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EN-PME-TEST

Project report

Determination of particulate matter emissions from solid biomass fuel burning appliances and boilers – Proposal for a common European test method

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Summary

The 20/20/20 target for Europe, i.e. to decrease the emissions of greenhouse gases by 20 % and to increase the use of renewable energy to 20% by the year 2020, will lead to an increased use of biomass combustion, e.g. by using wood logs and wood pellets for heating. On the other hand, the Air Quality Directive (2008/50/EC) lies down stringent requirements on maximum levels of particulate matter (PM) in the ambient air. Solid fuel burning appliances and boilers produce particulate matter emissions (PME) which are of concern to authorities and the public. The soot and organic components of these emissions are of most concern because they include compounds known for their potential impact on health and environment. Because of their small size, generally of the order of 1 micrometer, they readily pass through the nose and throat into the lungs. Some organic gaseous carbons (OGC) in the flue gas are precursors for secondary organic aerosols (SOA) formed in the atmosphere due to photo-oxidation under the influence of UV-radiation.

Many different methods have historically been used to measure PME from the flue gas of solid fuel-fired residential appliances and boilers. Confusion has arisen in the market as different and conflicting results have been quoted in manufacturers' literature. It became important to agree on a method applicable for all types of residential appliances and boilers burning solid fuels. This method shall give repeatable results that are of a guaranteed traceable accuracy, and by this means give the consumer reliable information on the suitability of a particular appliance or boiler.

In January 2012 the joint European Co-normative Research Project *Common European method for the determination of particulate matter emissions of solid fuel burning appliances and boilers* (EN-PME-TEST) started. Its aim was to develop and validate a common European test method to determine particle matter emissions from residential heating appliances and boilers burning solid fuels. The project group is a well balanced consortium of research and test establishments comprising some 18 partners from 10 European countries, coordinated by INERIS, France. The project has been performed under the umbrella of the ERANET Bioenergy. Special emphasis was given to the scientific basis for the candidate method and its relevance to health and environmental issues.

Following the work performed in the project, a method, designed to be standardised in the short term and to meet the actual EN standards for appliances and boilers has been selected. It is based on well known measurement techniques. It consists of the collection of the solid and liquid fraction (primary aerosols, PA) in the flue gas using a heated filter and the measurement of OGC using a FID analyzer. OGC are considered as good indicators of the quality of the combustion as well as primary organic aerosols (POA), they are also considered as SOA precursors. As a result, they appear as an interesting parameter to be included in a reference method in order to take into account the impact of wood combustion on air quality. Primary aerosols measured by heated filters at a specific temperature, referred to as PM_{HF} , and OGC sampling gas trains are kept at the identical temperature of 180°C. For the definition of the method, the parameters that have influence on the measurement result, such as temperature control, have particularly been tested. The choice has been made according to the following criteria:

- suitability of the parameters measured regarding impact on air quality;
- capability of the method to discriminate the performance of the tested appliances and boilers;
- reliability of the results obtained;
- availability, cost and simplicity of use of the proposed method, taking into account the fact that it should be used by notified bodies for type testing as well as by industry for product development.

The uncertainty of the method has been determined. The emission values for the expanded uncertainty of a pellet/woodchip boiler obtained are 34% for PM_{HF} in the range between 6 and 42 mg/m^3_{STP} and 30% for OGC in the range between 16 and 144 $C_{eq}mg/m^3_{STP}$. The PM_{HF} values for a wood log stove achieved an expanded uncertainty of 35% for PM_{HF} values between 41 and 104 mg/m^3_{STP} . The wood log stove emission values of uncertainty were achieved provided that the sample gas flow in the probe was higher than 7 m/s (typically 7 to 9 m/s).

Other methods that better address the issue of impact on air quality such as the use of a micro-smog-chamber (MSC) combined with total carbon measurements (TC) and the use of dilution with filtered air prior to sampling and online mass measurement have been evaluated. Although these methods are of interest, they do not appear mature enough to be proposed as candidate method at a European level right now. They are interesting options for the long term method, but further studies have to be performed.

Introduction

Context

The 20/20/20 target for Europe, i.e. to decrease the emissions of greenhouse gases by 20 % and to increase the use of renewable energy to 20% by the year 2020, will lead to an increased use of biomass combustion, e.g. by using wood and wood pellets for heating. On the other hand, the Air Quality Directive (2008/50/EC) lies down stringent requirements on maximum levels of particulate matter (PM) in the ambient air. Solid fuel burning appliances and boilers produce particulate matter emissions (PME) which are of concern to authorities and the public. The soot and organic components of these emissions are of most concern because they include compounds known for their potential impact on health and environment. Because of their small size, generally in the order of 1 micrometer, they readily pass through the nose and throat into the lungs. Some organic gaseous carbons (OGC) in the flue gas have the potential to be precursors for secondary organic aerosols (SOA) formed in the atmosphere by UV-radiation.

Many different methods have historically been used to measure PME from the flue gas of solid fuel fired residential appliances and boilers. Confusion has arisen in the market as different and conflicting results have been quoted in manufacturers' literature. It became important to agree on a method applicable for all types of residential appliances and boilers burning solid fuels. This method should give repeatable results that are of a guaranteed traceable accuracy, and by this means give the consumer reliable information on the level of performance of a particular appliance or boiler.

Further evidence for the need for a common standard was found in the Eco-Design Preparatory Study for "Solid Fuel Small Combustion Installations" (Lot 15/Lot 20) which is being made in order to propose implementing measures for the Ecodesign Directive (2005/32/EC) in this product area. It is concluded that the main environmental characteristics of the products covered by the Lot 15 / Lot 20 are the emissions, among them PME, and that existing standards are not sufficiently adequate to characterize these.

This is also verified by CEN/STAR, the Strategic Action and Advisory Group of the Comité Européen de Normalisation (CEN) which analyses the needs for Co-normative (CNR) and Pre-normative (PNR) research in relation to European standardization activities. In their resolution CEN/STAR 3/2008 endorsed the topic of "Test methods to determine particulate emissions from residential solid fuel burning appliances and boilers – relevance to health, environment, energy conservation as well as product development, type test and field inspection" for CNR research. The urgent need for a common European test method for the determination of PME is clearly endorsed by the standardization groups CEN/TC 57 (solid fuel burning boilers) and CEN/TC 295 (solid fuel burning room heaters). The road map towards a standardized European particulate matter emission measurement method published by CEN/TC 295 WG5 (Working Group Test Methods) defines the requirements for a new standard:

- Costs: The possible investment costs for the test laboratories should be kept as low as possible and the method must easily be incorporated in the already standardized test setup according to the relevant European harmonized standards.

- Low limit of quantification (LOQ): PME threshold limit values (TLV) are getting more stringent, therefore the method should be able to detect these low emissions with an acceptable fidelity.
- The uncertainty linked to those results must be evaluated by determination of reproducibility of the method during intercomparison exercises and must be kept as low as possible. This also implies that measurement practices are well described and implemented.
- It is absolutely necessary that the method can be calibrated according to existing standards reference methods.
- The standardized method is primarily intended for use in test laboratories. However, manufacturers must also be able to use it for development purposes and retrieved results should be comparable with those from test laboratories. Additionally, it might be useful if the method can be applied during field measurements.
- The standardized method must easily be adapted by all stakeholders (manufacturers, developers, installers, test laboratories, policy makers).
- The method should be able to take into account particles with diameters down to 10 nm, since there are indications that these particles have an adverse effect on human health.
- Additionally the method should probably take into account the fraction of volatile organic compounds and the emission during transient phases. Public awareness on these aspects will even enlarge the need for measurement methods that comply with this criterion.

Joint European co-normative research project EN-PME-TEST

Objectives and project description

In January 2012 the joint European Co-normative Research Project *Common European method for the determination of particulate matter emissions of solid fuel burning appliances and boilers* (EN-PME-TEST) started. The objective of the project was to develop and validate a common European test method to determine particulate matter emissions (PME) from residential heating appliances and boilers burning solid fuels. The test method shall be the basis for a European standard for PME-measurement. Special emphasis was given to the scientific basis for the candidate method and its relevance to health and environmental issues. The needs and requirements from the various stakeholders such as industry, authorities, standardization bodies and health and environment experts were taken into account during the study. Stakeholders were informed of the work carried out during European standardization meetings (CEN/TC 295/WG5, CEN/TC 57/WG1) and national committee meetings, as well as by results dissemination.

In a previous ERA-NET project, *Biomass PM¹*, all relevant aspects of PM emissions including possible measurement and characterization methods were thoroughly analyzed. Also recommendations on how to quantify and characterize the PME were given from scientific work in the field of health, environment and technology. However, the determination of PME in the context of product development, type test and field inspection poses specific requirements on ease of operation, costs, repeatability, traceability and transparency to non-specialists compared to R&D applications.

Research consortium partners

The project group is a well balanced consortium of research and test establishments comprising 18 partners from 10 European countries. The project has been performed under the umbrella of the ERANET Bioenergy call and was coordinated by INERIS, France. The contribution of the different consortium partners has been funded by their national funding agencies or by using self funding (a presentation of the project is given in Appendix 1).

¹ Biomass combustion in residential heating: Particulate measurements, sampling, and physicochemical and toxicological characterization, ERA-NET Bioenergy Programme 2007-2008, University of Kuopio, Fine Particle and Aerosol Technology Laboratory, Final report, August 2008

	Research consortium partner	Country
1	SP Technical Research Institute of Sweden, Energy Technology	Sweden
2	Centre of Appropriate Technology and Social Ecology, CATSE	Switzerland
3	University of Eastern Finland, Dept. of Environmental Science, Fine Particle and Aerosol Technology Laboratory, UEF	Finland
4	Danish Technology Institute, DTI	Denmark
5	BIOENERGY 2020+	Austria
6	University of Applied Sciences, Northwestern Switzerland, Institute of Aerosol and Sensor Technology, FHNW-IAST	Switzerland
7	University of Applied Sciences, Northwestern Switzerland, Institute for Biomass and Resource Efficiency, FHNW-IBRE	Switzerland
8	German Biomass Research Centre, DBFZ	Germany
9	Technology and Support Centre of Renewable Raw Materials, TFZ	Germany
10	French National Institute for Industrial Environment and Risks, INERIS	France
11	Centre Technique des Industries de la Fonderie, CTIF	France
12	Scientific and Technical Centre for Building, CSTB	France
13	University of Lorraine, Laboratory for Studies and Research on Wood Material, LERMAB	France
14	Innovhub-Stazioni Sperimentali per l'Industria, ISSI Agencia nazionale per le nuove tecnologie, l'energia e lo sviluppo economico sostenibile, ENEA	Italy
15	Technical Research Centre of Finland, VTT	Finland
16	SYMO	Finland
17	Energy Research, SINTEF	Norway
18	VŠB-Technical University of Ostrava, Energy Research Center, VSB-ERC	Czech Republic

Particulate emission in biomass combustion

A variety of terms are used to name the parameters studied when looking at residential wood combustion (RWC) emissions. It is of interest for the topic to define these common terms describing the parameters to be determined in the flue gases. The terms used in the project are compiled in Appendix 2.

Figure 1 gives the synoptic of pathways for the formation of particulate matter in the flue gas and the ambient air. Such flow charts have been suggested by other authors [Oberberger et al. 2001²; Nussbaumer 2010³] to illustrate the various pathways for particle formation. Here this approach has been focused to address the needs of test methods for type testing laboratories and field inspection. In particular the diagram highlights the ambivalence associated with volatile organic compounds (VOC), which can either be present in the gaseous or condensed phase, depending on sampling and filtration temperature.

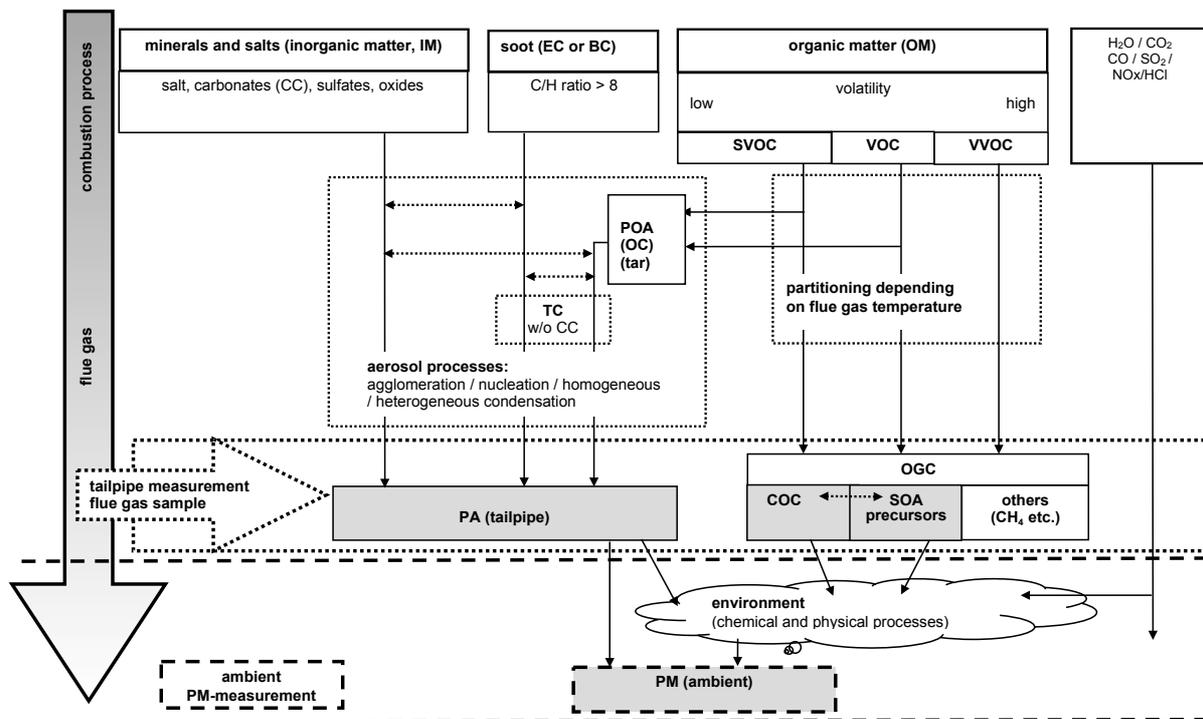


Figure 1 Synoptic of PM formation pathways in the flue gas and the ambient air and classification of products. The abbreviations used in the schematic are defined in Appendix 2

² Oberberger I., Brunner T., Jöller.: Characterization and formation of aerosols and fly-ashes from fixed-bed biomass combustion. Aerosols from biomass combustion, international seminar, International Energy Agency (IEA) and Swiss Federal Office of Energy, ISBN 3-908705-00-2, Zurich 2001

³ Nussbaumer T., Emissionsfaktoren von Holzfeuerungen und Klimaeffekte von Aerosolen aus der Biomasse-Verbrennung, 11. Holzenergie-Symposium, ISBN 3-908705-21-5, Zürich 2010

PME measurement techniques for residential biomass combustion

Evaluation of measurement techniques for type testing

During the initial phase of the project various techniques for PME measurement were investigated. Among them were particle counting, optical instruments, online mass measurements as well as elemental carbon (EC) and organic carbon (OC) analyzers. Methods of conditioning the aerosols in order to take into account primary organic aerosols (POA) and secondary organic aerosols (SOA) have also been evaluated. The requirements for a new standard defined by CEN/TC 295/WG5 as listed above limits the applicable measurement techniques substantially. Therefore the project consortium agreed upon a short term and a long term measurement method for the determination of PME.

Short term PME-measurement method

The short term method is designed to meet the actual EN standards for appliances and boilers. The method is based on well-known measurement techniques. It consists of the collection of the solid and liquid fraction (PA) using a heated filter (PM_{HF}) and the measurement of OGC using a FID analyzer. PME is described by the solid and condensed particulate matter in the flue gas (PA) and by OGC emissions as a guide value for condensables. Primary aerosols measured by heated filters at a defined temperature are referred to as PM_{HF} . PM_{HF} and OGC sampling gas trains are kept at a common temperature of 180°C. The instruments can be calibrated to guarantee accuracy for reliability and repeatability. The instruments can be acquired at reasonable costs.

The method is designed to meet the following boundary conditions:

Threshold limit values (TLV):

STP: standard temperature (293.15 K) and pressure (101.3 kPa)

- OGC: 40 ... 160 C_{eq} mg/ m³_{STP} @13%O₂
- PM_{HF} : 20 ... 150 mg/ m³_{STP} @13%O₂

Measuring range:

- OGC: 5 ...1'000 C_{eq} mg/m³_{STP} @13%O₂
- PM_{HF} : 5...200 mg/ m³_{STP} @13%O₂
- operation range for flue gas temperature: 40...400°C
(transient flue gas temperatures during sampling period)

Basic concepts of the short term measurement method are as followed:

- PM_{HF} are determined as solids and condensed particulate matter in the flue gas at the sampling temperature by gravimetric filter.
- The measurement of OGC by FID is used as a guide value of the condensable fraction in the flue gas.
- PM_{HF} and OGC values are reported separately (there is no relevance to fix a PME value as a combination of solid fraction and OGC).
- In order to prevent overestimation or underestimation of organic species, PA and OGC are sampled at the same temperature.

- Temperature levels in the sampling trains are crucial for accurate PM_{HF} and OGC measurement. The key design of the short term method is to maintain constant temperatures in all parts of the PM_{HF} and OGC sampling trains to prevent under or overestimating of PM_{HF} or OGC respectively.
- The temperature level in the PM_{HF} as well as OGC-gas sampling train is set at 180°C (max. deviation ± 10 K). The design temperature was chosen so that the use of PTFE-components is still possible.
- The aim of the probe is to achieve the required design temperature of 180°C \pm 10 K in the sample gas at the end of the probe, just before entering the filter holder, and its inner surface. The 2 meters probe with a resistive heating (electric current, probe tube acting as resistance) and a controlled constant temperature of 180°C covers the design needs over a wide range of flue gas temperature (40°C to 400°C).
- The temperatures of the PM_{HF}-probe and filter holder are kept at design temperature of 180°C. The measurement of the solid fraction in such conditions allows to improve accuracy in subsequent filter handling by preventing the evaporation of condensables or water and reduces deposits in the sampling train.
- Constant and homogenous temperatures in the PM_{HF} probe and in the filter holder improves repeatability during the entire sampling period: no super cooling in the PM_{HF} probe below temperature of 180°C, no over temperatures on the filter due to fluctuations of flue gas temperatures.
- A nozzle orientation rectangular to flow direction (90°-nozzle orientation), see Appendix 3, is proposed in order to increase the repeatability of PM_{HF}-measurement by separation of larger particles (randomly coarse or re-entrained particles in flue gas). Moreover this setting is more in line with ambient particle measurement with particle size sampling below 10 μ m (PM10).
- Probe deposits are added to gravimetric measurement after each run by blowing compressed air into the probe onto a conditioned filter.
- Improved limit of quantification (LOQ) by using a weighing scale for the gravimetric filters with a resolution of 0.01 mg.

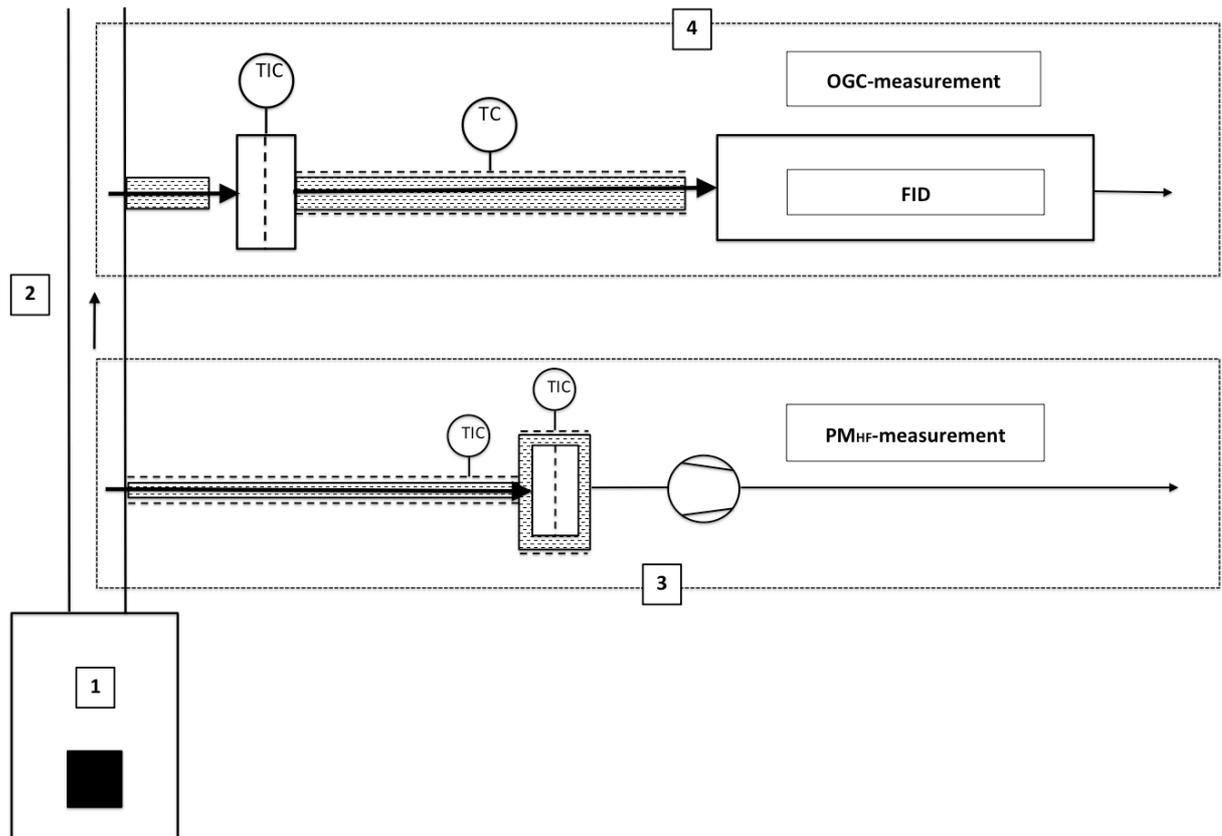


Figure 2 Short term PME-measurement method: synoptic of simultaneous PMHF- and OGC-measurement at identical temperature level of PMHF- and OGC-sampling train at temperature of 180°C.

- | | | |
|--|--|--|
| 1: test apparatus | 2: flue gas measurement section | |
| 3: PMHF-sampling train and measurement | 4: OGC-sampling train and measurement | |
| FID: flame ionization detector | OGC: organic gaseous carbons | PMHF: heated filter for PM-determination |
| TC: temperature control | TIC: temperature indicator and control | |

Long term PME-measurement methods

Current legislation for PME focuses on total particle emissions without differentiation among chemical composition or particle size. The short term method reflects this situation in order to make a transparent transition from the current legislation. The downside is that the combustion quality is only evaluated using the PA, CO and OGC value and the potential effect on health and the environment is not optimally reflected by these approaches. The actual short term approach cannot distinguish between particulate matter that mostly consists of inorganic material and particulate matter that consists of carbonaceous material which have a stronger impact on air quality and human health. As long as the threshold limit values are met, there is no motivation to improve a combustion with poor quality and a high level of carbonaceous material. Therefore the necessity to propose a method with a unique parameter that would reflect both combustion quality and potential effect on health and the environment still exists.

An ideal standard would reflect the impact on air quality from combustion emissions, based on the characterization of the chemical composition of PME. However, this would require an effort which is

beyond the possibilities available in type-testing. Therefore two more simple approaches are proposed here.

1. Total carbon (TC) measurements using a micro-smog chamber

A first approach that better reflects the impact of the emissions on air quality is to measure the particle-bound total carbon (TC). TC measurement allows excluding inorganic materials (e.g. salts) from the measurement but is not able to identify specific organic species. The procedure can be rather simple. Samples can be collected in filters and analysed using existing commercial devices. The final goal of this approach is to make it possible to define threshold limit values in terms of TC that incentivise the manufacturers to improve the quality of the combustion. Our measurements show that TC correlates well with PM_{HF} during the steady state operation of a specific appliance ($n=7$, $R^2=0.95$). This suggests that the non-carbonaceous fraction can be considered a baseline, independent of the quality of the combustion, for a specific operating point.

We have also evaluated a continuous-flow oxidation-reactor, called the micro-smog-chamber (MSC), to estimate the effect of atmospheric aging for different flue gases, a detailed description is provided in appendix 5. The oxidation of flue gas in the reactor serves two purposes. First, it promotes the formation of secondary organic aerosol (SOA) which would not be accounted for without this treatment. At the same time, oxidation reduces the volatility of the organic species and makes the sample more robust against artefacts from sampling temperature and dilution.

2. PME mass measurements using dilution

Another approach addressing this issue is the use of dilution and cooling to room temperature prior to measurement in order to force the condensation of primary organic aerosols (POA) on the solid fraction. Dilution is used in sample treatment before PME analyzes in scientific research and testing (NS3058⁴) of combustion emissions and for example in vehicle emissions studies. Most importantly, due to dilution primary organic aerosols (POA) condense on existing particles and are taken into account in particle phase in PME measurements, which is not the case when sampling using heated filter alone. Dilution quenches particle agglomeration, reduces concentrations and temperatures without condensation of water. Dilution also enables the use of online aerosol instruments and reliable use of impactors to define certain and sharp PME size class.

Dilution systems are often considered as too complicated for type testing. Within this project, a simplified dilution system was designed and tested. It consists of a heated probe, which stabilizes the dilution process, a porous tube diluter suitable for low and moderate dilution ratios, a $PM_{2.5}$ impactor and a filter collection. Dilution stabilizes sample temperatures and conditions at the filter are constant despite the sampling conditions. This approach tested in comparison with a hot filter candidate method showed higher emission factors, but a relatively good correlation ($n=$

⁴ Norsk Standard NS 3058 Enclosed wood heaters Smoke emission – Part 2: Determination of particulate emission

15, R^2 0.80). The porous dilution tube was also used in combination with a Tapered Element Oscillating Microbalance (TEOM) which provides continuous mass measurements and is recognized as equivalent to the reference method for ambient air measurements of PM₁₀. This approach correlates well with dilution tunnel (n=12, R^2 0.89) method and with the hot filter combined with washing bottles method⁵ (n=20, R^2 0.98). A porous tube alone is only applicable in certain sampling setups, because it is very sensitive for flows through the system which affects the variation in dilution ratios.

However, although those methods better address the issue of impact on air quality, do not appear as mature enough yet to be proposed as candidate method at a European level. They are interesting options for the long term method, but further studies have to be performed.

⁵ Definition and evaluation of a new method for the characterization of particulate emissions from domestic combustion devices using biomass, I. Fraboulet, S. Collet, S. Bachellez, L. Robert, Y. Rogaume, E. Smit, J.S. Andersen, J. Poulleau, International conference on emissions measurements CEM, Prague 2011

Conclusions

The joint European Co-normative Research Project *Common European method for the determination of particulate matter emissions of solid fuel burning appliances and boilers* (EN-PME-TEST) developed and validated a test method to determine particle matter emissions (PME) from residential heating appliances and boilers burning solid fuels.

The short term method developed can easily be adapted to the actual EN standards for appliances and boilers. It is based on well known measurement techniques. It consists of the collection of the solid and liquid particulate matter in the flue gas using a heated filter and the measurement of OGC using a FID analyzer. Particulate matter and OGC sampling gas trains are kept at a common temperature of 180°C. For the definition of the method the parameters that have influence on the measurement results, such as temperature control, have been particularly tested. The uncertainty of the method has been determined. The emission values for the expanded uncertainty of a pellet/woodchip boiler obtained are 34% for PM_{HF} (particulate matter collected on the heated filter) in the range between 6 and 42 mg/m^3_{STP} and 30% for OGC in the range between 16 and 144 $C_{eq} mg/m^3_{STP}$. The PM_{HF} values for a wood log stove achieved an expanded uncertainty of 35% for PM_{HF} values between 41 and 104 mg/m^3_{STP} . The wood log stove emission values of uncertainty were achieved during measurements where the sample gas flow in the probe was higher than 7 m/s (typically 7 to 9 m/s). The method combining the heated filter and the OGC measurement using FID has been selected as candidate for a common European method to be used by notified bodies to perform type testing. The choice has been made according to the following criteria:

- suitability of the parameters measured regarding environmental issues,
- capability of the method to discriminate the emission levels of appliances and boilers;
- reliability of the results obtained;
- availability, cost and simplicity of use of the proposed method, taking into account the fact that it should be used by notified bodies for type testing as well as by industry for product development.

Other methods that better address the issue of impact on air quality such as the use of a micro-smog-chamber combined with total carbon measurements (TC) and the use of dilution prior to sampling and online mass measurement have been evaluated. Although these methods are of interest, they do not appear mature enough yet to be proposed as candidate method at a European level. They are interesting options for the long term method, but further studies have to be performed.

Appendices

Appendix 1:

EN-PME-TEST project description

Residential heating using wood combustion is strongly involved in the development of renewable energy. However, it can be associated to high emissions of particulate matter characterized by a very fine size distribution and strong contribution of organic condensables. Recent discussion within the CEN TC 295 WG 5 looking at methods for the measurement of atmospheric emissions from domestic wood burning heating devices resulted in 2011 in the selection of two methods for the determination of particulate matter based on the DIN+ (heated filter) and the NS3051 (dilution tunnel) that were integrated in the prEN 16510.

However, until today, there has been no agreement on the choice of a unique European method for the measurement of particulate emissions from residential heating appliances and boilers burning solid fuels.

The objective of the EN-PME-TEST project has been to develop and validate a common European test method to determine particle matter emissions (PME) from residential heating appliances and boilers burning solid fuels. The test method shall be the basis for a European standard for PME-measurement. Special emphasis has been given to the scientific basis for the candidate method and its relevance to health and environmental issues.

The determination of PME in the context of product development, type test and field inspection poses specific requirements on issues such as ease of operation, costs, repeatability, traceability that have been dealt with during the EN-PME-TEST project. It was the clear aim of this project to provide a method that fulfils the particular requirements of type testing, product development and ideally field inspection.

The following table presents detailed information on the partners of the consortium. The work started in January 2012 and has been performed in five technical Work Packages with 18 partners from ten countries, and one Work Package for management and administration. The partnership is a well balanced consortium of research and test establishments. The project was scheduled to last three years. The project has been performed under the umbrella of the ERANET Bioenergy, it was coordinated by INERIS, France.



The contribution of the different consortium partners has been funded by their national funding agencies or by using self funding. The French contribution (CSTB, CTIF, INERIS, LERMAB) has been funded by ADEME, the Swiss contribution (CATSE, FHNW) has been funded by the Swiss Federal Office of Energy and the Federal Office for the Environment, the Austrian contribution (Bioenergy 2020+) has been funded by FFG, the Finnish contribution (UEF, VTT, SYMO) has been funded by TEKES, the Danish contribution (DTI) has been funded by Miljø Føderministeriet, the German (TFZ, DBFZ) contribution has been funded by FNR.



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The main stakeholders for the project were:

EU and Governmental Bodies:

- DG TREN
- DG ENV
- National Environmental Agencies
- National ministry of environment

Industrial organizations: National Manufacturer Organisations

European standardization committees:

- CEN TC 57 (Central heating boilers, e.g. residential wood log boilers and pellets boilers)
- CEN TC 295 (Residential solid fuel burning appliances, e.g. wood stoves)
- CEN TC 264 (Stationary Source Emissions)

- CEN SG 03 WG 2 (Sector Group on Space Heating Appliances)

The Work Package structure; as well as the WP Leaders are presented in the following table.

WP	Work Package	WP leader
0	Project coordination, management, liaison and dissemination	INERIS
1	Evaluation of existing PME measurement methods for application as test method and proposition of short and long term candidate methods	UEF
2	Detailed layout and validation of candidate method short and long term (s)	CATSE
3	Inter-laboratory comparison with candidate method(s)	DTI
4	Adaptation of candidate method(s) within field tests and downstream particle separation devices	DBFZ
5	Specific context related issues to test method	SP

Appendix 2

Terms and acronyms used in the EN-PME-TEST-project

acronym	term	remarks
BC	black carbon	soot fraction of particulate matter emissions (identical EC)
CC	carbonates	carbonates formed from ash components and carbon in fuel
COC	condensable organic compounds	organic compounds in gas phase, measured in the flue gas, condensing in the ambient air
EC	elemental carbon	soot fraction of particulate matter emissions (identical BC)
IM	inorganic matter	minerals and salts (carbonates, sulfates, oxides, etc.) as inorganic fraction of particulate matter emissions
NMOGC	non-methane organic gaseous carbon	potential SOA precursors and COC
OC	organic carbon	organic carbon fraction of particulate matter emissions resulting from incomplete combustion
OGC	organic gaseous carbon	OGC released with the flue gas to the atmosphere
OM	organic matter	SVOC, VOC and VVOC
PM	particulate matter	microscopic solid or liquid matter
PA	primary aerosols	PM released with the flue gas to the atmosphere (salt, minerals, soot and tar)
PM _{HF}	primary aerosols collected on a heated filter	PM _{HF} = PA @sampling temperature; in the short term method of the EN-PME-TEST project PM _{HF} is collected at 180°C
PME	particulate matter emissions	In the short term method of the EN-PME-TEST project PME is described by 2 separate values: 1) PM _H and 2) OGC
POA	primary organic aerosols	organic fraction of PA
SOA	secondary organic aerosols	particulate matter in the atmosphere as a result of transformed OGC by UV radiation
soot	elemental carbon	soot (C/H > 8), carbon particles fraction of particulate matter emissions resulting from incomplete combustion (stated as carbon only)
SVOC	semi volatile organic compounds	boiling range: > 250°C
tar	tar	condensed SVOC and VOC
tailpipe measurement	tailpipe measurement	capturing point at the end of the sampling duct for measurement of PME
TC	total carbon	carbonaceous particle fraction of particulate matter emissions TC = EC + OC (without carbonates, CC)
VOC	volatile organic compounds	boiling range: 20°C – 250°C
VVOC	very volatile organic compounds	boiling range: < 20°C

Appendix 3:

Short term PME-measurement method

Summary

The objectives to be pursued by the candidate method are to provide a reliable and simple approach to measure particulate matter emissions. Moreover it should be able to be applied for type testing, for product development and if possible for field measurements and should take into account the impact of wood combustion on air quality. The short term measurement method tested is based on a mass sampling combined with an OGC measurement. The solid fraction is collected on the heated filter, whereas OGC are measured by FID analysis. OGC are considered as good indicators of the quality of the combustion as well as POA, and they are also considered as SOA precursors. As a result, they are an interesting parameter to be included in a reference method in order to take into account impact of wood combustion on air quality.

Parameters with influence on PME measurement

The method should provide reliable results for a wide range of appliances and boilers with different flue gas characteristics especially in terms of temperature, particle size distribution, content of organics, levels of concentrations etc. The aim of the work performed on the short term PME measurement method was to propose an approach that would not be sensitive to the main influence parameters such as flue gas temperature variations, the presence of organics and of variable amount of large particles (randomly coarse or re-entrained particles in flue gas) that are particularly important in the case of bad combustion and that can lead dispersion of the results. As a result a special focus was put onto temperature control, measurement of the contribution of deposit in the probe, and the investigation of a simple manner to remove randomly coarse or re-entrained particles from the flue gas before sampling.

Temperature control

For the sampling of the solid fraction, since the temperature is one of the most sensitive influence parameter, temperature must be controlled in the whole sampling train in order to provide reliable results. This is performed by a sampling probe developed during the project with specifications which guarantee a temperature control at 180°C for a range of flue gas temperature between 40°C and 400°C.

Heated probe design

A sampling probe based on resistive heating (electric current, probe tube acting as resistance) method was developed to maintain the sample gas temperature in the heated filter at 180°C for a range of flue gas temperature in the duct from 40°C to 400°C. A schematic of the probe and its properties are presented in Figure 3.1.

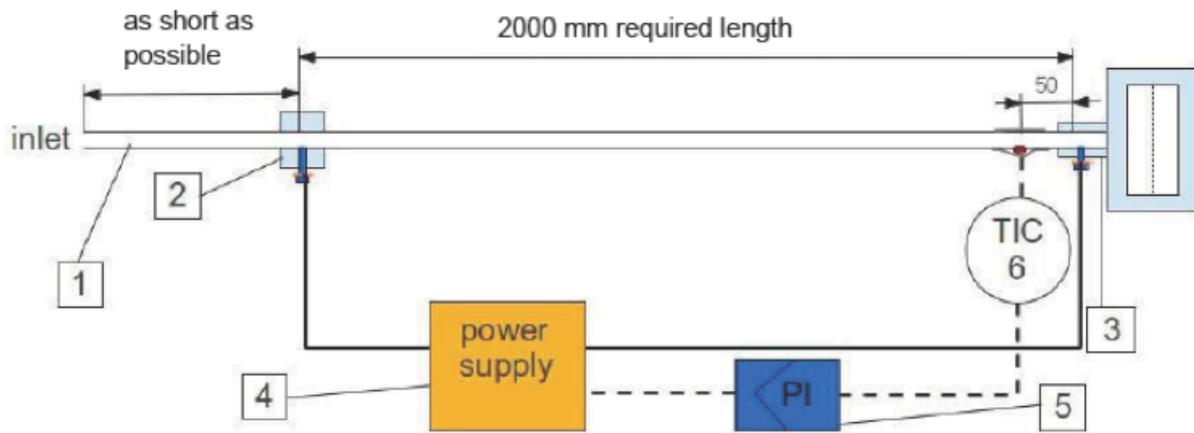


Figure 3.1 Schematic of the PM_{HF} sampling probe designed within the EN-PME-TEST-project
 1: sampling tube; 2 and 3: fitting acting as electrodes; 4: power supply for resistance heating; 5: temperature controller; 6: thermocouple soldered on the outer surface of the tube for measuring tube temperature; TIC: temperature indicator and control loop.

Various experiments showed that a tube heated at 180 °C with a total length of 2 meters and specifications for size and material given below allows a constant gas outlet temperature of $180^{\circ}\text{C}\pm 10\text{K}$ for inlet temperatures from 40°C to 400°C. If the tube is shorter than 2 meters, the outlet temperature is not independent from the inlet temperature or the flue gas will be cooled down below 180°C close to the probe walls which would result in undesirable condensation. Therefore a tube length of 2 meters was proposed.

The tube temperature (as input variable to the heating controller) must be measured close to the tube outlet but within the resistive heating section.

Tubing

For the tubing a thin-walled stainless steel tube is selected:

- material: 1.4301 stainless steel (X5CrNi18-10)
- outer diameter (OD): 8 mm
- inner diameter (ID): 7.5 mm
- wall thickness: 0.25 mm
- cross-section of tube wall: 6 mm²
- inner cross-section of tube: 44 mm²

The total length of the tube adds up of the proposed 2 m heating/cooling part of the tube and the desired length of the probe immersing the measurement section.

The following graph (Figure 3.2) presents the variation of flue gas temperature at the outlet of the probe for a flue gas temperature at the inlet varying between 40° and 400°C. It shows that for a set probe wall temperature of 180°C, the probe manages to maintain the flue gas at the outlet at the set temperature.

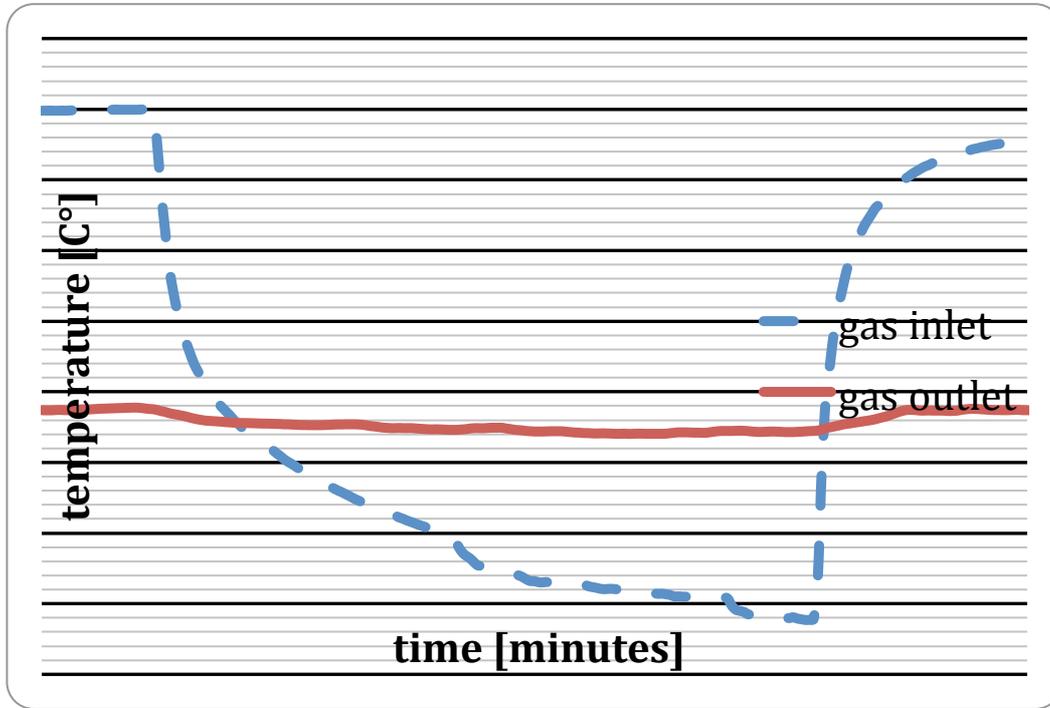


Figure 3.2 Temperature in the flue gas at the outlet of the probe in a range of flue gas temperature in the duct varying from 40°C to 400°C

Sampling velocity and nozzle orientation

Flue gases emitted by combustion of wood are characterized by a very low velocity in the flue gas duct (generally below 2 m/s). At these levels, maintaining isokinetic sampling is not possible because it is rather difficult to properly measure the flue gas velocity. Moreover, although the nozzle size can be adapted, low velocity generally leads to low sampled volume, which can affect the limit of quantification (LOQ) of the methods. Results obtained from previous projects and during this project show that isokinetic sampling is not necessary for wood combustion emissions that are free of coarse particles. The very fine size distribution mode of particles normally measured in flue gases of wood combustion does not require isokinetic sampling.

Sampling under tarry and sooty combustion conditions generally leads to less reproducible results compared to sampling under good combustion conditions. This is partly due to the presence of variable amount of large, randomly re-entrained particles in the flue gas. This causes an increase of measurement dispersion. A way of improving measurements reliability would be, to systematically remove this fraction of coarse particles. A simple manner of doing so has been investigated during the project. The idea was to study the impact of the angle between flue gas in the duct and nozzle orientation on the efficiency of particles collection. Three angles have been studied as shown in Figure 3.3:

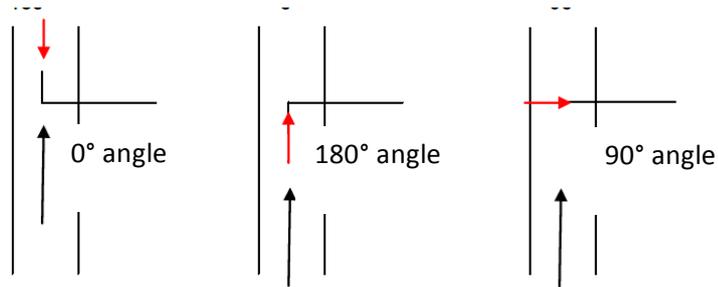


Figure 3.3 Sampling configurations studied (in black the flue gas flow direction in the measurement section and in red the sampling gas flow direction)

The study was based on experimental tests using the different sampling conditions in comparison with computational fluid dynamics (CFD) simulation and the conclusion of a paper looking at the impact of backward sampling on particle collection efficiency (Tsuji et al, 2001⁶). The main outcomes of the CFD studies are that, with a flue gas velocity in the duct of 2 m/s and using a 0° angle (reverse) or 90°, it is possible to remove the coarse particles (bigger than 20 μ m, according to the CFD calculation) as presented in the following graph showing the fraction of particles collected according to sampling conditions.

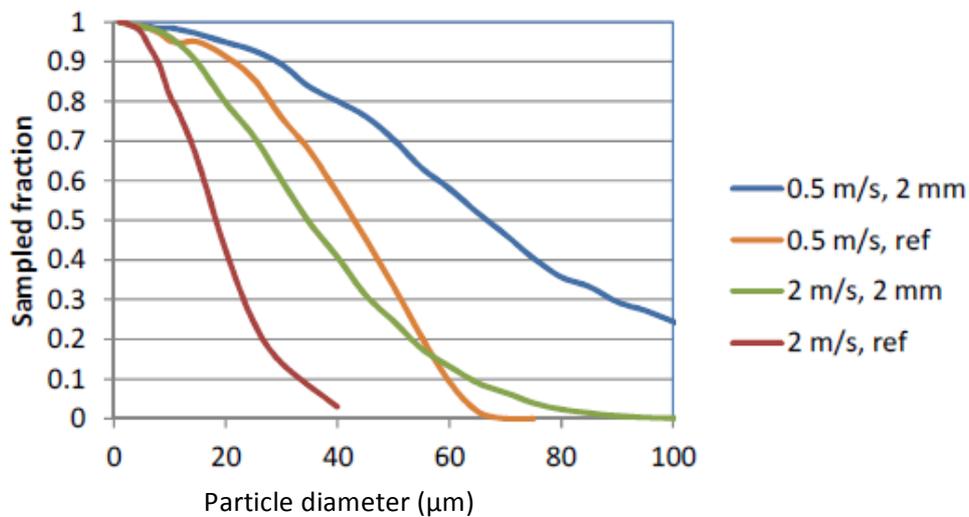


Figure 3.4 Particle collection efficiency obtained using reverse sampling according to flue gas velocity in the duct (0.5 m/s and 2 m/s) and nozzle diameter (ref stands for 8 mm nozzle diameter) at a sample rate of 10 l_{stp}/min

⁶ Classification and collection of fine particles by means of backward sampling H. Tsuji a, H. Makino a, H. Yoshida, Powder Technology 118 (2001). 45–52

Moreover, a comparison of 0° angle sampling at different sample gas velocities indicated that when sampling with a velocity of 7 m/s and above, the dispersion of results could be improved in comparison to sampling using a velocity below 2.5 m/s (average relative dispersion 18% against 70%).

Finally, since both approaches lead to similar results in terms of particles collection efficiency according to CFD simulations, the 90° angle was preferred to the 0° angle for the following reasons:

- in the case of 90°, no elbow in the probe implies less deposit,
- 90° is easier to handle in order to insert in and remove from duct, as a result, the probe can be cleaned more easily;
- with a 90° angle, there is less risk of confusion (with 180° angle) and no risk of mispositioning once the probe is inserted into the duct. no coarse particles from the chimney or from precipitators can fall into the probe.

Contribution of deposit in the probe

Results obtained at the VSB intercomparison campaign showed that the amount of deposit determined by probe rinsing was in most cases between 5% and 30% of the PM_{HF} mass (Figure 3.5), the highest contributions are observed at extraordinary high OGC contents.

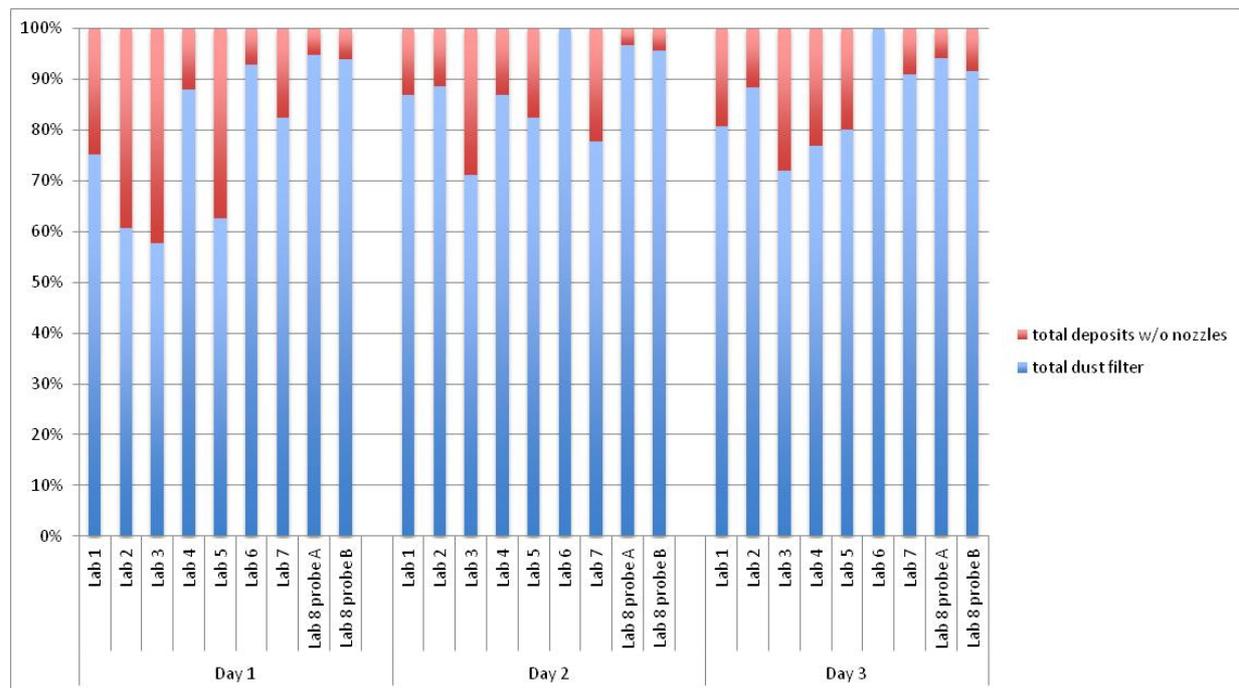


Figure 3.5 Contribution of deposits in the probe determined by rinsing to the total PM_{HF} mass (filter plus deposits) during the Ostrava intercomparison campaign

One way of decreasing the amount of deposit in the probe is to increase the sampling velocity, as presented in Figure 3.6.

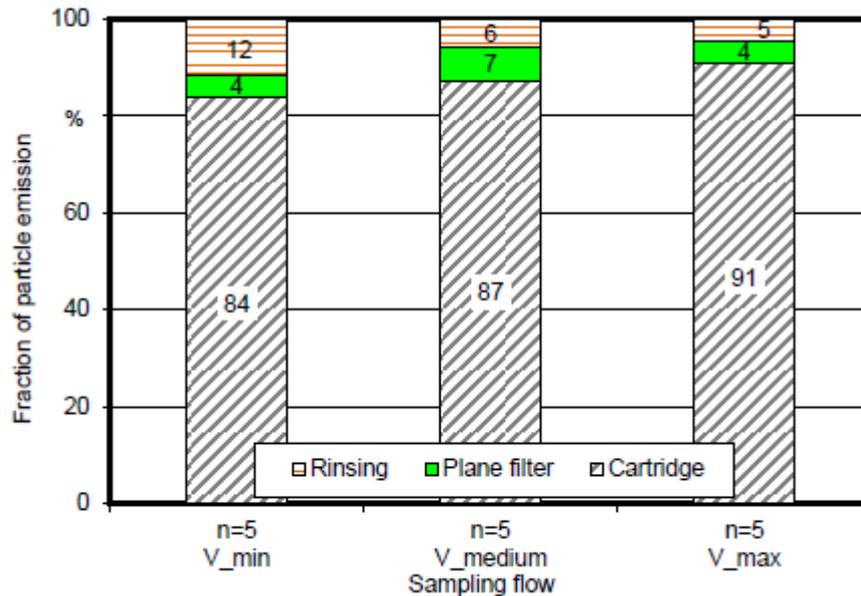


Figure 3.6 Share of mass deposited in the probe determined by rinsing to the total PM_{HF} mass for different sampling velocities

However the determination of the amount of dust deposited in the probe remains necessary especially when using a two meters long probe.

The typical procedure for determining the amount of dust deposited in the probe, as described in the EN13284-1 standard, is to rinse it with water and acetone and to evaporate the solvent to dryness and weigh the dry extract. However it is quite a laborious procedure that requires the use of chemicals and several hours of sample processing before obtaining a result. Moreover, the LOQ associated are often higher than the LOQ of filter weighing, which can be problematic especially at low levels of concentrations. In order to deal with the issue of high LOQ, the EN13284-1 standard offers the possibility to rinse the probe at the end of each day of sampling (i.e. several samples taken on heated filters) and to allocate the dry extract obtained after solvent evaporation according to the amount of dust collected on each filter. However, contrary to what can be expected from stationary sources, in the case of wood combustion sources, the amount of deposit in the probe is not linked to the quantity of the solid fraction (Figure 3.7).

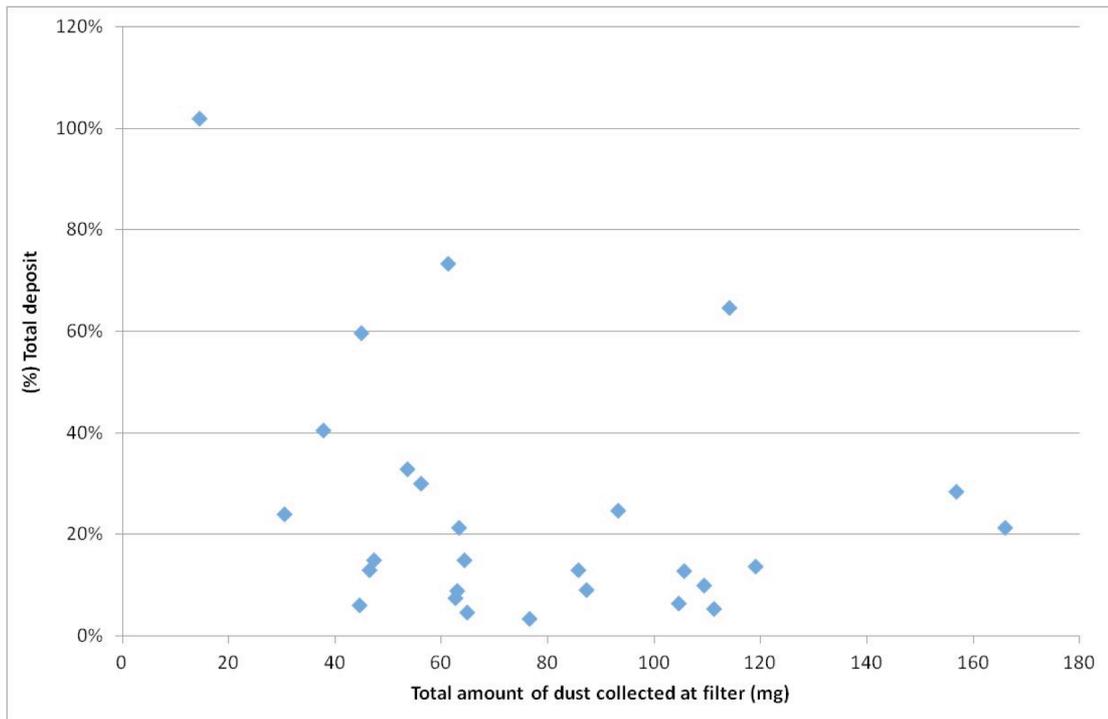


Figure 3.7 Total deposit determined in the probe against amount collected on the heated filter, Ostrava campaign

As a result, the approach defined in the current standard does not appear to be a reliable method for emissions from wood combustion appliances and boilers. Another approach has been investigated during the project; it consists of blowing into the probe using compressed filtered air and transport the deposits onto a weighed and conditioned filter placed in the filter holder. Tests have been performed in order to determine the amount of deposit collected in the probe after sampling by blowing with compressed air followed by rinsing with water and acetone. The following graph (Figure 3.8) shows the contribution of each approach (rinsing and blowing) to the total amount of deposit determined. The contribution of what can be determined by blowing over 7 tests performed varies from 30% to 80% of the total deposit determined, with an average of 63%.

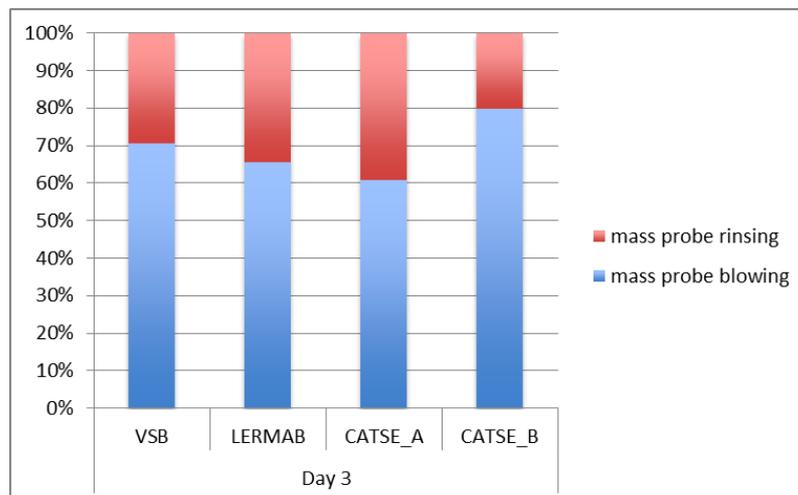


Figure 3.8 Contribution of deposit in the probe determined by rinsing and blowing

Taking into account the fact that deposits in the probe represents no more than 30 % of the total mass of PM_{HF} collected (see Figure 3.5), the use of blowing allows collecting about 90% of the total mass.

Following these results, we propose to determine the deposit in the probe after each test run by blowing compressed air into the probe onto a conditioned filter instead of rinsing the probe at the end of each sampling day and allocating the result according to the mass collected on each filter.

Comparison with prEN16510

The biggest improvements offered by the candidate method compared to the prEN16510 are the temperature control in the filtration area and the fact that temperature of both the solid particles and the OGC measurements are set to 180°C.

A comparison of the results obtained by the candidate method against prEN16510 method has been performed during the intercomparison at INERIS using a 40 kW pellet boiler as emission source. The graph obtained is presented in Figure 3.9. It shows a linear correlation characterized by a determination coefficient of 0.89. The results are of the same order, which would suggest that the limit values applied with the prEN16510 may remain if the candidate method proposed became a standard. It is important to note that in this case, the flue gas temperature in the duct was maintained at around 120°C, under such conditions the temperature in the filtration area is likely to be quite constant whatever the sampling method used.

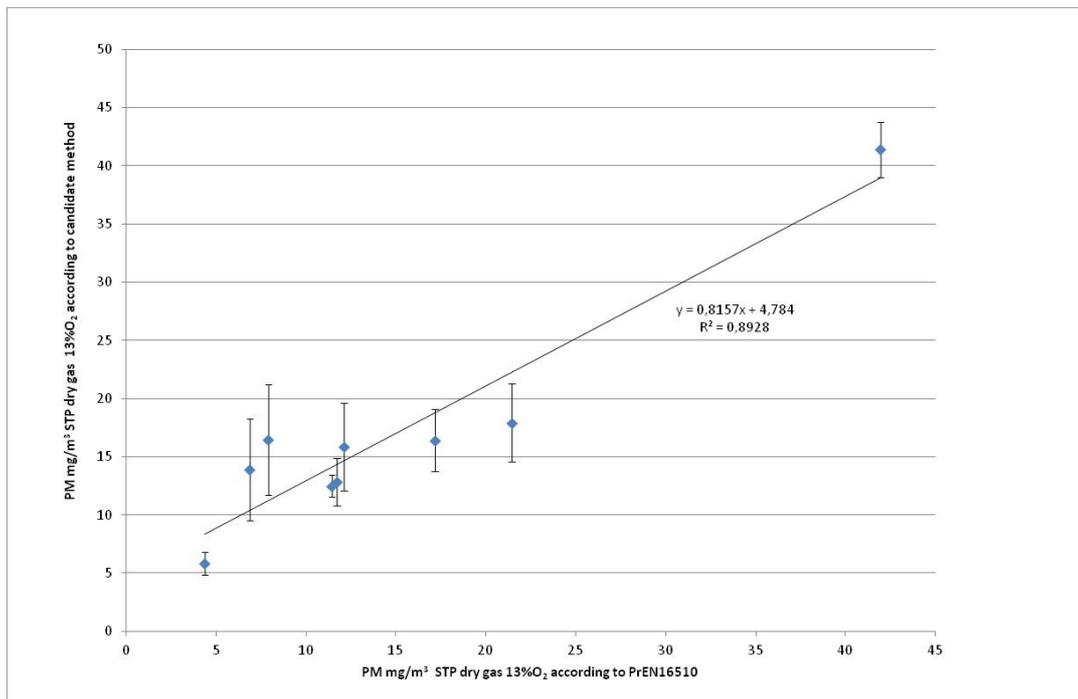


Figure 3.9 Comparison of PM_{HF} according to candidate method and prEN16510

However when sampling emission from a wood log appliance with changing flue gas temperature, the candidate method guarantees a stable and controlled flue gas temperature of 180°C at the filter which should improve the reproducibility of the results compared to prEn16510 and offer a better agreement with OGC measurement also set to 180°C.

OGC measurements

The results of the project show that OGC emissions are good indicators of the amount of the condensable fraction. This can be illustrated by the gap observed between results obtained on a heated filter (blue dots) and after dilution (red dots) as a function of OGC content presented in Figure 3.9.

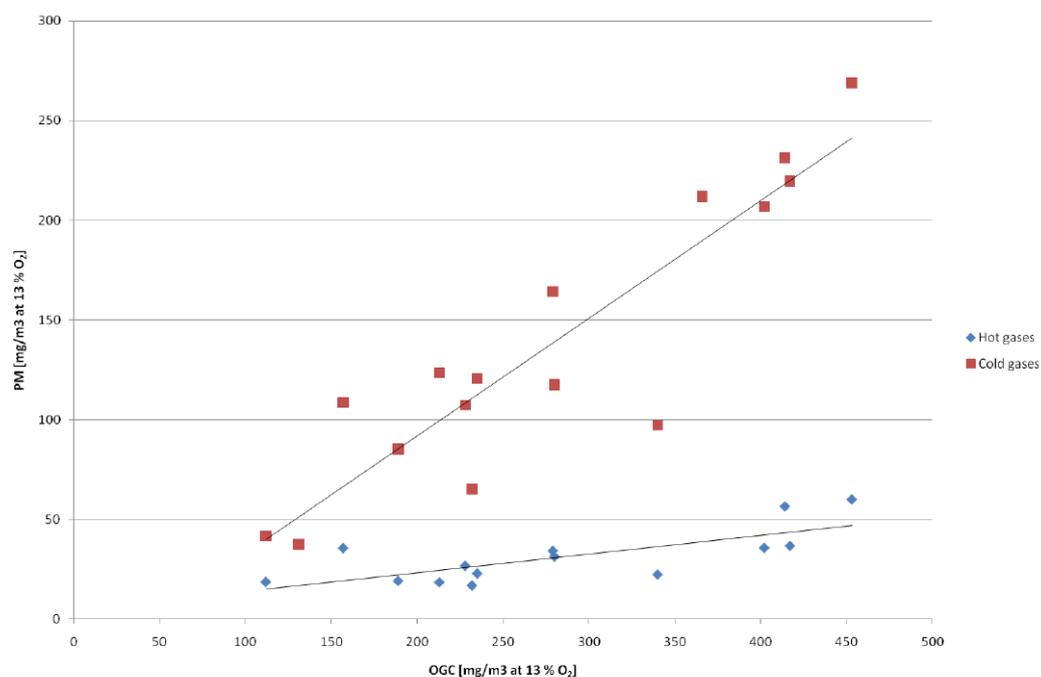


Figure 3.9 Comparison of concentrations of PM_{HF} measured using a hot filter and after a dilution tunnel as a function of OGC

Moreover since OGCs are precursors of SOA and are good indicators of combustion quality, it can be quite interesting to include them in a reference method when taking into account the impact of wood combustion on air quality. However, no correlation can be applied between the amounts of OGC measured by FID and the condensable fraction determined using washing bottles collection, as presented Figure 3.10 obtained with data collected during intercomparison (WP3) and during sampling campaigns performed in WP2. As a result, OGC concentration cannot be used to determine by calculation a concentration of the condensable fraction, it should be considered as an independent parameter that can be used as a good indicator for the amount of condensable components.

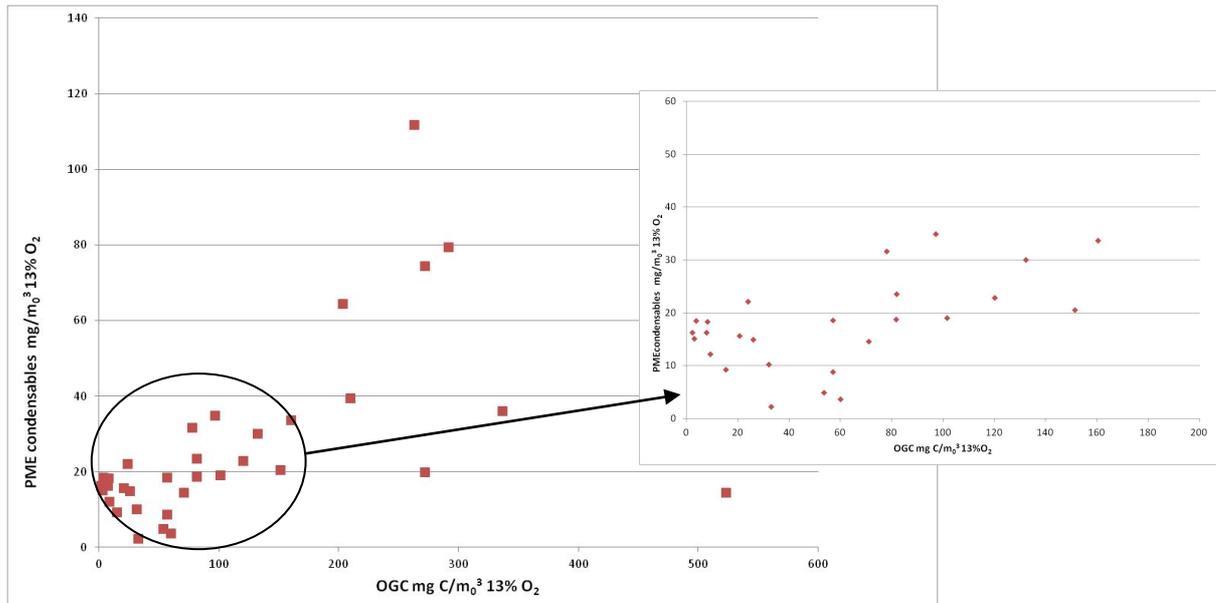


Figure 3.10 Concentrations of condensable fraction measured using washing bottles as a function of OGC

Amongst combustion gases, OGC are generally characterized by the highest uncertainty when performing intercomparison exercises involving stationary emissions control laboratories. This slightly higher dispersion of results compared to other combustion gases can be due to:

- Differences in response factors due to instruments burner design;
- lack of temperature control at the filtration stage and in the sampling line;
- O₂ interferences that can influence FID measurements by +/- 20% when measuring wood combustion emissions. FID devices must be checked for cross sensitivity.
- Memory effect in the area of the pre-filter as a result of missing temperature control.

In order to improve the quality of the measurement, the following instructions shall be followed:

- sampling at high temperatures (e.g. at 180°C as proposed by the short term method) can help reduce the memory effect, indeed one can assume that the higher the sample gas temperature in the FID, the fewer memory effects are present.
- the use of instruments that have proven to be reliable: certified instruments, good feedback from other labs;
- the temperature control in the filtration area and the sampling line should be carried out properly:
- good practices should be applied when performing sampling, this implies performing adjustments; leak tests every day of sampling
- Risks of interferences with O₂ have to be considered and addressed:
 - by using H₂/He mixture as fuel of the oven instead of H₂ alone;
 - by performing calibration using calibration gases containing 10% O₂.

Uncertainties

The uncertainty of the candidate method has been determined by performing intercomparison campaigns. Performing an intercomparison study is a possible way of evaluating the uncertainty of measurement methods. It is part of the standardisation process of measurement methods. It is a very valuable way of detecting major sources of uncertainty and to see on which input variable the metrological actions must be focused. It is also useful to disseminate good practices to evaluate the capabilities of different laboratories to apply standard measurement methods. A sample is provided to several laboratories and the results obtained are compared. This leads to the calculation of the global uncertainty of the method (ISO 5725-2⁷). Two inter-comparison campaigns have been performed within the EN-PME-TEST program:

- the first one at INERIS (France) in February 2014, using the testing bench for emission measurements, a horizontal testing facility equipped with twelve sampling ports and connected to a pellet resp. wood chip boiler ;
- the second one at VSB (Czech Republic), in October 2014, using a horizontal testing bench designed for the occasion connected to a wood log stove.

The detailed results of the intercomparisons performed are presented in a dedicated WP report⁸. These intercomparison campaigns lead to the determination of expanded uncertainties for both parameters determined with the candidate method, the results obtained are presented in the following tables. The values for the INERIS-campaign of expanded uncertainty (based on interlaboratory dispersion only) obtained are 34% for PM_{HF} in the range comprised between 6 and 42 mg/m^3_{STP} and 30% for OGC in the range between 16 and 144 $C_{eq} mg/m^3_{STP}$. As a comparison, during the last intercomparison campaign performed at INERIS for OGC by stationary emissions control laboratories, the expanded uncertainty was between 12.5% and 25% in, the range comprised between 5 and 15 mg/m^3_{STP} .

The PM_{HF} values for the wood log stove of the VSB-campaign achieved an expanded uncertainty of 35% for PM_{HF} values between 41 and 104 mg/m^3_{STP} . These values of uncertainty were achieved provided that the sample gas flow in the probe was higher than 7 m/s (typically 7 to 9 m/s). The specified suction volume of the sample gas of 10 litres/minute in the probe meets these boundary conditions.

Table 3.1 and Table 3.2 show the results in detail of the INERIS-campaign with the pellet/woodchips boiler for PM_{HF} resp. OGC emission and its uncertainties.

⁷ ISO 5725-2:1994 Accuracy (trueness and precision) of measurement methods and results, Basic methods for the determination of repeatability and reproducibility of a standard measurement method

⁸ EN_PME_TEST WP3 deliverable DTI

Table 3.1 Intercomparison results PM_{HF} for pellet boiler (INERIS-campaign)

Date	Fuel	i	Average	Std dev	Cv	uncertainty		avg. Uncertainty
			[mg/m ³ (stp)]		[%]	mg/m ³ (stp)	[%]	
04-feb-14	Pellets	1	42	3	6%	5	12%	32%
04-feb-14		2	17	3	15%	5	30%	
04-feb-14		3	18	3	19%	7	38%	
04-feb-14		4	6	1	18%	2	35%	
04-feb-14		5	41	9	22%	18	44%	
05-feb-14	Chips	6	21	2	11%	5	23%	36%
05-feb-14		7	13	2	16%	4	32%	
05-feb-14		8	17	5	29%	10	58%	
05-feb-14		9	17	2	14%	5	28%	
05-feb-14		10	14	4	28%	8	57%	
05-feb-14		11	13	1	8%	2	16%	

Table 3.2 Intercomparison results OGC for pellet boiler (INERIS-campaign)

Date	Fuel	i	Average	Std dev	Cv	Uncertainty		avg. U
			[mg/m ³ STP]		[%]	[mg/m ³ STP]	[%]	
04-feb-14	Pellets	1	95	12	13%	25	26%	42%
04-feb-14		2	31	7	22%	14	44%	
04-feb-14		3	21	5	24%	10	49%	
04-feb-14		4	16	4	26%	8	51%	
04-feb-14		5	18	4	19%	7	39%	
05-feb-14	Chips	6	144	17	12%	34	24%	24%
05-feb-14		7	53	4	8%	9	16%	
05-feb-14		8	87	8	9%	16	19%	
05-feb-14		9	71	8	11%	16	22%	
05-feb-14		10	71	7	11%	15	21%	
05-feb-14	11	56	12	22%	25	45%	23%	
06-feb-14	Chips	12	42	6	13%	11		27%
06-feb-14		13	31	4	11%	7		23%
06-feb-14		14	46	5	10%	10		21%
06-feb-14		15	40	4	11%	9		21%
06-feb-14		16	65	8	13%	16	25%	

In Table 3.3 the PM_{HF} values are shown for sample gas flows between 7 to 9 m/s.

Table 3.3 Intercomparison results PM_{HF} for wood log stove (VSB-campaign) at sample flow rates between 7 and 9 m/s

Date	Fuel	i	Average	Std dev	Cv	uncertainty		avg. Uncertainty
			[mg/m ³ (stp)]		[%]	mg/m ³ (stp)	[%]	
08-okt-14	Logs	6	69	7	10%	14	20%	38%
08-okt-14		7	61	20	34%	41	67%	
08-okt-14		8	104	27	26%	53	51%	
08-okt-14		9	62	12	20%	24	39%	
08-okt-14		10	104	7	7%	14	13%	
09-okt-14	Logs	11	73	6	8%	11	16%	32%
09-okt-14		12	49	7	14%	14	29%	
09-okt-14		13	53	17	31%	33	63%	
09-okt-14		14	41	8	19%	16	39%	
09-okt-14		15	87	7	8%	14	17%	

In the VSB-campaign there was also sample gas withdrawn from the flue gas at flow rates in the range of 3.5 to 5 m/s. The deviation in the low flow set up raises substantially (see Chapter *Sampling velocity and nozzle orientation*) leading to uncertainties of 79% with PM_{HF} values between 62 to 110 mg/m^3 (Table 3.4).

Table 3.4 Intercomparison results PM_{HF} for wood log stove (VSB-campaign) at sample flow rates between 3.5 and 5 m/s

Date	Fuel	i	Average	Std dev	Cv	uncertainty		avg. Uncertainty
			[$mg/m^3(stp)$]	[$mg/m^3(stp)$]	[%]	[$mg/m^3(stp)$]	[%]	
08-okt-14	Logs	6	62	32	53%	65	105%	79%
08-okt-14		7	62	20	32%	40	65%	
08-okt-14		8	95	34	36%	68	72%	
08-okt-14		9	76	28	36%	56	73%	
08-okt-14		10	110	44	40%	88	80%	

Conclusions: proposals made for a reliable method to measure PME from RWC

The main conclusions obtained are:

- The results of the project show that although OGC are good indicators of the amount of POA (condensable fraction) and combustion quality in high emission cases, no correlation can be applied between the amounts of OGC and POA. As a result OGC concentrations cannot be used to determine by calculation the concentration of the condensable fraction, it is used as a guide value of the amount of condensables.
- In order to prevent overestimation or underestimation of organic species, PM_{HF} and OGC should be sampled at the same temperature; a temperature of 180°C is proposed.
- A sampling probe, able to maintain the sample gas temperature to 180°C in the probe and at the outlet for a range of flue gas temperature in the duct between 40°C and 400°C, has been designed and validated.
- A sample gas velocity in the probe of about 7 m/s (corresponds to 10 l_{STP}/min at 7.5 mm inner probe diameter at 180°C) is proposed, following conclusions regarding over isokinetical sampling and influence of high velocity to decrease dust deposit;
- Taking into account the constraints associated with the determination of deposit in the probe by rinsing, it is proposed to determine the deposit in the probe after each run by blowing compressed air into the probe onto a conditioned filter.
- A simple manner of systematically removing the variable amount of large particles (randomly coarse or re-entrained particles) present in the flue gas is proposed. The impact of the angle between flue gas in the duct and flue gas sampling on the sampling efficiency of particles has been studied, it leads to the conclusion that using a straight probe (90° angle) allows removing larger particles and as a result improving measurement repeatability.
- OGC measurements are typically characterized by slightly higher dispersion (uncertainty 12.5 % at 10 mgC/m^3_{STP}) of results compared to other combustion gases. The following recommendations should be followed in order to improve quality of measurements: sampling at high temperature (above 160°C, in the method proposed: 180°C), use of instruments that have proven to be reliable, the temperature control in the filtration area and in the sampling line to be carried out properly, good practices to be applied, risks of interferences with O_2 to be considered and addressed.

Based on these proposals, a candidate method has been tested and its uncertainty determined, by performing intercomparison tests using both methods, the values of expanded uncertainty (based on interlaboratory dispersion only) obtained are 34% for PM_{HF} and 30% for OGC.

Appendix 4:

Proposal for a common European method to determine PME

The Term PME is described here by two separate values: PM_{HF} (solid and liquid particulate matter collected on the heated filter at the sampling temperature, in our case at 180°C) and OGC (a guide value for condensables).

The measurement method proposed consists of two parallel sampling lines, one for PM_{HF} sampling and one for OGC measurement. The PM_{HF} are collected on a heated filter and the OGC are measured using a FID. Both sampling lines are set to a fixed temperature of 180°C to limit overestimation or underestimation of organic species. The PM_{HF} sampling probe is placed in front of the OGC sampling probe to limit the disturbances between the two probes.

For PM_{HF} , the inlet of the probe (nozzle), is positioned at a 90° angle to the flue gas flow direction in the measurement section, this is to increase the repeatability of PM_{HF} measurement by separation of larger particles (randomly coarse or re-entrained particles in flue gas).

The PM_{HF} samples are taken at a flow rate of 10 l_{STP} /min using a straight probe with an inner diameter of 7.5 to 8 mm.

After each test run, the deposit in the probe is determined by blowing filtered compressed air into the probe, and collect the dust deposited onto a conditioned and weighed filter. For each test run, the total mass of PM_{HF} corresponds to the sum of the mass collected on the two filters used:

- the heated sample gas filter used to collect particulates in the sample gas during test run
- the deposits filter used to collect the deposits in the probe by blowing compressed air through it.

The parameters for PM_{HF} and OGC are reported independently, PM_{HF} is expressed as mg/ m³_{STP} and OGC as C_{eq}mg / m³_{STP}, of dry gas; based on the O₂ reference value.

Schematic showing the detailed layout of the method

The PM_{HF} sampling line is composed of :

- a straight or coiled probe heated to 180°C for heating and cooling the sample gas
- a filter casing holding a filter heated to 180°C;
- a system used to remove the water vapour to express results as dried gas ;
- a cold sampling pump;
- a sampling volume measurement device equipped with temperature and pressure monitoring to express the results in STP conditions.

The OGC sampling line is composed of:

- a pre filter set at the temperature of 180°C;
- a heated line set at temperature slightly above 180°C to avoid condensation of OGC;
- a device to measure water content of the flue gas.

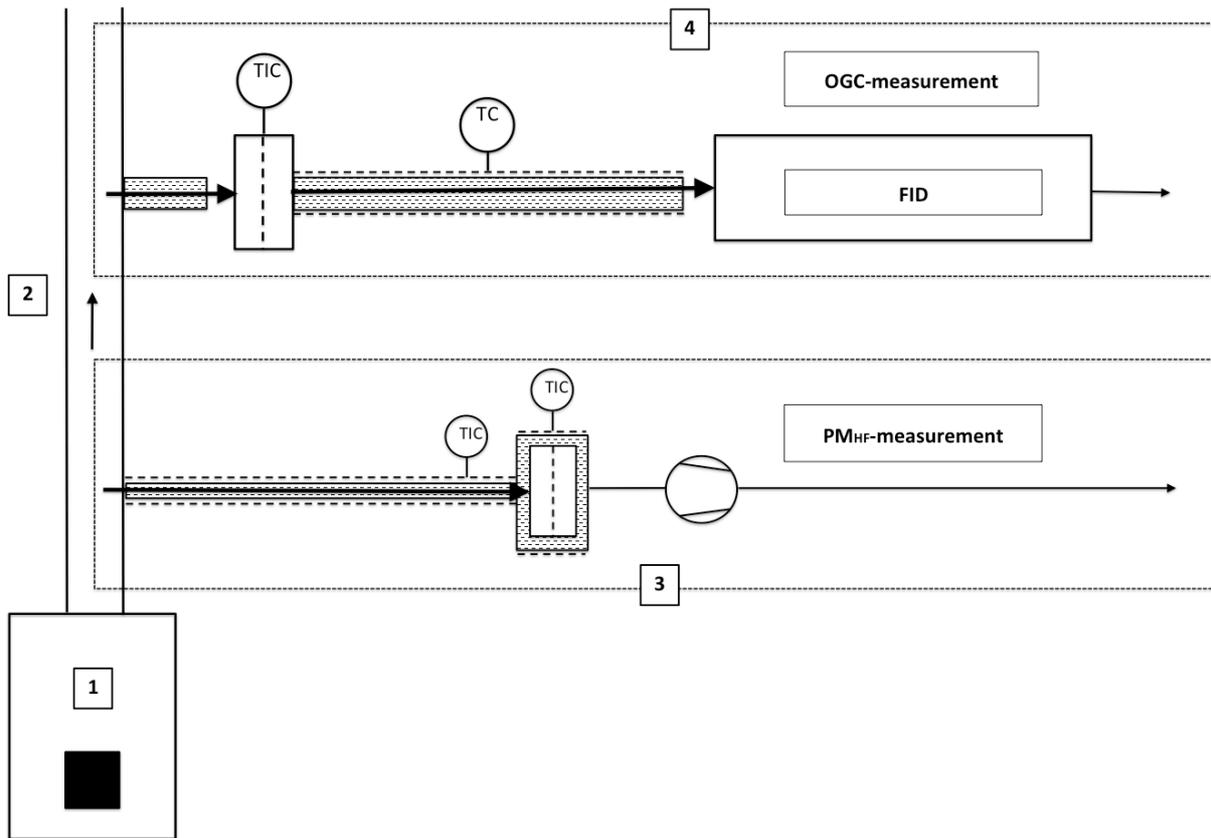


Figure 4.1 Short term PME-measurement method: synoptic of simultaneous PM_{HF} - and OGC-measurement at identical temperature level of PM_{HF} - and OGC-sampling train at temperature of 180°C.

- 1: test apparatus
- 2: flue gas measurement section
- 3: PM_{HF} -sampling train and measurement
- 4: OGC-sampling train and measurement

Detailed description of the PME-measurement method

List of material

Probe

The goal of the probe design is to achieve the required design temperature of $180^{\circ}\text{C} \pm 10 \text{ K}$ in the sample gas at the end of the probe and its inner surface. The probe is made of a 2 meter long stainless steel tube with an inner diameter of 7.5 to 8 mm. The tube can be straight or coiled. If the tube is coiled, the characteristics for convection cooling of the tube must be similar to that of a straight tube.

Probe heating

The 2 meters probe with a resistive heating (electric current, probe tube acting as resistance) and a controlled constant temperature of 180°C covers the design needs.

Remarks

The proposed probe design guarantees the required design temperature of $180^{\circ}\text{C} \pm 10 \text{ K}$ of the sample gas independently from the flue gas temperatures which can vary between 40°C and 400°C . The probe temperature is not changed, neither in the heating nor in the cooling mode.

Only measuring the outlet temperature of the probe is not sufficient. In such a setup it would be possible to work with much shorter probes (1 meter or less) but in order to cool down the flue gas within short distances the surface temperature of the probe must be reduced substantially below design temperature of 180°C . This results in undesirably condensation on cold surfaces and increases undesired particle deposition on the probe surfaces due to thermophoresis.

Nozzle

For PM_{HF} the inlet of the probe (nozzle), is positioned at a 90° angle to the flue gas flow direction in the measurement section, as illustrated in Figure 4.2. This is to increase the repeatability of PM_{HF} measurement by separation of larger particles (randomly coarse or re-entrained particles in flue gas).

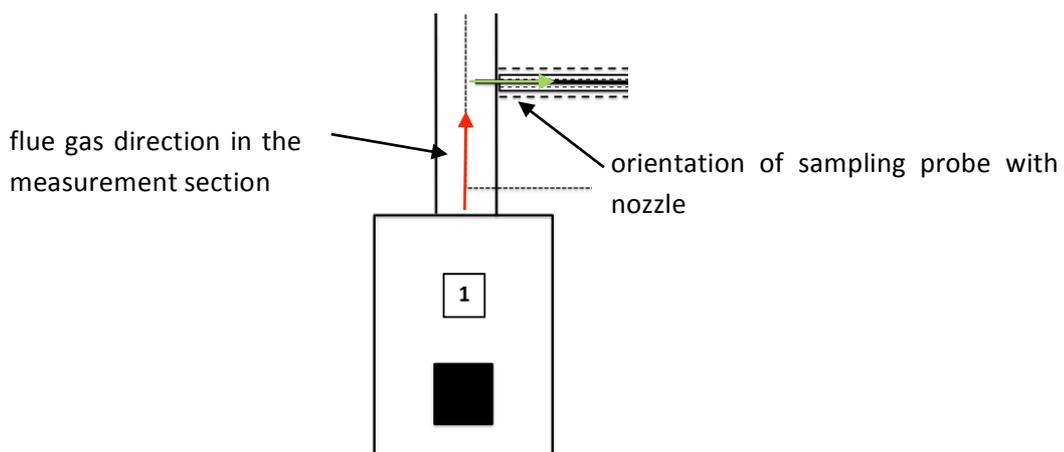


Figure 4.2 PM_{HF} -measurement: orientation of probe nozzle

Filter casing:

The filter is placed into a sealed filter holder or casing heated to 180°C .

Filter material

A filtering material following CEN Standard EN13284-1 specifications should be used. More specifically the retention should be above 99.95% for a particle size of 0.3 μm . Two filters per test run are necessary, one for sampling PM_{HF} and one for collecting the deposit into the probe after sampling. The size of the filter should be adapted according to the amount of PM_{HF} to be collected.

PM_{HF} sampling pump

The sampling train is equipped with a system used to remove moisture placed before the pump, its aim is to protect the sampling pump and to measure the volume sampled as dry gas.

PM_{HF} sampling volume measurement device

A sampling volume measurement device equipped with temperature and pressure monitoring is necessary to express the results in STP conditions.

FID analyser

The OGC concentration is determined using a flame ionization detector (FID) following the requirements of the EN12619⁹ standard, calibrated using a mixture of C_3H_8 with 10% O_2 .

Measurement section

The measurement section is characterized by a diameter D and a length L. A straight duct of 4-5D length should be placed before the PME measurement section. The measurement section diameter should be adapted to obtain a duct velocity higher than 2 m/s duct.

Sampling procedure

PM_{HF}

Filter conditioning and weighing

Before sampling :

Filters are conditioned in an oven at 200°C for 1 h and let to cool down in a desiccator for 8 h. The filters are weighed according to EN13284-1¹⁰ but using a weighing scale with a resolution of 0.01 mg. The filters are then stored in a dry place (ideally in a desiccator) before sampling.

⁹ EN 12619:2013 Stationary source emissions. Determination of the mass concentration of total gaseous organic carbon. Continuous flame ionisation detector method

¹⁰ EN 13284-1:2002 Stationary source emissions – Determination of low range mass concentration of dust – Part 1: Manual gravimetric method

After sampling :

After sampling the filters are conditioned in an oven at 180°C for 1 h, and cooled down in a desiccator for 8 h. The filters are weighed according to EN13284-1¹⁰ but using a weighing scale with a resolution of 0.01 mg.

Sampling

Both sampling lines are set to 180°C to limit overestimation or underestimation of organic species.

The PM_{HF} samples are taken at a minimum flow rate of 10 l_{STP} /min using a 7.5 to 8 mm inner diameter straight probe. Sampling duration is not defined in this procedure.

Determination of the contribution of deposit in the probe:

Deposit in the probe is collected at the end of each test run by inserting a conditioned and weighed filter into the filter holder and blowing filtered compressed air (with an air blow gun at 6 bar) into the inlet of the probe for 30 seconds. The deposits filter is then weighed following the weighing procedure.

OGC measurements:

OGC measurements are performed according to CEN standard EN12619⁹. The pre filter temperature should be 180°C and the heated line temperature should be above 180°C to avoid condensation. The results are expressed as C_{eq}mg /m³_{STP} dry gas STP at O₂ reference value. In case the raw data are expressed in ppm CH₄ in the wet gas it must be converted into C_{eq}mg /m³_{STP} dry gas STP at O₂ reference value by applying Formula 2 (see below). When calibrating and processing data, a specific attention should be paid to the ratio of 3 between the calibration gas C₃H₈ and unit of expressing the results C_{eq}

Quality assurance/Quality control**Probe cleaning:**

At the end of each sampling day, the probe and the filter holder should be cleaned by rinsing three times using water and acetone.

Field blank:

A field blank should be taken for each batch of samples taken, it consists of a weighed conditioned filter, inserted into the filter holder without sucking flue gas. The filter is conditioned and weighed following the above procedures. The value of the field blank is considered as acceptable if the ratio between the measurement and the field blank expressed as collected masses is > 10.

Leak test:

The sampling line is assembled and the absence of leak is verified following the CEN standard EN13284-1. The control is made by closing the inlet of the sampling line, turning on the sampling pump and measuring the flow rate at the outlet of the sampling line using an appropriate rotameter.

The leak flowrate should be lower than 2% of the nominal sampling flowrate. If it is higher, the leak should be identified and repaired before starting sampling.

Periodic quality control

Quality control of the FID analyser, weighing scale, the pump and the volume measurement device should be performed according to requirements specified in the appropriate standards.

Adjustment and drift evaluation of the FID measurement line

The FID analyser and sampling line should be adjusted at the beginning of each sampling day using a mixture of C₃H₈ with 10% O₂, in order to lower the effect of O₂ interferences.

It should then be verified at the end of each day in order to evaluate the drift according to the following criteria.

- If the drift is below 2%, no action to be taken;
- if the drift is between 2 % and 5 %, the data collected during the day should be corrected;
- if the drift is higher than 5% the data collected during the day should be considered as invalid.

Limits of quantifications LOQ

The LOQ are determined by performing repeated measurements at low level of concentration. For OGC a method of determination of LOQ is presented in the EN 15267-3¹¹ standard, for PM, it is described in the ISO 15767¹² standard.

Calculations

PM_{HF}

The concentration of PM_{HF} stated as mg/m³_{STP} corresponds to the particulate mass collected on the two filters (heated sample gas filter and deposits filter) divided by the volume dry gas sampled expressed under STP conditions and according to an O₂ reference value:

¹¹ EN 15267-3:2007 Air quality. Certification of automated measuring systems. Performance criteria and test procedures for automated measuring systems for monitoring emissions from stationary sources

¹² ISO 15767:2009 Workplace atmospheres. Controlling and characterizing uncertainty in weighing collected aerosols

Formula 1

$$PM_{HF} [\text{mg}/\text{m}^3_{\text{STP dry gas @ } O_{2 \text{ ref}}}] = (m_1+m_2)/V_{\text{STP dry gas}} * (21- O_{2 \text{ ref}}) / (21-O_{2 \text{ measured}})$$

where:

m1 is the particulate mass collected on the heated sample gas filter

m2 is the particulate mass collected on the deposits filter

$V_{\text{STP dry gas}}$ is the dry sampling gas volume of the test run expressed according to standard conditions of temperature and pressure (STP)

$$V_{\text{STP dry gas}} = V_{\text{measured}} * 273/(273+T_{\text{measured}}) * P_{\text{measured}}/P_{\text{standard}}$$

$O_{2 \text{ measured}}$ is the mean value of O_2 determined over a test run

$O_{2 \text{ ref}}$ is the reference value for oxygen (e.g. 13% O_2)

OGC

Formula 2 (According to EN12619⁹)

$$OGC [C_{\text{eq}} \text{ mg}/\text{m}^3_{\text{STP dry gas @ } O_{2 \text{ ref}}}] = OGC [\text{ppm}] * 12/22.4 * 100/(100- \text{moisture}\%) * (21- O_{2 \text{ ref}}) / (21-O_{2 \text{ measured}})$$

where:

OGC [ppm] is the mean value of OGC concentration determined over the sampling period and expressed as ppm of C;

moisture% (by volume) is the amount of humidity of the flue gas

$O_{2 \text{ ref}}$ is the reference value for oxygen (e.g. 13% O_2)

Method characteristics**Measuring ranges**

- OGC: 5 ...1'000 C_{eq} $\text{mg}/\text{m}^3_{\text{STP @ } 13\%O_2}$
- PM_{HF} : 5...200 $\text{mg}/\text{m}^3_{\text{STP @ } 13\%O_2}$
- flue gas temperature: 40...400°C (transient flue gas temperatures during sampling period)

Uncertainty determined

Uncertainty have been determined by performing intercomparison tests using both methods, the values of expanded uncertainty (based on interlaboratory dispersion only) obtained are 34% for PM_{HF} and 30% for OGC.

LOQ to be expected

For PM_{HF} measurements, using a weighing scale with a resolution of 0.01 mg, a LOQ of 3 mg/m^3_{STP} can typically be obtained, taking into account a flow rate of $10 \text{ l}_{STP}/\text{min}$, for a sampling time of 30 minutes.

For OGC a LOQ of $10 C_{eq} \text{ mg/m}^3_{STP}$ can typically be obtained.

Appendix 5:

Long Term Approach using a Micro Smog Chamber and Total Carbon Measurement

Our goal for the long term approach is to develop a method for quantification of particulate matter emissions that reflects the quality of the combustion. Instead of focussing on the total mass, we propose to measure only the particle-bound carbon atoms by means of a total carbon (TC) analysis. This would motivate appliance manufacturers to improve the combustion efficiency of their devices.

An advantage of the TC analysis is that this parameter is already well established for ambient pollution monitoring. Thus, TC is a better metric for comparing emissions against ambient measurements. However, a TC measurement would not give a complete picture of the emissions without including some sort of potential for secondary organic aerosol (SOA) formation. Ambient measurements establish particle bound organic carbon (OC) as the largest carbonaceous fraction from wood burning emissions. In turn, the SOA produced by atmospheric aging may amount to more than 50% of the atmospheric OC related to this type of combustion (Lanz *et al.*, 2007). SOA is therefore one of the most important atmospheric pollutants in Europe (Denier van der Gon *et al.*, 2014).

We will explain in this appendix how we produce SOA by means of a micro smog chamber. We will also show how this technique compares against ambient measurements and other experimental methods for establishing a SOA potential. Finally, we will share our findings when combining the use of the micro smog chamber and the TC analysis for wood burning characterization.

The Micro Smog Chamber

The Micro Smog Chamber is a simple continuous-flow tube reactor that oxidizes OGC to form SOA (Keller and Burtscher, 2012). Emissions are first exposed to UVC light (20 watts of optical power at the 184 and 256 nm emission lines) produced by means of five low pressure mercury lamps and then to UVA light (30 watts on a broad spectrum) from a high pressure halogen lamp. A short residence time of 10 seconds is enough to oxidize the precursor substances and form SOA. This fast oxidation allows for a time-resolved characterization. The reactor can be used either to expose 1) total, slightly diluted, emissions or 2) only the gas-phase. The latter setup is used to study exclusively the SOA potential without interference from primary PME (see, e.g., Figure 5.1). Our results in terms of SOA yield are comparable to previously published data from smog-chamber experiments.

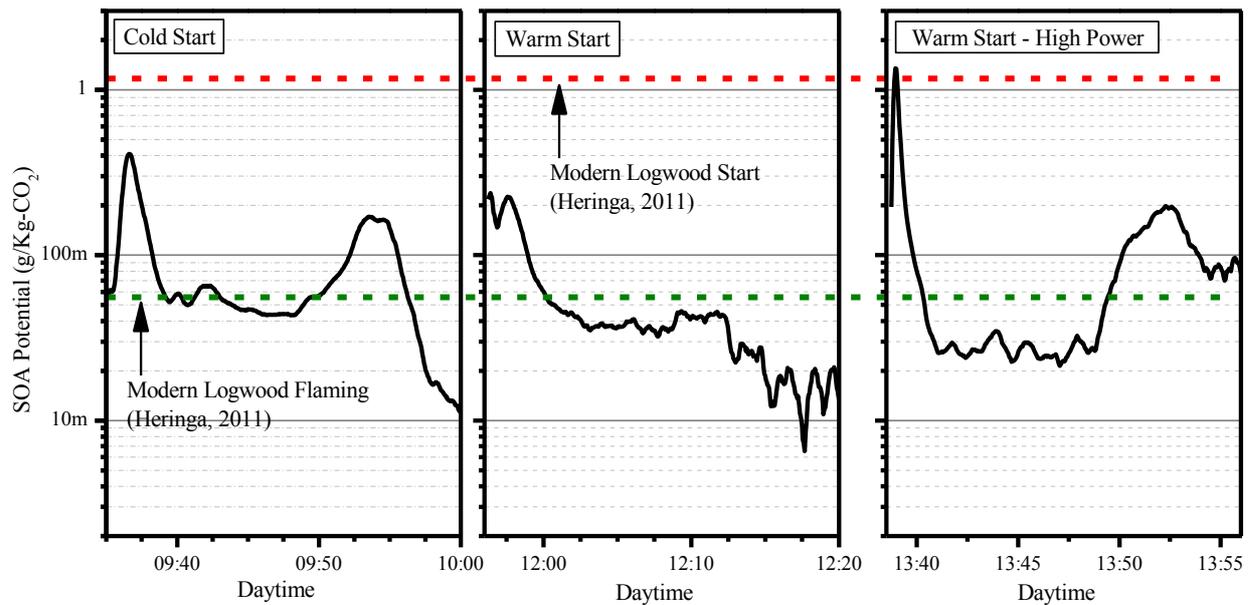


Figure 5.1 Time resolved SOA Potential, measured by means of a TEOM, after approximately 10 seconds residence time in the micro smog chamber. The curves correspond to the emissions from the log-wood cooking stove for three different cycles: (a) a cold start, (b) warm start, and (c) warm start with increased flow of primary air. The TEOM curve represents a 2 min running average. Also shown are reference lines to the factors calculated by Heringa et al. (2011) using a smog chamber and a residence time of 5 h. Source: Keller and Burtscher, 2012.

The micro smog chamber is intended as a conditioning system for comparing the emissions from wood-burning devices taking the SOA production potential into account with reproducible results. It has been evaluated at test bench experiments using different small combustion installations (SCI) as well as during field measurements performed on medium size boilers (180 to 450 kW) burning wood chips and wood pellets. The actual potential depends upon several factors and is a combination of the emissions caused during the start and restart phases, which in general have higher emission factors, and the steady state combustion.

Throughout the duration of the EN-PME-TEST project, we have compared the SOA production potential against other emission parameters including gas-phase data (CO, OGC, non-methane OGC, and NO_x) as well as against the particle phase in form of total PME and EC. We have not found any useful correlation that could predict the amount of SOA. Our tests show that the SOA production potential varies throughout several orders of magnitude, from a neglectable contribution to the total PM emissions (Figure 5.2a) to the same order of magnitude than current emission limits (Figure 5.2.b). Non-certified or badly operated appliances can cause the SOA potential to increase further orders of magnitude even during steady state combustion (Figure 5.2 c).

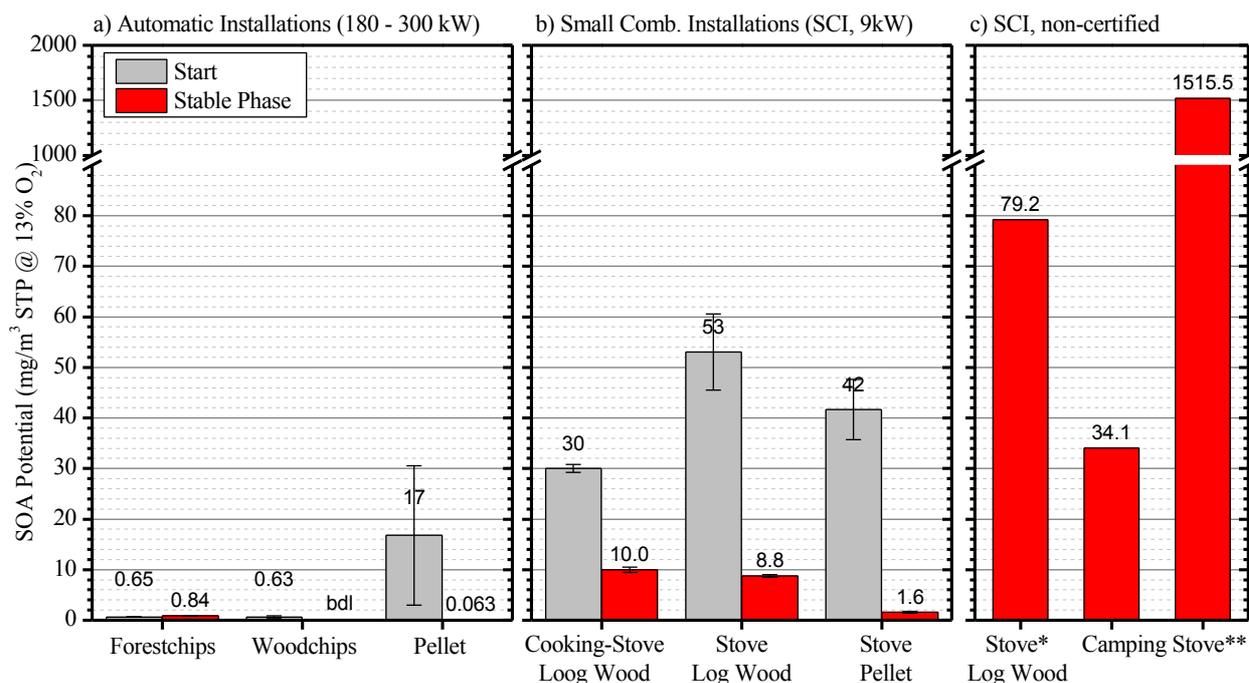


Figure 5.2 Average SOA production potential from a) 3 automatic medium size boilers, compared against the potential from b) 3 modern small combustion installations measured in the laboratory, and c) the SOA potential for 3 log-wood stoves that do not fulfill the LRV standards. The data on a) and b) was measured by means of the micro smog-chamber, whereas c) presents traditional smog-chamber experiments from the literature (*Heringa *et al.*, 2011, and **Grieshop *et al.*, 2009). bdl = below detection limit.

Atmospheric Relevance of the Organic Aerosol produced by the Micro Smog Chamber

Photo-oxidation, also referred to as atmospheric aging, is the process that transforms gas-phase organic carbon into SOA. This process is slow due to the low concentrations of reactive species in the atmosphere. The fact that the atmosphere is a mixture of aerosol from different sources makes aging difficult to follow experimentally. A variety of tools are used to simulate atmospheric aging and study the production of SOA in the laboratory. They include smog-chambers as well as flow reactors. The preferred method to evaluate these devices is the use of a chemical analysis technic, e.g. an aerosol mass spectrometer (AMS, Aerodyne Inc.), in combination with a source apportioning study like the positive matrix factorization (PMF). When used correctly, they can separate the organic aerosol from different combustion sources or, depending on the particular experiment, separate primary and secondary organic aerosol within the same combustion event.

Whereas, from the scientific point of view, it is important to establish the atmospheric relevancy of the organic material produced by photo-oxidation, a type approval approach only needs to provide a reliable and reproducible technique that can be linked to the actual emission values or SOA production potential. However, SOA production is a complex process. It is more likely that an approach mimics the potential atmospheric yields if the chemical composition makes sense from an atmospheric point of view. We will show that this is the case when using the Micro Smog Chamber. We have performed two measurement campaigns that make use of the MSC, an AMS/SP-AMS and PMF to characterize the primary emissions and the potential for secondary organic aerosol

production of logwood and pellet stoves. Details of these campaigns can be found in Bruns *et al.* (2015), Corbin *et al.* (2015) and Corbin *et al.* (2016). Here we briefly mention some important results.

On a first campaign (Corbin *et al.*, 2015, and Corbin *et al.*, 2016), the emissions from a pellet stove and a logwood stove were analyzed by means of a dual-vaporizer aerosol-particle mass spectrometer (SP-AMS, Aerodyne Inc.). The SP-AMS provided information on the OM, BC, and surface composition of the soot. The emissions were analysed in three different types of experiments: 1) total emissions without UV-conditioning conditioning, 2) total emissions after UV-conditioning in the micro smog chamber, and 3) filtered emissions, i.e. only the gas phase, and UV conditioning. These experiments provide the chemical signature of primary emissions, aged primary and secondary emissions, and pure secondary organic aerosol respectively. In addition, a tapered element oscillating microbalance (TEOM 1405, Thermo Scientific) and a SMPS system provided information about mass yields and size distribution of the resulting aerosol.

Oxidation of wood-stove emissions in the Micro Smog Chamber generated organic aerosol that was more-oxidized than expected for atmospheric observation. A lower oxidation degree can be obtained by reducing the residence time in the reactor. Nevertheless, the SOA production potential derived from the micro smog chamber was within the range expected from a previous smog-chamber study in a logwood stove (Heringa *et al.*, 2011). This consistency supports the intended use of the MSC as a simple online tool for SOA-formation-potential estimation.

High resolution PMF analysis shows that the primary, non-conditioned, emission can be described by two main factors that were identified with the start- and flaming-phases of the combustion cycle. The mass spectra of the start-phase were highly correlated with pyrolysis products like levoglucosan (uncentered $r = 0.84$), whereas the mass spectra of the flaming-phase were well correlated with lignin-combustion organic material (uncentered $r = 0.79$). The highest primary organic aerosol emission factors happened during the start-phase. In the case of the aged emissions also two PMF factors are enough to model the combustion cycle. The assignment to pyrolysis products or lignin-combustion is not straightforward due to the changes induced by photo-chemical aging. They can, however, still be identified by the moment of the cycle when their contribution is more important. Again, the highest emission factor can be assigned to the starting phase of the cycle when pyrolysis is the dominant process.

The second campaign took place at the Paul Scherrer Institute (PSI) in Villigen. The campaign focus was the quantity and chemistry of organic aerosol from the oxidation of emissions from a logwood appliance as well as the oxidation of a well-known precursor molecule (i.e. α -pinene). The portable smog chamber (SC) from PSI, the micro smog chamber (MSC) and a second flow tube reactor (PAM chamber) were used to oxidize the samples. High resolution time-of-flight aerosol mass spectrometer (AMS) measurements provided insight into particulate chemical composition and a proton transfer reaction time-of-flight mass spectrometer (PTR-MS) was used to determine OH exposures (i.e. an indicator of the atmospheric equivalent oxidation) for comparison of the different reactors.

A very marked difference between the three systems is the size of the particles containing SOA. The size is directly influenced by the speed of oxidation. The largest particles, caused mostly by condensation or coagulation with existing primary aerosol, come from the smog-chamber which is the slowest system. Primary particles are referred to as seed in smog-chamber literature because they capture the extremely low-volatility organic compounds (ELVOCs) formed by aging before they

are irreversibly lost to the chamber walls. Seed particles however may not be enough to prevent losses. For instance, at atmospheric relevant concentrations, a significant portion of the ELVOCs will still be lost to the chamber walls (see, e.g., Ehn et al., 2014). During α -pinene experiments, nucleation was observed in all three systems, higher OH concentrations increased the rate of nucleation and, depending on the residence time, similar OH exposures produced a range of OA sizes (see Figure 5.3).

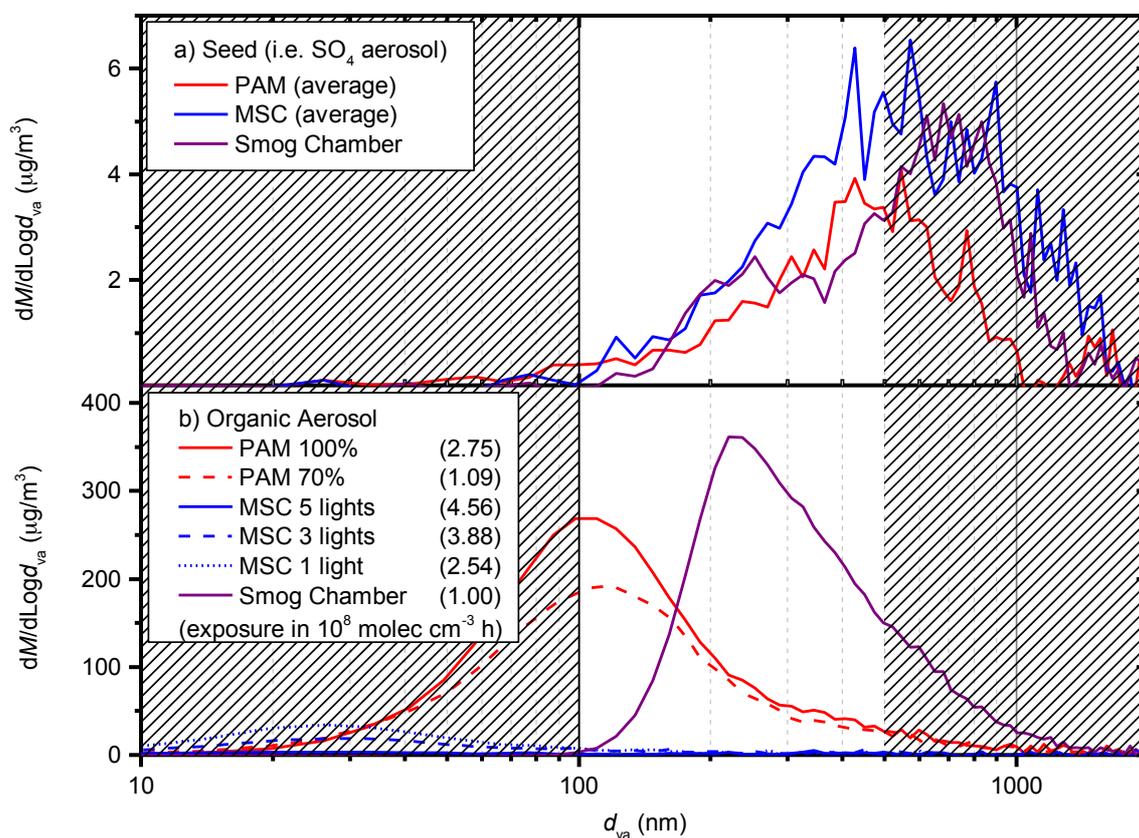


Figure 5.3 Sulfate and organic mass based size distributions from an α -pinene oxidation experiment measured by AMS of (a) $(\text{NH}_4)_2\text{HSO}_4$ seed in the SC prior to oxidation and (b) resulting organic aerosol particles after oxidation in the PAM, MSC and SC. The initial α -pinene mixing ratio was 200 ppbv. Wall and transmission losses have not been taken into account. The numbers in parenthesis refer to the OH-exposures in 10^8 molecules cm^{-3} h. The dashed regions correspond to the data beyond the optimum transmission size of the AMS. The detection efficiency in these regions is poor and cannot be used to calculate aerosol yields. Adapted from Bruns *et al.*, 2015.

The MSC has the fastest oxidation and can achieve the highest OH-exposure. This promotes the formation of a nucleation mode. Depending on the type of experiment, condensation on top of seed particles does not contribute significantly to the formation of SOA. The measured range OH-exposure for the MSC during this campaign was $(1.7\text{-}4.6)\times 10^8$ molecules cm^{-3} h for α -pinene experiments and $(0.32\text{-}3.4)\times 10^8$ molecules cm^{-3} h for wood burning. This corresponds to an equivalent atmospheric aging of 7-19 days and 1-14 days within 13 seconds of reaction time. The OH-exposure can be controlled by adjusting the intensity of the UVC light, the length of the MSC, or by changing the dilution and thus the concentration of the precursor molecules.

The difference in particle size poses a problem for the system measuring organic aerosol, the widely used AMS, which has a 50% size-cut at an aerodynamic diameter of $d_{vo} \sim 100\text{nm}$ (Lui et al., 2007). Our experiments show that the organic aerosol mass mode after oxidation in the MSC can easily be located at sizes $d_{vo} < 60\text{nm}$. A calibration of the AMS for such small particles is difficult due to large uncertainties and could involve correction factors larger than one order of magnitude. Without this calibration, the AMS reported lower organic aerosol yields for the MSC than the other systems for most experiments. Some groups argue that the lower yields can be attributed to wall losses in flow-reactors. However, this cannot be the case in our setup. The low dilution factors (typically 1:4 to 1:8) of the wood burning experiments create a condensational sink (i.e. the capture of ELVOCs by primary particles) 10 times faster than wall losses in the MSC already for primary PM concentrations as low as a few mg/m^3 . Furthermore, the α -pinene and wood burning experiments show that homogeneous nucleation may be the predominant mechanism for SOA formation in the MSC. Neither the fast condensational-sink nor the wall-losses are enough to prevent the formation of a nucleation mode. The AMS can thus deliver information about the chemical composition of the emissions but cannot be used as a tool for measuring the total organic aerosol after aging in the MSC.

One concern with the ability of flow reactors to simulate atmospheric processes is that slower processes contributing to the evolution of the particle phase (e.g., condensed phase reactions) are not able to proceed during the relatively short residence time in these flow reactors. However, the similarity in terms of yields and composition between the SC and the PAM indicate that either these slow processes do not significantly alter bulk aerosol yields or composition or that these slow reactions are accelerated and/or compensated for by the fast oxidation in the PAM. Yield comparison against the MSC was not possible due to significant mass below the AMS detection range. Nevertheless, the conclusions from the PAM can probably be extended to the MSC since the residence time in the MSC is only a factor 4 shorter than the PAM (the PAM simulates up to 10 days of oxidation in 53 seconds and is thus 3 orders of magnitude faster than the atmosphere). In addition to that, even though the OH exposure in the MSC was usually higher than both PAM and SC, the chemical signature of the SOA produced in the MSC compares well to chemical signatures found in atmospheric studies (Figure 5.4).

We want to point out that the high OH exposures reported for the MSC during this campaign are a consequence of the experimental design which required high dilution ratios. As mentioned before, our typical experimental setup is performed in only slightly diluted emissions. Thus, the primary pollutant concentration will be higher and the OH exposure closer to what the SC and PAM achieved during this study (see, e.g., the black circles on the lower panels of Figure 5.4).

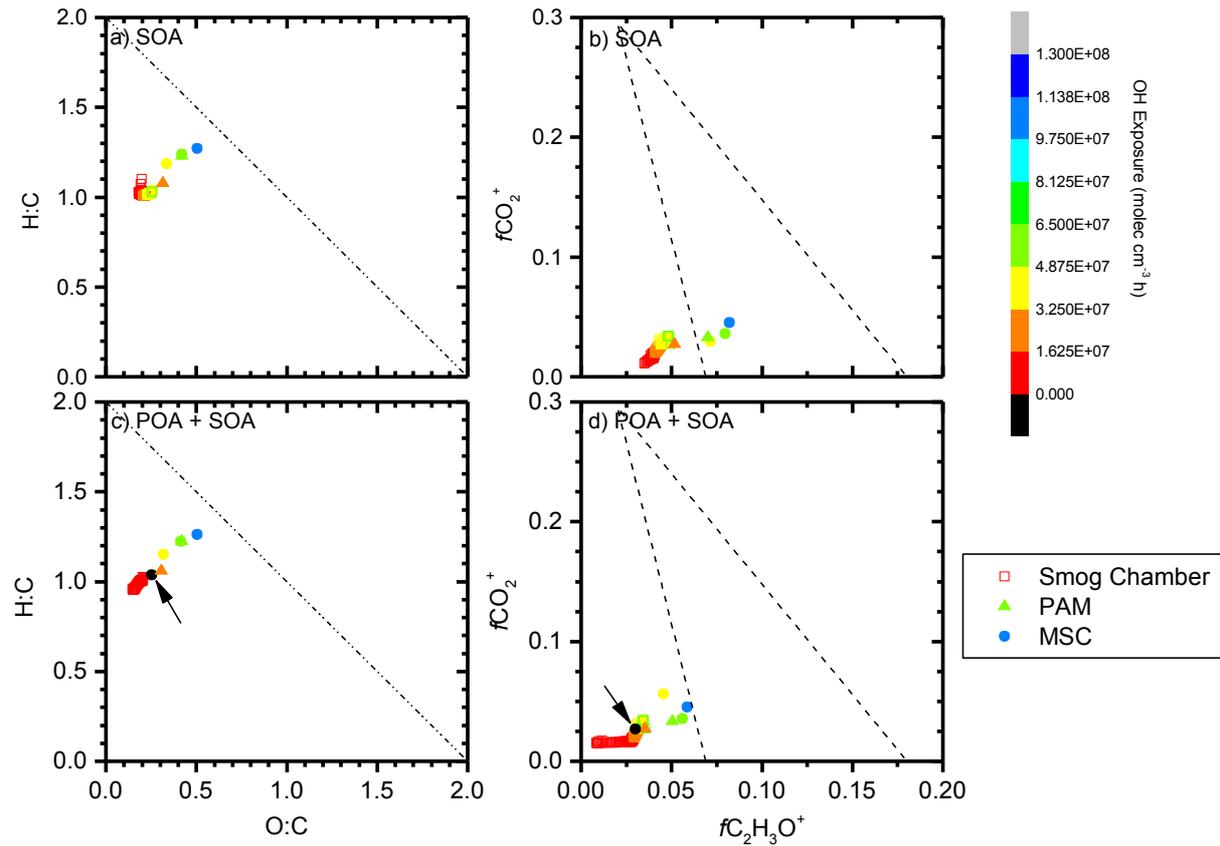


Figure 5.4 Elemental ratios of SOA and bulk organic aerosol (primary organic aerosol, POA, and SOA) generated during a wood burning experiment (panels a and c respectively) and their corresponding mass fractions $f\text{CO}_2^+$ as a function of $f\text{C}_2\text{H}_3\text{O}^+$ (panels b and d). Color data points represent the organic aerosol aged in the SC (open squares) and the PAM (triangles) and MSC (circles) when sampling from the SC (prior to starting SC oxidation). The color scale shows the equivalent OH-Exposure. The black circles on the lower panel represent a direct sampling experiment with the MSC, i.e. sampling directly from the combustion source at higher concentrations than the other data points. This is the way the MSC is designed to work. The dashed line on panels a) and c) shows a minus one slope. Atmospheric observations have been found to be close to this line (see Heald *et al.*, 2010). The dashed lines on panels b) and d) delimit the region where most ambient measurements have been observed. Adapted from Bruns *et al.*, 2015.

Total carbon measurement and volatility of SOA precursors

We tested a simplified measurement system based on a total carbon (TC) analysis. The idea behind this system is to provide a measurement procedure that includes the potential for secondary organic aerosol formation and is compatible with type-approval testing as well as field measurements. The idea was tested in several measurement campaigns. TC includes the PM fraction relevant to the combustion quality and probably serves as a better marker for toxicity compared to total PM since the carbonaceous fractions, i.e. soot and organic material, have been related to the health impact.

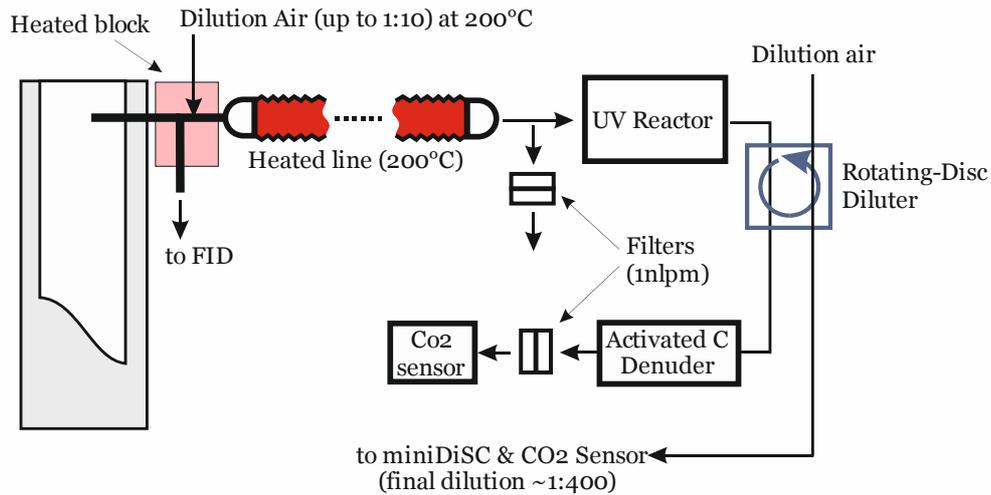


Figure 5.5 Measurement setup for off-line total carbon analysis. The sample is extracted from the stack and immediately diluted by a factor 1:4 to 1:10 using hot air. The sample is then oxidized in the micro-smog-chamber (MSC). A filter sample is collected before and after the oxidation during a typical period of 30 minutes. After the MSC, an activated carbon denuder removes the remaining gas-phase hydrocarbons and O_3 produced in the MSC preventing artefacts and further oxidation in the filter. A rotating-disc-diluter is used to further dilute the emissions and obtain time resolve data by means of a size distribution measurement using, e.g., a miniature diffusion size classifier (miniDiSC) or an SMPS system. The absorption of gas-phase hydrocarbons on the filter prior to the MSC are estimated by means of a backup filter.

Figure 5.5 shows the experimental setup of our TC sampling system. The analysis is performed off-line by means of thermo-optical analysis using the EUSAAR 2 protocol. It is important to note that TC is not the total carbonaceous PM mass. Total carbon is defined as the sum of organic carbon (OC) and elemental carbon (EC) as $TC=OC+EC$ and thus accounts only for the mass of the carbon atoms. Factors between 1.6 and 2 are typically used to obtain the organic mass (OM) from OC.

Figure 5.6 shows results from measurements performed on different appliances using different combustion conditions. Note that TC analysis clearly separates the two types of installations. The automatic boiler has an efficient combustion and low TC emission factor. The manually operated logwood stove has a TC emission factor one order of magnitude larger than the boiler during the type approval test. This trend would be similar but not as pronounced for gravimetric measurements. Changes in the combustion conditions affect the contribution of OC and EC and also have an impact on the TC. This is more pronounced for the logwood stove; modification in the combustion protocol can increase the TC emission factor by an order of magnitude. The changes are not so drastic for EC (within a factor 3 and 4 for the woodchip boiler and the logwood stove respectively) as they are for OC (factors 10 and 100).

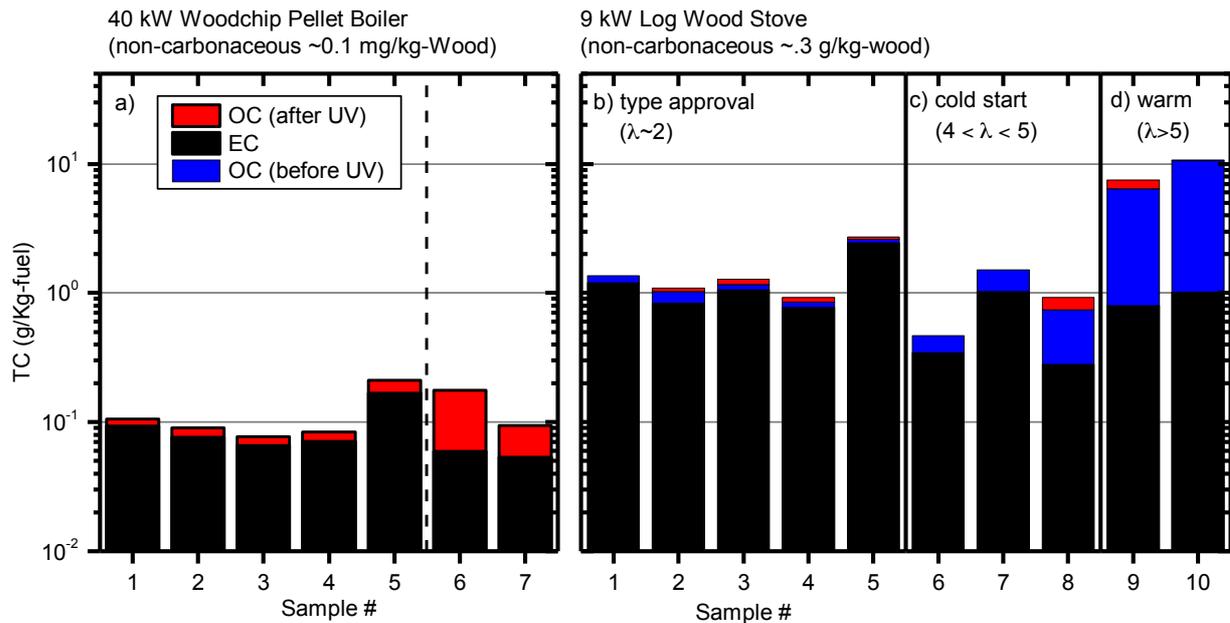


Figure 5.6 TC emissions divided into their organic carbon (OC) and elemental carbon (EC) fractions for a woodchip boiler and a logwood stove in different operating conditions. The dashed line between filter 5 and 6 of the woodchip boiler shows a readjustment of the operating conditions. The average air to fuel ratio, λ , is given for the tests with the logwood stove. a) Type approval runs of the logwood stove represent warm starts. c) Increased λ operation obtained by not readjusting the air supply of the stove after the logs ignited properly. All other settings were identical between a) and c).

An interesting and unexpected result is the fact that there is almost no difference in the amount of OC before and after UV exposure. This is certainly not the case at higher dilution ratios or during atmospheric observations, where the oxidation process can increase OM several fold. Figure 5.7 shows a measurement performed during the same campaign at a higher dilution ratio. Turning off the UV lights decreases the total PM by a factor of 2. At low dilution ratios and low temperature the vapour pressure is high and the partitioning is shifted towards the particle phase, whereas at a higher dilution a higher fraction of the organic material will remain in the gas-phase. Oxidation in the MSC lowers the volatility of these compounds and makes them remain in the particle phase even at higher dilution ratios.

In other words, dilution tunnel measurements may reflect a PM emission factor that is closer to the atmospheric emission factor after aging. However, partitioning without oxidation can be affected by changes in dilution or temperature. A temperature difference of tens of degrees or a misadjustment in the dilution factor could result in drastically different emission factors. Oxidation in the MSC makes the sample robust against these changes. We have seen this in experiments performed on the same stove at similar conditions by changing the dilution ratio by up to a factor of four prior to exposure to UV light. This did not seem to affect the production of SOA.

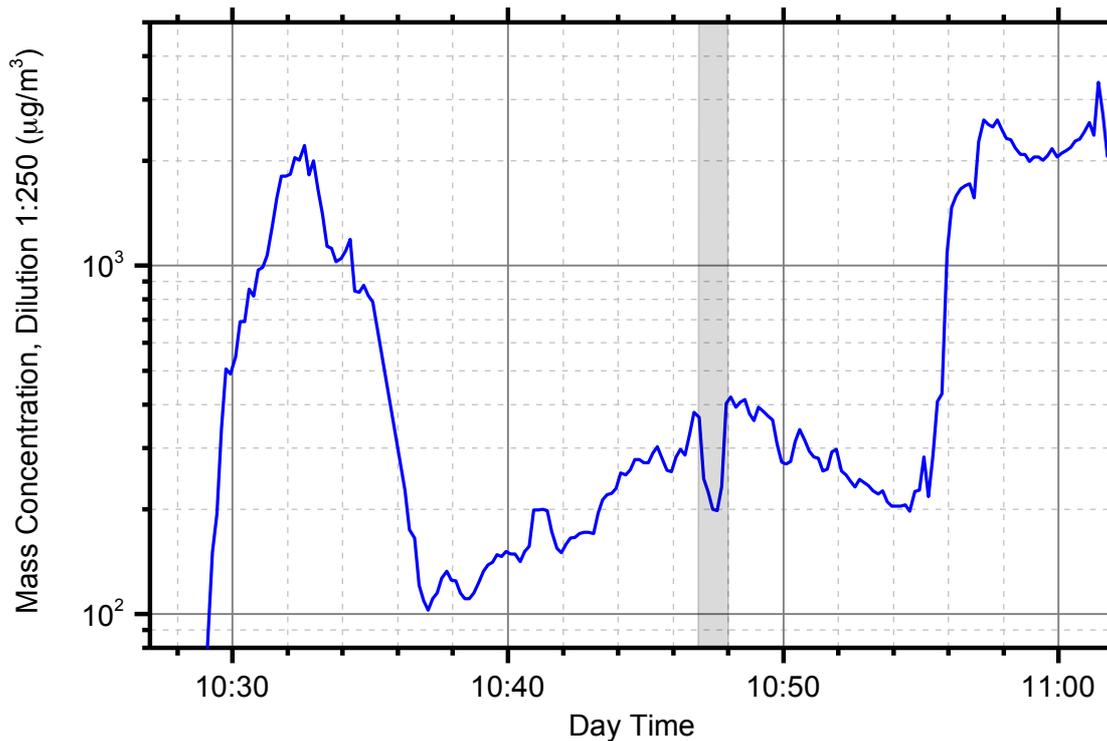


Figure 5.7 Real time particle mass concentration measured by means of a miniDiSC (assuming a particle density of 1200 kg/m³) for filter #7 of the logwood experiments (see Figure 5.6). For simplicity in the discussion, the data has not been corrected by dilution or O₂ content. The grey region in the figure shows a one minute interval during which the UV light of the MSC was turned off.

These results give us a better understanding of the production of SOA from the emissions modern combustion appliances. We have seen that the amount of total OC after oxidation is very close to the OC concentration prior to oxidation at room temperature and low dilution ratios (i.e. the CO₂ concentration $c(\text{CO}_2)$ was $1\% < c(\text{CO}_2) < 2\%$ during exposure to UV). This suggests that SOA from modern appliances comes mainly from hydrocarbons that are in the particle-phase under those conditions but are transported to the gas-phase at atmospheric dilution levels. This is also compatible with a series of observations made during far worse combustion situations by other groups. For instance, Robinson et al. (2007) made studies with diesel emissions and showed that at least 85% of SOA originates from the least volatile OGC-fraction (SOA almost doubled the total PM). The same group (Grieshop et al., 2009) observed a similar trend using a non-certified camping-tent stove. The PM increase due to SOA was almost 3-fold and came from non-traditional precursors (i.e. the authors speculate that low volatility vapors contribute to 85% of SOA). Vakkari et al. (2014) studied 60 biomass burning plumes (open fires) in southern Africa and observed significant changes on plume properties within the first 2-4 hours. The effect was enhanced in plumes with higher contribution from smoldering (i.e. higher contribution of pyrolysis). Both the fast changes and the higher contribution from smoldering suggest that low volatility species are causing this effect. Finally, Pieber et al. (2014) reported the reduction of SOA from wood burning using a catalyst. Their source was a certified 9 kW logwood stove. Already low catalyst temperatures ($\sim 200^\circ\text{C}$) cause a reduction of 50% OGC, which translates to 94% less SOA. This demonstrates that not all hydrocarbons have the same potential for building SOA.

Finally, we have performed measurements using an emissions conditioning system called NOSMOG (prototype developed by Hexmodul AG, Oekosolve AG and Salermo Engeler GmbH). NOSMOG is a multifunctional flue-gas conditioning system with particle-precipitation properties for biomass combustion in SCI. The system reduces the temperature of the flue-gas down to $\sim 50^{\circ}\text{C}$, affecting partitioning and therefore the emission of SOA precursors. Measurements performed on a logwood stove are shown on Figure 5.8. When the electrostatic precipitator (ESP) was operated at cold temperatures, the SOA production potential was decreased significantly, especially during the start-phase of the cycle. At low temperatures (in this case below 70°C), the raw gas partition is shifted towards the particle phase and, thus, the ESP is capable of removing the substances that would otherwise produce secondary organic aerosol. There was, however, no evident reduction of OGC due to the use of NOSMOG (Figure 5.8c). This suggests that NOSMOG removes only a small fraction of low-volatility OGC which is responsible for most of the SOA production. This is on the same line as our hypothesis that only a small fraction of low-volatility OGC is the main source of SOA precursors. As the system is heated up again (experiment 4 and Figure 5.8b), the captured low-volatility species will be resuspended and cause the production of SOA and a higher concentration of OGC is measured after the ESP.

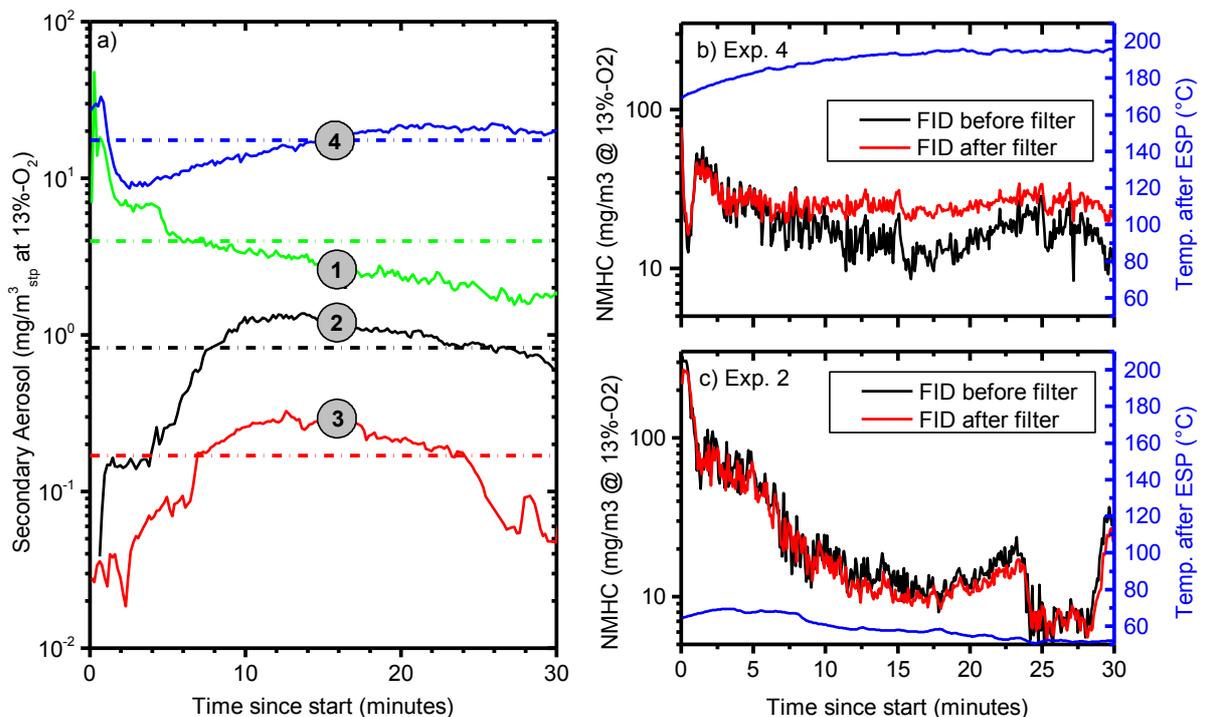


Figure 5.8 Secondary organic aerosol production potential during four warm start experiments of a 9 kW logwood stove and the NOSMOG system (a). The curves represent: 1) a warm start using only the electrostatic precipitator (ESP) but no cooling system, 2) and 3) two warm starts with a reduced temperature at the ESP, and 4) a final warm start using the NOSMOG system after turning off the ESP cooling. The dashed lines show the average SOA production potential for the 30 minutes measurement. Panels b) and c) show the concentrations of non-methane hydrocarbons, as measured by an FID, before and after the ESP and the raw gas temperature after the ESP for experiments 4 and 2 respectively.

Conclusions and outlook

The micro smog chamber produces SOA with an oxidation degree at the upper level of atmospheric observations within a few seconds. For overlapping OH exposures, the chemistry of SOA is similar to what is produced during smog-chamber experiments. Particle size, however, is smaller due to fast nucleation of low volatility organic species. Higher OH exposures still produce SOA with a reasonable chemical signature (fC₂H₃O⁺ vs fCO₂⁺ and O:C vs H:C), similar to atmospheric observations.

Most of the SOA emitted in modern appliances comes either during intervals where pyrolysis dominates the production of organic material or during high lambda operation. Even in these modern appliances SOA (measured at high dilution ratios) can multiply the total emissions several fold. The least-volatile VOC-fraction from wood burning emissions contributes the most to SOA formation. We have indications that this is also the case for automatic appliances.

Sampling at high concentrations and low temperatures (e.g. dilution tunnel) will capture more organic carbon than samples collected using heated gravimetric filters or at atmospheric dilution levels. UV treatment in the MSC reduces the volatility of the sample and makes it robust against differences in temperature or dilution factor.

The fact that most of these SOA precursors are in the particle phase at high concentrations and low temperatures can be used to construct systems, like NOSMOG, that target the secondary emissions. Rinsing the organic material (deposited in the ESP) and maintaining a low temperature is crucial for efficient removal of SOA precursors.

Finally, total carbon analysis could be used as an alternative metric for particulate matter emissions from wood burning appliances. SOA production potential can be included in the metric by means of photo-oxidation of the emissions using, e.g., the micro smog chamber. For this purpose, we are currently developing an automatic TC analysis system to be use on site at the laboratory as well as during field measurements.

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