance method. Also occurred problem may have noticed earlier if there would have been other system to provide better on-line information of the CO<sub>2</sub> emissions instead of the precision scales used by standard method.

The uncertainty analysis of direct measurement and energy balance method were made only for type A measurement uncertainties. However, other kind of uncertainties might be even more significant in real processes, so special attention must be paid to the validity of the used measurements. Therefore, online monitoring of key measurements has a major benefit also in these applications.

## 6.5 Applicability of energy balance method with other fuels and emissions

The quantities of fuel components may vary to some extent between fuel analyses, and presumably the conditions for emissions also vary, which is challenging for CO<sub>2</sub> modelling. For many standard fuels, like oil or gas, the modelling of flue gas flow and CO<sub>2</sub> amount should give reliable results. Fuel consumption for these fuels can be determined the same way like in this thesis, indirectly from the energy balance,

although gas and liquid fuel flows can be also relatively easily measured directly. Instead solid fuel consumption is usually harder to determine instantaneously with traditional measurements, so the use of indirect system, like energy balance method, may give more reliable results.

Although CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O are emitted during the combustion of fossil fuels, CO<sub>2</sub> accounts for the majority of greenhouse gas emissions from most combustion plants that generate electricity, heat, and/or steam. The method developed to estimate CO<sub>2</sub> emissions differs significantly from that required to estimate CH<sub>4</sub> and N<sub>2</sub>O emissions. A combustion process itself can involve fluctuations that remain undetected and result in undesired consequences such as an increased level of emissions. The energy balance method works reasonable well in cases where certain variables correlate strongly with each other, as it is in the case of modelling CO<sub>2</sub> emission. Less perceivable but still important phenomena may remain undetected behind the characteristic behaviour of the process. These phenomena can be important when considering the formation of other emissions than CO<sub>2</sub>. While CO<sub>2</sub> can be reasonably estimated by applying energy balance method and fuel analysis, estimating CH<sub>4</sub> and N<sub>2</sub>O depends not only upon fuel characteristics, but also on technology type and combustion characteristics, usage of pollution control equipment, and environmental conditions. Emissions of these gases also depend more on the efficiency and combustion technology, as well as maintenance and operational practices. Due to this complexity, a much greater effort is required to estimate CH<sub>4</sub> and N<sub>2</sub>O emissions from energy balance method.

## 7 CONCLUSIONS

In this master's thesis three independent methods were presented and applied to determine CO<sub>2</sub> emissions in power plants that cover new requirements set by European Commission for the third ETS period. The presented methods were standard method, direct measurement method and energy balance method. The methods were applied in Salmisaari power plant of Helsingin Energia.

The results indicate that the flue gas measurement and energy balance methods provide possibilities for CO<sub>2</sub> monitoring, as the new requirements are considered in sensor calibration protocols. More weight for these estimates can be put when this issue is also considered.

The energy balance calculation method can be used as emissions trading observation method or in combination with approved methods within certain limits. If more than one fuel is used in the boiler, energy balance method can be used as an additional assurance.

In order to meet the accuracy of emissions trading requirements when using energy balance method, the most important energy flow measurements must be calibrated. Minor energy flows can be dealt with as a part of the boiler losses as to simplify error analysis.

Balance calculations are also useful in the management of errors. Primary monitoring method and the authentication method should be selected so that they are not based on the same measurements. With this approach dependence of individual measurements can be avoided. Then the problems are more likely detected and they can be addressed with determination.

When the accuracy of the presented observation methods are examined and compared, for direct measurements should be used at least calibration accuracies and for standard and energy balance methods it is also needed to take into account other factors affecting the accuracy. In particular, the performance of the energy balance method is quite dependent on accuracies of the fuel analysis and process measurements. However, taking into account the limitations, the energy balance method can provide fairly consistent and reliable estimate of CO<sub>2</sub> emissions together with standard and direct measurement methods. Therefore it is reasonable easy to recommend the use of energy

balance method as a relatively cheap, accurate and simple way of determining flue gas flow rate and CO<sub>2</sub> emissions.

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## APPENDIX I

<b>GENERAL LEVEL QC PROCEDURES</b>	
<b>QC Activity</b>	<b>Procedures</b>
Check that assumptions and criteria for the selection of activity data and emission factors are documented.	<ul style="list-style-type: none"> <li>• Cross-check descriptions of activity data and emission factors with information on source categories and ensure that these are properly recorded and archived.</li> </ul>
Check for transcription errors in data input and reference	<ul style="list-style-type: none"> <li>• Confirm that bibliographical data references are properly cited in the internal documentation.</li> <li>• Cross-check a sample of input data from each source category (either measurements or parameters used in calculations) for transcription errors.</li> </ul>
Check that emissions are calculated correctly.	<ul style="list-style-type: none"> <li>• Reproduce a representative sample of emissions calculations</li> <li>• Selectively mimic complex model calculations with abbreviated calculations to judge relative accuracy.</li> </ul>
Check that parameter and emission units are correctly recorded and that appropriate conversion factors are used.	<ul style="list-style-type: none"> <li>• Check that units are properly labelled in calculation sheets.</li> <li>• Check that units are correctly carried through from beginning to end of calculations.</li> <li>• Check that conversion factors are correct.</li> <li>• Check that temporal and spatial adjustment factors are used correctly</li> </ul>
Check the integrity of database files.	<ul style="list-style-type: none"> <li>• Confirm that the appropriate data processing steps are correctly represented in the database.</li> <li>• Confirm that data relationships are correctly represented in the database</li> <li>• Ensure that data fields are properly labelled and have the correct design specifications.</li> <li>• Ensure that adequate documentation of database and model structure and operation are archived.</li> </ul>
Check for consistency in data between source categories.	<ul style="list-style-type: none"> <li>• Identify parameters (e.g. activity data, constants) that are common to multiple source categories and confirm that there is consistency in the values used for these parameters in the emission calculations.</li> </ul>
Check that the movement of inventory data among processing steps is correct	<ul style="list-style-type: none"> <li>• Check that emission data is correctly aggregated from lower reporting levels to higher reporting levels when preparing summaries.</li> <li>• Check that emission data is correctly transcribed between different intermediate products.</li> </ul>
Check that uncertainties in emissions and removals are estimated or calculated correctly	<ul style="list-style-type: none"> <li>• Check that qualifications of individuals providing expert judgement for uncertainty estimates are appropriate.</li> <li>• Check that qualifications, assumptions and expert judgements are recorded. Check that calculated uncertainties are complete and calculated correctly.</li> <li>• If necessary, duplicate error calculations or a small sample of the probability distributions used by Monte Carlo analyses.</li> </ul>

Undertake review of internal documentation.	<ul style="list-style-type: none"> <li>• Check that there is detailed internal documentation to support the estimates and enable duplication of the emission and uncertainty estimates.</li> <li>• Check that inventory data, supporting data, and inventory records are archived and stored to facilitate detailed review.</li> <li>• Check integrity of any data archiving arrangements of outside organisations involved in inventory preparation.</li> </ul>
Check methodological and data changes resulting in recalculations.	<ul style="list-style-type: none"> <li>• Check for temporal consistency in time series input data for each source category.</li> <li>• Check for consistency in the algorithm/method used for calculations throughout the time series.</li> </ul>
Undertake completeness checks.	<ul style="list-style-type: none"> <li>• Confirm that estimates are reported for all source categories and for all years from appropriate base year to the period of the current inventory.</li> <li>• Check that known data gaps that result in incomplete source category emissions estimates are documented.</li> </ul>
Compare estimates to previous estimates.	<ul style="list-style-type: none"> <li>• For each source category, current inventory estimates should be compared to previous estimates. If there are significant changes or departures from expected trends, recheck estimates and explain any difference.</li> </ul>