



STUDY ON ALCOHOL-POWERED FLUELESS FIREPLACE COMBUSTION AND ITS EFFECTS ON INDOOR AIR QUALITY

Final Report



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ABSTRACT	11
1 INTRODUCTION	12
1.1 ETHANOL AS A FUEL	12
1.2 THE COMBUSTION PROCESS IN DOMESTIC APPLIANCES	13
1.3 AIR NEED AND VENTILATION	13
1.4 INDOOR AIR QUALITY GUIDELINES	17
1.5 INDICATIONS ABOUT POSSIBLE HAZARDS	24
1.6 FACTORS AFFECTING EXPOSURE TO COMBUSTION PRODUCTS	26
2 CHARACTERISTICS OF ALCOHOL-POWERED FLUELESS APPLIANCES	28
2.1 TECHNICAL AND AESTHETIC CHARACTERISTICS	28
2.2 SELECTION CRITERIA OF THE TESTED APPLIANCES	30
2.3 DESCRIPTION OF THE APPLIANCES	31
3 COMMERCIAL ALCOHOL-BASED FUELS	34
3.1 COMPOSITION AND DENATURATION OF LIQUID ETHANOL	34
3.2 GEL FUELS: CHARACTERISTICS AND USES	34
3.3 FUEL-APPLIANCE MATCHING	35
3.4 SELECTED FUELS	35
4 POLLUTANTS EMITTED FROM ETHANOL COMBUSTION	40
4.1 EXPERIMENTAL TESTS ON SELECTED APPLIANCES	40
4.1.1 DIRECT COMBUSTION TESTS	40
4.2 CORRELATIONS BETWEEN EMISSION FACTORS AND FUELS/APPLIANCES	54
4.3 EXPERIMENTAL TESTS IN A SEALED CHAMBER	57
5 EFFECTS ON INDOOR AIR QUALITY	59
5.1 EXPERIMENTAL TESTS IN A VENTILATED CHAMBER	59
5.1.1 RESULTS	61
6 PREDICTIVE MODELLING OF INDOOR AIR QUALITY AND ROOM VENTILATION	79
6.1 BASIC PRINCIPLES OF NUMERICAL MODELLING	79
6.2 DEVELOPMENT OF A PREDICTIVE MODEL	79
6.3 MODEL VALIDATION	81
6.4 EFFECTS OF VENTILATION	83

7	CONCLUSIONS	86
8	RECOMMENDATIONS	88
9	GLOSSARY	90
10	REFERENCES	92
	ANNEX A - EXPERIMENTAL RESULTS	94
	ANNEX B - SUMMARY OF INTERNATIONAL AIR QUALITY STANDARDS AND GUIDELINES	106
	ANNEX C - PREDICTIVE MODELLING OF INDOOR AIR QUALITY AND ROOM VENTILATION (IN EXCEL FORMAT)	107
	ANNEX D - WELL MIXED ROOM MODEL: USER'S GUIDE	108

List of Figures

Figure 1 Physical-chemical properties of the selected fuels.....	36
Figure 2 Further physical-chemical properties of the selected fuels	36
Figure 3 IR spectra of the three gels (see peaks in the spectral region 1100-1180 cm ⁻¹).....	37
Figure 4 Weight loss vs time (@50°C) for the investigated fuels	38
Figure 5 Device used for hob gas tests according to EN 30-1-1:2008	40
Figure 6 IR images of: a) appliance A b) appliance B c) appliance C d) appliance D e) appliance E and f) appliance F	41
Figure 7 Temperature decrease after switching off appliance E	42
Figure 8 CO and NO _x average emissions in direct analysis of combustion tests.....	45
Figure 9 TOC average emissions in direct analysis of combustion tests	47
Figure 10 CO and NO _x average values for fuels and appliances	48
Figure 11 TOC average values for fuels and appliances.....	49
Figure 12 Repeatability of direct combustion tests, for appliance E.....	51
Figure 13 Variability of different fuels tests, for appliance E	51
Figure 14 Repeatability of direct combustion tests, for appliance A (as a function of time)	52
Figure 15 Variability of different fuels tests, for appliance A (as a function of time)	52
Figure 16 Main results of Sealed Chamber tests performed with the investigated appliances (as a function of time)	57
Figure 17 Results of CFD simulations representing the temperature distribution inside the test chamber without (left) and with (right) a fan to promote mixing of the internal air	59
Figure 18 PM trends during a typical test (as a function of time).....	61
Figure 19 Repeatability of ventilated chamber test (appliance E)- (as a function of time).....	62
Figure 20 Variability with fuels in ventilated chamber tests (appliance E) – (as a function of time).....	62
Figure 21 CO level in ventilated chamber tests in the first cycle.....	64
Figure 22 CO level in ventilated chamber tests in the OFF cycle.....	65
Figure 23 CO level in ventilated chamber tests in the second cycle	66
Figure 24 NO _x level in ventilated chamber tests in the first cycle.....	67
Figure 25 NO _x level in ventilated chamber tests in the OFF cycle.....	68
Figure 26 NO _x level in ventilated chamber tests in the second cycle.....	69
Figure 27 CO ₂ level in ventilated chamber tests in the first cycle	70
Figure 28 CO ₂ level in ventilated chamber tests in the OFF cycle.....	71
Figure 29 CO ₂ level in ventilated chamber tests in the second cycle.....	72
Figure 30 Carbonylic compounds in ventilated chamber tests (active sampling)	74
Figure 31 Carbonylic compounds in ventilated chamber tests (passive sampling).....	75
Figure 32 VOCs in ventilated chamber tests: comparison of the different appliances and the blank (which refers to the empty chamber with no appliances)	76
Figure 33 Effect of ventilation on VOC	77
Figure 34 Effect of changing fuel	77
Figure 35. Sketch of a representative scenario for the exposure assessment (well-mixed environment)	80
Figure 36 Comparison of experimental results and perfectly mixed model predictions on selected cases: Blue, Black and Green lines represent the experimental trends of CO, NO _x and CO ₂ , respectively; Red lines represent the corresponding model profiles.....	81
Figure 37 Average concentration values obtained for different fuels and appliances: comparison of experimental and model predictions.....	82
Figure 38 Effect of ventilation on CO ₂ concentration, estimated through the well mixed model.....	83

Figure 39 Comparison of experimental tests at different ventilation rates on the B appliance	84
Figure-A 1 Summary of direct combustion test for appliance A	93
Figure-A 2 Summary of direct combustion test for appliance B	94
Figure-A 3 Summary of direct combustion test for appliance C	95
Figure-A 4 Summary of direct combustion test for appliance D	96
Figure-A 5 Summary of direct combustion test for appliance E	97
Figure-A 6 Summary of direct combustion test for appliance F	98
Figure-A 7 Gas concentration in ventilated chamber test, for appliance A.....	99
Figure-A 8 Ultrafine particles concentration in ventilated chamber test, for appliance A	99
Figure-A 9 Gas concentration in ventilated chamber test, for appliance B	100
Figure-A 10 Ultrafine particles concentration in ventilated chamber test, for appliance B	100
Figure-A 11 Gas concentration in ventilated chamber test, for appliance C.....	101
Figure-A 12 Ultrafine particles concentration in ventilated chamber test, for appliance C	101
Figure-A 13 Gas concentration in ventilated chamber test, for appliance D.....	102
Figure-A 14 Ultrafine particles concentration in ventilated chamber test, for appliance D	102
Figure-A 15 Gas concentration in ventilated chamber test, for appliance E	103
Figure-A 16 Ultrafine particles concentration in ventilated chamber test, for appliance E.....	103
Figure-A 17 Gas concentration in ventilated chamber test, for appliance F	104
Figure-A 18 Ultrafine particles concentration in ventilated chamber test, for appliance F.....	104

List of Tables

Table 1 Summary of stoichiometric exhausts data	14
Table 2 Summary of exhausts data at 1% O ₂ in the dry fumes	14
Table 3 Air supply requirements for solid fuel appliances in England and Wales	16
Table 4 Specification of the investigated fireplaces and fuel samples (Schrupp et al., 2014)	18
Table 5 Summary of the results in terms of main combustion products and by-products, total organic carbon (TOC), formaldehyde and particle number concentration (PNC) obtained during the burning phase (Schrupp et al., 2014).	20
Table 6 Selection of recommended guideline values	21
Table 7 List of common denaturants used in different EU countries (all values are indicated for 1 litre of pure alcohol)	22
Table 8 Concentrations of CO, CO ₂ and NO _x measured in indoor air by Guillaume et al. (2013). Bold values are over the limits admitted by the French standard INRS ED 984.	22
Table 9 Concentrations of aldehydes measured in indoor air by Guillaume et al. (2013). Bold values are over the limits admitted by the French standard INRS ED 984.	23
Table 10 Ethanol-powered Appliances and Burn Hazards	24
Table 11 Ethanol-powered appliances and possible carbon monoxide Intoxication Hazards	25
Table 12 Ethanol-powered appliances and possible VOC Intoxication Hazards.....	25
Table 13 Experimental array for appliances/fuels combinations	30
Table 14 Main characteristics of the selected appliances	32
Table 15 Denaturing formulas for selected liquid ethanol fuels.....	35
Table 16 Physical-chemical properties of the selected gel fuels	35
Table 17 Emission factors for appliances and fuels	54
Table 18 Mass Fluxes for appliances and fuels	55
Table 19 Examples of emission factors for different class of combustion devices from Migliavacca et al (2006), Marengo et al (2009) and Derudi et al. (2012)	55

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ABSTRACT

The aim of this document is to provide an evidence base to inform and guide policy development for the use of flueless ethanol-fuelled appliances. The document reviews the data for the levels of pollutants produced by these burners or fireplaces, and summarises the evidence for an association between use of these appliances and adverse health outcomes (based on a review of the scientific literature).

The purpose of the study has also been to conduct laboratory experiments in order to:

- determine the emissions into indoor air due to different models of alcohol-powered flueless fireplaces; the study has comprised five models of alcohol-powered flueless fireplaces of different heat outputs burning six varieties of ethanol fuel (half in liquid and the other half in gel form) under conditions of proper and of poor ventilation.
- elaborate and validated a calculation model for emissions of combustion products based on the laboratory experiments
- interpret the results against existing exposure limit values identified during the review of the scientific literature and technical regulations.

This document provides general information about alcohol fireplaces, their characteristics and use, as long as specific original data produced by a laboratory work performed in the framework of this study.

1 INTRODUCTION

1.1 Ethanol as a fuel

Ethanol is a chemical compound, also known as ethylic alcohol, constituted of carbon, hydrogen and oxygen; like any other organic compound it can react with molecular oxygen, producing carbon dioxide and water. This oxidation process is the combination of several chemical reaction and is globally exothermic, for this reason, ethanol can be used as a fuel in many different applications. The main one is presently in the automotive sector as a substitute or additive of gasoline.

Ethanol for industrial and domestic uses has been produced for decades starting from crude oil through petrochemical processes. On the contrary, the biological fermentation of vegetal materials (grapes, wheat, malt, ...) was limited, in the past, to the production of alcoholics for the human consumption. Nowadays large amounts of bio-ethanol are produced in the world, by means of the industrial fermentation of biomasses, in order to get a renewable fuel for the energy applications.

In this sector bio-ethanol is referred to as first generation, when produced from corn, wheat or other plant species used in the human alimentation, while it is named second or third generation bio-ethanol when it is produced starting from ligno-cellulosic biomasses or waste materials that are not in competition with the food supply chain. Many doubts exist about the actual sustainability of first generation bio-ethanol, mainly due to the large amount of carbon dioxide equivalent emitted in the cultivation phase of the raw materials used, so a massive switch to second and third generation bio-fuels is expected in the next decade.

As previously stated, the main use of ethanol as a fuels is in the automotive sector, because it has suitable characteristics to replace partially or totally gasoline in the internal combustion engines. For this specific application the chemical and physical properties of the fuel must comply with the European quality Standards defined in two European Standards (CEN/TS 15293, 2011) and (EN 15376, 2011), mainly to prevents problems of compatibility with the constructive materials used in the vehicles.

The other fuel uses of ethanol are very limited in terms of total consumptions, even though an increasing diffusion in the market of fireplaces and other household appliances for aesthetic purposes has been reported in Europe and other industrialized countries. These applications are limited by the high cost of the fuel, compared with its direct competitors like wood pellet and logs, but the increasing availability of bio-ethanol in the fuel market, to comply with the renewable energy targets, might change the future situation.

1.2 The combustion process in domestic appliances

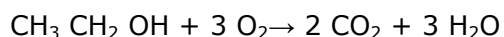
Most domestic combustion appliances, used for cooking (hobs, cookers,...), heating (boilers, stoves, fireplaces, space heaters,...) or aesthetic purposes are based on the direct combustion of the fuel with ambient air, producing a flame. This flame may be confined in a closed or open combustion chamber, provided with a burner or without it. The main role of the burner, when present, is to supply the correct amount of fuel and air and mixing them in order to maintain the optimal combustion conditions. Under these conditions the maximum efficiency of combustion and the minimum production by-products due to incomplete combustion are achieved. Many different burner configurations have been developed for gaseous, liquid and even solid fuels (wood pellet). Where a burner is not present the fuel burns freely until all the fuel loaded is consumed. In these cases the flame is largely uncontrolled, since the air supply only is responsible for the combustion rate and this parameter is generally fixed or only manually controlled by the user.

Any real combustion process, produces not only carbon dioxide (CO_2) and water (H_2O), as indicated by the theoretical combustion reactions, but they also produce other chemical species often responsible for pollution and detrimental effects on the human health. Among them carbon monoxide (CO), nitrogen and sulphur oxides (NO_x , SO_x), volatile organic compounds (VOC), polycyclic aromatic hydrocarbons (PAH), polychlorodibenzodioxines and furanes (PCDD-PCDF), heavy metals and particulate matter (PM) are the most relevant and potentially harmful.

The nature and quantity of the pollutants produced depends on many factors related to the composition of the fuel, the characteristics of the appliance and the service behaviour and maintenance. The composition of the fuel determines the possibility of formation of some species, for instance a fuel not containing sulphur cannot produce SO_x while if it does not contain chlorine PCDD-PCDFs are not formed and a fuel without metal compounds cannot generate metals in the fuel gases. Besides the chemical composition, also the physical state of the fuel influences its combustion behaviour and eventually its reaction products. For example, gaseous fuels are easily mixed with air and burn directly through gas phase reactions, while liquid and solid fuels have to be vaporized before combustion takes place. The configuration of the appliance is equally important in determining the amount of pollutants produced through combustion. The appliance design controls the conditions of combustion in terms of fuel/air ratio, temperature, residence time of the fumes in the combustion zone, mixing and turbulence; all these aspects have a strong effect on the combustion process and the mechanisms of formation. For example, a reduced oxygen concentration and/or a low temperature produce high amounts of carbon monoxide, while high temperatures enhance the synthesis of nitrogen oxides. An extensive description of the complex mechanisms of formation of the different pollutants is highly technical and outside the scope of this report, specific notes about them will be provided in the text when necessary.

1.3 Air need and ventilation

As already described, the combustion process of hydrocarbons consists of several chemical reactions producing the overall oxidation of the carbon and hydrogen content of the fuel to carbon dioxide and water. In the case of ethanol, the global reaction is expressed as follows:



1

This stoichiometric equation gives the theoretical amount of oxygen required to completely oxidize a molecule of ethanol, this amount is 3 molecules of oxygen, producing 2 molecules of carbon dioxide and 3 of water. This is a theoretical relation, because in practice much more oxygen is required to have a good and complete combustion process, the actual excess air needed to burn a specific fuel in a particular combustion appliance is a fundamental parameter to be found by the manufacturer of the appliance, by the installer and even by the final user, when adjustments on site are possible. Besides this, it is also important to bear in mind that the most conventionally used oxidizer is not pure oxygen but air, and air consists of only 21% of oxygen and about 79% of nitrogen. This nitrogen “dilutes” the combustion products and reduces the temperature of combustion, but it is also responsible for the formation of nitrogen oxides, which are formed at high temperatures of the flame even if the fuel does not contain nitrogen.

In **Table 1** and **Table 2** the main data calculated directly from reaction stoichiometry are reported. In particular, Table 1 summarizes the flow rate and composition of the exhaust gases produced by burning 0.5 kg/h of ethanol, which is the average consumption rate of alcohol fireplace, in air at stoichiometric conditions; in these conditions the concentration of CO₂ is 12.2%, but it becomes 15% when reported to dry basis, that means after elimination of the water content. This parameter is important because most limit values, used in the national standards, are referred to the 15% of CO₂ in the dry flue gases just for this reason. In **Table 2** the same data are calculated for a CO₂ concentration in the fumes equal to 1% (on dry basis), this means that the amount of air supplied for combustion is greater than the minimum required by stoichiometry, and enough to reduce the concentration of CO₂ at only 1%. This parameter is important as well, because the French and Italian standards refer to this value as testing conditions for alcohol fuelled appliances.

Table 1 Summary of stoichiometric exhausts data¹

Stoichiometric exhausts from 0.5 kg/h ethanol					
Air flow rate		(Nm ³ /h)	3.52	(Nm ³ /GJ)	251.4
		(kg/h)	4.50	(kg/GJ)	321.7
Exhausts flow rate		(Nm ³ /h)	4.00	(Nm ³ /GJ)	28.6
		(kg/h)	5.00	(kg/GJ)	357.4
Average Molecular Weight		(g/mol)	28.01		
Density		(kg/Nm ³)	1.25		
Exhausts composition			Flow rates		
		mg/Nm ³	kg/h	Nm ³ /h	kg/GJ
CO ₂ (%)	12.2	238710	0.956	0.487	68.3
H ₂ O (%)	19.5	156638	0.627	0.780	44.8
N ₂ (%)	68.3	854313	3.421	2.737	244.3

Table 2 Summary of exhausts data at 1% O₂ in the dry fumes

Exhausts from 0.5 kg/h ethanol at			1% CO ₂ (dry basis)			
			1310.63	% excess air		
Air flow rate		(Nm ³ /h)	49.70	(Nm ³ /GJ)	3549.9	
		(kg/h)	63.59	(kg/GJ)	4542.4	
Exhausts flow rate		(Nm ³ /h)	50.18	(Nm ³ /GJ)	3584.5	
		(kg/h)	64.09	(kg/GJ)	4578.1	
Average Molecular Weight		(g/mol)	28.63			
Density		(kg/Nm ³)	1.28			
Exhausts composition			Flow rates			
			mg/Nm ³	kg/h	Nm ³ /h	kg/GJ
CO ₂ (%)	1.0	19046	0.956	0.487	68.3	
H ₂ O (%)	3.0	24102	1.21 ²	1.50	86.4	
N ₂ (%)	77.0	962502	48.3	38.6	3450	
O ₂ (%)	19.0	271524	13.62	9.54	973	

In real combustion appliances the way the air is supplied is as important as the quantity of air supplied, in fact only the air entering directly in the flame zone (primary air), or just downstream of the flame (secondary air) are involved in the combustion process, while any further air supplement, added in the low temperature region, simply dilutes the fumes, but it does not interact chemically with the combustion products in the short time. Secondary reactions, involving the pollutant species emitted from combustion, may happen in the atmosphere in a longer range of time.

Many strategies have been developed in combustion engineering to optimize the injection and mixing of air in the flame zone, in order to maximize the combustion efficiency and minimize the pollutants formation. These strategies often involve the

¹ Nm³ stands for m³ of gas in normal conditions (273 K, 101325 Pa)

² The value includes the moisture content of ambient air (50%RH)

configuration of the burner and design of the combustion chamber and in most advanced appliances, they include automatic control devices.

Once the combustion products have been released in the ambient, they are mixed with the room air; then the concentration of the different species in the room depends on the flow rate of each compound, produced by the appliance, the dimension of room and the air exchange rate (AER). These concentrations vary in time with a rate depending on each of the aforementioned parameters. The composition of the indoor air is not generally uniform throughout the room, since in the real life a room is not perfectly mixed. Convective flows, produced by differences in the local density of the air, may create vertical gradients of temperature and composition: hot and light gases move up to the ceiling, while cold and heavy gases move down towards the ground. These flows induce some circulation of the indoor air that can be modified by any obstacle in the room; all these aspects may create zones of different composition inside the same room.

The two aspects here described, the need for combustion air and the room ventilation, have to be linked together in order to analyse the situation produced in a room where a flueless combustion appliance is working. Combustion subtracts oxygen from the room air, producing mainly carbon dioxide and water vapour, along with some pollutant species, in the same time it releases heat in the room, increasing the inside temperature. Hence, ventilation must supply enough air to replace the oxygen consumed by the combustion process, the fresh air entering the room cools down the indoor atmosphere and reduces the inner concentration of combustion products, that are drained out of the room along with the vitiated air, which is progressively replaced by the fresh one.

Most domestic combustion appliances are connected to a stack in order to convey the flue gases outside, but they often get the needed combustion air from inside the room, then the technical standards, in these cases, only require a vent, connecting the room with the outdoor atmosphere, large enough to supply the air for combustion, according to the power of the appliance. In those few cases of flueless appliances, like hobs, catalytic space heaters and alcohol fireplaces, a major attention should be devoted to the accumulation of harmful species, affecting the indoor air quality. For example, for gas appliances, the following relation (UNI 7129-2, 2008) can be used to calculate the size of the vent in a room where an appliance of power Q is installed:

$$S = K \cdot Q \geq 100 \text{ cm}^2 \quad 2$$

where:

S = area of the vent in cm^2 (it must be greater than 100 cm^2 in any case)

K = ventilation coefficient equal to $6 \text{ cm}^2/\text{kW}$

Q = power in kW

Other national regulations define the minimum ventilation requirements for a room where combustion appliances are installed in terms of vent dimension. For example the Approved Document on Combustion appliances and fuel storage system, a document

issued to provide practical guidance on ways of complying with Building Regulations 2000 (SI2000/2531) for England and Wales, reports the following table (**Table 3**) to define the minimum vent dimensions for appliances burning solid fuels with a rated output up to 50 kW.

Table 3 Air supply requirements for solid fuel appliances in England and Wales

Table 1 Air supply to solid fuel appliances				
Type of appliance	Type and amount of ventilation (1)			
Open appliance, such as an open fire with no throat, e.g. a fire under a canopy as in Diagram 23.	Permanently open air vent(s) with a total equivalent area of at least 50% of the cross sectional area of the flue.			
Open appliance, such as an open fire with a throat as in Diagrams 22 and 29.	Permanently open air vent(s) with a total equivalent area of at least 50% of the throat opening area. (2)			
Other appliance, such as a stove, cooker or boiler, with a flue draught stabiliser.	Permanently open vents as below: If design air permeability $>5.0\text{m}^3/(\text{h.m}^2)$ then 300mm ² /kW for first 5kW of appliance rated output 850mm ² /kW for balance of appliance rated output If design air permeability $\leq 5.0\text{m}^3/(\text{h.m}^2)$ then 850mm ² /kW of appliance rated output (4)			
Other appliance, such as a stove, cooker or boiler, with no flue draught stabiliser.	Permanently open vents as below: If design air permeability $>5.0\text{m}^3/(\text{h.m}^2)$ then 550mm ² /kW of appliance rated output above 5kW If design air permeability $\leq 5.0\text{m}^3/(\text{h.m}^2)$ then 550mm ² per kW of appliance rated output (4)			
Notes:				
1. Equivalent area is as measured according to the method in BS EN 13141-1:2004 or estimated according to paragraph 1.14. Divide the area given in mm ² by 100 to find the corresponding area in cm ²				
2. For simple open fires as depicted in Diagram 29, the requirement can be met with room ventilation areas as follows:				
Nominal fire size (fireplace opening size)	500mm	450mm	400mm	350mm
Total equivalent area of permanently open air vents	20,500mm ²	18,500mm ²	16,500mm ²	14,500mm ²
3. Example: an appliance with a flue draught stabiliser and a rated output of 7kW would require an equivalent area of: $[5 \times 300] + [2 \times 850] = 3200\text{mm}^2$				
4. It is unlikely that a dwelling constructed prior to 2008 will have an air permeability of less than $5.0\text{m}^3/(\text{h.m}^2)$ at 50 Pa unless extensive measures have been taken to improve air-tightness. See Appendix F.				

1.4 Indoor air quality guidelines

Both indoor and outdoor sources, including room users behaviour and activities, affect the concentration and composition of pollutants in indoor air. It is usually easier to find information on emission characteristics of outdoor pollutants sources (Estrellan and Iino, 2010) than of indoor ones. However, the quantification of emissions from indoor sources is of paramount importance for assessing the human exposure to pollutants (Ott and Siegmann, 2006). The most significant sources, for indoor environments, include tobacco smoking, cooking, kerosene heating, candles and/or incense use, as well as wood burning (Derudi et al., 2012; Derudi et al., 2014, Tuckett et al., 1998; Fan and Zhang, 2001). Combustion processes are the main indoor sources of both smaller particles and different gaseous pollutants; these products play an important role because they can affect directly the human health or they can act as precursors of secondary particles in the indoor environment, through the process of gas-to-particle conversion (Rohr et al., 2003).

A alcohol fireplace is a type of fireplaces and furnaces with combined zones generation of heat and technological process-combustion of fuel (denatured alcohol). According to

manufacturers, this kind of fireplaces does not require a chimney and their installation is possible at any point in a room. The main part of each bio fireplace is the burner, typically realized by a simple metal container whose shape and dimensions may be different (Bertagna et al., 2013). The burner is filled with fuel, usually it is bioethanol. Fuel is poured into the burner and lit with an extended candle lighter as suggested. These fireplaces are available in several different designs: wall-mounted design can be built into a drywall wall or recessed; free standing or stand-alone ethanol fireplaces are portable and can be used in any architectural setting, including indoors and out. Table-top ethanol fireplaces are also available; they represent the smallest versions of ethanol fireplaces.

In principle, a chemically complete combustion of the fuel is expected by the manufacturers, so “only” carbon dioxide (CO₂) and water should be the products of the combustion process. As a matter of fact, considering the poor design of the burner, the typical absence of fans to promote forced ventilation or devices to check the degree of mixing within air and fuel vapours in the core of the appliances, the possibility that different pollutants could be produced due to incomplete combustion conditions and released into indoor environments cannot be neglected.

Schripp et al. (2013) evidenced that alcohol fireplaces can be a strong source for ultrafine particles (UFP), even though they show no significant visible smoke; in particular the authors performed a series of experimental tests within a stainless steel ventilated room of 48 m³ (according to DIN 4734-1) aimed at analysing the emissions by different fireplaces fed with a series of liquid and gel fuels mainly constituted by ethanol. According to the analysed appliances, the burning phase lasted between 70 and 240 min; the emissions were monitored during and until 12 h after a single burning phase by means of several online detectors (for CO₂, CO, NO_x, formaldehyde and particles) and offline methods (for VOC, Volatile Organic Compounds). It was found that the operation of ethanol fireplaces can significantly affect the air quality into the test chamber. During the tests, with some appliances, the German guideline values for CO₂ (2000 or 1000 ppm, considered as hygienically unacceptable and hygienically conspicuous, respectively) and NO₂ (350 µg/m³) were exceeded. Due to the high flame temperatures, always approx. 1000°C, which affects a direct oxidation of the atmospheric nitrogen according to the thermal-NO_x mechanism, a continuous formation and release of NO and NO₂ was observed, thus resulting in an unavoidable exceedance of the NO₂ limit of all the investigated appliances (Schripp, 2013). Some systems showed also a relevant release of formaldehyde.

About UFP emissions, the authors highlighted that the devices were not constant emitters of particles, showing large differences between different cycles; the average diameter of the detected particles was in the range 10-65 nm, that is a typical dimension for organic soot produced by furnaces and ovens during incomplete combustion processes. This low particles size, also in the case of secondary growth of the particles due to electrostatic phenomena, coagulation or gas-solid reactions, allows deep lung penetration down to the alveolar region. For the air stream containing such UFP, it was estimated that about 60% of the total lung particle deposition can occur in the lower alveoli, thus creating a possible health problem in the case of frequent exposures to this environment.

The same authors (Schripp et al., 2014) studied also the influence of different fireplaces and fuels (3 liquid samples, 5 gel-type samples) on the pollutants emissions in a 48 m³ test chamber, as summarized in **Table 4**.

Main results obtained in the above-mentioned experimental campaign are reported in **Table 5**.

A relevant number of both national and international guideline values are available for evaluating the concentrations measured; a selection of these limits is reported in **Table 6**. With reference to these limits, the authors evidenced that the use of ethanol fireplaces did not exceed the limits for CO in all the experiments, while NO_x emissions were always above the limit; this can be ascribed also to the fact that some nitrogen-containing species can be present in the denaturizing agent or into other components of the fuels, as underlined by the typical features of several denaturants of **Table 7** (Guillaume et al., 2013).

Table 4 Specification of the investigated fireplaces and fuel samples (Schripp et al., 2014)

sample	ID	max. filling capacity [mL]	heating value ^a [kJ/kg]	min. room volume ^b [m ³]	comments ^b
fireplace 1	O1	580	-	66	150 min max. operation time
fireplace 2	O2	150	-	66	70 min max. operation time
fireplace 3	O3	500	-	~90 ^c	-
fireplace 4	O4	240	-	~45	-
ethanol 1	E1	-	22052	-	"organic ethanol" (98.2%); contains ethanediol (1.8%)
ethanol 2	E2	-	23570	-	"organic ethanol" (94%)
ethanol 3	E3	-	24505	-	"organic ethanol" (94%); contains 2-butanone (MEK) and denatonium benzoate
gel 1	G1	-	22600	-	"organic ethanol"
gel 2	G2	-	20770	-	"organic ethanol"; contains isopropyl alcohol
gel 3	G3	-	20550	-	"organic ethanol"; contains isopropyl alcohol, dye and thickening agent
gel 4	G4	-	25797	-	"organic ethanol"; contains isopropyl alcohol
gel 5	G5	-	20023	-	"organic ethanol"; contains isopropyl alcohol

^aMeasured according DIN 51900-1 and DIN 51900-2.

^bFrom the manual of the device/fuel.

^cEstimated from the minimum room area specification of 35–40 m².

Moreover, it was highlighted that the predominant emissions released from the ethanol fireplaces are VOCs; in some cases, a direct emission of the denaturing agent was

detected into the test room (i.e., 2-butanone). For gel-based fuels, significant emission of 2-propanol were usually detected, while these emissions were not present for the liquid fuels. Several oxygenated species were also detected into the exhausts and this was not unexpected; the fact that formaldehyde, in particular, is produced when alcohol is burnt is a known phenomenon and has led to countries which use large amounts of ethanol (i.e., for road vehicles) having outdoor air formaldehyde concentrations higher than the indoor levels (Salthammer, 2013); the maximum formaldehyde values were for some configurations, in terms of type of fireplace and kind of fuel tested, significantly above the WHO recommended values.

A similar study, with the aim to assess the impact of ethanol fireplaces on indoor air quality has been also carried out in a 37.5 m³ test chamber by Guillaume et al. (2013) at an air exchange rate (AER) of 0.4 h⁻¹. They measured the release of VOC, CO₂, CO and nitrogen oxides from 4 ethanol appliances, performing also some experiments in which the exhausts were directly sampled and analysed at the exit of the different equipment. Apart from the characterization of the emissions during both the burning and the extinguishment phase, whose results are summarized in Table 8 and Table 9, the authors evaluated also the risks of flash and burn injuries; different risks have been identified concerning heat injuries during the combustion or refill of the fireplace, basically confirming the hazardous conditions defined by other studies (Kraemer et al., 2011; http://www.cotemaison.fr/energie-chauffage-climatisation/on-a-teste-la-cheminee-ethanol_5371.html, Commission de la sécurité des consommateurs, 2008).

Different problems concerning the unsafe structure of some fireplaces and the eventual lack of warnings and markings on several of these products have been also recorded in the RAPEX (Rapid Alert System for non-food dangerous products) notifications database in the last few years (2015, http://ec.europa.eu/consumers/consumers_safety/safety_products/rapex/index_en.htm).

Table 5 Summary of the results in terms of main combustion products and by-products, total organic carbon (TOC), formaldehyde and particle number concentration (PNC) obtained during the burning phase (Schrupp et al., 2014).

Parameter		E101	E201	E301	E302	G103	G203	G303	G404	G503
air exchange [h⁻¹]		0.69	0.69	0.69	0.69	0.91	0.91	0.91	0.43	0.91
burning time [h]		1.70	1.40	1.45	1.20	3.10	2.60	3.20	2.50	2.80
applied fuel [mL]		500	500	500	150	500	500	500	240	500
fuel consumption [mL/h]		294	357	345	125	161	192	156	96	179
NO [ppm]	max	0.60	0.31	0.22	0.17	0.40	0.26	0.33	0.23	0.30
	min	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	mean	0.11	0.01	0.06	0.02	0.06	0.01	0.02	0.01	0.01
	exp. (0.5 h)	0.56	0.27	0.21	0.15	0.39	0.25	0.32	0.22	0.29
NO₂ [ppm]	max	0.84	1.27	1.59	0.40	0.36	0.31	0.29	0.40	0.41
	min	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	mean	0.16	0.04	0.45	0.04	0.06	0.02	0.02	0.02	0.02
	exp. (0.5 h)	0.79	1.11	1.40	0.36	0.36	0.29	0.28	0.38	0.40
NO_x [ppm]	max	1.45	1.57	1.78	0.57	0.74	0.51	0.57	0.63	0.71
	min	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	mean	0.27	0.05	0.50	0.06	0.12	0.03	0.03	0.04	0.03
	exp. (0.5 h)	1.35	1.40	1.57	0.50	0.73	0.50	0.56	0.61	0.69
CO [ppm]	max	8.6	14.2	16.5	4.6	9.3	9.4	12.0	7.1	5.8
	min	0.3	0.2	0.6	0.4	0.3	0.4	0.3	0.5	0.3
	mean	5.0	9.0	9.4	2.6	3.7	4.1	4.2	4.0	2.8
	exp. (0.5 h)	6.9	12.9	15.1	3.8	6.5	7.5	8.6	5.9	3.9
	exp. (1 h)	6.2	11.1	12.1	3.2	5.7	6.3	7.2	5.5	3.6
CO₂ [ppm]	max	5124	5899	5637	2239	3717	3364	3396	2890	3303
	min	504	488	513	501	458	550	492	514	466
	mean	3620	4060	3801	1589	2941	2579	2736	1988	2563
TOC^a [ppm]	max	3.7	7.3	14.4	2.3	4.4	15.8	5.7	9.8	12.0
	min	0.7	2.9	2.1	0.4	0.4	0.7	0.3	1.3	2.0
	mean	3.1	5.7	9.2	1.5	1.3	1.6	0.7	7.2	7.6
formaldehyde [ppb]	max	210	456	35	n.d.	129	177	202	67	47
	min	0.4	7.8	<0.1	n.d.	9.6	9.2	8.8	4.6	4.3
	mean	131	259	17	n.d.	56	60	54	39	36
benzene [ppb]	BP ^b	0.6	3.7 ^d	12.7	1.2	0.3 ^d	4.0	0.6	16.1	0.9
	FP ^c	1.2	2.8 ^d	14.3	1.9	2.2 ^d	10.2	3.7	10.5	8.1
PNC [# /cm³]^e 5–560 nm	max	671000	483000	2250000	6190	353000	405000	1320000	214000	366000
	min	551	2100	686	745	241	5730	1510	993	754
	mean	441336	192616	1166485	4441	36891	44794	224064	29638	33072
PNC [# /cm³]^f 0.3–20 µm	max	3.3	10.2	13.4	4.3	18.7	9.3	9.5	10.6	10.1
	min	1.4	2.6	7.5	2.5	2.0	2.3	2.1	4.2	2.1
	Mean	2.0	6.1	9.9	3.3	6.1	4.5	3.7	7.8	4.1

^aReference: propane.

^bBP: burning phase.

^cFP: falling phase.

^dSorbent: Tenax TA.

^eFMPS (Δt = 30 s).

^fAerosol spectrometer 1.08 (Δt = 6 s); n.d.: not determined.

^gThe different air exchange rates are chosen according to the minimal room volume specifications of the manufacturer.

Table 6 Selection of recommended guideline values

	DIN 4734-1	DIN 13779	Germany	WHO	USA (NAAQS, EPA)	IAQMG (Hong Kong)
CO₂	5000 ppm	≤800 ppm (high IAQ)	<1000 ppm (harmless)			<800 ppm (excellent class)
		>800–1000 ppm (medium IAQ)	1000–2000 ppm (elevated)			<1000 ppm (good class)
		>1000–1400 ppm (moderate IAQ)	>2000 ppm (unacceptable)			
		>1400 ppm (low IAQ)				
CO	30 ppm		RWII 15 mg/m ³ (8 h) (≈13 ppm)	100 mg/m ³ (15 min) (≈87 ppm)	9 ppm (8 h)	<1.7 ppm (excellent class)
			RWII 60 mg/m ³ (0.5 h) (≈52 ppm)	35 mg/m ³ (1 h) (≈30 ppm)	35 ppm (1 h)	<8.7 ppm (good class)
			RWI 1.5 mg/m ³ (8 h) (≈1.3 ppm)	10 mg/m ³ (8 h) (≈8.7 ppm)		
			RWI 6 mg/m ³ (0.5 h) (≈5.2 ppm)	7 mg/m ³ (24 h) (≈6.1 ppm)		
NO₂			RWII 0.06 mg/m ³ (1 week) (≈0.032 ppm)	200 µg/m ³ (1 h TWA) (≈0.106 ppm)	100 ppb (8 h)	<21 ppb (excellent class)
			RWII 0.35 mg/m ³ (0.5 h) (≈0.185 ppm)	40 µg/m ³ (1 a TWA) (≈0.021 ppm)	53 ppb (1 a TWA)	<80 ppb (good class)
HCHO			0.1 ppm	0.08 ppm (0.5 h avg)	0.1 ppm	<24 ppb (excellent class)
						<81 ppb (good class)

Table 7 List of common denaturants used in different EU countries (all values are indicated for 1 litre of pure alcohol)

	Smell	Taste	Tracker	Colorant
Austria	MEK (1.25%) Gazole (0.35%)	Fusel oil (0.6%)	–	–
Belgium	–	–	Methanol (5%)	Methylene blue
Denmark	MEK (2%)	–	–	–
France	–	–	Methanol (3.5%) Isopropanol (1%)	–
Finland	MEK (2%)	Bitrex	Acetone (3%)	–
Germany	MEK (1%)	Bitrex	–	–
Greece	Kerosene (0.5%)	Turpentine (1%)	Methanol (5%)	Methylene blue
Ireland	Oil (0.375%)	Pyridine (0.5%)	Methanol (10%)	Methyl violet
Italy	MEK (2%)	Bitrex	–	Red 51
Luxemburg	–	–	Methanol (5%)	–
Netherlands	–	Fusel oil (0.55%)	Methanol (3%) Acetone (1%)	–
Portugal 1	Oil (2%)	–	Methanol (5%)	Methylene blue
Portugal 2	Turpentine (2%)	–	–	Malachite green
Spain	MEK (2%)	Bitrex	–	Methylene blue
Sweden	MEK (2%)	–	–	–
United Kingdom	Oil (3.75%)	Pyridine (0.5%)	Wood naphta (9.5%)	Methyl violet

MEK: Methyl ethyl ketone.

Table 8 Concentrations of CO, CO₂ and NO_x measured in indoor air by Guillaume et al. (2013). Bold values are over the limits admitted by the French standard INRS ED 984.

Fireplace	Test duration	CO ₂ max (%)	CO _{max} (µL/L)	CO _{mean} (µL/L)	NO _{max} (µL/L)	NO ₂ max (µL/L)
S1	2 h 25	1.41	51.6	18.4	0.4	1.7
S2	5 h 15	2.10	40.1	17.7	1.1	2.1
S3	2 h 29	1.05	15.1	8.5	0.4	1.8
S4	2 h 43	1.84	32.3	17.6	0.3	3.3

Table 9 Concentrations of aldehydes measured in indoor air by Guillaume et al. (2013). Bold values are over the limits admitted by the French standard INRS ED 984.

Concentration at extinguishment (mg/m ³ at 25 °C)	S1	S2	S3	S4
Formaldehyde	0.794	0.763	0.425	0.885
Acetaldehyde	1.835	2.157	1.135	2.232
Acrolein	1.108	0.080	0.032	0.061
Acetone	0.026	0.016	–	–
Propionaldehyde	0.303	0.479	0.329	0.116
Crotonaldehyde	–	–	–	–
Methacrolein	0.721	–	–	–
2-Butanone	–	–	–	–
Butyraldehyde	–	–	–	–
Benzaldehyde	0.012	0.024	0.017	0.010
Valeraldehyde	–	0.033	0.018	0.026
m-Tolualdehyde	–	–	–	–
Hexaldehyde	0.007	0.010	0.008	0.008

As previously mentioned, another important factor can be the fuel composition because usually it is not 100% pure ethanol; it contains additives such as denaturizing agents, fragrances and other combustible species. Burner fuel is often a liquid or gel preparation with 95 or 96% of 'neutral rectified' ethyl alcohol (ethanol) and denatured additives to which manufacturers sometimes add colouring agents and perfumes. Lloyd and Visagie (2007) specifically tested a range of gel fuels with appliances designed for alcohol burning. The tests comprised the determination of the efficiency of the fuel/appliance combination when boiling water at full and, where possible, minimum power, and the measurement of CO, CO₂ and unburned hydrocarbons collected in a hood at the burner level in normal operation. The tests were repeated with paraffin-fuelled appliances, propane gas appliances and an electric stove. In the majority of cases it was found that the gel fuels did not meet emissions standards for CO and that they gave off excessive unburned hydrocarbons. It was suspected that this had to do with the mixing of the fuel vapour with air, because tests with pure ethanol in various appliances gave similar results. Tests in which appliances were modified to improve the air/fuel mixing showed that the hypothesis was valid. A subsidiary finding of the tests was that some gel fuels had excessive water, and that in these cases the condensation of the water vapour on the base of a cooking pot was so extensive that it could extinguish the flame. This leads to a recommendation that a standard for gel fuels be established.

1.5 Indications about possible hazards

As alcohol fireplaces have come onto the market recently, no data about burn or intoxication accidents caused by ethanol-powered appliances has yet been published. However, several possible hazards can be defined on the basis of similar experiences related to ovens, stoves and other kind of domestic appliances, as reported in

Table 10 for burn hazards and in **Table 11** and **Table 12** for intoxication hazards.

Table 10 Ethanol-powered Appliances and Burn Hazards

Generating Event	Origin (due to product)	Origin (due to use)
Contact with the flames	No fire screen	Installed in a place that is overexposed to draughts
	Body has openings on several sides	
Contact with the hot parts of the appliance (burner, body, fire screen)	Appliance built with conducting materials and no insulation on the outside walls	Appliance is handled when hot (filling; transport)
	No body	Installed in an inappropriate location (passageway)
Deflagration and/or explosion	Burner is sealed closed and the ethanol vapours concentrate inside the appliance	Hot appliance is relit without waiting for the time required for the burner to cool down, or without refilling with cold fuel
	No time delay-trip to prevent filling a hot appliance	
Backfire	No fuel supply hatch	Fuel is poured directly into burning chamber of a hot appliance
	Tank has no anti-spill system	Faulty control of filling operation (from a very large can)
Combustion starts up spontaneously after an attempt to extinguish a hot appliance, or after an apparent spontaneous flameout (low tank, draught, and so on)	Lack visibility of boiling fuel surface	Shape of the burner
	Faulty sealing of system closing the burning chamber	The burning chamber is not fully closed or closing system gets stuck
	Incandescent components in the burner (very thin metallic walls, steel filings, and so on)	Burning chamber is reopened immediately after an attempt to extinguish a hot appliance
Untrained person lights the appliance	Burning chamber has no lock system	Appliance is turned off with a full tank
		Unsafe storage of the fuel and lighting accessories

Volatile organic compounds may cause irritations and allergies of the respiratory tracts, eyes and skin over the short-term. Over the long-term, some compounds such as formaldehyde and benzene are reputedly carcinogenic. As previously evidenced, ethanol-powered appliances produce VOCs in several different situations.

Table 11 Ethanol-powered appliances and possible carbon monoxide Intoxication Hazards

Generating event	Origin (due to product)	Origin (due to use)
Carbon monoxide output	Large capacity tank	Appliance operates in a very small space, or faulty ventilation causing CO ₂ accumulation
	Flames cool due to burner shape	Flame confined inside burner (deliberately slow rate, or opening blocked by accessories)
	No CO detector built into the appliance	Appliance is used in an extant fireplace, which is not closed off, but emissions are driven back into the room (hazard if a CMV is installed)

Table 12 Ethanol-powered appliances and possible VOC Intoxication Hazards

Generating Event	Origin (due to product)	Origin (due to use)
Volatile organic compound (VOC) output	Poor fuel quality	Inappropriate choice of fuel
	Additives in the fuel produce VOC	
	Component materials of the device are damaged	A hot appliance is turned off, or an appliance is turned off in a hot atmosphere (> 15°C), tank is still full, and ethanol vapours disperse in the atmosphere
	Burner shape	Contact with the flames, or products heat and may emit VOC (wall hangings, paints, varnishes, wood panels, and so on)

1.6 Factors affecting exposure to combustion products

The actual exposure of people, that use a particular appliance, does not depend on the appliance only, but also on the dimension and ventilation of the room where it is installed, as already explained, and also on the particular habits of the users, as well as the presence of other indoor sources. Ventilation itself is often a matter of habits: someone is used to open the windows frequently or at least to keep the inner doors open, allowing a better dispersion of the combustion products in a larger volume, other people always keep doors and windows closed, depending on the structure and

dimension of the houses and most important due to the climate conditions. Nowadays modern buildings and regulations suggest to maintain the maximum thermal insulation, for energy saving reasons, reducing, at the same time, the extent of unwanted ventilation in the rooms. All these aspects must be taken into account when indoor air pollution is considered. Aesthetic appliances, like flueless alcohol fireplaces should be, are supposed to be used for a short time during the day and mainly in some specific occasions. A continuous use, as for heating appliances, is not considered in the existing national standards, but in the real world it cannot be ignored, because a not clear and correct communication can induce the consumers to purchase such appliances as heating supplementing units, especially where the climate is not rigid enough to justify a heating plant. In this case, it is likely that people try to optimise the heating performances, keeping the rooms as sealed as possible, increasing in the same time their exposure to toxic by-products.

Another important aspect to be considered is the location of the fireplace respect to the people; into a real room the air cannot be considered perfectly mixed and the local concentration of the pollutants near the source is always much higher than the average one. If the flueless appliance is placed on a table or near an armchair, people sitting there may be exposed to level of pollution higher than expected.

Last but not least, it is important to consider that most alcohol appliances have a free flame only partially protected by some kind of shield or structure. A free standing flame is very sensitive even to very small variations in the local air flow, producing a large increase of the emissions. Hence even the movement of people around the flame can influence very much the local exposure.

A final consideration should include the possibility to use more appliances simultaneously; it may happen more likely in public places, where such appliances are used as decorations, and where other sources of indoor pollution, like candles or air fresheners, may be used in the same time, producing a cumulative effect to be accounted for.

2 CHARACTERISTICS OF ALCOHOL-POWERED FLUELESS APPLIANCES

2.1 Technical and aesthetic characteristics

Flueless alcohol fireplaces have a much greater variability in their shape and technical characteristics, compared to other kind of appliances, because they have mainly a decorative scope and their aspect and design is more important than their operating properties. Some general characteristics are common to all the appliances and can be used to describe and classify them. They are here listed and defined:

Power: this term is typical of heating appliances and refers to the amount of thermal energy released through combustion in a unit time, it is expressed in kW. For aesthetic appliances this definition should not be used, because the heat production is not important for a device that should not be used for heating purposes. The rate of fuel consumption, expressed in terms of kg or litres of alcohol burned per unit time should be a more proper parameter to be used and the existing national standards usually do. Anyway, a direct and very simple relation exists between the two parameters, as the former is just calculated from the latter multiplied by the calorific value of the fuel, which is nearly the same for all ethanol based fuels.

$$Q = HCV \cdot R/3600$$

1

where:

Q = power in kW

HCV = calorific value in kJ/kg (approximately 28000 for ethanol based fuels)

R = fuel consumption rate in kg/h

The concept of power is generally associated with that of efficiency, because in most heating appliances part of the heat produced is dissipated along with the flue gases and only the remaining part is available as useful heat. This principle does not apply to flueless fireplaces because there is no dissipation of heat from a combustion appliance which is not in any way connected to the outside. This fact can be considered a positive aspect, but it should be disregarded for appliances that are not supposed to be used for heating.

Fuel tank capacity: this characteristic refers to the total amount of fuel stocked in the appliance, expressed in kg or litres; this parameter, along with the fuel consumption rate, defines the maximum working time of the appliance. In most cases, the fuel tank coincides with the bottom of the burner itself, but in the advanced automated appliances a separate tank is present, from which the fuel is pumped to the burner. A large tank allows a long autonomy of the appliance, but increases the amount of pollutants released in the indoor air; for this reason some national standards define a maximum volume allowed for the fuel tank, in order to limit the working time of the

appliance. Tanks must be refilled manually by the user, this operation can be potentially dangerous if the fuel enters in contact with surfaces still hot enough to ignite the alcohol vapours during refilling. For this reason, instruction manuals generally suggest to refill only after a proper cooling period. In manual appliances this is left to the good practices of the users, while in automatic appliances a thermal sensor is often used to prevent dangerous operations.

Burner type: the configuration of the burner is fundamental to get good combustion performances but, differently from other type of combustion appliances where some standardized burner configuration is always adopted, in alcohol fireplaces the burner configuration is defined by the designer of the appliance, without specific technical rules or standards to comply with. In most cases the burner is very simple, consisting of a metal cup, not larger than a common food tin. This cup is the fuel tank and the burner in the same time; for liquid fuel a glass wool filling is often placed inside the cup to absorb the fuel and maintain a stable combustion of the alcohol vapours, evaporating from the wool. A perforated metal plate or a slot is often used to cover the cup and control the combustion rate. Sometimes the holes or slots in the upper plate, where the flames come from, can be partially closed manually by the user to reduce or eventually shut down the flame. The amount of liquid in these burners changes continuously from a maximum at the beginning to a minimum at the end of a combustion cycle. Thus producing an unsteady combustion process, whose emission may be very different in the different stages. The advanced automatic burners are based on steady evaporation of a known amount of liquid fuel pumped from the tank through a mechanical pump. The burner generally consists of circular or linear vessel, electrically heated to produce the vapours that are ignited by an incandescent wire. In this appliances the consumption rate can be finely regulated by an electronic control unit according to the user's request (a power level is generally set either on the control unit or on remote). Moreover the control unit allows to define limit values, in terms of temperature, CO₂ or CO concentration, at which the appliance is automatically shut down. Modulation is even possible to maintain the desired level of comfort. All these features make these devices very similar to modern pellet stoves or fireplaces used for heating.

Combustion Chamber type: in most combustion devices, combustion itself takes place in a closed chamber made of high temperature resistant materials, where the combustion air is supplied naturally or forced. This is not the case of alcohol fireplaces that often works with an open chamber, similarly to open wood fireplaces, or even in the open air. The fact they are flueless, makes it possible to place them everywhere in a room, without any constrain due to the connection to a stack. Hence many designers gave free rein to their imagination, producing "objects" of any shape, structure, dimension and colour. In many of them a free standing flame is present, only partially shielded by glass or metal walls, that does not constitute a real combustion chamber, but which can still modify the combustion conditions. The control of the air inflow is a fundamental characteristic of a combustion chamber, governing the combustion process; even where a real combustion chamber does not exist any obstacle and obstruction can modify the flow of the incoming air in the flame, producing strong effects on the combustion performances. This fact must be taken into account by designers, manufactures, installers, sellers and final users.

Aesthetics and price: alcohol fireplaces are supposed to be aesthetic objects, sold as articles of furniture or knick-knacks and used mainly in some special occasions, similarly to candlesticks. For this reason their appearance is an essential element for the purchaser, who wants an object that fits in his house, and for the manufacturer, who wants to maximise the aesthetic appeal of his product. It follows that the price of these appliances is often determined by factors that have little to do with the technical characteristics of the product, contrary to what happens with other domestic devices. In this case the price can not be considered an index of the high technical quality of an appliance. Advanced automatic appliances in general are relatively expensive, comparable with pellet stoves, but also very basic appliances, having a luxurious design, are sold at a similar price, while other appliances, equally simple, are available on the market at much lower prices.

2.2 Selection criteria of the tested appliances

Six different appliances, ranging in power from 2 up to 6 kW, have been selected according to the most common technical characteristic of the flueless alcohol-powered fireplaces in the European market. The features evaluated have been the type of burner, the level of automation, construction materials, fuel tank capacity and filling device. These and other information on their utilization conditions (proper liquid/gel fuels, proper ventilation, maximum allowed operating time) have been requested from manufacturers through user's manuals and direct contact with the main European producers and importers.

In particular, in order to represent the different main types of appliances, according to their usage, the different devices have been selected in the following categories:

Desktop or floor "lamps", used as decorative accessories mainly in hotel rooms, restaurants, offices. They are typically used for short periods and people are exposed to their emissions only in particular occasions. Their burner technology is extremely simple, being generally constituted of a simple metal container with one or more slots on the top, while the aesthetic features of their design are the fundamental characteristics for the end user. The flame is generally completely open or only partially shielded by small glass walls. The reference power for the this type of appliance is lower than 2 kW and their typical capacity is less than 1 litre.

Fireplace-like appliances, that are similar in dimensions, aspect and usage to wood fireplaces. Their look may either resemble a classical fireplace or have some modern design, but they are always characterized by some sort of frame, surrounding the flame zone, where one or more burners are located. In few cases some decorative elements are used to simulate the aspect of wood logs. The reference power for this type of appliance is about 4 kW and their typical capacity is between 2 and 5 litres.

Stove-like appliances, typically sold and used as an auxiliary heating appliance, even if not explicitly declared. They are often similar in aspects to a pellet stove and may have electronic controls for automatic switch on and off, power or thermostatic regulation and forced convection for a more efficient diffusion of warm air. The reference power for this type of appliance is about 5 kW and their typical capacity is larger than 3 litres with the possible presence of an auxiliary fuel tank.

The selected appliances are specifically designed and declared to work with liquid or gel only. Moreover, gel burners usually consist of a small metal can, so that to get a higher power two or more cans are simultaneously used, getting an overall power generally lower than 4 kW.

For the above-mentioned reasons, it has been preferable to test different appliances for different fuels and to replace the larger gel appliance (of about 6 kW) with a smaller one, increasing the representativeness of the ensemble of selected appliances. In fact, most of them have a power in the range from 3 to 4 kW, while bigger appliances are uncommon and seldom used indoor.

Therefore, the following fuel/appliances combinations adopted and set of tests reported in **Table 13** has been carried out in the study.

Table 13 Experimental array for appliances/fuels combinations

APPLIANCES			1.5 - 2.5 kW		3.5-4.5 kW			~ 6 kW
			A	B	C	D	E	F
FUEL	Gel	G1						
		G2						
		G3						
	Liquid	L1						
		L2						
		L3						

2.3 Description of the appliances

Appliance A. It is a gel ethanol circular stainless steel burner of 290 mm diameter. The tank capacity is 2 litres; the nominal power output is 2.7 kW. Filling and ignition are manual; the burner has a manual system of power regulation between two positions (minimum and maximum) that varies the opening of the six holes on the burner cover. The flame zone is surrounded and protected by a heat resistant tempered glass cylinder, 260 mm high. It is thought to be inserted in furniture elements specifically designed for it, like small tables.

Appliance B. The apparatus, suitable for only liquid ethanol may be considered a table lamp having a square base of about 120 mm side in which the seat that contains the burner is positioned. It consists of a small cylindrical container of about 0.8 litres capacity, inside which is placed a "sponge" of fibrous material which supports the perforated circular grid closing of the cup. Filling and ignition are manual. On each side of the base four glass interlocking panels (350 mm high) are positioned, that ensure protection from the flame and at the same time ensure an inflow of air to the flame.

itself which makes it assume a swirling appearance. The nominal output of the burner is 2.0 kW.

Appliance C. This device is powered by ethanol gel and it belongs to the category of powder-coated metal decorative wall burners. The burner consists of three gel-fuel steel tins of capacity of 0.5 liters each; its dimensions are 600 mm width / 420 mm height / 210 mm depth. The declared power output is 4 kW. Filling and ignition are manual for each cup.

Appliance D. This model of apparatus consists of a painted steel ground fireplace provided with a decorative frame open on one side. Its dimensions are 600 mm height / 900 mm width / 240 mm depth. The tank capacity is 3 litres and the thermal power output is 3.5 kW. The peculiarity of the burner with respect to the other selected devices is to have an internal filling of ceramic material (a kind of refractory ceramic brick) that facilitates the evaporation of ethanol and at the same time makes it more difficult any spillage of liquid. Filling and ignition are both manual.

Appliance E. It is a stove-like appliance, in which the steel burner is positioned inside a closed combustion chamber, a maximum of 5 litres of liquid ethanol can be loaded. The nominal output of the unit is equal to 4.0 kW. The combustion air enters the combustion chamber through the slots at the base of the chamber itself, while the products of combustion flow through two sets of slits: a front, towards which the exhaust gases are conveyed by an internal baffle plate, and the other on the top of the stove. This type of stove, quite different from the others, is equipped with a ventilation system and automatic ignition; it is also possible to automatically adjust the power as a function of the set temperature in the environment in which it is placed.

Appliance F. It is a burner equipped with electronic and remote controls, along with detectors for fuel level, CO₂, and heat sensors. It is suitable for fireplaces and insert installations inside walls or furniture. The stainless steel combustion tray has 5 litres capacity and the nominal thermal power output is 6.2 kW. Its dimensions are: 1000 mm length, 113 mm height, and 238 mm depth.

In

Table 14 the main characteristics of the selected appliances are summarized.

Table 14 Main characteristics of the selected appliances

Appliances	Fuel: liquid (L) / gel (G)	Tank capacity (l)	Ignition: Manual (M) / Automatic (A)	Nominal thermal output (kW)	Experimental thermal output (kW)	Maximum working time (h)	Price segment ³ (€)
A	G	2.0	M	2.7	1.7	7.2 ⁴	800-1000
B	L	0.8	M	2.0	3.5	1.4	< 100
C	G	1.5	M	4.0	4.0	2.3	≈ 150
D	L	3.0	M	3.5	3.8	4.8	1000-1500
E	L	5.0	A	4.0	4.0	7.7	1500-2000
F	L	5.0	A	6.2	6.2	4.9	≈ 2500

³ Data refer to prices in the Italian market (VAT not included).

⁴ This nominal value, calculated from the maximum volume of the tank, is overestimated in practice; because the flame likely extinguishes well before the tank is completely empty. The actual value is highly variable between 1 and 2 hours.

3 COMMERCIAL ALCOHOL-BASED FUELS

3.1 Composition and denaturation of liquid ethanol

As stated in the very beginning of this report, ethanol is a well identified chemical compound, having specific and well known chemical and physical properties; while commercially speaking, the names ethanol, bioethanol or simply alcohol are referred to a series of products mainly constituted of ethanol, but containing other minor components in variable proportions.

The first and most important characteristic, which makes one ethanol different from another, is the method of alcohol denaturation. In Europe has been recently published the COMMISSION IMPLEMENTING REGULATION (EU) N. 162/2013 of 21 February 2013 amending the Annex to Regulation (EC) N. 3199/93 on the mutual recognition of procedures for the complete denaturing of alcohol for the purposes of exemption from excise duty. It establishes that a denaturing procedure consisting of 3 litres of isopropyl alcohol (IPA), 3 litres of methyl ethyl ketone (MEK) and of 1 g of denatonium benzoate per hectolitre of absolute alcohol, could be considered for adoption as a common denaturing procedure for the purposes of completely denaturing alcohol. One of the main advantages of this common procedure is that it is likely to replace several individual procedures of the various Member States.

However, in Annex 1 to the Regulation many other allowed denaturation methods are listed for different Member States.

It is worth to be stressed that each single denaturing method is not exclusive of each state, but everyone can use one of available methods. Some exceptions, if any, laid down by the domestic law of each State, regarding the commercialisation.

Even though the main components of each formulation are similar, the relative amount of each one may vary significantly and flavour and odour of the final product may be consequently different. Some denaturation formulas, conventionally used for domestic usage, are not suitable for fuel applications, because the smell produced is too strong and some components can have irritating effects; while others are considered, by the commercial distributors, much more suitable, due to their delicate and good flavour.

3.2 Gel fuels: characteristics and uses

As many other domestic liquid products such as detergents, soaps and disinfectants, also alcohol based fuels are nowadays available in an alternative gel formulation. The possible advantages of these products rely on their higher viscosity and lower flammability, which allows a safer handling and usage, compared with liquid ethanol. In fact, in case of accidental spillage or overturning of a filled appliance, is more unlikely the gel catches fire and propagate it through spreading on the floor. Even the evaporation process, that releases ethanol vapours even when the appliance is off, takes place at a lower rate with gels, compared to liquids. On the side, but due to the same properties, these products are less suitable to be used as fuel because of the difficulties they have to ignite and burn.

For gel fuels the commercial situation is not very clear, because there is not any specific regulation about them: they are commercialized in different forms, under different names, without a clear specification of their composition, they are usually coloured and may have some perfume inside; their formulation largely depends on the producers. The most common jellifying agent is the Xanthan Gum, but also other compounds, able to make the ethanol denser and more viscous are used, for example 2-methyl-heptanone. These fuels are not distributed everywhere and there are also some ethanol based products distributed on the market, that are mainly used for cooking (for some particular dishes like fondue) or for food warming, but they can also be used in specific fireplaces and constitute a specific categories of fuels and appliances.

3.3 Fuel-appliance matching

An important aspect to consider is the correct matching between the fuel and the appliance: most alcohol fired fireplaces are intended to burn liquid ethanol and in general the manufacturers or the local distributors suggest a specific fuel, sold under some particular trade name. The use of other types of commercial ethanol, sold for generic domestic use, is sometimes discouraged in the user manuals. This behaviour reflects in part a correct information to the consumers, because different alcohol based products might produce a different effect when burnt, but in the same time it is also due to the commercial policy of the supplier of the device, who sells also that particular brand of fuel.

On the other hand, the situation is very different if we consider gel appliances, in this case the user manual generally indicates clearly that the appliance is designed for gel fuels.

3.4 Selected fuels

The standard of the European Union is to date very little used (also because of the strong odour that emanates), while the most common for the use of our interest seems the German one.

For this study, it has been decided to provide samples of ethanol for the tests to be run on the selected devices denatured according to the following formulation:

- German (the most common)
- Slovenian (with less pronounced odour)
- European (indicated in the REGULATION (EU) N. 162/2013)

The three formulations have also some different characteristics. In the following **Table 15** the denaturing formulas are specified.

Table 15 Denaturing formulas for selected liquid ethanol fuels

Denaturing formulation per 100 l of liquid ethanol	European EU	German D	Slovenian S
isopropyl alcohol (IPA)	3 L		1580 g (2 L)
methyl ethyl ketone (MEK)	3 L	0.95-0.96 L	
denatoniumbenzoate	1 g	1 g	0.79 g
methyl isopropyl ketone		0.025-0.003 L	
ethyl sec-amyl ketone		0.0015-0.002 L	
tert-butyl alcohol			790 g

Also three commercial gel products, distributed in several European countries have been selected. In particular the first product selected is a yellow coloured ethanol gel from Holland; the other two products are transparent and odour-free gels coming from France and Germany.

In **Table 16** the physical-chemical properties of the fuels are summarized.

Each selected fuel has been analysed to determine its composition, density, calorific value (HCV), flash point, initial boiling point (Tb in), autoignition temperature (**Figure 1** and **Figure 2**).

Table 16 Physical-chemical properties of the selected gel fuels

	Flash Point (°C)	HCV (MJ/kg)	Delay (s)	HCV (cal/g)	Tb in (°C)	T autoign. (°C)
L1 Liquid ethanol EU den.	12.5	27.33	14	6526.6	78	423
L2 Liquid ethanol D den.	12.5	28.03	13	6694.7	78	407
L3 Liquid ethanol S den.	13.5	28.06	9	6701.6	78.3	407
G3 Gel Ethanol (German)	16.5	24.72	13	5903.1	78.5	439
G2 Gel Ethanol (French)	16.5	24.35	18	5816.1	78.8	429
G1 Gel Ethanol (Holland)	17.5	19.60	21	4681.8	79.6	431

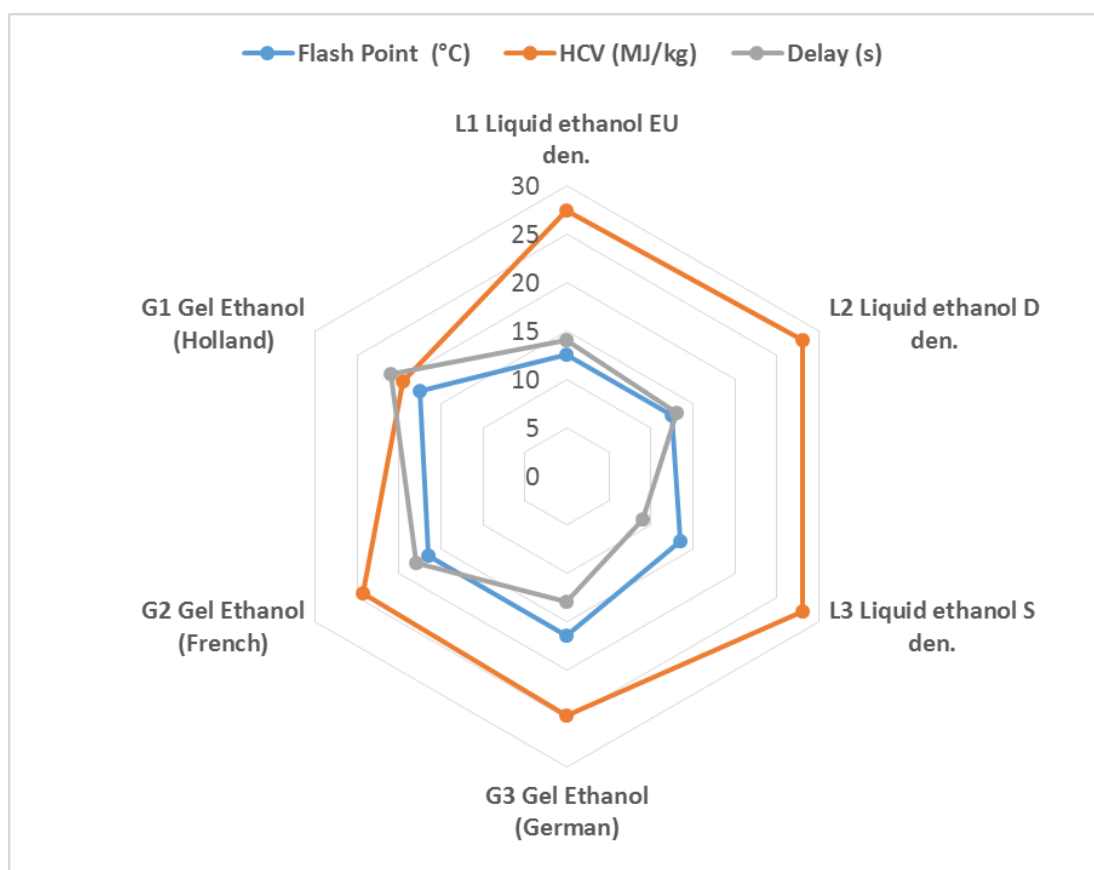


Figure 1 Physical-chemical properties of the selected fuels

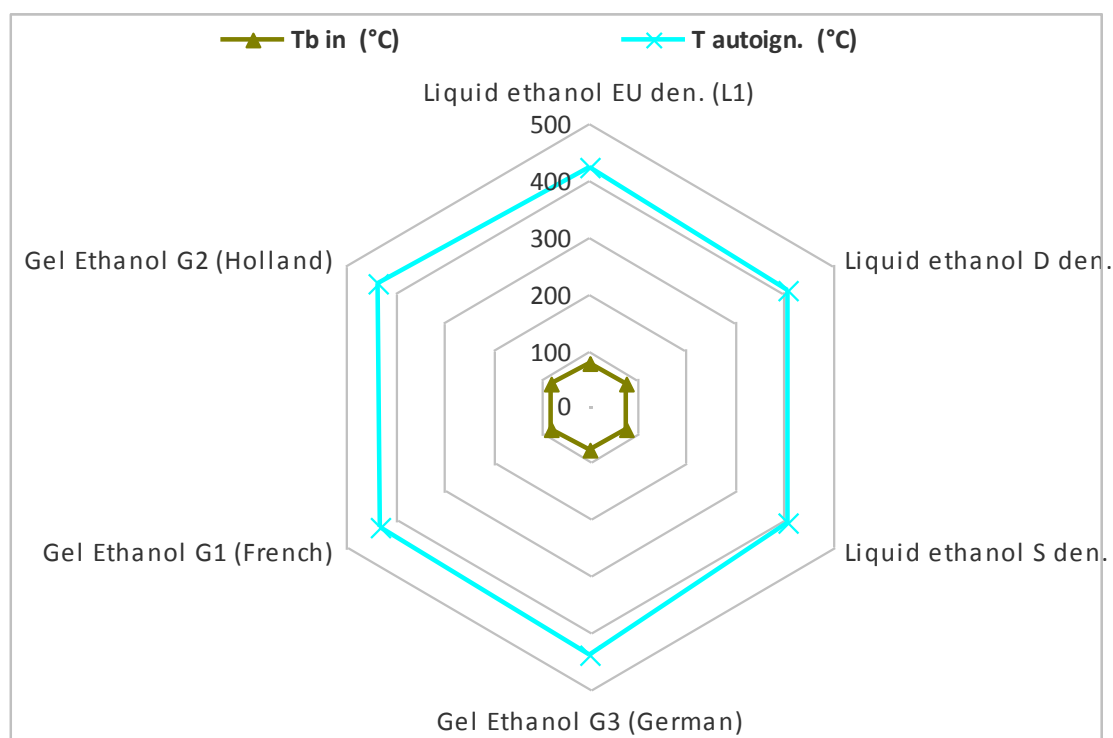


Figure 2 Further physical-chemical properties of the selected fuels

The results of the analysis show that the characteristics of the liquid fuels are quite similar, despite the different denaturation, while gel fuels have lower calorific values and higher flash points compared to the liquids. That implies a different behaviour of the gels when used in a combustion appliance, in particular they show a more difficult ignition and release less heat while burning. In particular, G2 gel fuel has a very low calorific value and high flash point, it is the only coloured fuel included in this study and this might influence its properties. The infrared spectra of the three gels are very similar, except some additional peaks in the spectral region 1100-1180 cm^{-1} detected in the G2 sample (**Figure 3**). Only in the case of gel G2 the GC-MS (Gas Chromatography–Mass Spectrometry) analysis has allowed to detect the presence of limonene flavour.

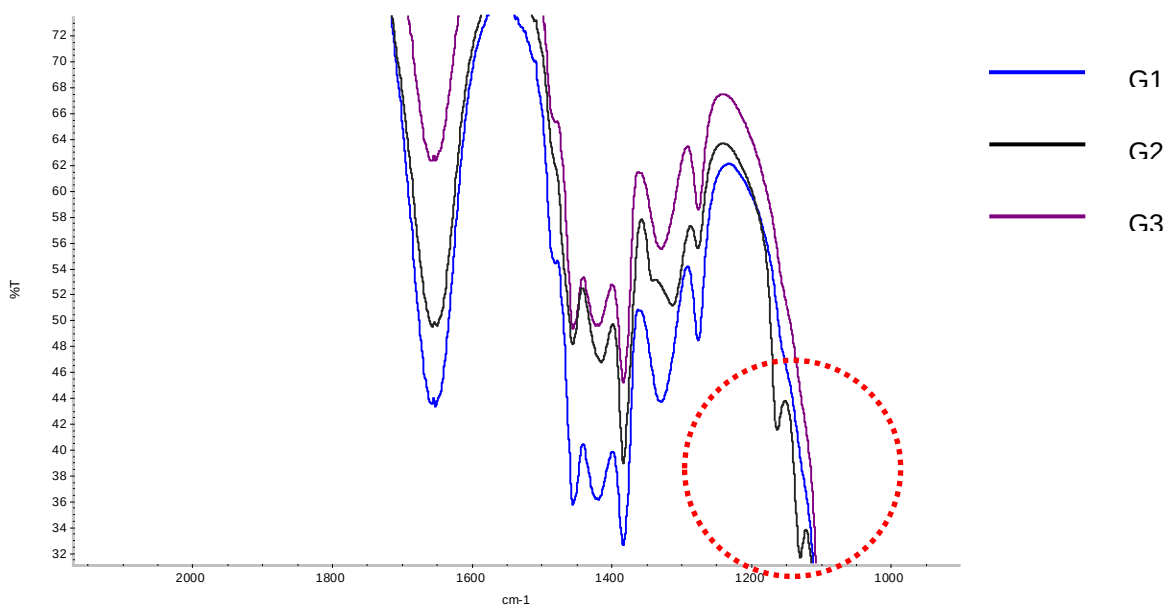


Figure 3 IR spectra of the three gels (see peaks in the spectral region 1100-1180 cm^{-1})

Liquid and gel fuels have been tested in a thermo-gravimetric apparatus in order to evaluate their behaviour in the evaporation phase. The oven has been heated up at the temperature of 50°C, which is representative of the typical temperature of the burner after it is switched off. The figure below shows the weight loss of each fuel sample. It allows to compare the evaporation rates of the liquid and gel ethanol. A very different behaviour is observed for the liquids and for the gels. The slope of the weight-loss curve represents the rate of evaporation, which is almost constant in the time interval greyed in the figure, because in this interval the temperature is constant and also the amount of fuel in the crucible can be considered relatively constant, so that the evaporation process is nearly steady, hence these values can be used for direct comparison. The gels show a residual amount of about 1% in weight, which does not evaporate at this temperature, that can be attributed to the gelling agent. This parameter is very important because the evaporation rate governs the combustion rate, since only the vaporised fuel can burn; in combustion conditions the heat of the flame itself is partially transferred to fuel to vaporise it.

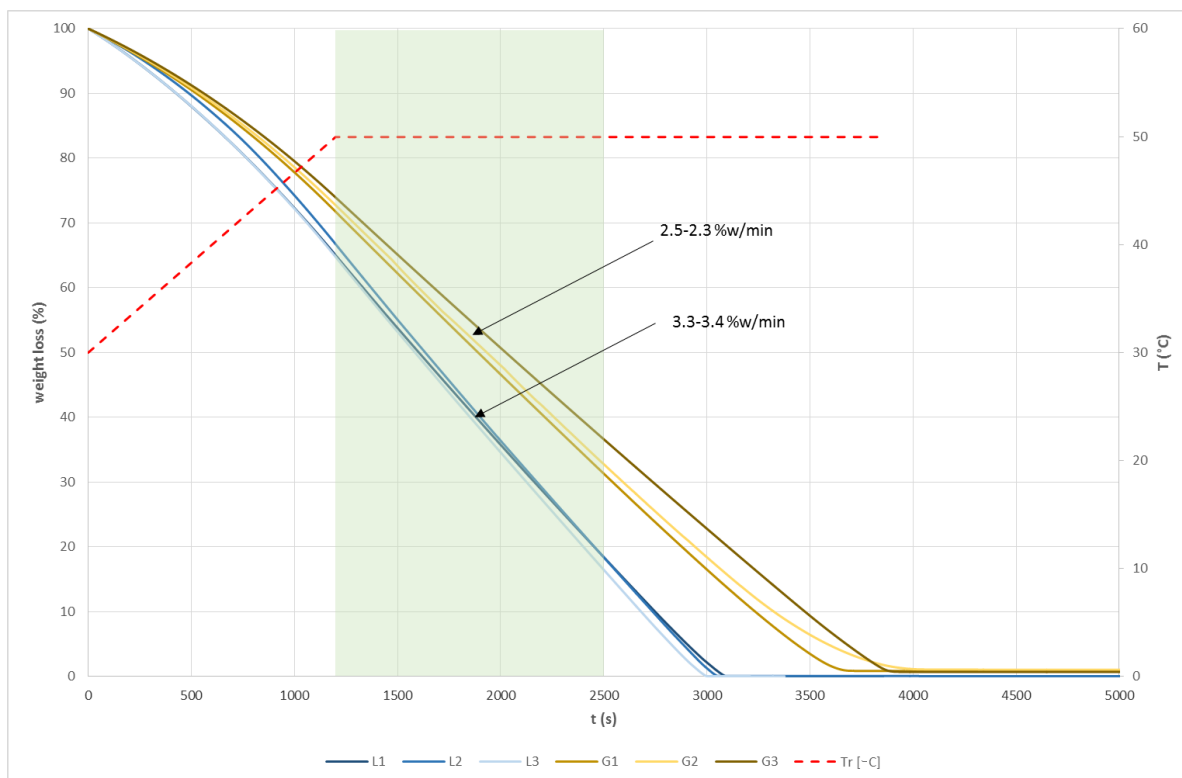


Figure 4 Weight loss vs time (@50°C) for the investigated fuels

4 POLLUTANTS EMITTED FROM ETHANOL COMBUSTION

4.1 *Experimental tests on selected appliances*

Several different tests have been carried out in order to characterise the pollutant emissions produced by alcohol fireplaces.

- **Direct combustion tests:** flue gases are conveyed through a hood to measure the concentration of the combustion products at a known dilution ratio with ambient air
- **Sealed chamber tests:** each appliance is placed in a sealed chamber (18 m³ in volume) and the inner concentration of CO and CO₂ is measured in parallel up to a pre-defined CO₂ level (2.3 %)
- **Ventilated chamber tests:** each appliance is placed in a ventilated chamber (30 m³ in volume) where the main emission parameter (CO₂, CO, NO_x, VOC, PAH, PM) are measured under two different ventilation conditions (0.5 and 0.2 AER). The test is carried out following a three hours on-off cycle to simulate a real live use of the appliance

The experimental design and results are reported in the following sections.

4.1.1 *Direct combustion tests*

For each combination appliance-fuel, combustion tests have been performed so as to convey the combustion products through a hood, allowing in such a way sampling and analysis of the emissions (referring to specific national standard: e.g. the French standard for "Appareils fonctionnant à l'éthanol" NF D 35-386 and the Italian Technical Specification "Apparecchi a etanolo – requisiti e metodi di prova", UNI 11518:2013). These standards refer to a hood designed according to Figure 5 for small appliances (in turn derived from standard EN 30-1-1:2008 on tests of hob gas burners), while for large ones a different solution has been arranged, according to the specific geometry of the appliance. The hood conveys the flue gases produced by combustion and some ambient air; the height of the hood base, referred to the burner plane, is adjusted so that the CO₂ measured concentration is as close as possible to 1%, to prevent any possible influence of the hood itself on the combustion process.

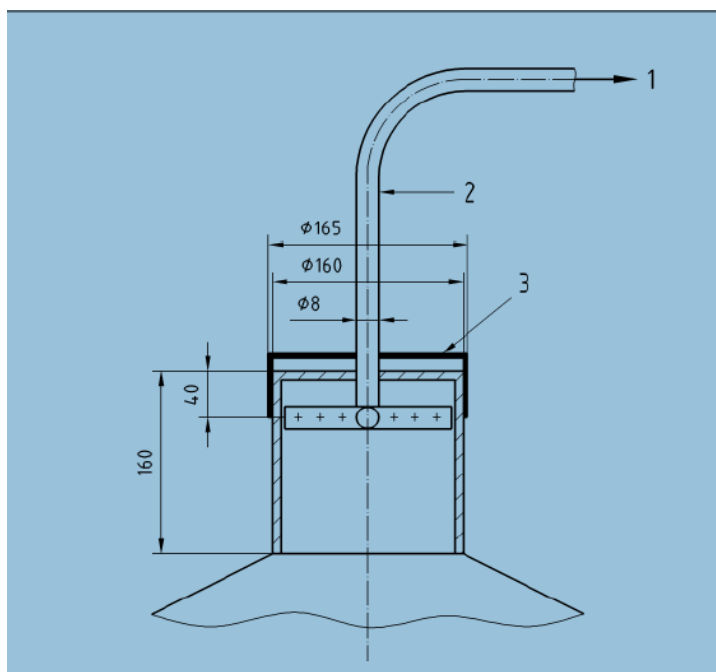
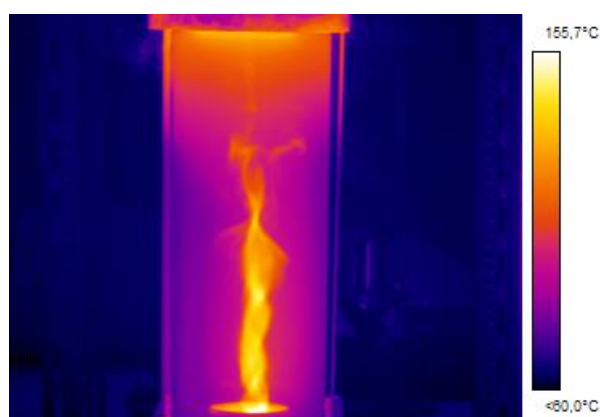


Figure 5 Device used for hob gas tests according to EN 30-1-1:2008

These tests are very important to characterise the behaviour of the appliances and to plan the optimal test conditions for each one.

Some thermographic images have been acquired in order to compare the different behaviour of the appliances in terms of distribution of temperatures and thermal convection of the combustion products. Some examples are reported in **Figure 6**.



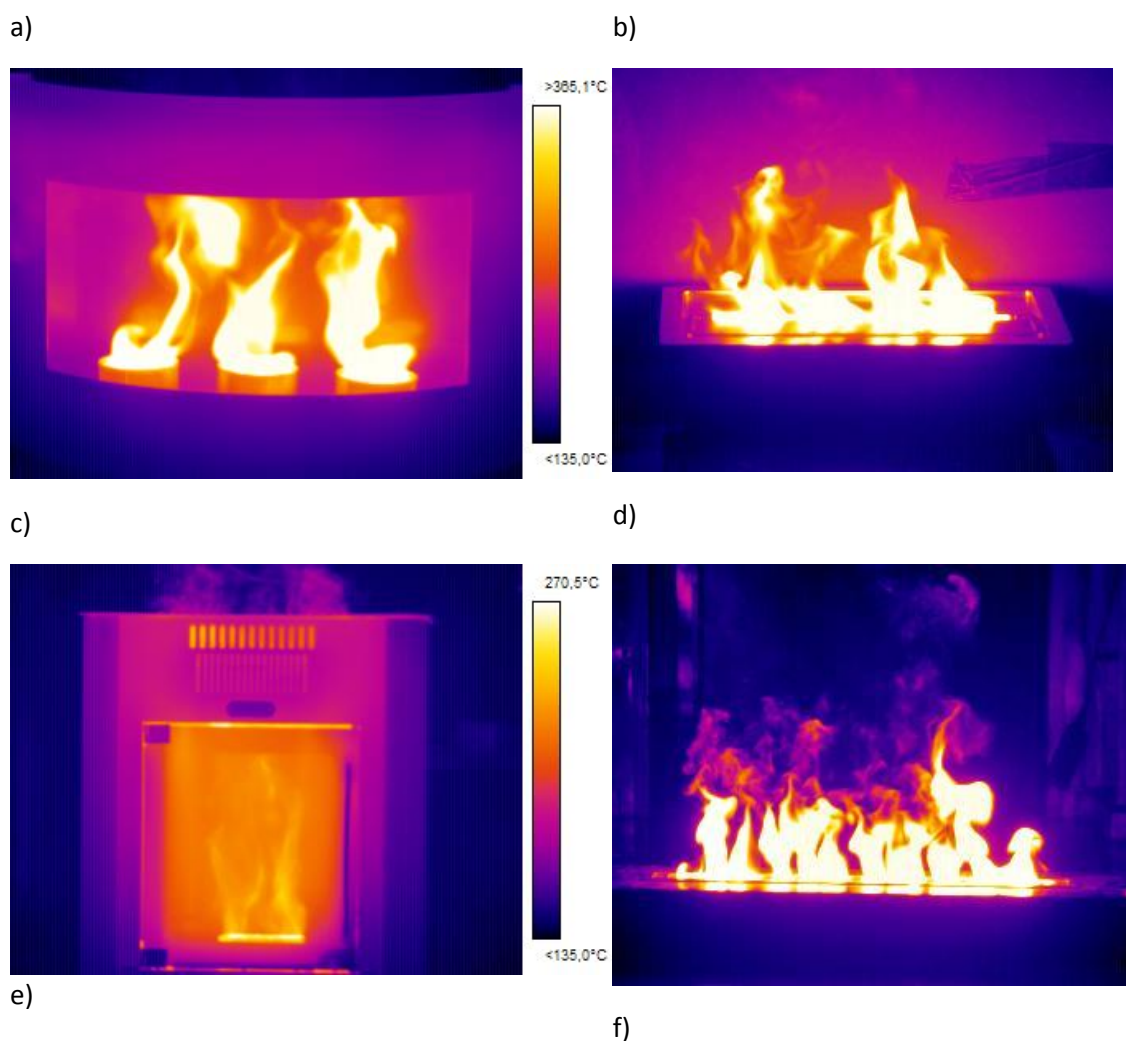


Figure 6 IR images of: a) appliance A b) appliance B c) appliance C d) appliance D e) appliance E and f) appliance F

For example in **Figure 6-a)** it is possible to observe the very unstable and fluctuating flame of appliance A. In **Figure 6-b)** the cold air entering in the combustion zone from the lateral vertical slits is clearly visible and produces the typical swirled shape on the flame. In the upper section hot flue gases are homogeneously distributed before leaving the appliance. **Figure 6-c)** and **Figure 6-d)** show the wall gel-fuelled fireplace and the slot burner during the steady combustion phase. In **Figure 6-e)** the combustion chamber is visible long with the hot fumes leaving it from the slots placed on the top of the stove, where they are conveyed to the hood; also the appliance surface is hot enough to radiate heat as a typical stove. In the last picture (f) of **Figure 6** the log linear flame produced by burner F is shown in its stable and uniform shape.

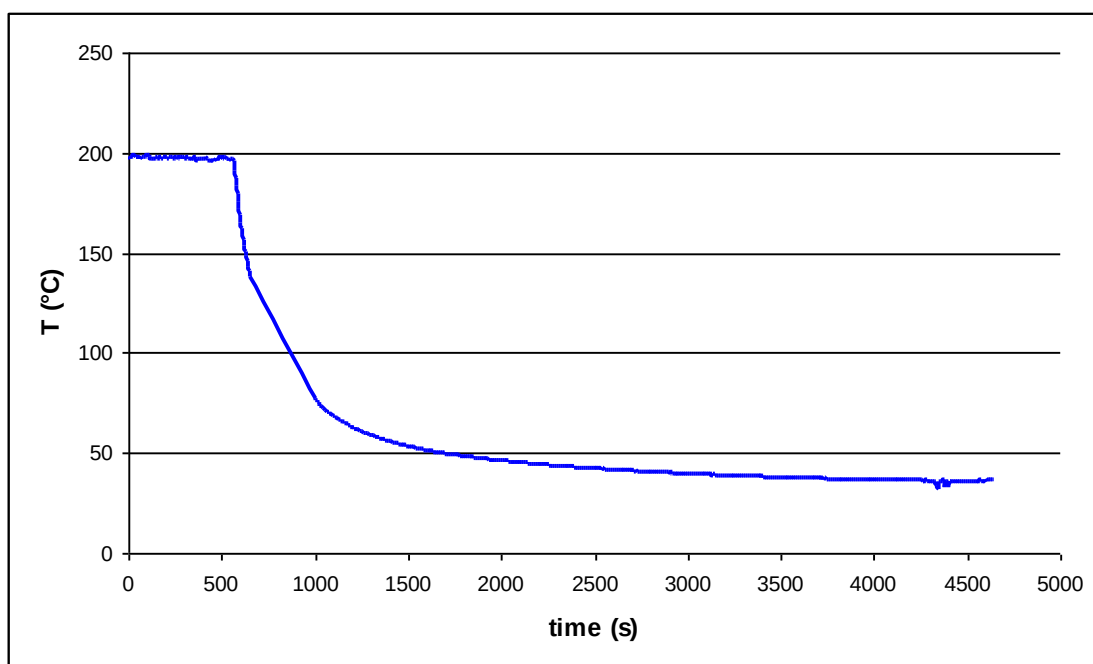


Figure 7 Temperature decrease after switching off appliance E

In **Figure 7** the decrease of the surface temperature of the burner of appliance E is shown as measured by means of the thermographic analysis. It is possible to observe that the upper part of the burner initially in direct contact with the flame has a very high temperature (200°C), that quickly decreases, but it maintains a temperature around 50°C for a relatively long time.

Different appliances have different burner configurations, tank capacities and switching procedures; all these technical aspects have a strong influence on the behaviour of the appliance, modifying the test conditions to be adopted. Combustion tests have shown that most appliances have an initial peak of CO and TOC (Total Organic Carbon) emissions, corresponding to the ignition phase. Then a steady combustion phase begins, with emission levels nearly constant in time, but different for each appliance. This period lasts for a time as long as the capacity of the fuel tank, but when the tank is nearly empty the flame starts vanishing, becoming shorter and only partially visible. During this phase the pollutant emissions of unburnt substances, produced by the fading flame, increase greatly. In this period the behaviour is very erratic and strongly dependent on the burner configuration. The CO emission reaches a maximum, corresponding to the complete extinction of the flame, then it falls down suddenly, while the TOC measured is further increased and remains very high for a long period of time because of the evaporation of the residual fuel. Also this evaporation phase depends very much on the type of appliance. Examples of emission trends are reported in Annex A, in the figures from **Figure-A 1** to **Figure-A 6**. They are representative of the different behaviour of each appliance tested in this study under the same experimental conditions.

In **Figure 8** and **Figure 9** the main results on CO, NO_x and TOC are summarized in graphic form.

All the parameters have been monitored using a combined set of different experimental techniques, in particular macro species, such as CO₂, CO, NO_x, have been measured using continuous analysers (NDIR and chemiluminescence, respectively). A FID (Flame Ionization Detector) on-line analyser has been used to monitor the total hydrocarbons emissions during both the combustion and cooling phases of each appliance. All instruments are managed according to technical standards, namely:

NO _x	UNI EN 14792:2006
CO	UNI EN 15058:2006
O ₂	UNI EN 14789:2006
TOC	UNI EN 12619:2002
CO ₂	ISO 12039:01

Specific sampling techniques have been adopted to collect, identify and quantify some micropollutant species such as Aldehydes, VOCs and PAHs. Specific sorbent (Tenax™ and Carbosorb™ cartridges for VOCs and PAHs, DNPH for carbonylic compounds) have been adopted for sampling and proper analytical techniques (HPLC, GC-MS,...) have been applied.

Particulate matter has been sampled through filtration and gravimetrically determined, but it resulted undetectable.

4.1.1.1 CO emissions

The CO concentration directly measured in the flue gases at about 1% CO₂, as recommended in French and in Italian standards, is around 10 ppm in the stationary combustion phase. It means that when reported at 15% CO₂ (reference condition for stoichiometric combustion) the CO concentration in some cases exceeds the limit value of 100 ppm defined in these standards. Namely appliances A and B never respect the limit, while appliance C produced ambivalent results. Only for the three appliances D, E and F this limit is nearly always respected. A particular situation is observed for burner A, where the CO measured emission ranges between 28 and 45 ppm, becoming 350-650 ppm in reference conditions; a large variability is observed for the different gels and within the different tests.

In the vanishing phase the CO concentrations appear generally increasing, but not in the same proportions; in some cases the average CO concentration is doubled if compared to stationary conditions, in other cases these concentrations remain nearly constant. There is not a clear correlation of this behaviour with the burner or gel type used and it appears much more related to the random behaviour observed in the fading flames. Anyway it is important to single out that for automatic appliances (E and F) this phase does not exist and even for the D fireplace, equipped with a ceramic brick burner this phase is hardly detectable and it is not considered in our results.

4.1.1.2 NO_x emissions

For NO_x emissions the measured values are closer to each other, the average concentration in stationary conditions is around 3 ppm; when reported to reference conditions, these values are in the range 30-60 ppm. Most of them exceed the limit value of the French standard (33 ppm of NO_x) but, in this case, the comparison is not fully applicable, because the French standard requires to measure NO_x at 5% CO₂ concentration, while these experimental tests have been carried out in the same hood configuration used to measure CO emissions, at about 1% CO₂.

In the case of NO_x the higher values are observed for those appliances which produced lower CO emissions, as a consequence of the different mechanisms producing these species. In fact, the reducing environment, due to the presence of CO, is not favourable to the formation of NO_x.

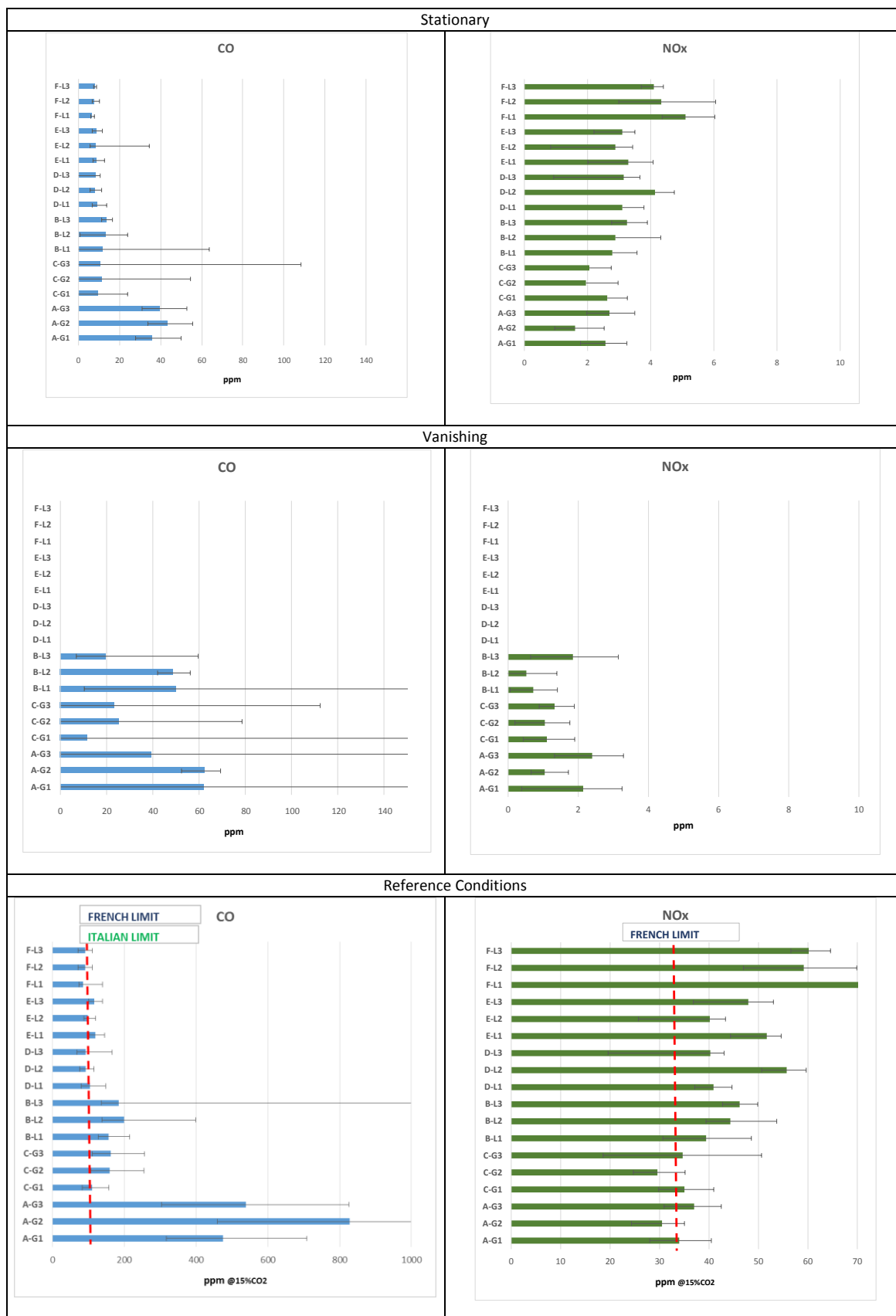


Figure 8 CO and NOx average emissions in direct analysis of combustion tests

4.1.1.3 TOC emissions

Unburnt organic species, measured as Total Organic Carbon (TOC) using a FID analyser, have been determined in the stationary combustion phase, in the vanishing phase and also after the complete extinguishment of the flame, in order to evaluate the evaporation of residual fuel from the hot device (Figure 9).

TOC average concentration in stationary stage is always below 10 mg/m³ except in one case, even though large fluctuations are observed. In the vanishing phase the measured concentrations are always increased by a factor of 10, due to the poor combustion conditions encountered in the final life of the flame. It is noteworthy to observe that the highest concentrations of TOC are measured after the complete extinguishment of the flame; this is due to evaporation of the residual fuel in the burner and in the tank, where a fuel-blocking device is not present. In appliance A evaporation is particularly pronounced as a consequence of the large dimensions of the vessel; but also in appliances B and D a large evaporation is observed, due to the presence of a "spongy" material retaining the fuel and increasing the evaporating surface. In all these tests it has been assumed that the user let the appliances spontaneously switching off, without manually closing the burner plates (appliances A, B, C, and D); these considerations are not valid for automatic appliances (E, F) where the switching off of the device is electronically controlled.

It is important to underline that the very high TOC concentrations, measured when the flame is off, are not directly comparable with the values measured during the combustion phase, because they are not representative of the same mass flux, due to a lacking of convection; these values are, on the contrary, representative of an average concentration in the steady atmosphere in the area surrounding the burner.

In **Figure 10** and **Figure 11** the average values for fuels and appliances are reported. They confirm lower specific emissions for liquid fuels than for gels in terms of CO and TOC, while for NO_x liquids are, on average, worse than gels. Comparing the appliances we can state that CO and TOC emissions are similar except for appliance B for liquids and especially A for gels.

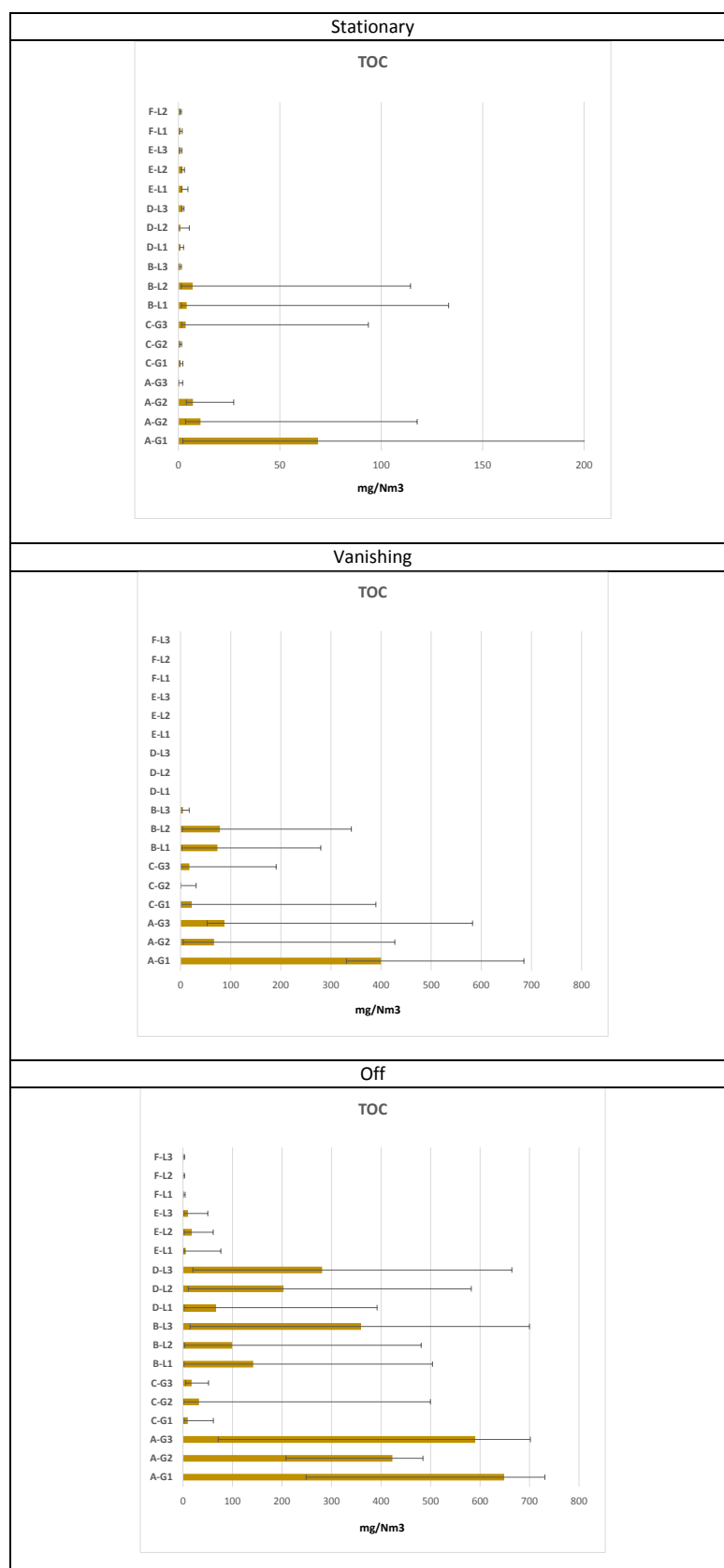


Figure 9 TOC average emissions in direct analysis of combustion tests

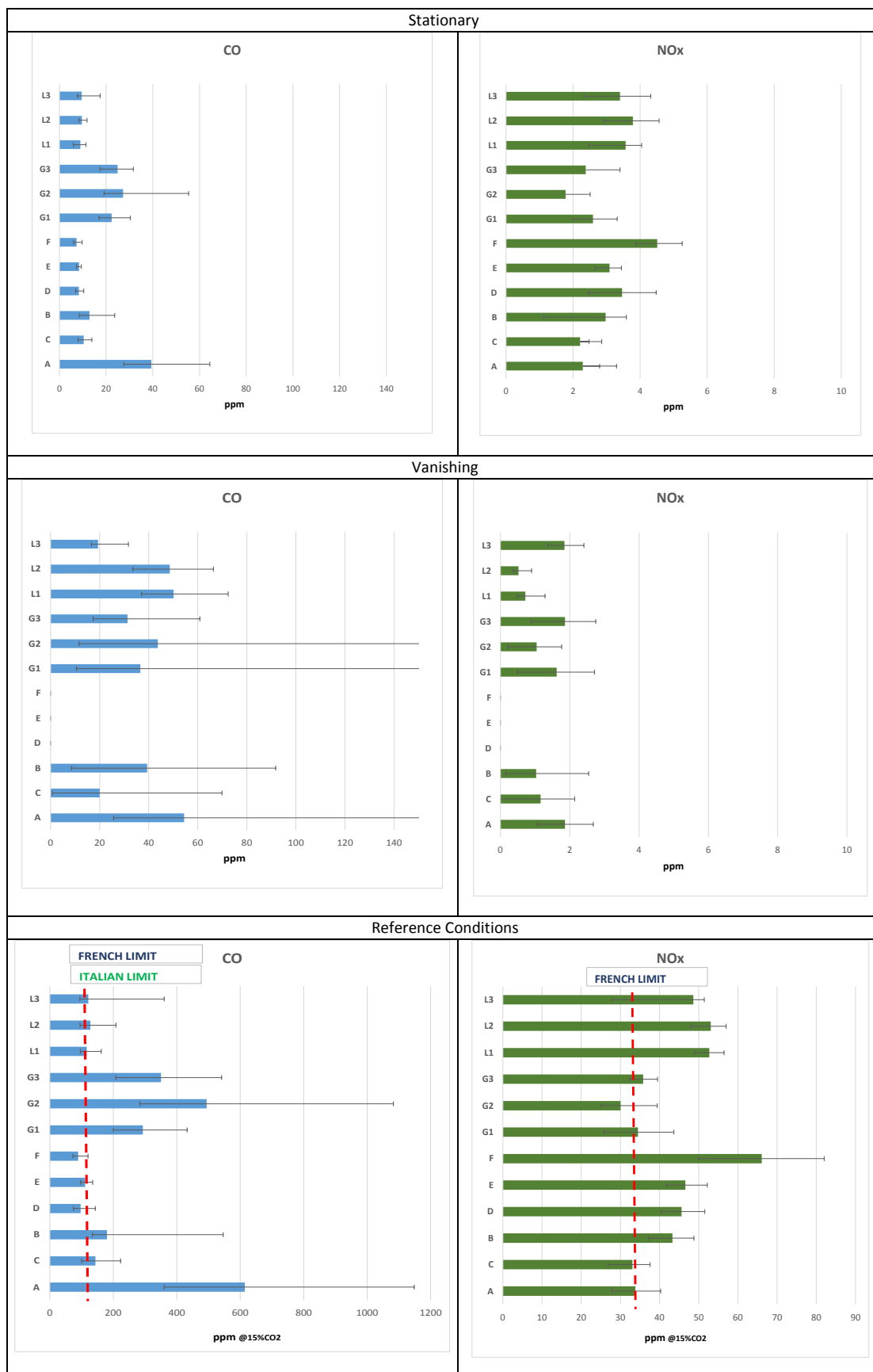


Figure 10 CO and NOx average values for fuels and appliances

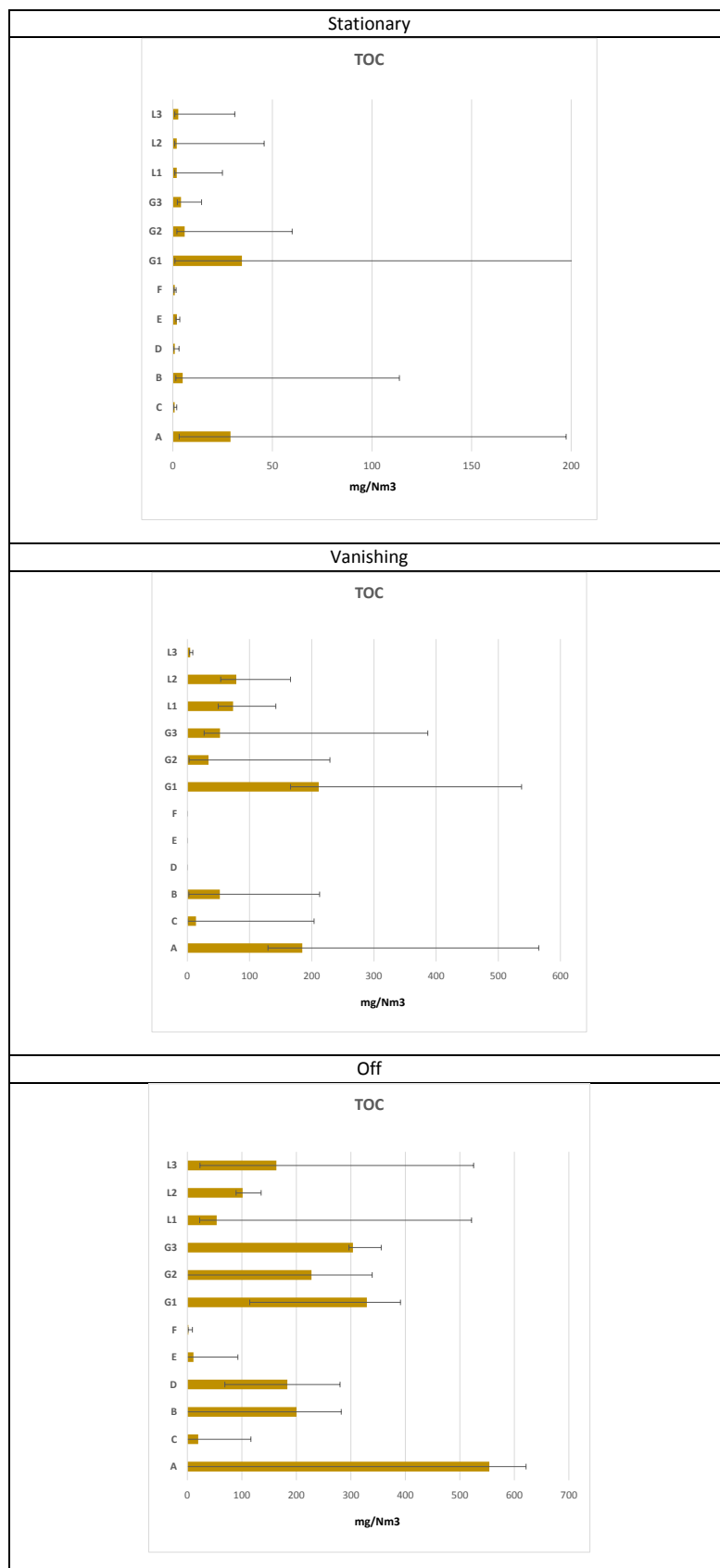


Figure 11 TOC average values for fuels and appliances

4.1.1.4 Repeatability of results

Repeatability of the tests is an important aspect to evaluate the significance of the results here presented. Besides the uncertainty of the measurement tools used in the experiments, there is an intrinsic variability in the tests due to the not perfectly repeatable behaviour of the appliances. For manual appliances, even small differences in the initial level of the fuel, in the ambient temperature may influence the burning conditions and hence the results of the tests. Automatic appliances are much more stable because of the electric control devices. In the same time the free flames (not protected by a combustion chamber) are very sensitive to air circulation around the burner, this is another source of random variations in the outcomes of the tests. In order to provide a proof of the validity and reliability of results some comparisons of different tests are here reported.

In **Figure 12** experimental data coming from three different tests, performed on the stove named E, which is the most stable and automated appliance, are reported for CO, CO₂ and NO_x, during steady combustion conditions. The instantaneous average concentration curve is reported too, along with the standard deviation represented by the vertical bars. The shaded area emerging from summing up all the standard deviation bars is a pictorial representation of the variability of a set of tests performed on a particular appliance.

In **Figure 13** the same average curves and variability areas are reported and compared with the concentration curves coming from test performed on the three different liquid fuels. It is interesting to notice that variability due to the fuel is not greater than the intrinsic variability of the tests in case of CO, while it is slightly higher for NO_x, but this topic will be discussed in details later in the text.

A similar comparison is shown in Figure 14 and Figure 15 for appliance A, which can be considered the most erratic and unpredictable appliance among those tested in this work. Here the fluctuations in the concentrations, registered during a single repeated test, are very large, mainly for CO, as a consequence of the extreme unsteadiness of the combustion conditions typical of this particular burner. Also in this case the variations, related to the fuel type, are not much greater than those observed for different tests with the same fuel.

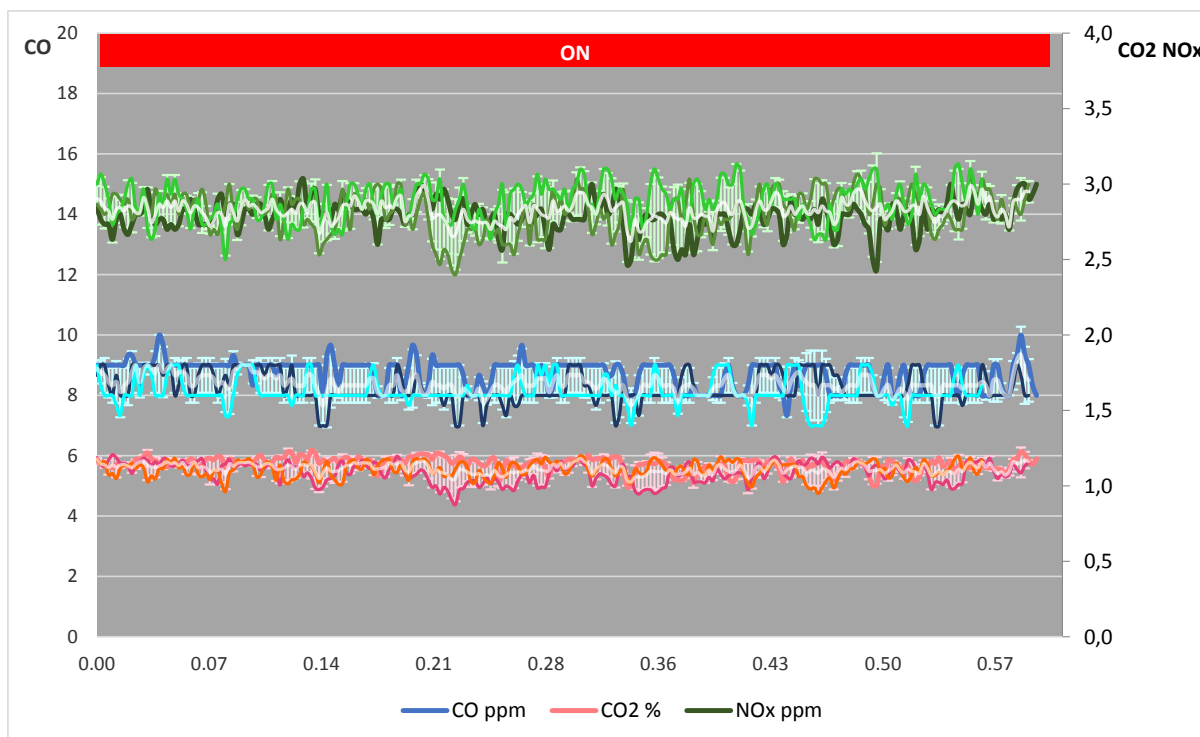


Figure 12 Repeatability of direct combustion tests, for appliance E

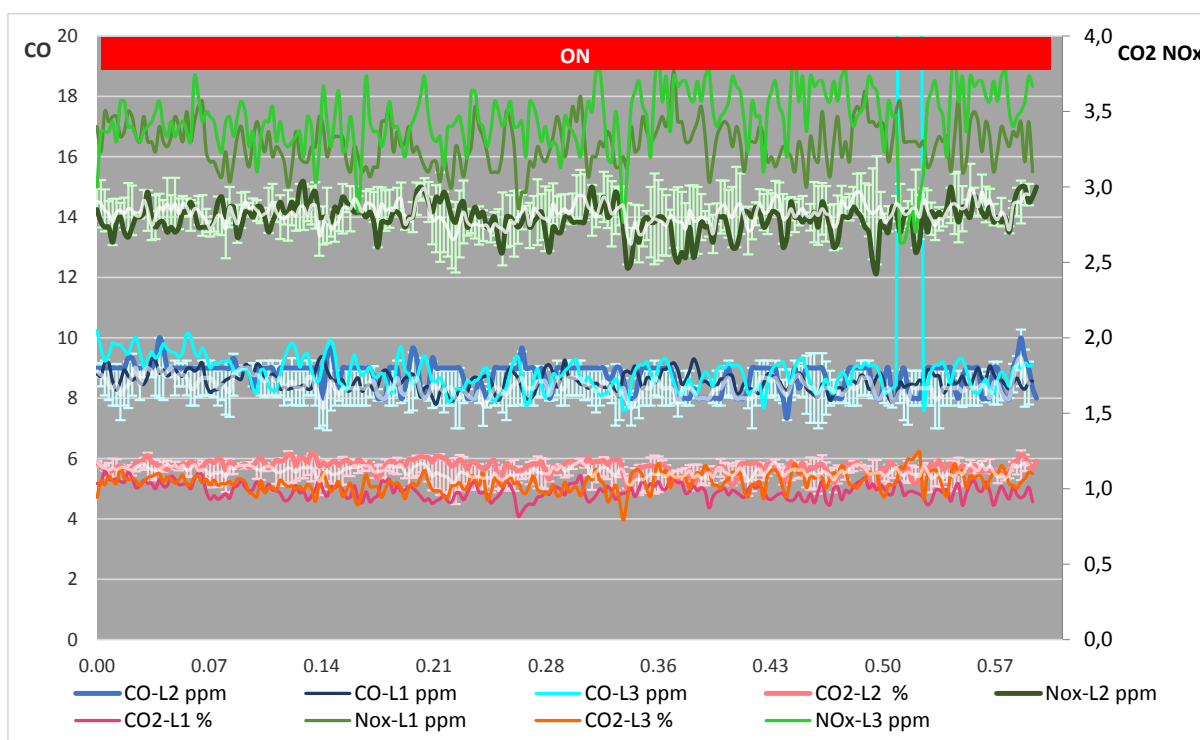


Figure 13 Variability of different fuels tests, for appliance E

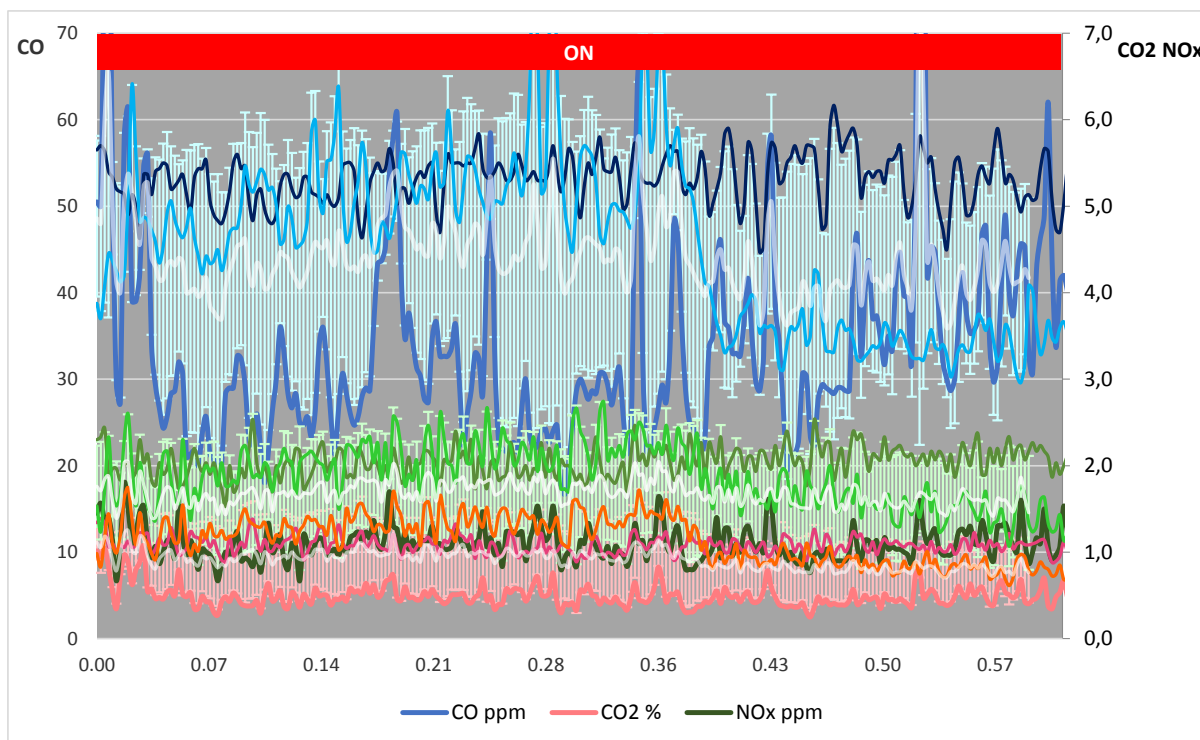


Figure 14 Repeatability of direct combustion tests, for appliance A (as a function of time)

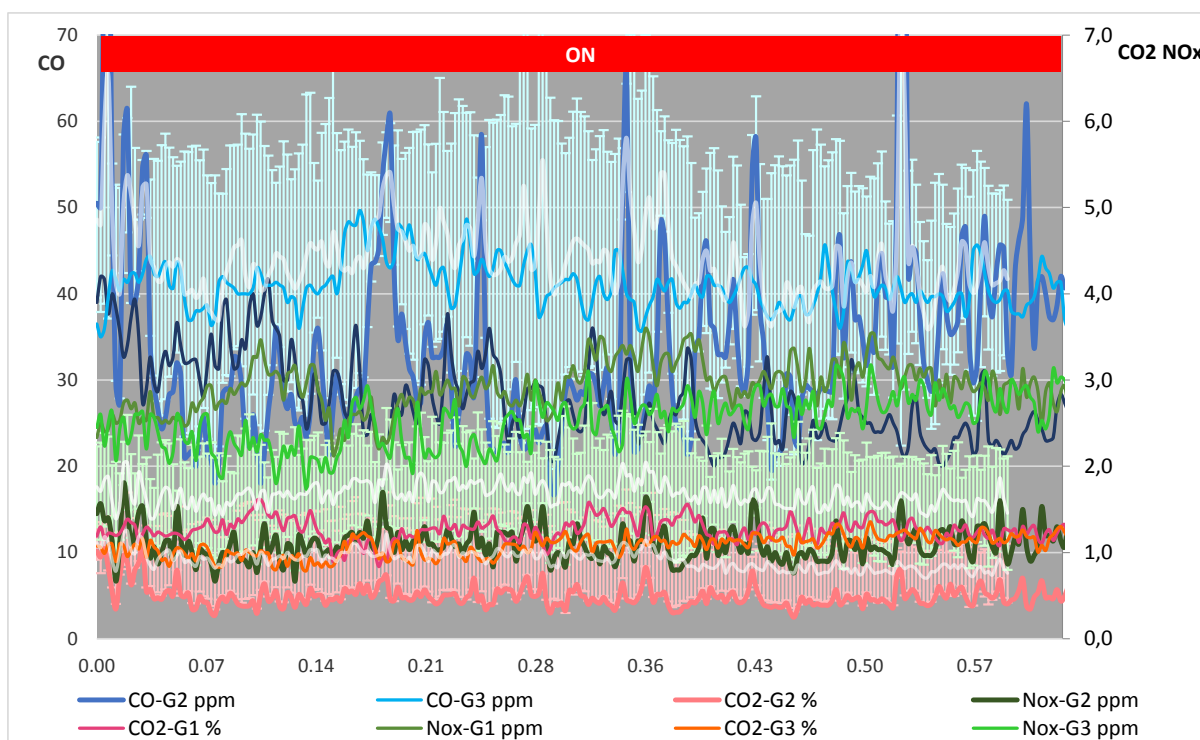


Figure 15 Variability of different fuels tests, for appliance A (as a function of time)

4.2 Correlations between emission factors and fuels/appliances

Emission factors (EF) are defined as the amount of some pollutants emitted from a source per unit of either mass of fuel burnt or energy produced or any other parameter of interest (for example km in the automotive sector). Emission factors are useful to compare different emission sources on the same basis and to compare the environmental performances of appliances and fuels. For instance a CO emission of 100 mg/kg fuel indicates that a specific appliance produces 100 mg of CO when 1 kg of fuel is burnt. The same concept could be expressed in terms of g/MJ using the calorific value of the fuel as reference parameter.

Another useful parameter, often reported to quantify and compare emission sources, is represented by the mass flux or emission rate, that is the total mass of any pollutant emitted per unit time (expressed in g or kg per unit time). This parameter expresses the actual impact of an emission source on the surrounding environment.

These two parameters have been calculated from the tests previously described and they are reported in Table 17 and **Table 18**. The comparison of emission factors clearly indicates the very high specific emission of gel appliance A and partially C, in terms of CO and TOC. The emission factor for CO₂ is the same in all the cases, because it comes directly from the stoichiometry of reaction. In **Table 19** some examples of emission factors for other combustion devices are reported, it is important to underline that many of them are referred to appliances compulsory connected to a stack, while only candles are flueless. However, it is possible to notice that CO and TOC emission factors of ethanol fireplaces are similar to the corresponding emission factors of different kind of burners and stoves, while NO_x factors are usually below the values obtained for boilers and stoves. With respect to scented candles, ethanol fireplaces seem to emitted less NO_x (and this could be ascribed to the flame temperatures that with alcohol fuels are lower than with waxes) but more TOC emissions.

On the other side, mass fluxes takes also into account the power of the appliance, it is particularly evident for CO₂, that is directly estimated from the consumption rate of each appliance, hence even appliances with a lower specific emission may have a relatively high mass flux, if they have a higher power.

These factors are commonly considered in numerical models to predict the possible concentrations of pollutant substances that could be found into an indoor environment, such as a ventilated room, when these appliances are present and used.

Table 17 Emission factors for appliances and fuels

EMISSION FACTORS										
	CO	NO _x	TOC	CO ₂	HCHO	CO	NO _x	TOC	CO ₂	HCHO ⁵
	<i>mg/kg fuel</i>	<i>mg/kg fuel</i>	<i>mg/kg fuel</i>	<i>kg/kg fuel</i>	<i>mg/kg fuel</i>	<i>g/GJ</i>	<i>g/GJ</i>	<i>g/GJ</i>	<i>kg/GJ</i>	<i>g/GJ</i>
A-G1	3600	428	5775	1.91	86.9	128.57	15.29	206.25	0.068	3.1
A-G2	6322	387	1310	1.92	123.5	225.79	13.82	46.79	0.069	4.4
A-G3	4356	490	655	1.91	86.8	155.57	17.50	23.39	0.068	3.1
C-G1	937	437	44	1.91	3.6	33.46	15.61	1.57	0.068	0.13
C-G2	1388	390	109	1.91	7.3	49.57	13.93	3.89	0.068	0.26
C-G3	1410	457	112	1.91	2.1	50.36	16.32	4.00	0.068	0.07
B-L1	1314	506	331	1.91	24.0	46.93	18.07	11.82	0.068	0.86
B-L2	1617	576	412	1.91	36.1	57.75	20.57	14.71	0.068	1.3
B-L3	1486	591	644	1.91	26.9	53.07	21.11	23.00	0.068	0.96
D-L1	913	516	84	1.91	5.3	32.61	18.43	3.00	0.068	0.19
D-L2	872	752	80	1.91	34.0	31.14	26.86	2.86	0.068	1.2
D-L3	823	524	80	1.91	-	29.39	18.71	2.86	0.068	-
E-L1	1042	658	217	1.91	17.8	37.21	23.50	7.75	0.068	0.63
E-L2	898	523	183	1.91	-	32.07	18.68	6.54	0.068	-
E-L3	1008	604	193	1.96	-	36.00	21.57	6.89	0.070	-
F-L1	719	927	101	1.91	3.7	25.68	33.11	3.61	0.068	0.13
F-L2	847	787	95	1.91	13.7	30.25	28.11	3.39	0.068	0.49
F-L3	847	787	95	1.91	-	30.25	28.11	3.39	0.068	-

⁵ HCHO= formaldehyde

Table 18 Mass Fluxes for appliances and fuels

MASS FLUXES				
	CO	NOx	TOC	HCHO ⁶
	mg/min	mg/min	mg/min	mg/min
A-G1	13.5	1.6	21.7	0,33
A-G2	28.9	1.8	6	0,56
A-G3	22.6	2.5	3.4	0.45
C-G1	8	3.7	0.4	0.03
C-G2	11.8	3.3	0.9	0.06
C-G3	12	3.9	1	0.02
B-L1	9.4	3.6	2.4	0.17
B-L2	12.8	4.6	3.3	0.29
B-L3	10.9	4.3	4.7	0.2
D-L1	7.6	4.3	0.7	0.04
D-L2	7	6.1	0.6	0.27
D-L3	6.8	4.3	0.7	-
E-L1	9.4	5.9	2	0.16
E-L2	7.9	4.6	1.6	-
E-L3	8.9	5.4	1.7	-
F-L1	9.6	12.4	1.3	0.5
F-L2	11.3	10.5	1.3	-
F-L3	11.3	10.5	1.3	-

Table 19 Examples of emission factors for different class of combustion devices from Migliavacca et al (2006), Marengo et al (2009) and Derudi et al. (2012)

	CO	NOx	TOC	HCHO	
	g/GJ	g/GJ	g/GJ	mg/kg	
Gasoil Boiler	20 - 125	50 - 60	5 - 30		CF ⁷
Natural gas Boiler	20 - 320	26 - 47	40 - 60		
Fuel Oil	45	50 - 170	2 - 5		
Pellet Stove	300	25	15		
Closed fireplace	1725	80	200		
Traditional stove	3400	30	355		
Burning wood ⁸				180–1165	
	(mg/g)	(mg/g)	(µg/g)		
Scented candles jar ⁹	2.5 - 4	0.8 – 0.9	13- 23		FL ¹⁰

⁶ HCHO= formaldeehyde

⁷ Conveyed Flue

⁸ Salthammer et al. 2010

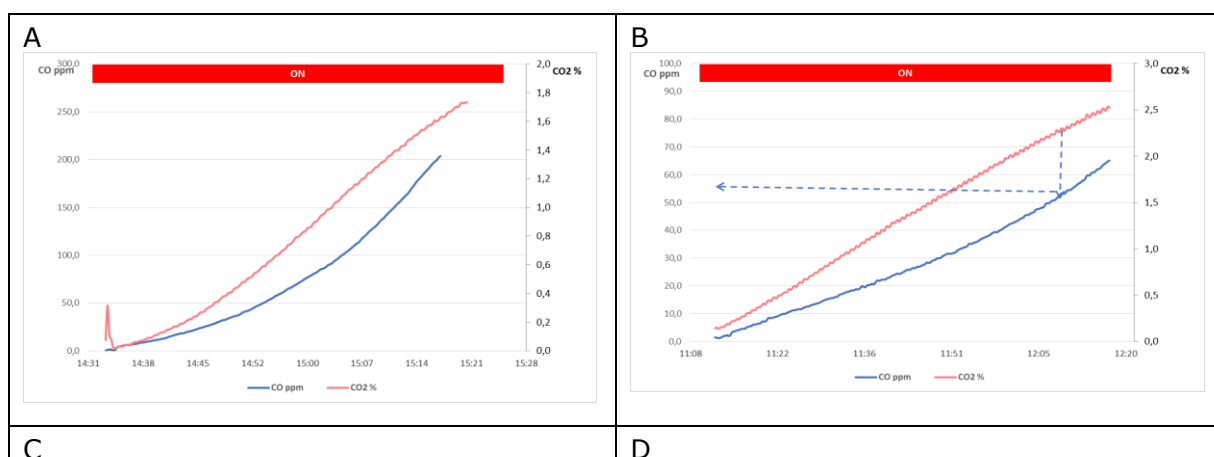
⁹ Derudi et al. 2012

4.3 Experimental tests in a sealed chamber

A sealed room (with dimensions 2.0 m x 3.6 m x 2.5 m, for a total volume of 18 m³) built according to cited French standard NF D 35-386 has been used to carry out tests in worst ventilation conditions.

The appliance, placed inside the room, is lighted on at its maximum power and the room immediately sealed. The test stops when either the CO₂ concentration in the chamber reaches a value of 2.3% or the flame extinguishes spontaneously. By means of a continuous analyser the concentration trends of each parameter (CO₂, CO, NO_x, relative humidity and temperature) have been recorded and compared. The maximum CO value can be compared with the limit value defined in the French standard, which is fixed at 80 ppm. In **Figure 16** results are reported for each appliance with one single fuel, because the fuel type resulted ineffective on these tests.

As shown in Figure 16 three of the six appliances (namely B, C, and E) fully respect the French standards with CO concentrations well below the limit. For appliance F the situation is peculiar, because the embedded sensors shut the appliance off before 2.3 % of CO₂ concentration is reached; as a consequence it is not possible to say that the test is passed. It is easy to extrapolate anyway that if the test went on up to the CO₂ reference condition the limit would be respected. Similarly, appliance A does not reach the CO₂ reference value because of the flame vanishes spontaneously, but in this case the CO concentration reached is well above the aforementioned limit. Finally, for appliance D the test is carried out properly, but the limit value is largely exceeded. It is important to underline that, while liquid appliances produce very repeatable results, the gel appliances have a quite erratic behaviour.



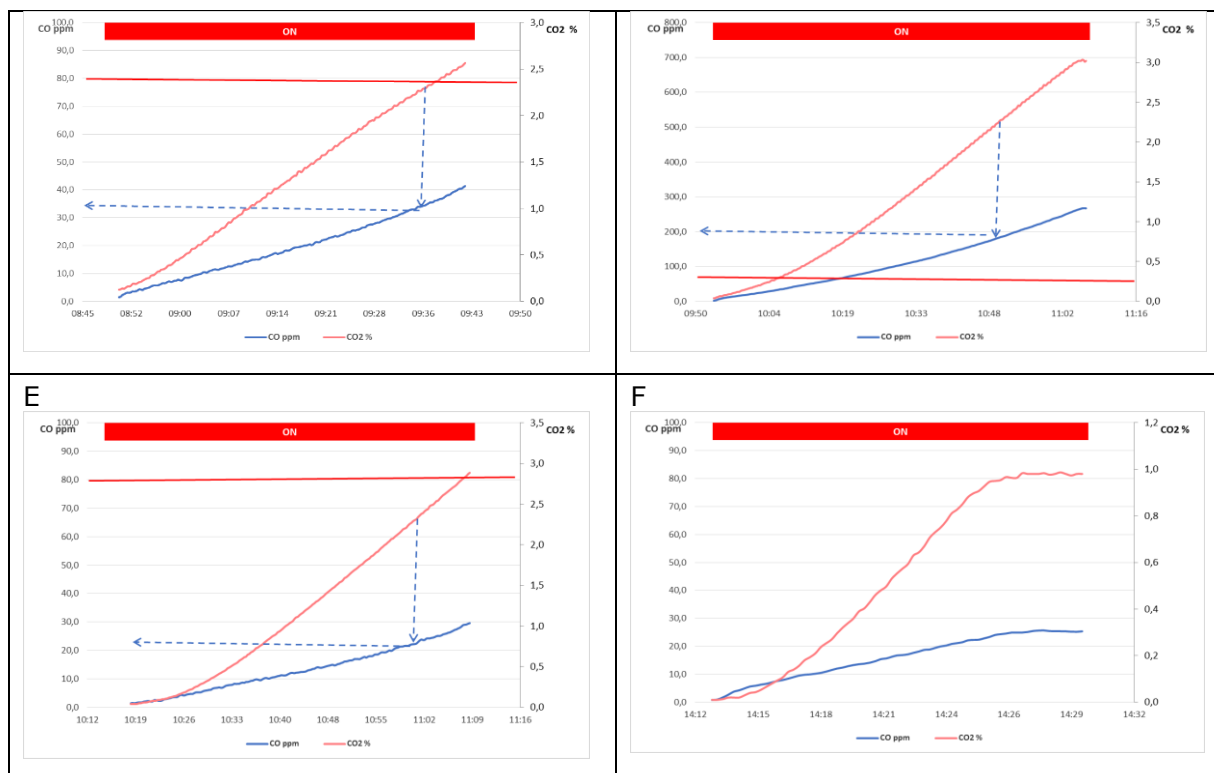


Figure 16 Main results of Sealed Chamber tests performed with the investigated appliances (as a function of time)

5 EFFECTS ON INDOOR AIR QUALITY

5.1 Experimental tests in a ventilated chamber

In order to study the direct effect of the use of alcohol flueless fireplaces on the indoor air quality, a series of tests has been carried out in a ventilated chamber.

The ventilated chamber, specifically set up for this application, has the dimensions of 3.4 m x 2.9 m x 3.0 m, for a total volume of 29.6 m³. A known amount of pre-filtered ambient air is injected into the chamber to get the desired ventilation conditions. Gas analysers, sampling probes and other specific instruments have been used to determine the pollutants emissions conveyed out of the chamber through the outlet duct. Automatic analysers able to work at ppb-level concentration are used to measure CO, CO₂, NO_x and methane and non-methanic hydrocarbon species; active and passive sampling systems are used to collect and subsequently analyse aldehydes, VOCs, and PAHs. Particulate matter concentration is determined by means of an optical instrument, that measures the number concentration of particles in the range 1-10 µm and then converts these data in an estimation of mass concentrations expressed as PM₁-PM_{2.5}-PM₁₀. In addition, the number concentration and distribution of particles in the range 5 nm–1 µm are measured on line using an UFP particle sizer, based on electrostatic detectors.

A complete test, in the ventilated chamber, consists of on/off cycles reproducing the typical conditions of the usual domestic operation of these appliances. The room is preliminary purged with filtered air and the blank concentrations are recorded for 1 hour at least; then the appliance is put in the room and lighted on, the door is closed again for one hour while the fuel burns. After about one hour, the door is open to switch the appliance off, manually or automatically according to the specific type of appliance. The door is closed again for one hour, while the ventilation air purges the chamber. Then the appliance is switched on for one hour again and hence the test is concluded. During the whole period of the test (three hours globally, the ventilation rate is kept constant and the on-line parameters are recorded, including temperature and relative humidity. Every time the door is opened (three times a test) some fresh air enters the room producing a discontinuity in the trends of the parameters recorded. Inside the room a fan, placed on the floor and directed towards the ceiling is used to ensure a good mixing of the inside air and to get homogeneous concentrations during the test.

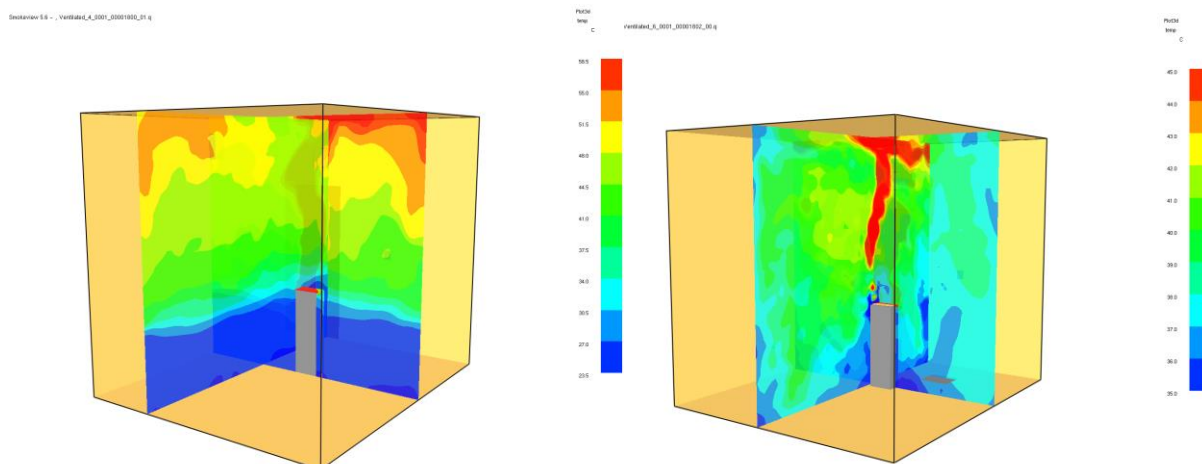


Figure 17 Results of CFD simulations representing the temperature distribution inside the test chamber without (left) and with (right) a fan to promote mixing of the internal air

A preliminary CFD (Computational Fluid Dynamics) numerical simulation has been carried out to analyse the dynamics of the system. In particular the best placement of the internal fan has been analysed. In fact the option of putting the fan on the ceiling of the room has been discarded, because it disturbs the flame too much, for some appliances at least. Mixing is needed because the high temperature of the combustion products produces a two layers situation, where upper layer of hot gases is not well mixed with the lower one.

In **Figure 17** the predicted temperature field is shown without mixing on the left and with a fan on the floor, oriented vertically, in the picture on the right.

The FDS simulation code (McGrattan et al. 2007), developed by NIST (National Institute of Standards and Technology) and available freeware, has been used for these calculations.

In the Figures from **Figure-A 7** to **Figure-A 18** some representative results from each appliance are reported to exemplify the behaviour of the different appliances in the ventilated chamber tests. The entire three hours period of the tests is shown in Figures; for each appliance the concentration curves of CO, CO₂ and NO_x are reported: as expected, the concentration of these species increases rapidly with a rate proportional to the power of the appliance and its specific emission factor, after one hour the same concentrations suddenly fall because the door is opened and the appliance is switched off. From now on, for one hour, the decrease in the concentrations is governed by the air exchange rate of the room. Then, when the appliance is switched on again, more combustion products are released and, because the starting level is generally higher than in the beginning, the concentrations in the second cycle rises higher than in the first cycle. In each plot, a red shaded area covers the periods of time, during the tests, in which the CO₂ concentration exceeds the value of 5000 ppm (i.e. 0.5%), that is considered the maximum allowed level in the German Standard. Even though carbon dioxide is not intrinsically toxic, staying for a long period at CO₂ concentrations higher than this level is not advisable, also because the oxygen content of the air is proportionally reduced.

5.1.1 Results

In one case only (namely for appliance A), also a blue shaded area is shown, corresponding to the period of time in which the CO concentration exceeds the TLV-TWA threshold of 25 ppm for workplaces.

Since the curves are nearly specular in the three phases, the average concentrations are quite constant during the tests.

In the reported Figures the ventilation has been fixed at 0.5 air exchanges per hour (AER), that is usually accepted as a proper room ventilation. Each test has been carried out also at a lower ventilation (about 0.2 AER), in order to simulate conditions of poor ventilation.

The experimental results clearly indicate that, even at 0.5 AER, quite inhospitable conditions are quickly reached in the room, in terms of temperature, which rises up to 45-50°C, starting from 25°C, and CO₂ level. These conditions are extreme enough to trigger the control devices of automatic appliances, that act by modulating (in the case of appliance E) or switching off (for the F one) the appliance itself. This is the reason why in **Figure-A 15** the curves show a peculiar jagged aspect, while in Figure-A 17 the "on phase" is shorter than the expected one hour.

For each appliance, a Figure showing the ultrafine particle concentration in the room is also reported: in nearly all the cases, a peak is observed during combustion, likely produced mainly in the vanishing phases. It is interesting to notice that only small particles are produced, while the concentration of the big ones are not significantly affected. This behaviour is confirmed by the optical PM monitor that does not measure any appreciable increase in the PM₁-PM_{2.5}-PM₁₀ concentrations, as shown in **Figure 18**, where the typical trend of the PM concentration is shown. The baseline PM concentration in the chamber is around 2-3 µg/m³ because the inlet air is filtered through an HEPA filter, but every time the door is opened the PM₁₀ increases due to the particulate introduced from the outside. These data clearly indicate that alcohol fireplaces do not increment the PM concentration, but they produce ultrafine particles.

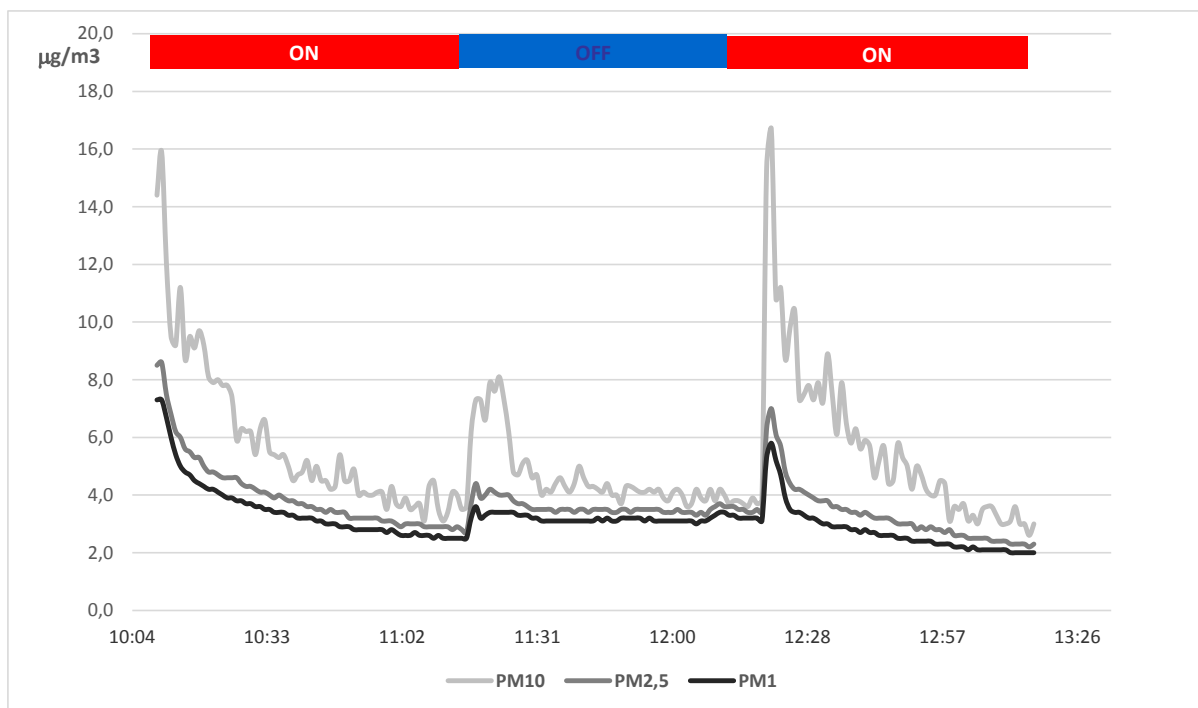


Figure 18 PM trends during a typical test (as a function of time)

Repeatability of the tests is shown in **Figure 19** and **Figure 20**, similarly to what previously done for direct combustion tests. Again, in this case three repeated tests on the same appliance (E) with the same fuel (L1) are compared and their average curve and the corresponding standard deviation are shown as a shaded area. Then the corresponding tests, performed on the same appliance, in the same conditions, but with the three different fuels are compared in **Figure 20**, here again the variability due to the fuel is comparable with the intrinsic variability of the tests.

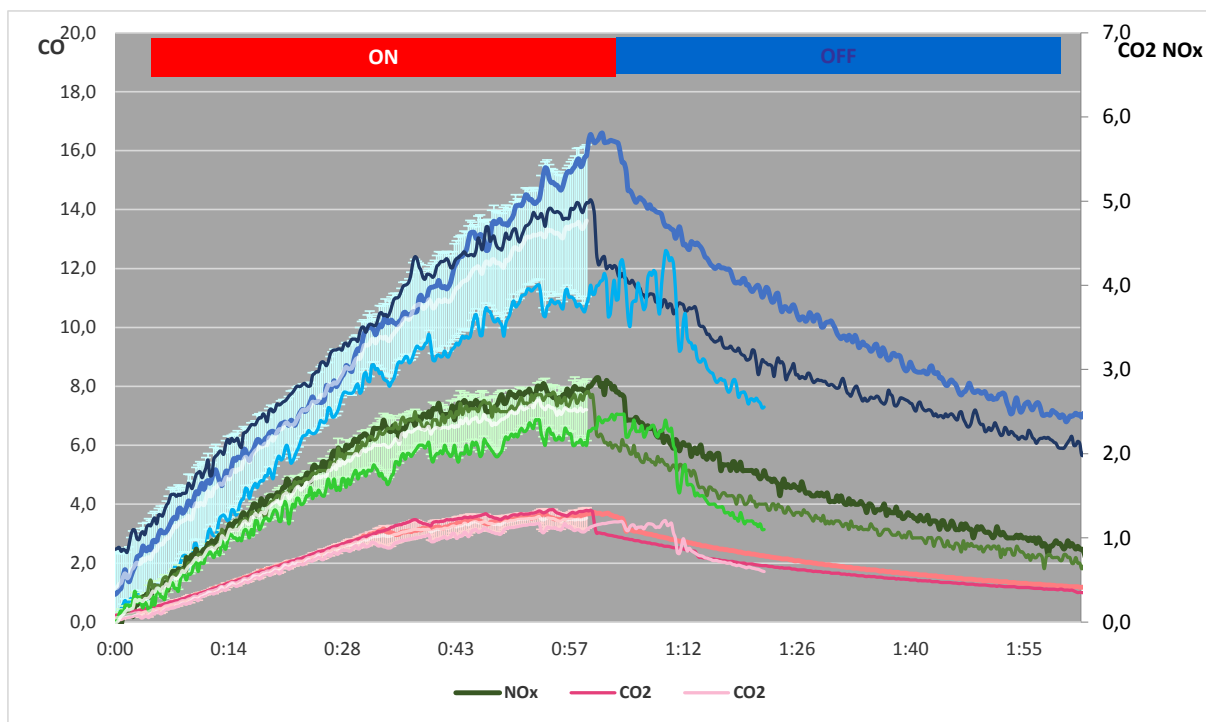


Figure 19 Repeatability of ventilated chamber test (appliance E)- (as a function of time)

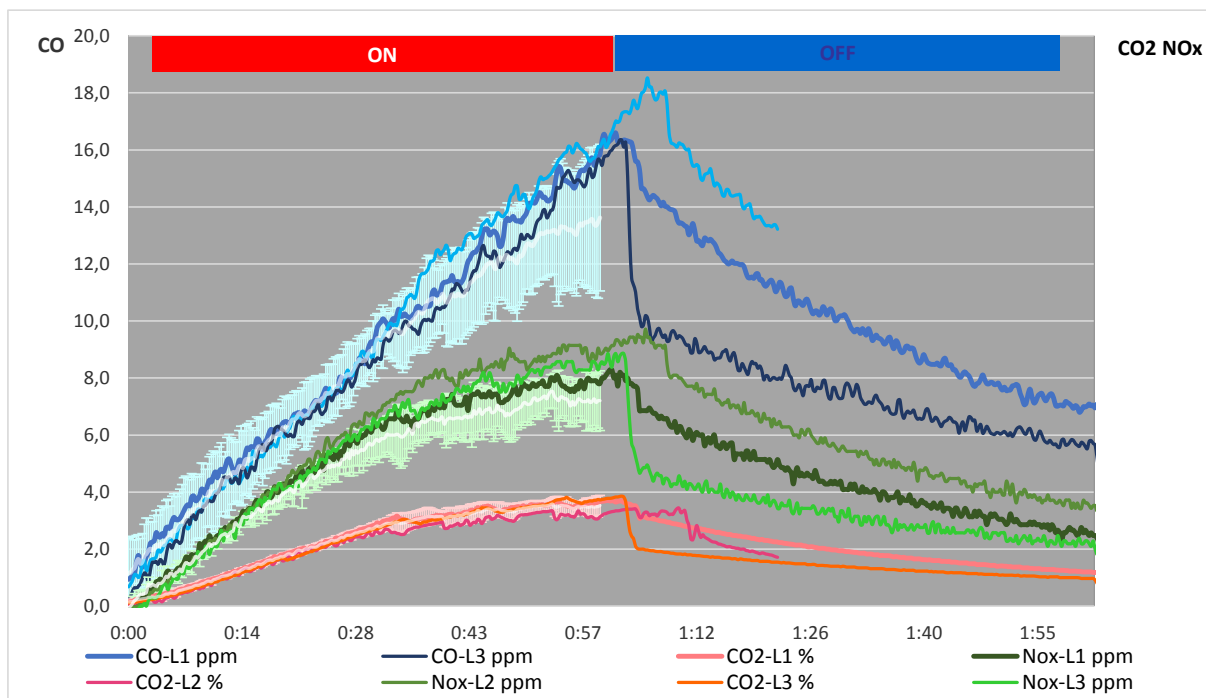


Figure 20 Variability with fuels in ventilated chamber tests (appliance E) – (as a function of time)

A summary of all the results produced in the ventilated chamber, in terms of CO, CO₂ and NO_x average, maximum and minimum concentrations are reported in the Figures from **Figure 21** to **Figure 29**. In the Figures the bars represent the average values of the tests, while the maximum and minimum values measured during the same tests are reported like "error bars". Both high ventilation (HV) and low ventilation (LV) tests are shown, even if the difference between these two conditions are not very evident. This fact is due to the small variation in the ventilation conditions used. This difference is further reduced because the room is not sealed and when the room is full of hot gases, they expand naturally and can leave the room spontaneously even when the forced ventilation is very low.

5.1.1.1 CO levels

In the Figures the threshold values are reported as well, the TLV-TWA for CO is 25 ppm, but this same value is the used in the French Standard as a limit, which considered the weighted average concentration on 1 hour in the ventilated chamber tests at 0.5 AER. These Figures show that the average values measured in the different phases of the tests are almost always below the TLV-TWA of CO in the first and second hour and also the maximum values seldom exceed this value. It is not true for appliance A, which shows extremely high CO levels, even much higher of what expected from the direct combustion tests. Also appliance D sometimes goes beyond this limit, but only in the maximum values in the first cycle. Appliance B and C in some cases exceed the limit during the second cycle. For appliance with a quite regular and steady emission, the accumulation effect is predominant in the second cycle, while appliances characterised by high emission spikes, this rule is not necessarily respected.

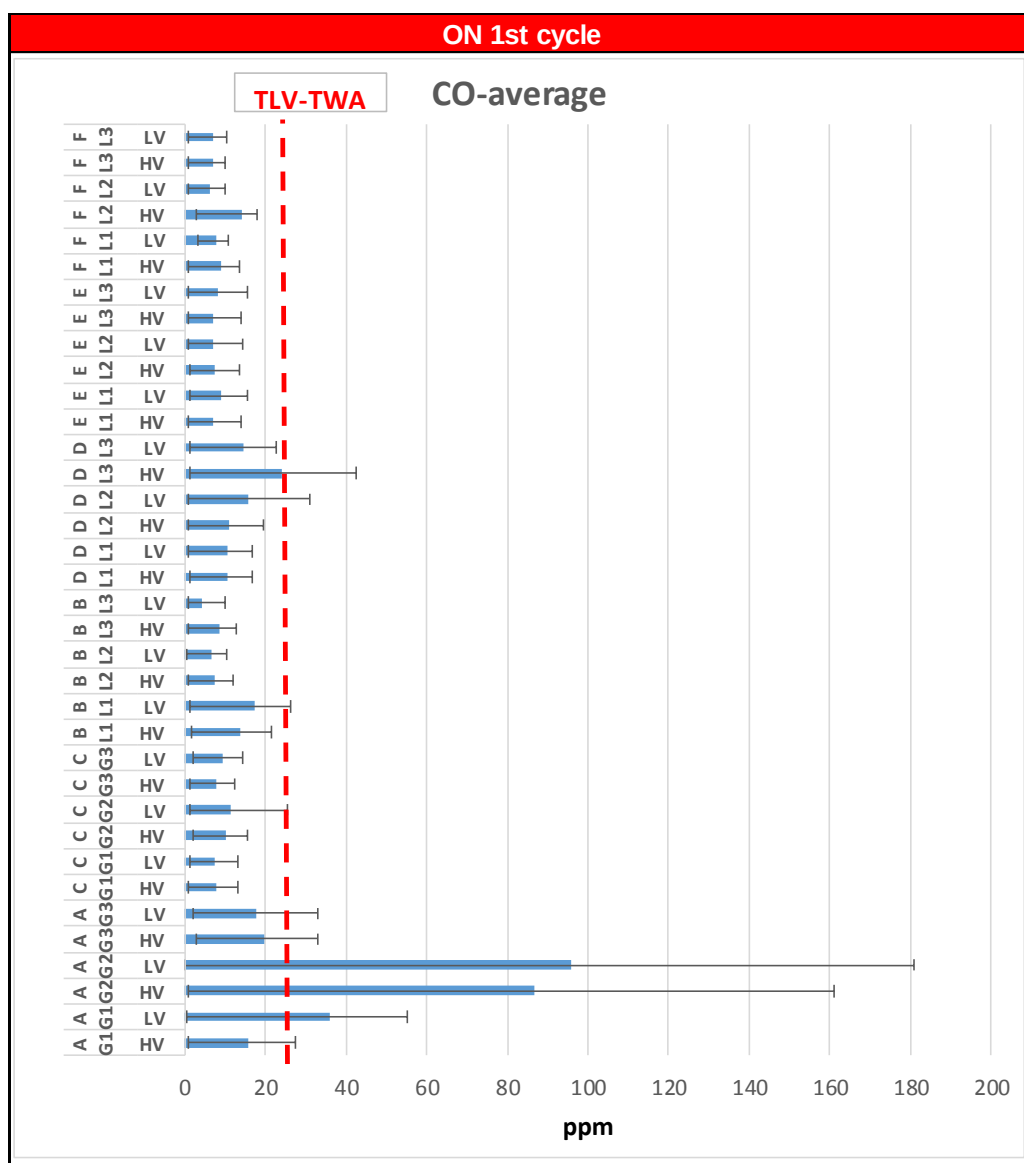


Figure 21 CO level in ventilated chamber tests in the first cycle

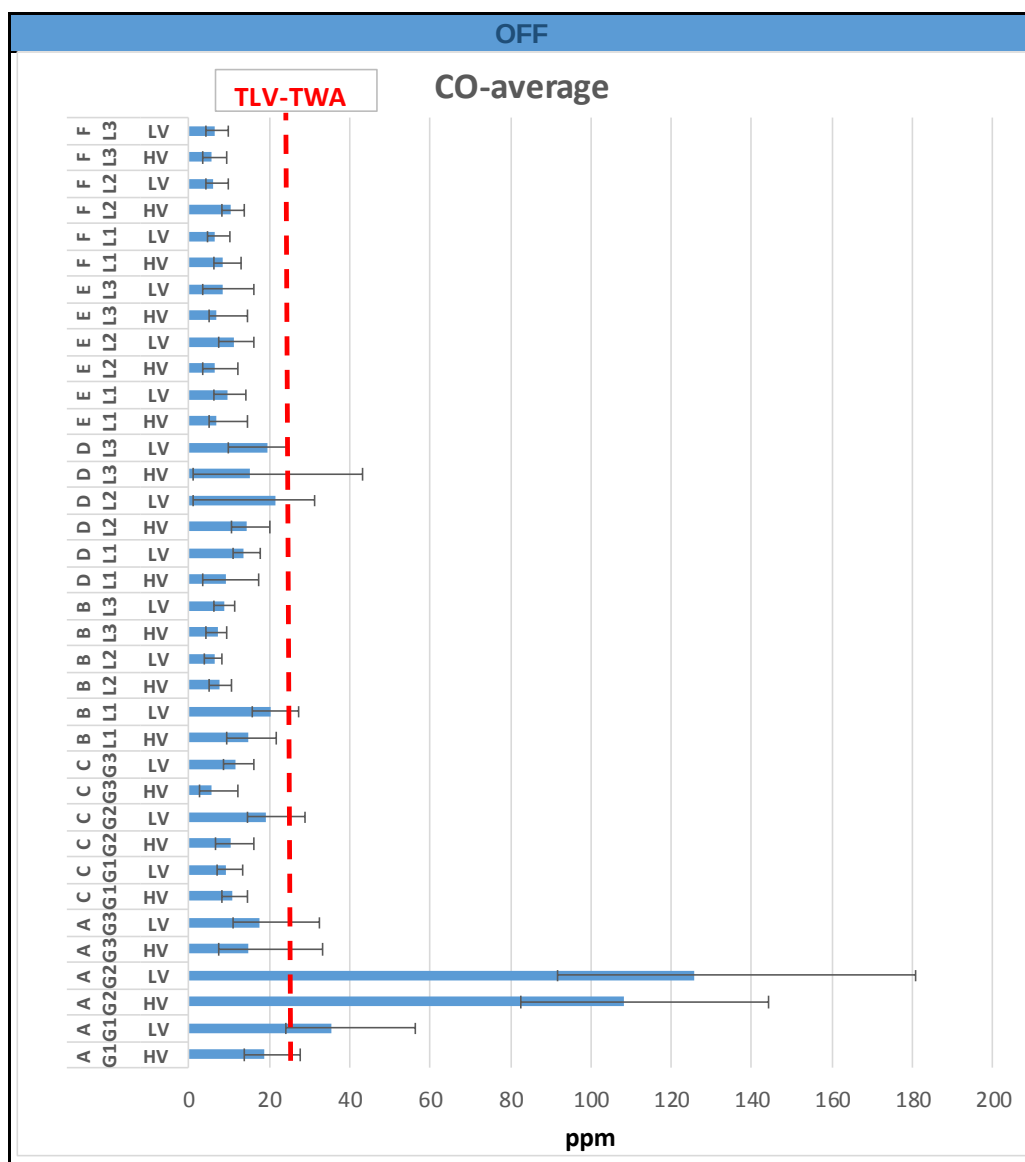
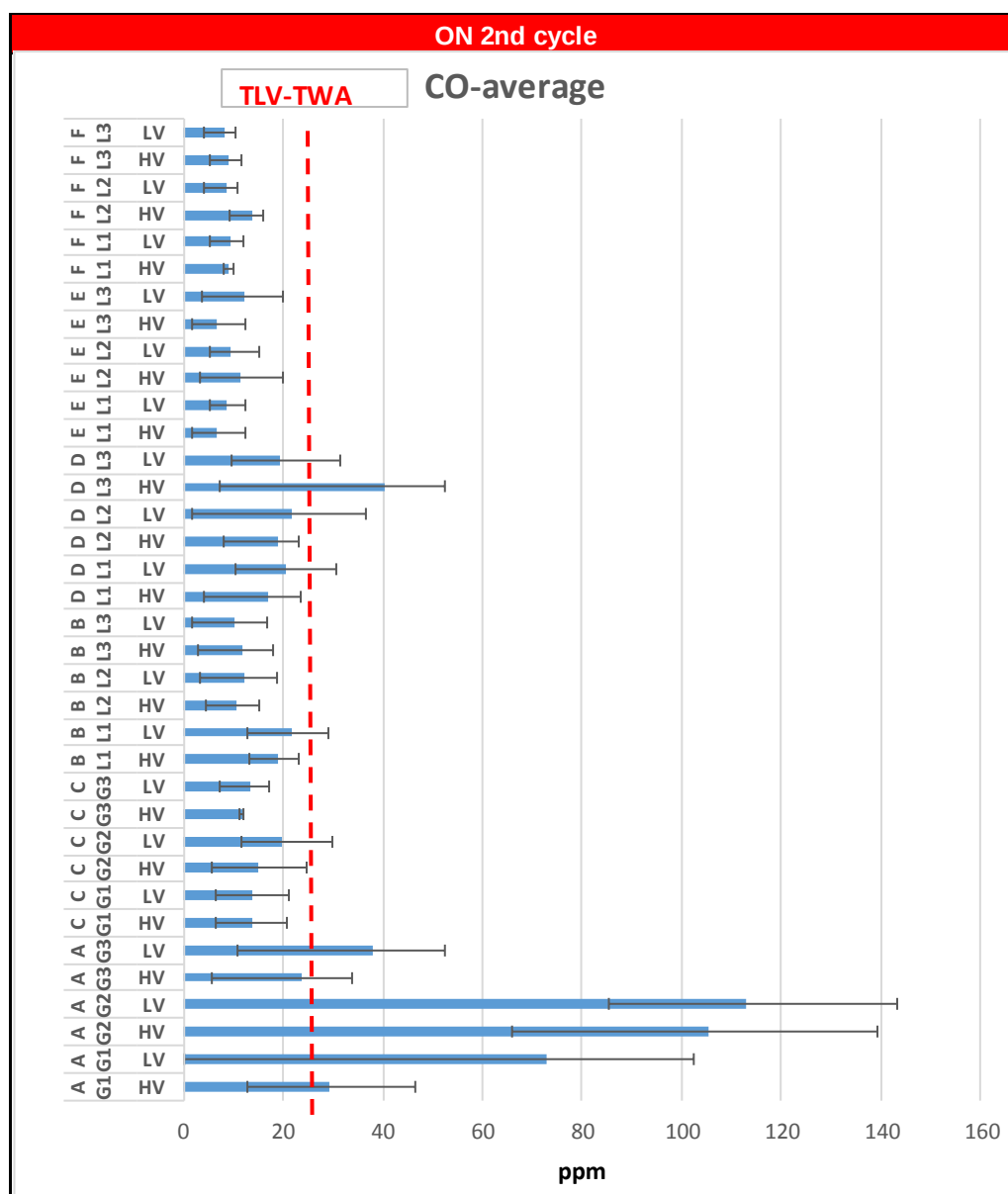


Figure 22 CO level in ventilated chamber tests in the OFF cycle



5.1.1.2 NO_x levels

NO_x levels are similar in all the test conditions, showing an average concentration always below the limit value of 3 ppm and maximum concentrations that only rarely exceed it, mainly in the second cycle. The chosen threshold value of 3 ppm is the TLV-TWA for NO₂, which is the predominant species measured in the room air, while the corresponding limit for NO is 25 ppm, consequently the most restrictive value has been adopted.

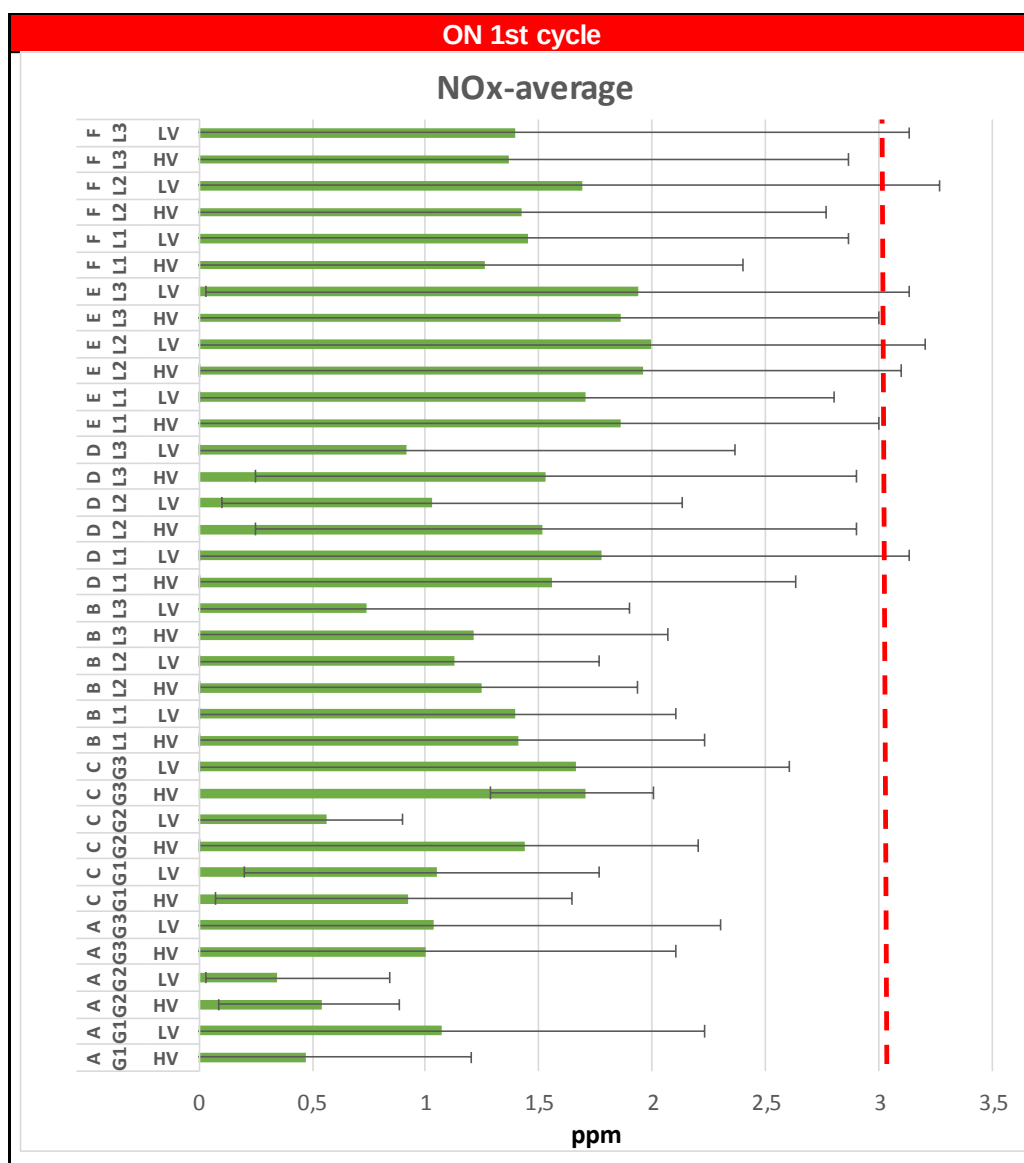


Figure 24 NOx level in ventilated chamber tests in the first cycle



Figure 25 NOx level in ventilated chamber tests in the OFF cycle

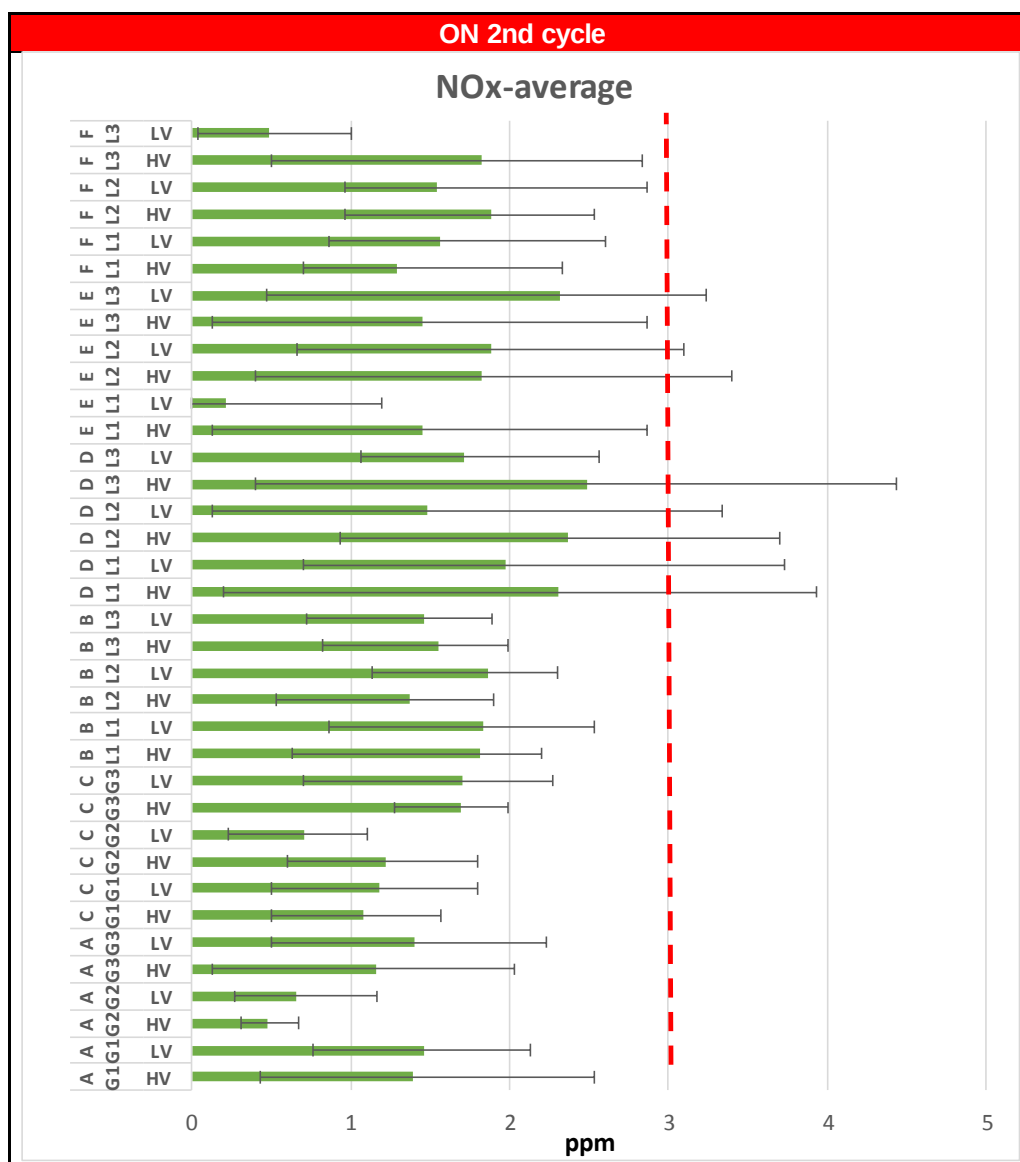


Figure 26 NOx level in ventilated chamber tests in the second cycle

5.1.1.3 CO₂ levels

The CO₂ concentration, measured in the room air during the tests, is directly related to the fuel consumption rate of the appliances and hence it is a function of their power. The threshold limit of 5000 ppm, defined in the German Standard, is always exceeded, even for small appliances.

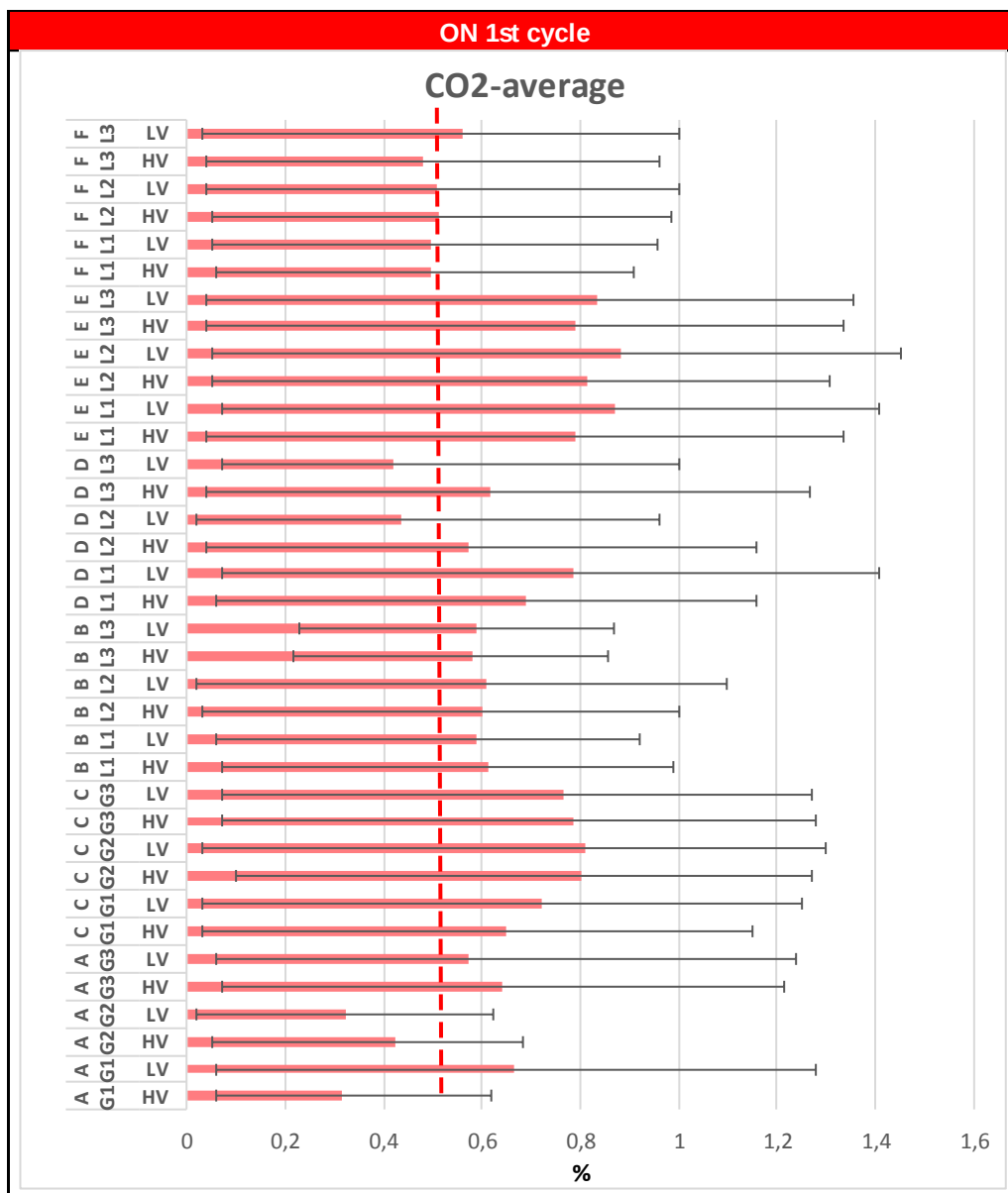


Figure 27 CO₂ level in ventilated chamber tests in the first cycle

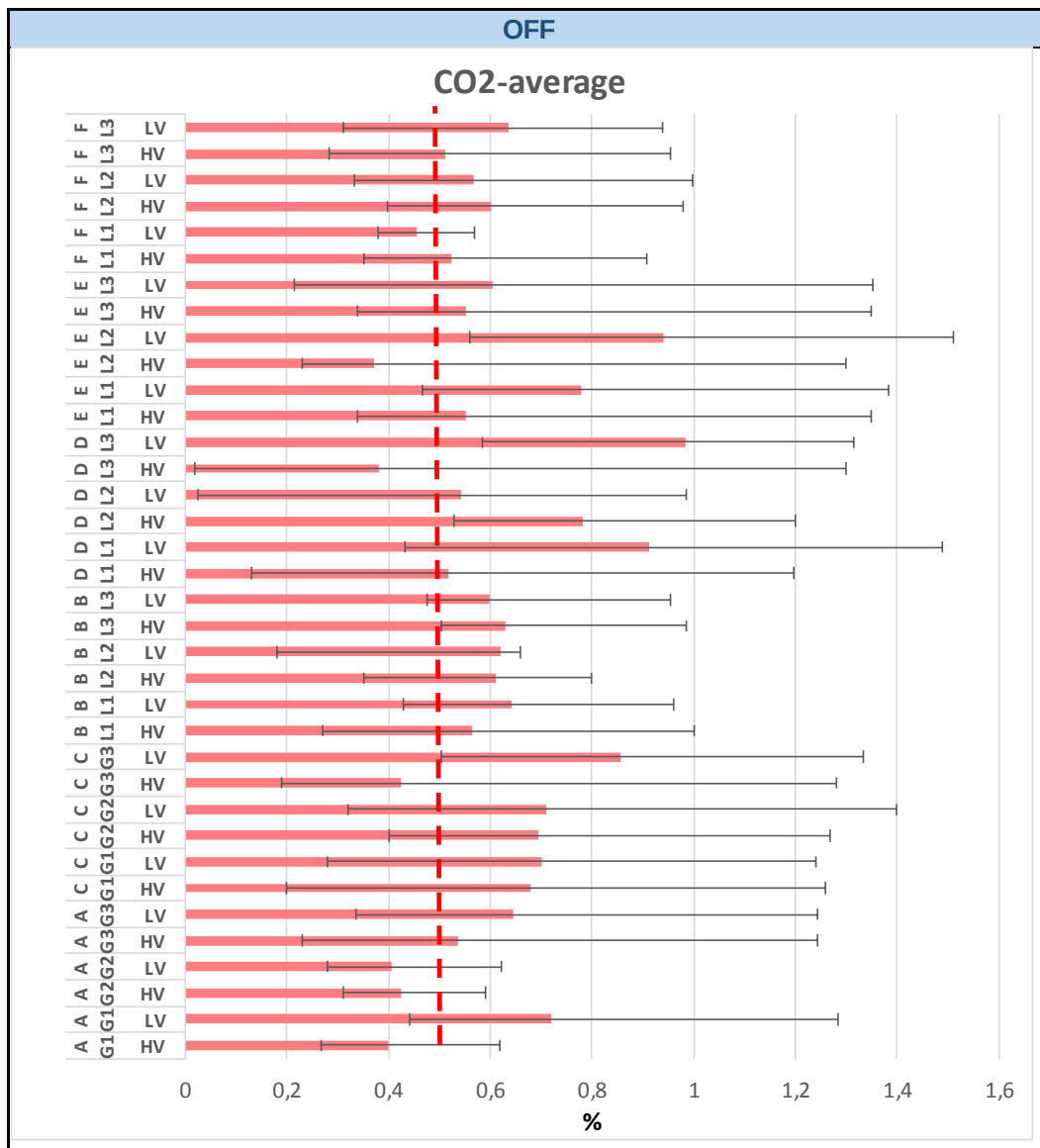


Figure 28 CO₂ level in ventilated chamber tests in the OFF cycle

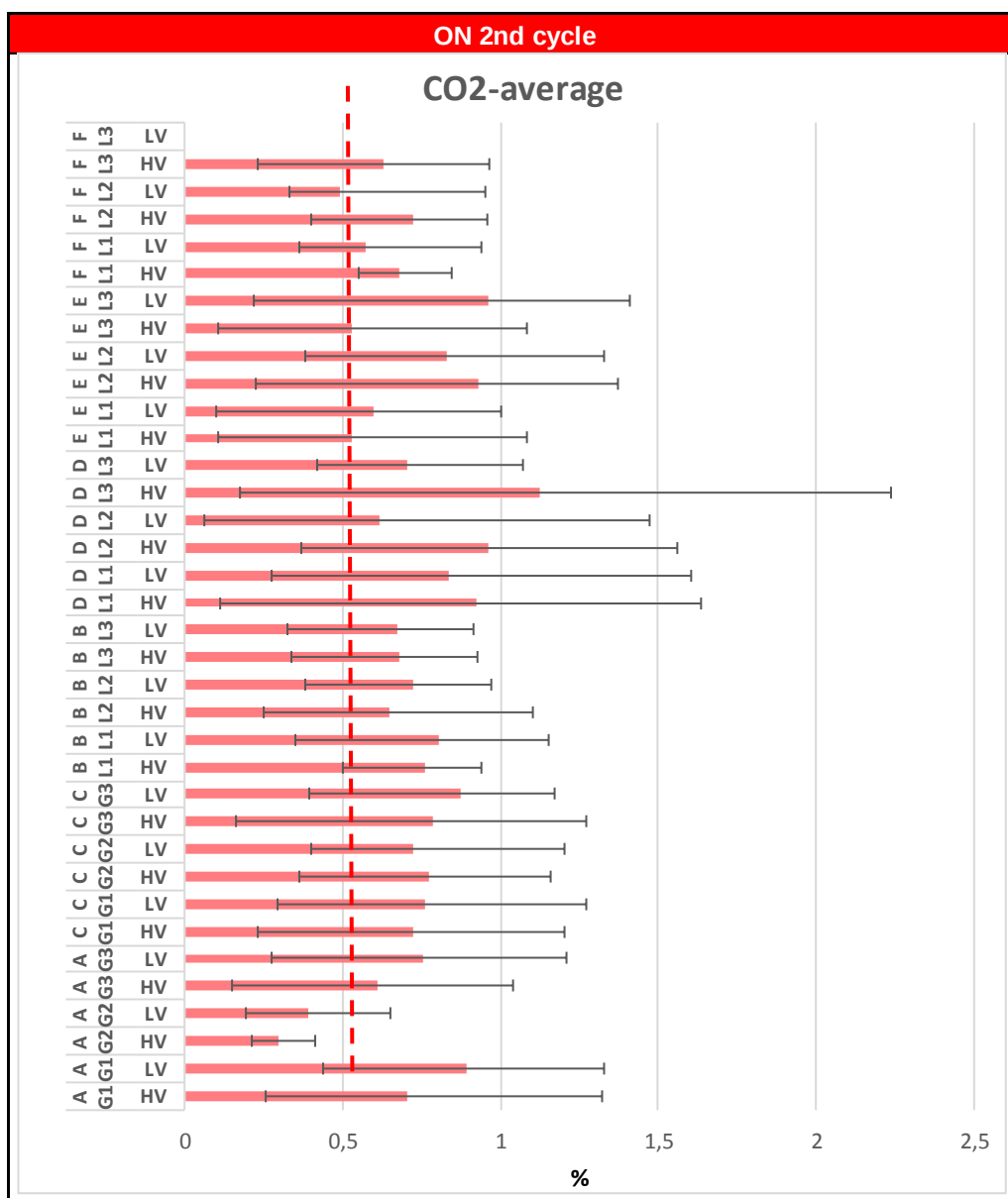


Figure 29 CO₂ level in ventilated chamber tests in the second cycle

5.1.1.4 VOC levels

The VOC concentration has been determined by means of sorbent cartridges using both active and passive sampling techniques. In particular, active samplings, by means of a pump, have been carried out for both generic VOC (using Tenax + Carbosorb cartridges) and specifically for aldehydes and ketones (DNPH cartridges). Samplings have been performed, during each test, when the CO₂ concentration was in the range between 0.4 and 0.5%, these conditions can be assumed as the acceptable limit for people to stay in the room, higher concentrations are not considered representative of a real life situation. In the same time, the passive samplers have been located in the ventilated chamber at the beginning of the each test and removed at the very end,

after three hours. The concentration measured in this way are representative of the average conditions during a series of on/off cycles.

In **Figure 30** and **Figure 31** a summary of carbonylic species (light aldehydes and ketones) measured in the ventilated chamber tests is reported, for active and passive sampling respectively. The major species observed is always acetaldehyde, followed by formaldehyde, while acetone and acrolein are measured only in trace concentrations. In most cases, both the acetaldehyde and formaldehyde concentration are below 1 mg/m^3 , with the exception of appliance A, which exceeds this level greatly, and appliance D. A good agreement is observed between the two series of data (active and passive samplings), this indicates that the concentration of pollutant species, observed at about 0.5% of CO_2 is representative of the average value of the whole on/off cycle. It is also noteworthy that these levels of concentration largely exceeds the sensitiveness level generally accepted. According to the WHO Guidelines (WHO, 2010) *"the lowest concentration reported to cause sensory irritation of the eyes in humans is 0.36 mg/m^3 for four hours. Increases in eye blink frequency and conjunctival redness appear at 0.6 mg/m^3 , which is considered equal to the no observed adverse effect level (NOAEL) The perception of odour may result in some individuals reporting subjective sensory irritation, and individuals may perceive formaldehyde at concentrations below 0.1 mg/m^3 . However, this is not considered to be an adverse health effect."*

The case of appliance A, mainly when burning the gel G2 is peculiar, because very high concentrations of pollutants have been measured, often exceeding the limit values of personal exposure, with more than 5 mg/m^3 of formaldehyde (TLV-STEL = 0.37 mg/m^3) and more than 20 mg/m^3 of acetaldehyde (TLV-STEL = 45 mg/m^3). The resulting indoor air could be potentially harmful for the human health, even though the direct perception by the people of these conditions could be enough to prevent a long exposure to these detrimental conditions.

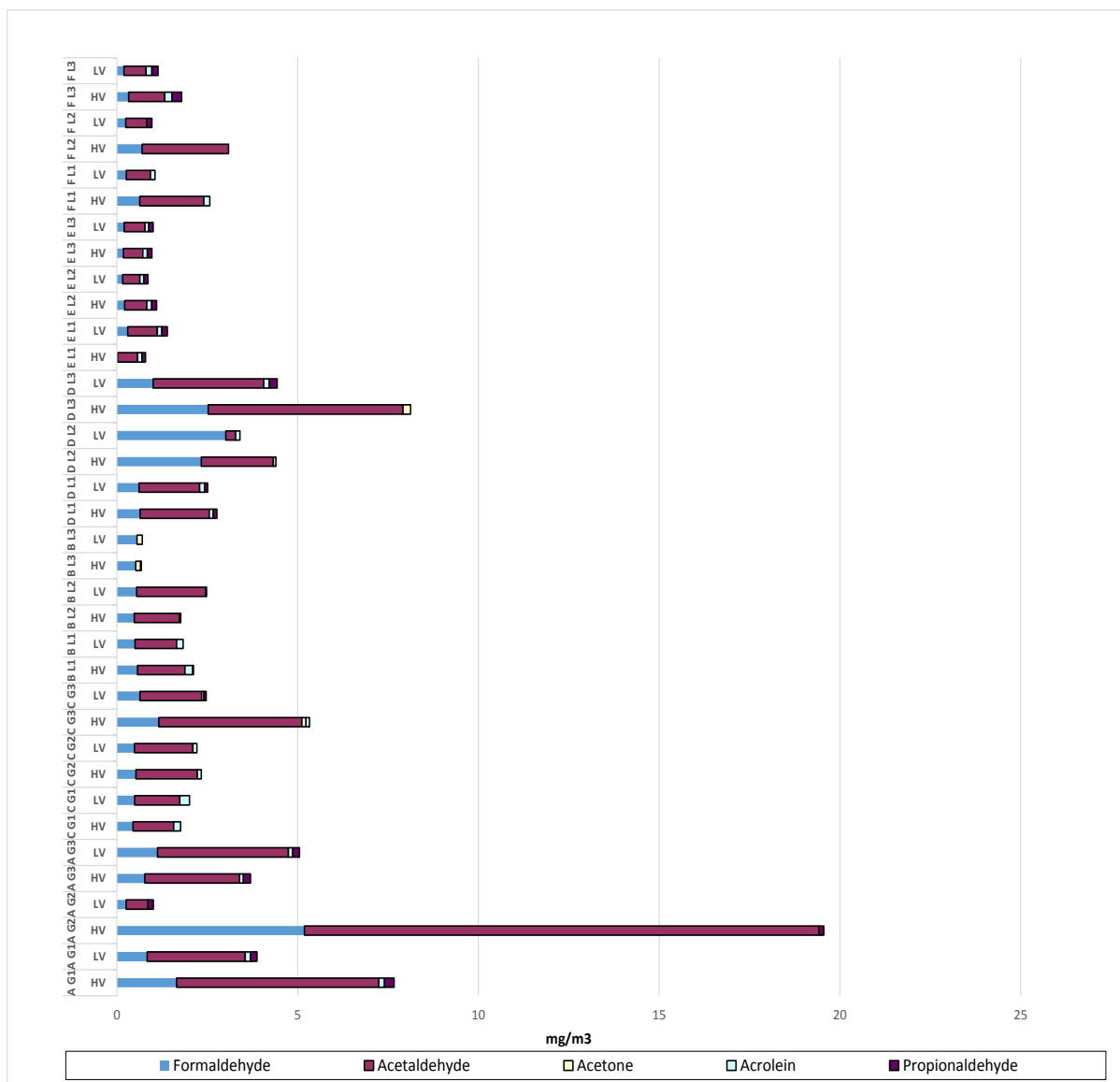


Figure 31 Carbonylic compounds in ventilated chamber tests (passive sampling)

The VOCs concentration has been measured using sorbent cartridges and GC-MS analysis, while no data from on-line FID analyser are available for these tests because, as soon as the appliance is filled with the fuel in the ventilated chamber, the concentration of ethanol released in the indoor air increases so much to go beyond the maximum range of the instrument. Hence, only off-line data have been collected from active and passive sampling. The same sampling procedure described for aldehydes has been adopted for general VOCs.

The chemical compound present in the largest amount is ethanol, that resulted often oversaturated; among the other species, observed in much lower concentrations, heavier alcohols, like 2-propanol, are quantified at a level of 1 mg/m³ along with other oxygenated species, but also aliphatic hydrocarbons and some aromatics (toluene in particular) are observed at a level of hundreds of micrograms. In **Figure 32** a comparison of the 6 appliances is shown, while in **Figure 33** the effect of ventilation is reported, finally in **Figure 34** the effect of the fuel is analysed. The trends observed for

VOCs are similar to what already described for carbonilic compounds, with appliance A burning gel G2 showing as usual the worst performances.

PAHs have not been found in measurable amounts, the detection limit of the applied technique has been estimated in 0.1 ng of naphthalene, 0.2 ng of anthracene and 0.4 ng for any other compound in each cartridge, these amounts have never been reached in any sampling.

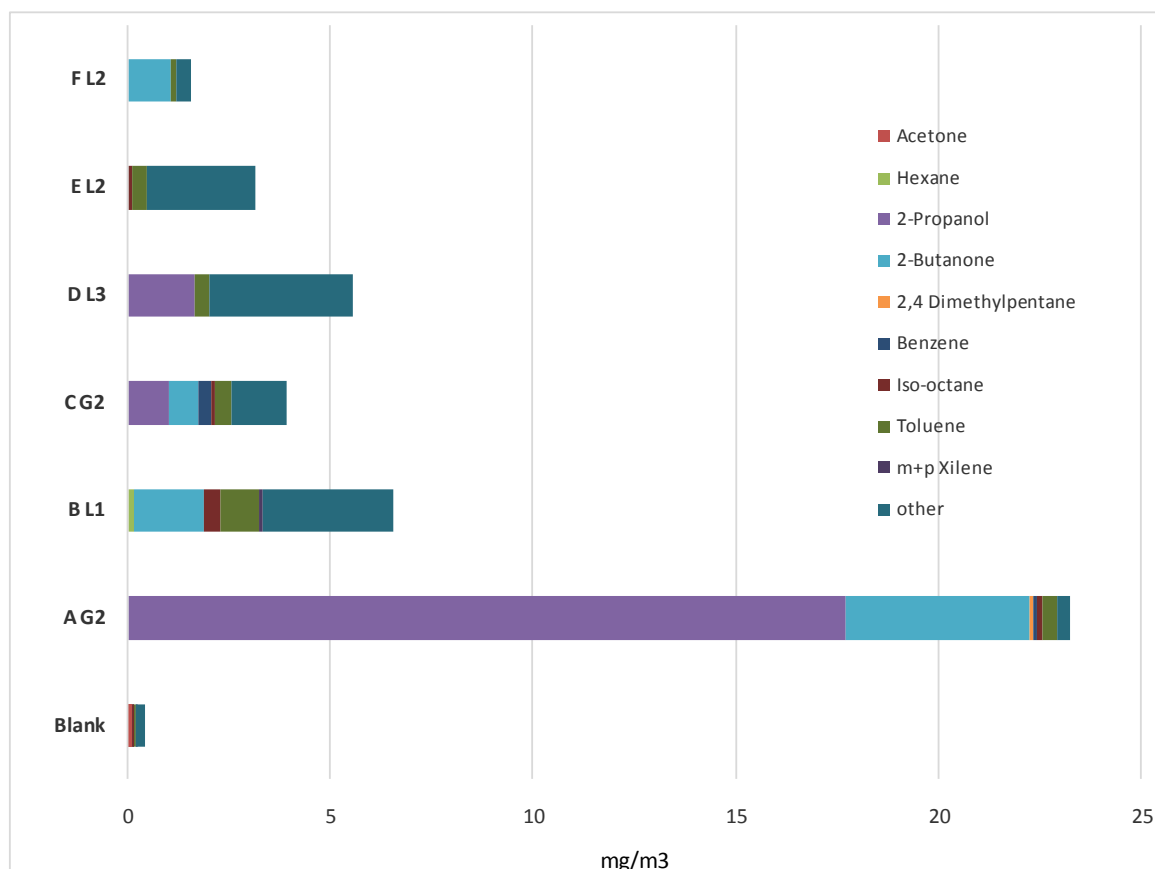


Figure 32 VOCs in ventilated chamber tests: comparison of the different appliances and the blank (which refers to the empty chamber with no appliances)

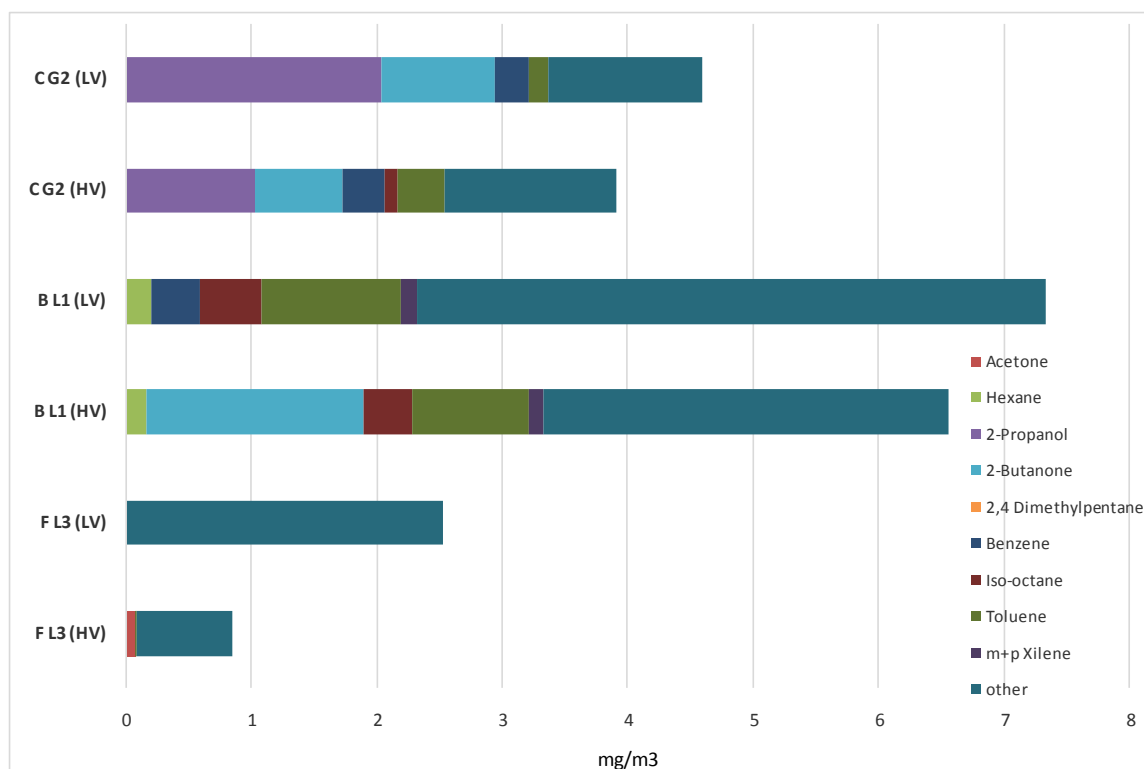


Figure 33 Effect of ventilation on VOC

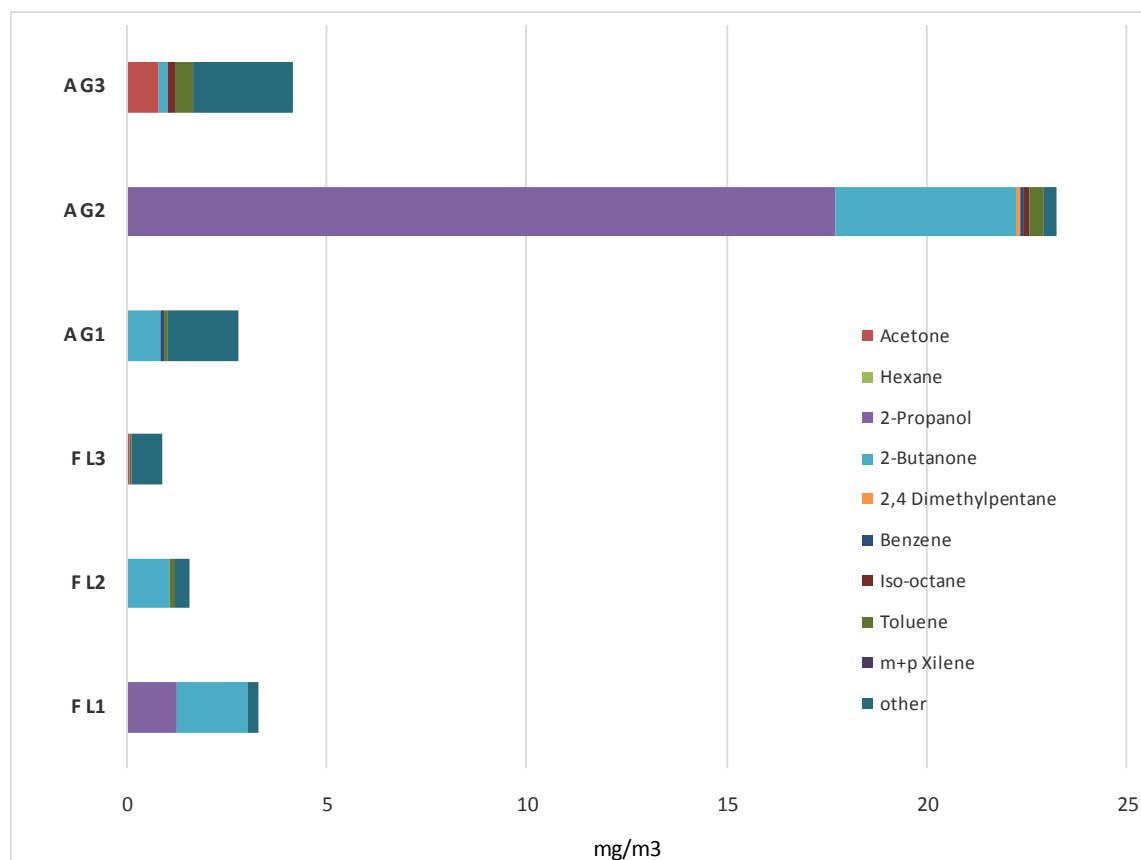


Figure 34 Effect of changing fuel

6 PREDICTIVE MODELLING OF INDOOR AIR QUALITY AND ROOM VENTILATION

6.1 Basic principles of numerical modelling

Numerical modelling allows to predict the behaviour of a physical system starting from basic assumptions on the nature of the system and the physical phenomena taking place, possibly introducing some empirical consideration and using calculation techniques. Numerical modelling is a powerful tool for analysing different possible scenarios and conditions and to predict the effect of different actions and modifications that can be applied to the system itself.

6.2 Development of a predictive model

A simple model can be defined to estimate the indoor air quality and, consequently, the human indoor exposure to combustion products emitted from alcohol-based fuels in the alcohol-powered flueless fireplaces. Starting from the information related to the emission rates (or mass fluxes or emission factors) obtained from the experimental studies, with reference to the characteristics of the ventilated chamber, a 1-box model can be defined to conservatively estimate exposure concentrations to main combustion products, as well as those of other relevant pollutants, as a function of different parameters, such as the source term, the room volume and its air exchange rate, the efficiency of the ventilation system, etc. According to the European Chemicals Agency (ECHA) classification, this model can be considered as a Tier 1 model; Tier 1 models are screening-level conservative deterministic models that allow a conservative, bounding estimate of exposure or risk using relatively little input information. Exposure determinants are single values and the approach results in high-end exposure estimates. The model assumes a constant release rate of pollutants, originated from a point-source (namely, one of the investigated appliances), and that the removal of volatile compounds and particles from the indoor environment is solely a function of the air exchange. Although removal of several pollutants, such as VOCs or particulates, due to adsorption or deposition ('sinks') is known to readily occur in common living spaces, such removal is usually not considered increasing the conservatism of the exposure estimations. The proposed model can be used to determine peak and time-weighted average exposure concentrations at maximum emission rates during, and following, the use of the appliances. Considering a short burning time and a rapid decay of the airborne pollutant concentration, no accumulation of pollutants needs to be considered; different parameters, such as the room volume, burn duration, time and air flow rates can be varied in order to calculate the emissions trends, built-up and decay dynamics of the pollutant substances, as well as the steady-state concentrations for many reference exposure scenarios. The estimated concentrations can be compared with the exposure limits proposed by several national and/or international agencies; a summary table containing different air quality standards for some potentially harmful substances is reported in Annex B.

Under normal burning conditions, the concentration of the desired pollutant reaches an equilibrium that depends only on the product emission rate and the ventilation rate. The room volume and the ventilation rate determine the time it takes to reach equilibrium conditions in the considered environment. Therefore, indoor concentrations can be estimated using a single-compartment mass balance model assuming uniform mixing between pollutants and indoor air (**Figure 35**). Equation 4 must be applied until the end of fireplace burning ($t=t_{\text{gen}}$), while Equation 5 has to be used over the remaining exposure period if the considered pollutant substance is not released also when the appliance is switched off; otherwise only Equation 4 must be taken into account, defining a proper emission factor for each phase:

$$t \leq t_{\text{gen}}$$

$$C(t) = \frac{E + C_{\text{in}} \cdot Q}{Q + k_l \cdot V} \left[1 - \exp\left(-\frac{Q + k_l \cdot V}{V} t\right) \right] + C_0 \cdot \exp\left(-\frac{Q + k_l \cdot V}{V} t\right) \quad 4$$

$$t > t_{\text{gen}}$$

$$C(t) = C_0 \cdot \exp\left(-\frac{Q + k_l \cdot V}{V} t\right) \quad 5$$

where $C(t)$ is the pollutant concentration into the environment (mg/m^3), C_0 the concentration of the pollutant into the room at the beginning of the considered emission period (mg/m^3), C_{in} the concentration of the pollutant in the supplied air, E the emission rate (mg/h), V the room volume (m^3), α the specific ventilation rate (number of air changes per time unit, defined as the ratio between the ventilation flow-rate Q and V) (h^{-1}), k_l the decay constant (h^{-1}) and t the time (h). In cases where the emission rate is constant, an asymptotic increase of the concentration can be seen until equilibrium is theoretically reached. Therefore, calculating an equilibrium concentration at the highest measured emission rate represents the worst case scenario (for this reason the decay constant k_l must be set to zero) for the exposure assessment ($C_{\text{ss}} = E/Q$). In reality, indoor air concentrations in homes and workplaces are however lower as a result of sink effects or higher air exchange rates. The emission rates of several combustion products and by-products have been determined by means of the experimental tests performed with the investigated fuels and appliances; in the case of inhomogeneous distribution conditions of the pollutants within the ventilated chamber, a correction factor (the efficiency factor ε) can be applied to the proposed well-mixed model, in order to recalculate the pollutants concentrations in a more realistic and conservative situation (so, at steady-state the concentration is $C_{\text{ss}} = E/(\varepsilon \cdot Q)$). The experimental measurements can be used to estimate the mixing efficiency of the reference experimental setup in order to properly calibrate the model parameters and to recalculate the pollutant trends in a more realistic situation.

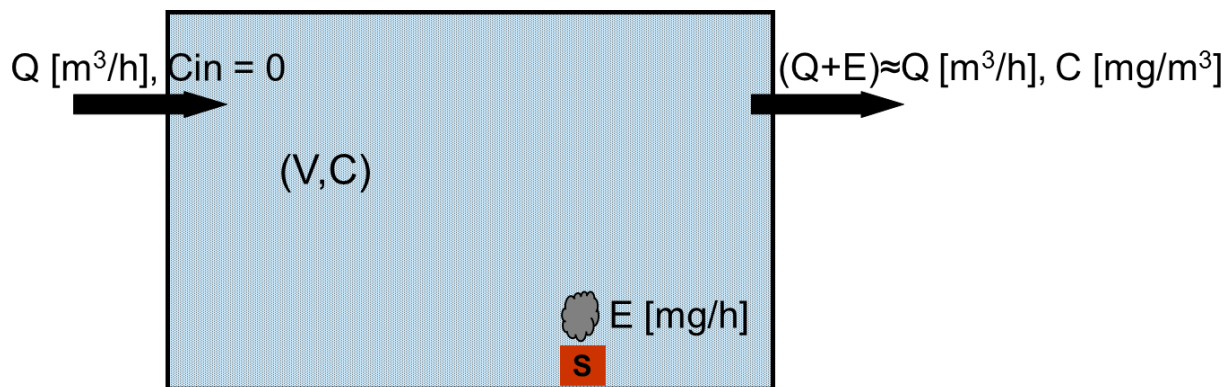


Figure 35. Sketch of a representative scenario for the exposure assessment (well-mixed environment)

6.3 Model validation

The model can be validated by comparing the concentration trends, predicted by the model based on the known characteristics of the chamber, the ventilation and the emission factors estimated in the direct combustion tests.

Some comparisons of model predictions and experimental trends are shown in **Figure 36** for the main substances detected during the tests. Different combustion cycles have been simulated and compared in order to test the model capability to predict the rise of the indoor pollutants concentration also when the starting level of pollutant substances is not zero. Decay phases, where burners are switched off and only the ventilation is active, have not been used for validation because it is not possible to directly compare model predictions and experimental data in these cases. As previously mentioned, at the end of the first cycle and before to start the second one, the door of the ventilated chamber is briefly opened to act on the burner (tank refill, switch off and on of the burner,...); the 1-box simple model here defined cannot take into account these effects, so its predictions are surely more conservative with respect to the real situation.

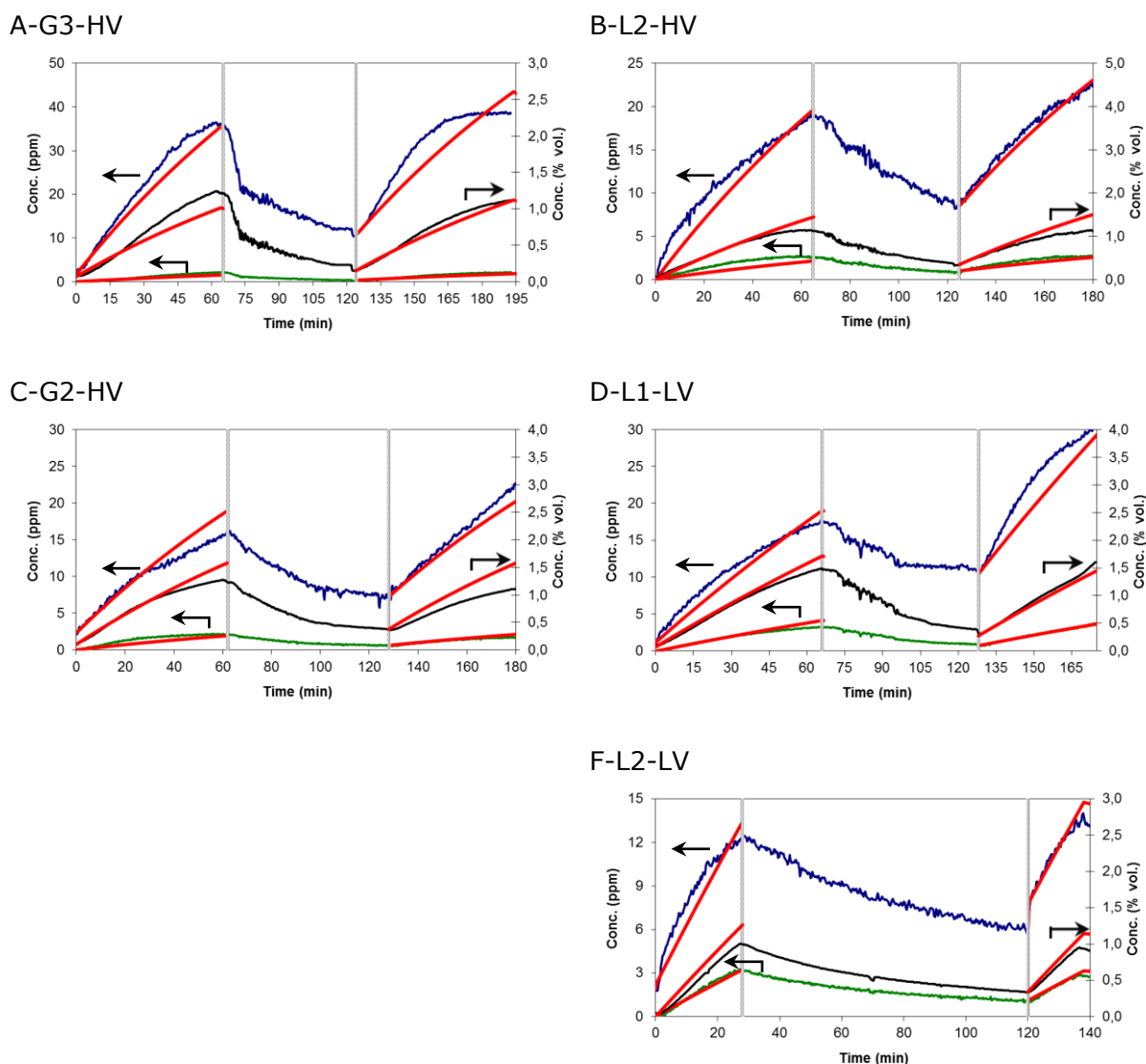


Figure 36 Comparison of experimental results and perfectly mixed model predictions on selected cases: Blue, Black and Green lines represent the experimental trends of CO, NO_x and CO₂, respectively; Red lines represent the corresponding model profiles

Figure 36 highlights a quite good agreement between model predictions and experimental data, thus underlying that the proposed model can be used as a predictive tool to analyse in a realistic way a lot of different possible scenarios, with different ventilation conditions or room volumes, etc. The model is also able to reasonably predict the average concentration values (as well as the peak concentrations) of the selected pollutants over a period of interest, as evidenced by the blind comparison of Figure 37; the central solid line of these plots represents the ideal values (where a full agreement between experimental data and model results could be obtained), while the dashed lines represent a deviation of $\pm 50\%$ from the ideal values. For the model it was assumed a well-mixed room condition; about NO_x emissions, it was considered that about 1/3 of the emitted nitrogen oxides are lost due to secondary reactions and/or adsorption phenomena (a large amount of water vapours, that can interact with NO_x, is generated during each experimental test). As can be seen from the Figure, most of the data are located around the ideal line; this confirms that the model

is able to predict with a good flexibility the behaviour of different fireplaces, during both high and low ventilation conditions, and with different liquid or gel fuels.

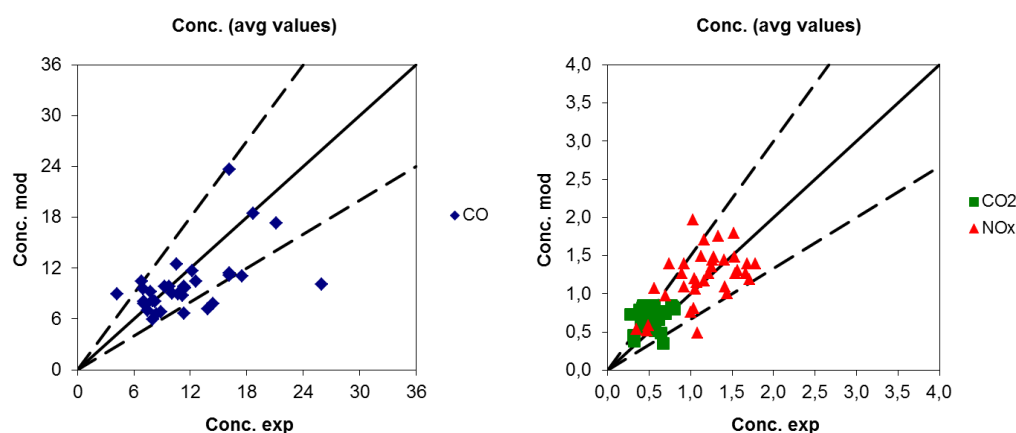


Figure 37 Average concentration values obtained for different fuels and appliances: comparison of experimental and model predictions

6.4 Effects of ventilation

As explained in the introductory chapter, ventilation is a very important parameter for the effect of a pollutant source on the indoor air quality. The theoretical tool developed in this study is able to give us a clear understanding of this effect. In Figure 38 some simulated profiles of the CO₂ concentration are shown for the same room (30 m³) in which a 3.4 kW appliance is burning for one hour and then is switched off, while the chamber is purged for the following hour. The different curves corresponds to different ventilation rates, from 0.2 up to 1.6 h⁻¹. As shown in the figure, ventilation rate affects both the maximum concentrations, reached in the burning phase which varies between 1.3% and 0.7%, and the slope of the curves. As a consequence of this different slope, even in the purging phase, the final concentration in the room shows a larger spread, compared with the maxima. Anyway, for limited variations in the ventilation rate (e.g. in the range 0.2-0.5 AER) the concentrations in the room are not very different, as observed in the experimental tests performed in the ventilated chamber.

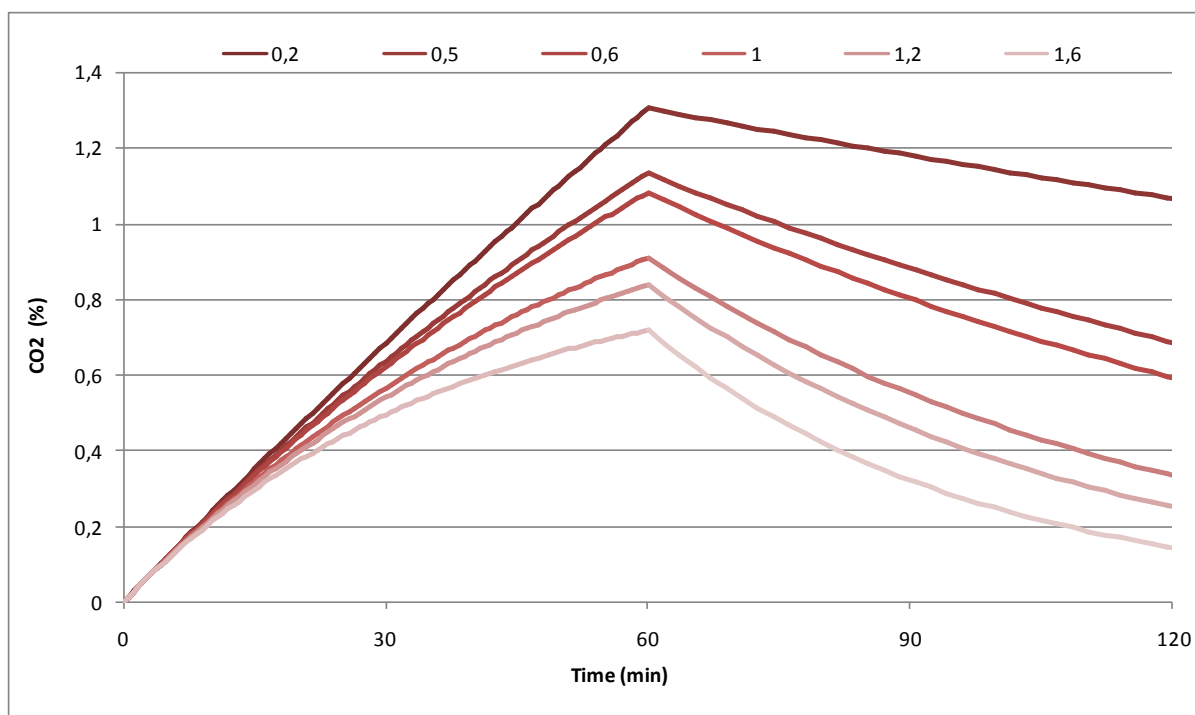


Figure 38 Effect of ventilation on CO₂ concentration, estimated through the well mixed model

In **Figure 39** three experimental tests, performed on appliance B at three different ventilation rates (0.2-0.5-1) are compared for CO₂, CO, and NO_x. The trends for CO₂ are very similar to the theoretical ones, also the curves for CO and NO_x are similar, but for these species the reaction kinetic may influence the results as long as the ventilation itself.

The model is delivered separately on electronic version to the Contracting Authority.

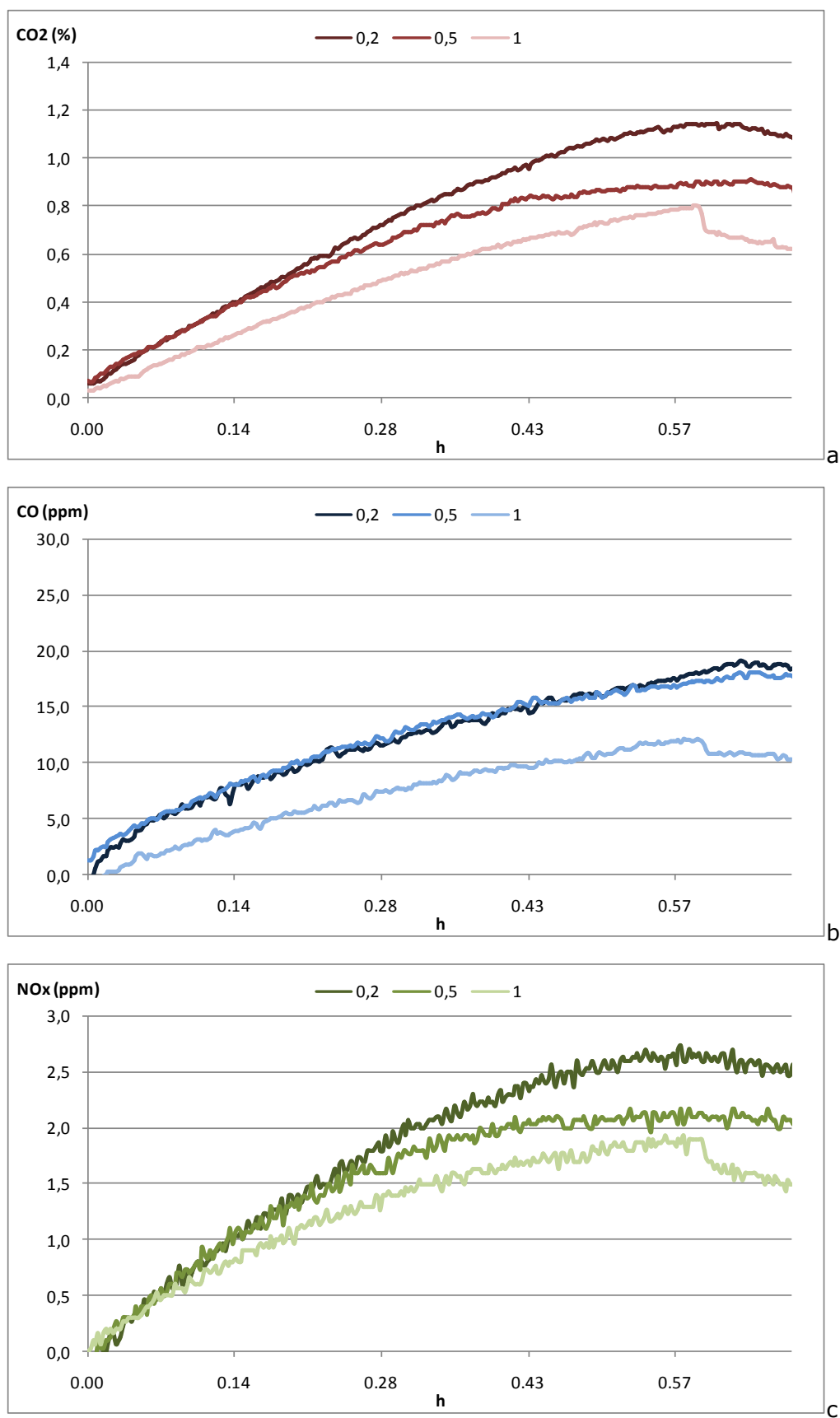


Figure 39 Comparison of experimental tests at different ventilation rates on the B appliance

7 CONCLUSIONS

The outcomes of this study can be summarised in the following conclusions:

1. Flueless alcohol appliances show a large variability in terms of designing configuration, technology, automation level, influencing their behaviour and performances. In any case, alcohol fireplaces and other similar commercial products are combustion appliances and must be considered as such. Similarly to heating appliances they produce heat, even if they are considered simply aesthetic objects; the temperature in a room, where these fireplaces are in use, can be significantly increased and the oxygen content of these rooms is depleted by combustion. An inadequate design can result in high emissions of pollutant substances and toxic species. Supplying the proper amount of air is a basic aspect to be considered, but also the direct impact of the flame on any cold surface must be avoided.
2. Similarly to hobs or cookers, catalytic heaters and any other flueless combustion appliance, alcohol fireplaces release the chemical products of combustion in the indoor environment, producing potentially toxic atmosphere. This aspect must be accounted for when similar appliances are installed and used. Many chemical compounds are released during the combustion and not combustion phases: CO and carbonylic compounds are the most abundant along with the components of the fuel itself (mainly ethanol and heavier alcohols). These species are produced in amounts large enough to heavily influence especially the indoor air quality of small room even if ventilated.
3. The emission rates of pollutants strongly depend on the technical characteristics of the appliances, while they are almost independent from the type of fuel. For CO they range from 700 up to 6000 mg/kg of fuel burnt, for NO_x they are between 400 and 900 mg/kg of fuel. For VOCs they are very variable, ranging from 80 up to 6000 mg/kg of fuel, if measured in terms of TOC, while formaldehyde, the most harmful species among those detected in this study, is emitted at a rate from 2 up to 120 mg/kg of fuel. These emission factors largely exceed most of other domestic sources.
4. The volume of the room, where these appliances are used, is very important in determining the actual exposure of the users to potentially toxic species. A frequent and continuous usage of such appliances in a poorly ventilated room may have a detrimental effect on the human health.
5. In some cases, from the experimental tests performed in this study, harmful conditions for the consumers have been reached. In the case of a gel appliance, CO concentrations up to 100 ppm have been detected and up to 5 mg/m³ of formaldehyde. It is not known if they can be considered representative of a large segment of appliances in the market or simply a limit worst case situation. Further investigations on a larger ensemble of appliances would be necessary to

increase the statistical significance of the results produced. Anyway, in most cases the CO average concentration is below 25 ppm and below 1 mg/m³ for formaldehyde.

6. Advanced automatic appliances have much better characteristics and performances: they work at optimised combustion conditions and their automatic controls and sensors allow to limit the production of pollutants and to prevent that harmful conditions can be reached.

8 RECOMMENDATIONS

This study has mainly the purpose to evaluate the effect of the usage of alcohol unflued fireplaces on the indoor air quality of a room where they are installed and used, producing some basic data, useful to infer possible effects on the human health. From the outcomes of the study it is possible to draw a number of considerations and some specific recommendations that are here summarised:

1. Most of the fuel burning appliances are required to undergo specific tests defined in the product standards, for their placing on the market. A similar regulation could be properly implemented also for alcohol fireplaces, at least above the very small scale (>1 kW) in order to prevent the commercial distribution of dangerous products. Below this power limit they could be assimilated, in terms of power, to the air fresheners and multiple candles.
2. The national standards presently available consider only CO (and NO_x for the French standard) as a relevant emission parameter; on the contrary other species are released in not negligible amount, that could be potentially harmful to human health. Aldehydes in particular should be accounted for in the evaluation of the performances of a product.
3. Technical standards and/or legal regulations should indicate clearly the minimum volume of the room as a function of the power (or fuel consumption rate) of a specific appliance and this indication should be clearly reported on the product manual and possibly on the appliance itself.
4. Ventilation holes should be compulsorily prescribed in technical standards and/or legal regulations, at least for appliances having a power greater than 4 kW.
5. Very clear recommendations should be indicated on the user manuals for a good and continuous ventilation of the ambient where these appliances are in use.
6. Consumers should be made aware that these appliances produce CO and other pollutants potentially toxic in case of long lasting exposure; a prolonged use should be discouraged anyway also in the users manuals.
7. Users should be advised to pay attention to any unpleasant odour produced during the combustion process, because they are an indication of poor and improper combustion and formation of pollutants.
8. Designers and manufacturers should be aware, as well, that they are producing and commercialising combustion appliances, which must be designed according to specific criteria, to get good combustion performances, because they are responsible for the products they introduce in the market.
9. The maximum capacity of the fuel tank should be limited to prevent a long lasting combustion and the appliances should be always provided with a covering cap or closing slot to be used to shut down the flame and cover the

burner when not in use. It may help to reduce the evaporation of the fuel. Besides the toxicity aspects, evaporation of the fuel may produce a flammable atmosphere surrounding the appliance, which can produce safety issues mainly in the refilling and re-ignition phase.

10. Further investigations on a larger ensemble of appliances would be necessary to increase the statistical significance of the results produced.

9 GLOSSARY

- **Air Exchange Rate (AER):** ventilation index of a room referred to the volume of the room itself. It is expressed in terms of volumes per hour; the exchange rate is 1 when a volume of fresh air, equal to the volume of the room, flows in the room in 1 hour, displacing an equal volume of room air.
- **Aldehydes:** a class of organic chemical compounds belonging to the larger class of carbonylic compounds. Formaldehyde is the simplest one, having a single carbon atom, followed by acetaldehyde containing two carbon atoms. Many aldehydes have a pungent odour and cause irritation when inhaled at concentrations higher than a threshold limit depending on the specific compound, but also variable from person to person. Some aldehydes can also produce more serious toxic effects.
- **Computational Fluid Dynamic (CFD):** a computer-based numerical tool able to solve the governing equations of fluid mechanics and often also heat exchange and chemical kinetics equations. It is used to perform simulation work to predict the behaviour of complex systems where the dynamics of the gas phase is essential.
- **Ethanol:** chemical compound having the molecular formula $\text{CH}_3\text{CH}_2\text{OH}$, it belongs to the class of chemicals named alcohols and it is commonly referred to simply as alcohol or ethyl alcohol.
- **Fuel:** any material, constituted of a single compound or a mixture of compounds in solid, liquid or gaseous form which can react with oxygen (oxidizer) through a process that can be used to produce energy (exothermal process).
- **Particulate Matter (PM):** solid or liquid particles suspended in the atmosphere or in any other gas. Along with many other possible sources, PM may be produced in the combustion processes in the form either of unburnt carbon (soot) or inorganic suspended ashes. The dimension of these particle is one of their most important characteristics, small particles are considered much more harmful for the human health compared with large ones, because they can easily penetrate the human tissues when inhaled. The main classifications of PM includes PM_{10} - $\text{PM}_{2.5}$ - PM_1 representing the mass concentration of particle (μg of particles per cubic metre) having a diameter smaller than 10, 2.5 and 1 μm respectively. Particles with a diameter lower than 100 nm (i.e. 0.1 μm) are defined ultrafine particles (UFP) and their concentration is usually reported in terms of number instead of mass (number of particles per cubic metre).
- **Polycyclic Aromatic Hydrocarbons (PAH):** hydrocarbon compounds composed of two or more aromatic rings. Many of them have been identified as carcinogenic and mutagenic compounds.
- **Stoichiometry:** it is a quantitative relation existing among reagents and products of a chemical reaction; it allows to calculate exactly the amount of products generated from a known amount of reagents when a specific reaction takes place and vice versa.
- **Threshold Limit Value (TLV):** limit concentration of chemical compounds in ambient air below which no negative effects have been reported for the health of workers daily exposed to it. TLV-TWA in particular refers to the time-weighted average on a working day of 8 h. TLV-STEL is the limit concentration, averaged

on 15 minutes, which can be exceeded only four times and for a short period in a working day.

- **Volatile Organic Compounds (VOC):** chemical organic compounds constituted of carbon, hydrogen and possibly oxygen, nitrogen and sulphur in minor quantities; characterised by a high vapour pressure at ambient temperature and hence usually present in vapour phase especially when an heat source is present. They may be produced in various processes, including combustion, or released from different materials through evaporation, sublimation, and/or decomposition. Some of them have a recognised high toxicity.

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ANNEX A - EXPERIMENTAL RESULTS

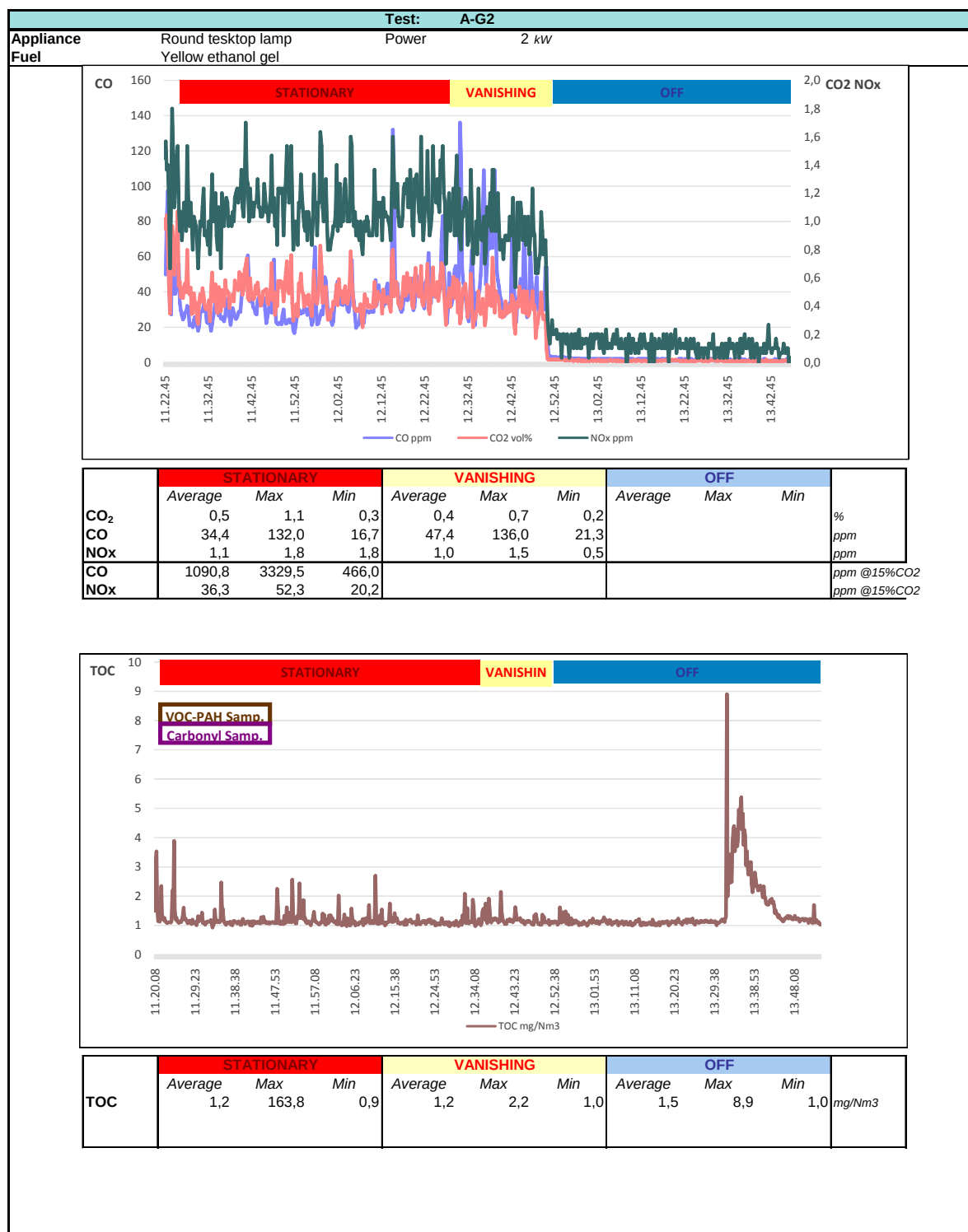


Figure-A 1 Summary of direct combustion test for appliance A

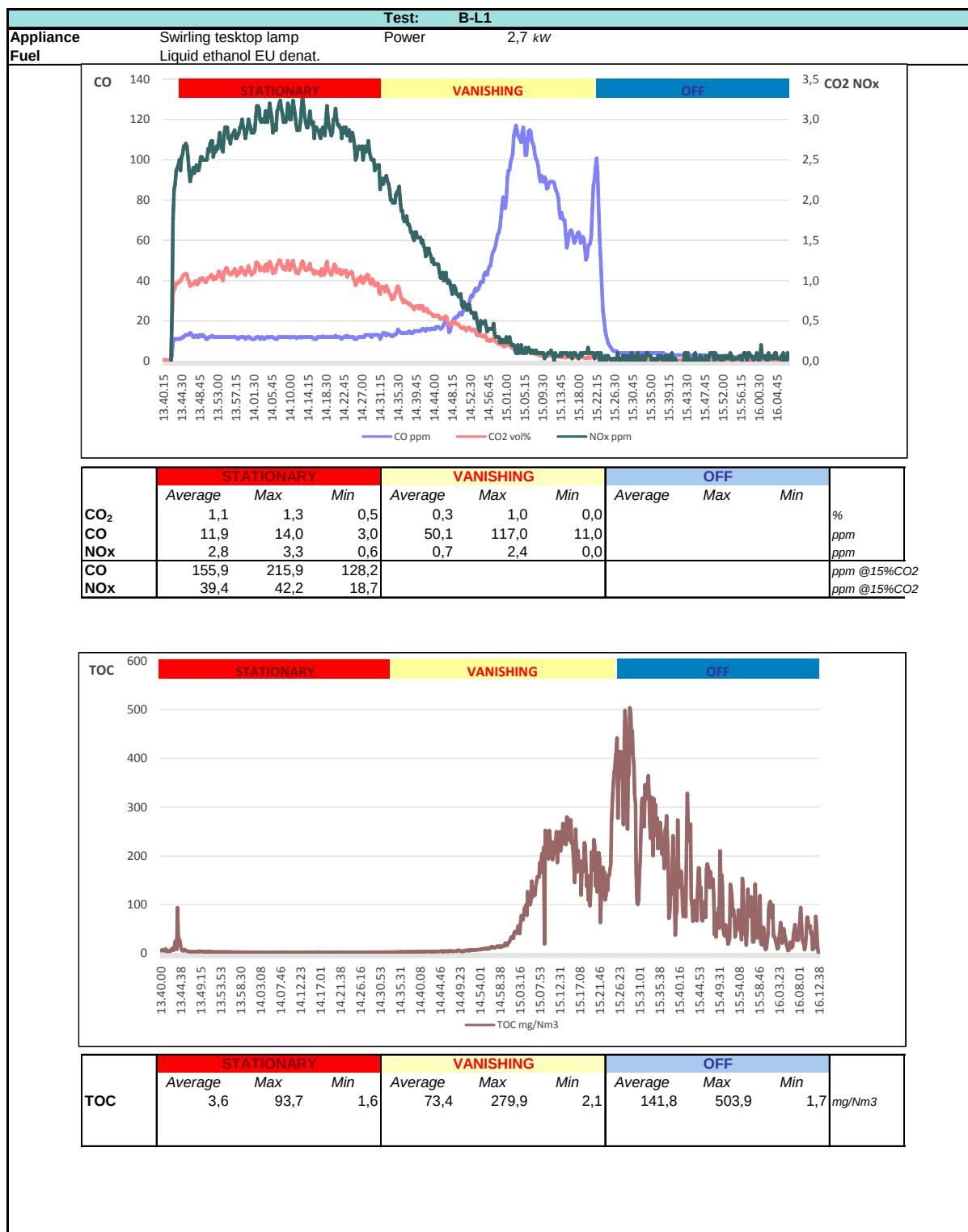


Figure-A 2 Summary of direct combustion test for appliance B

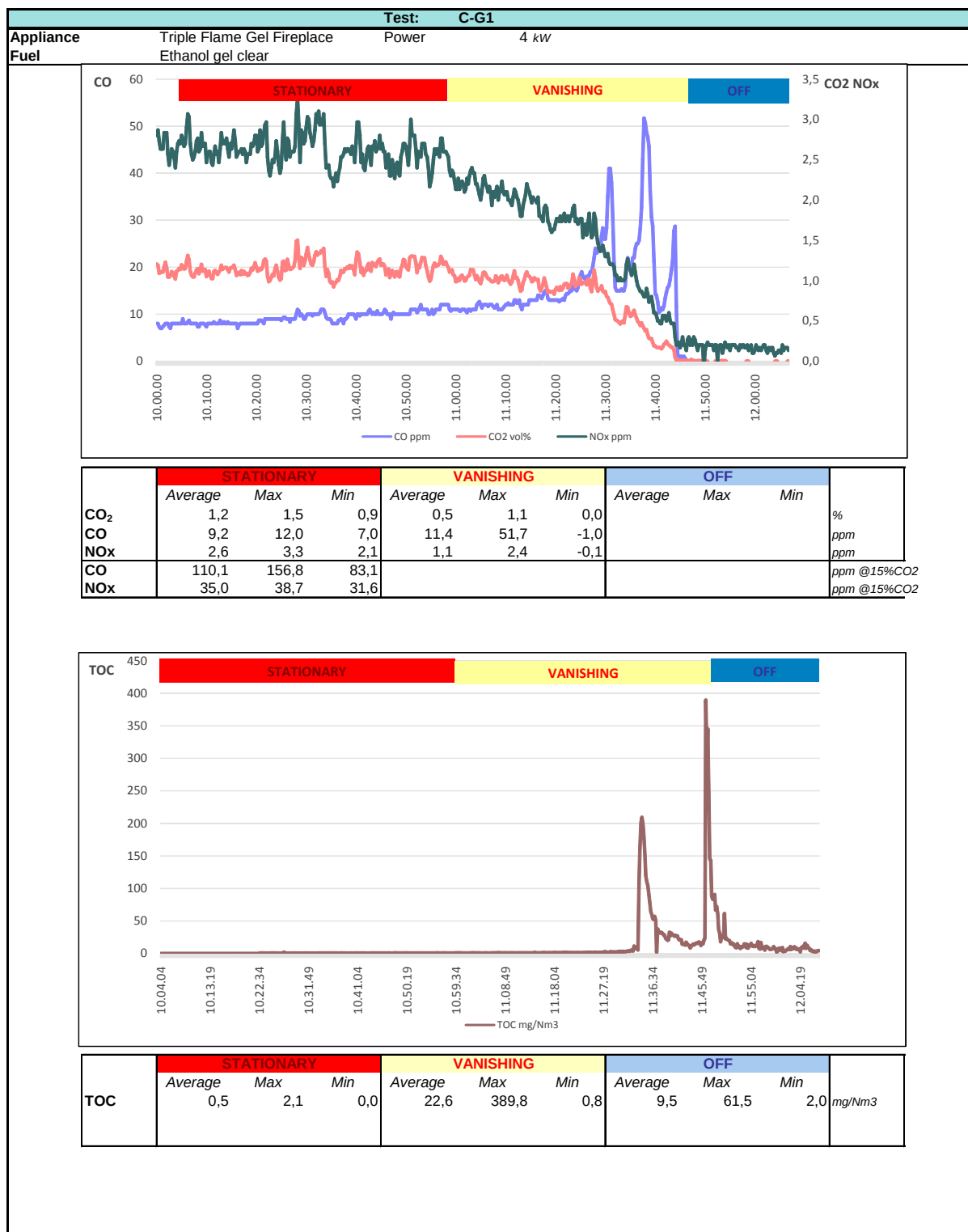


Figure-A 3 Summary of direct combustion test for appliance C

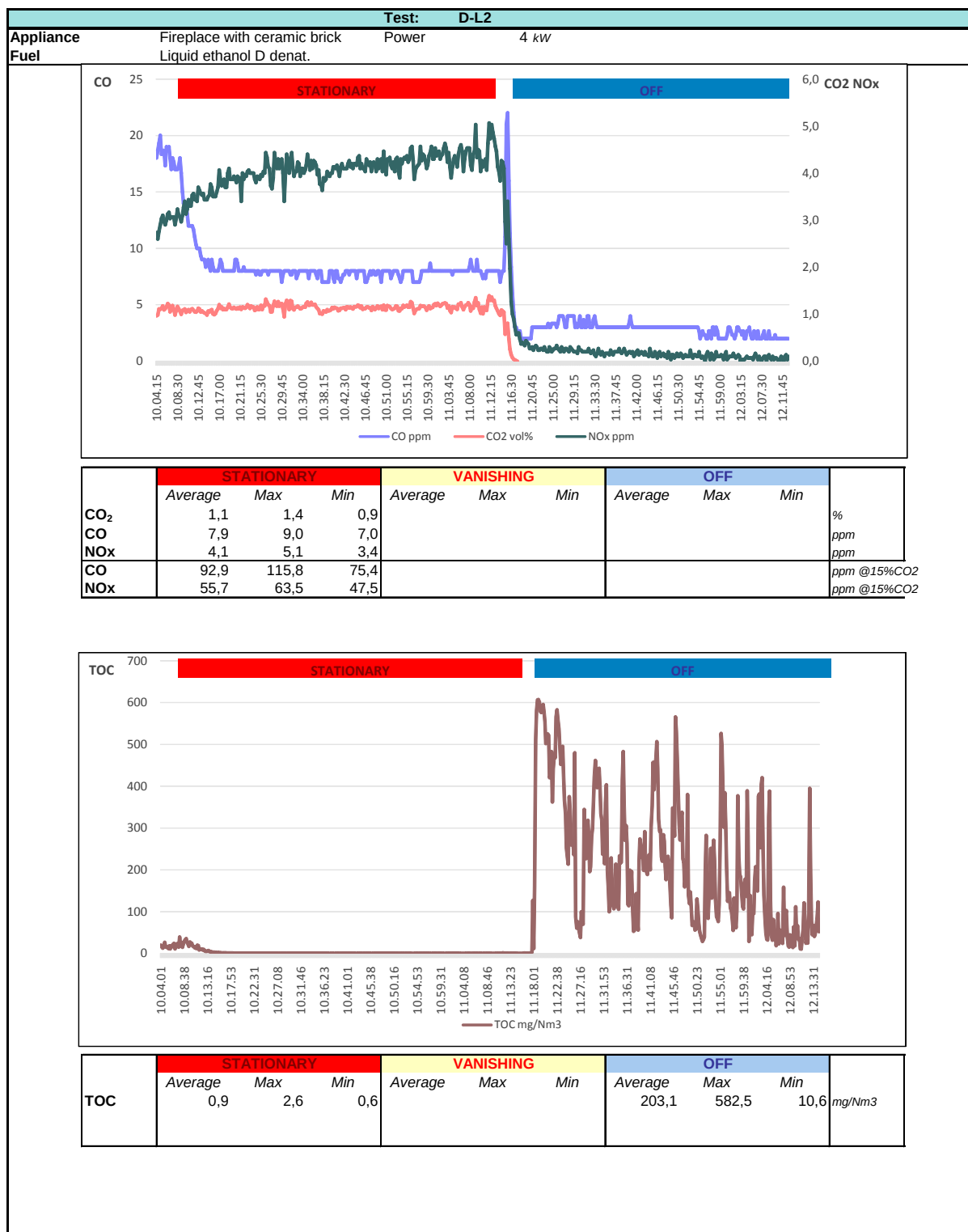


Figure-A 4 Summary of direct combustion test for appliance D

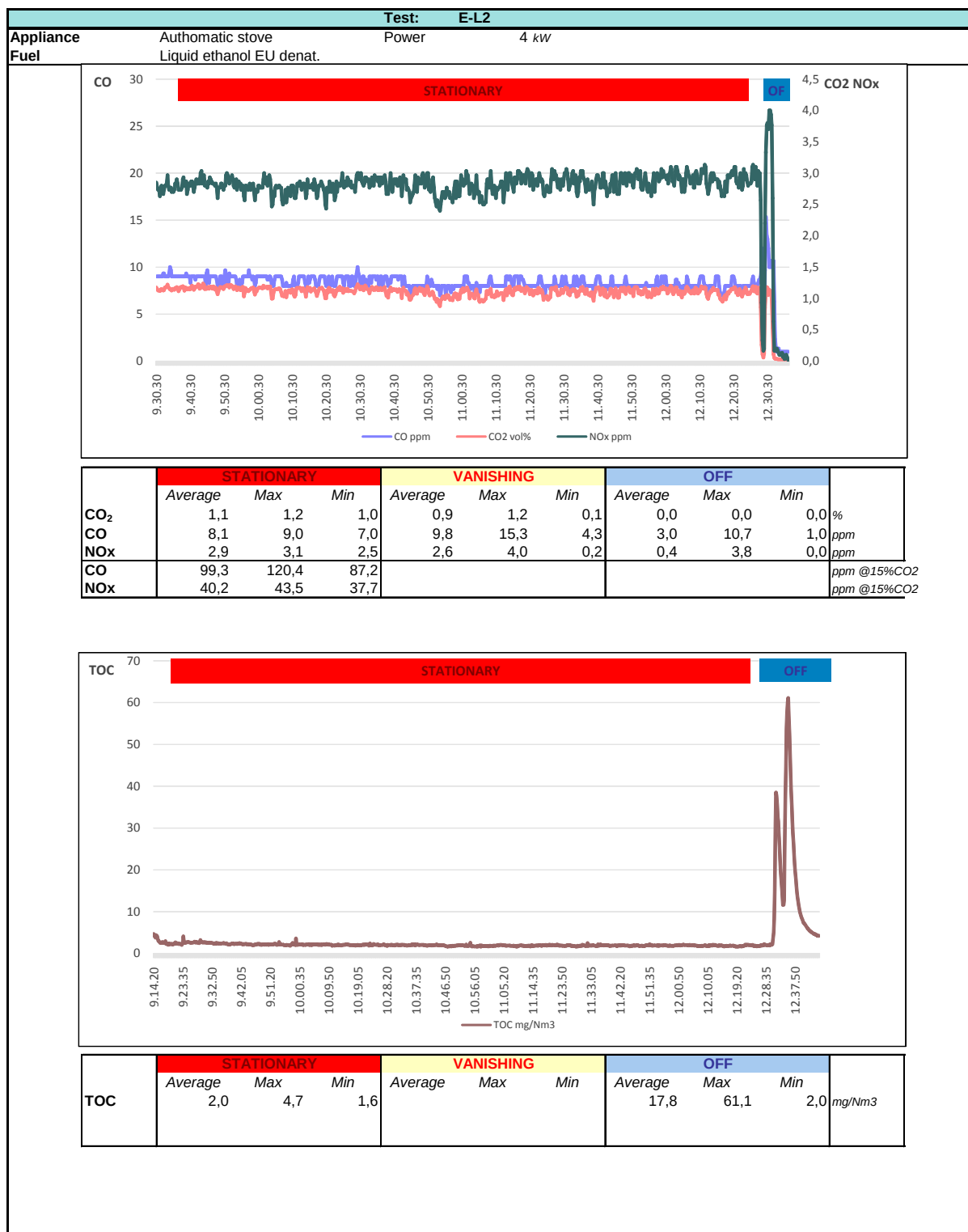


Figure-A 5 Summary of direct combustion test for appliance E

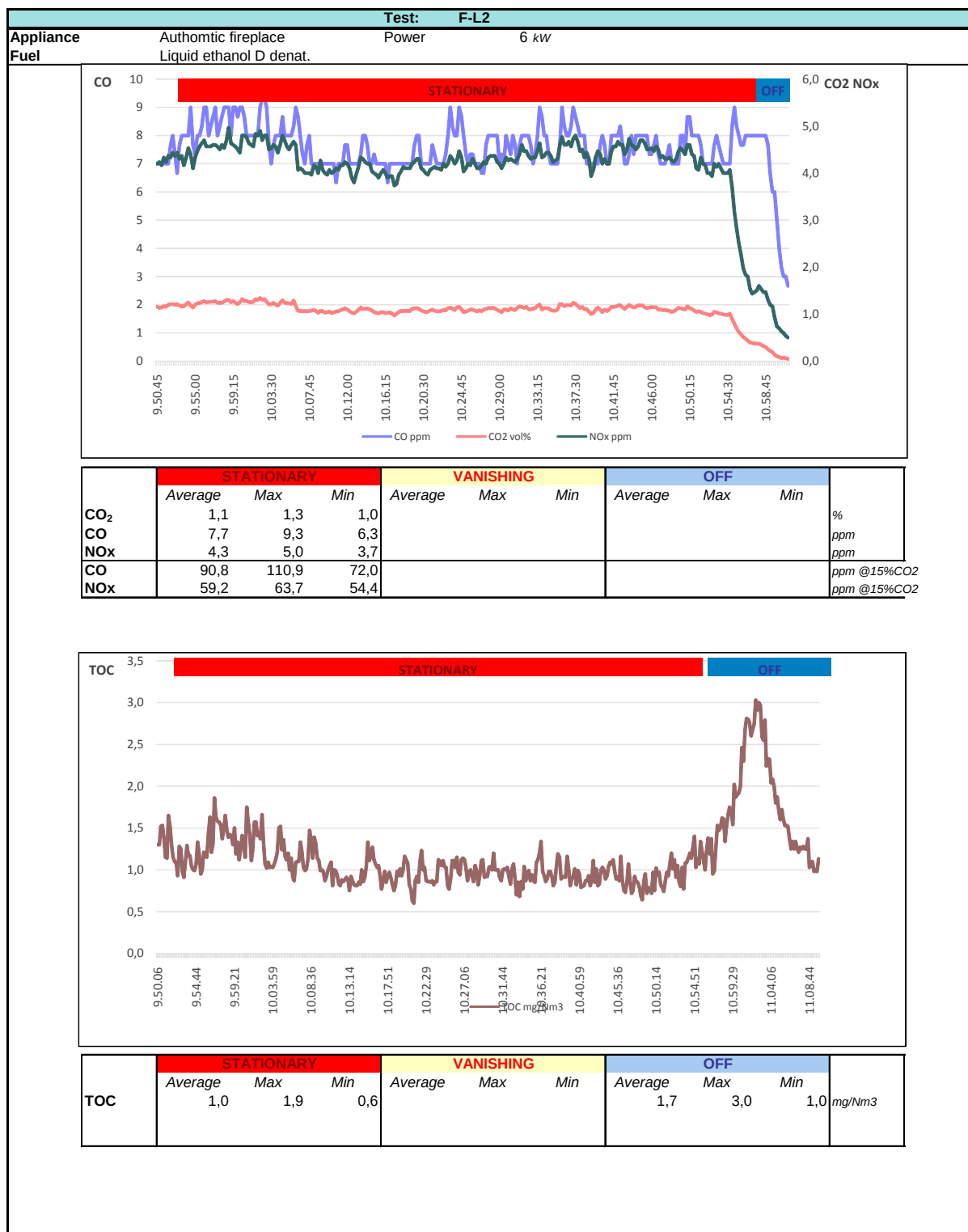


Figure-A 6 Summary of direct combustion test for appliance F

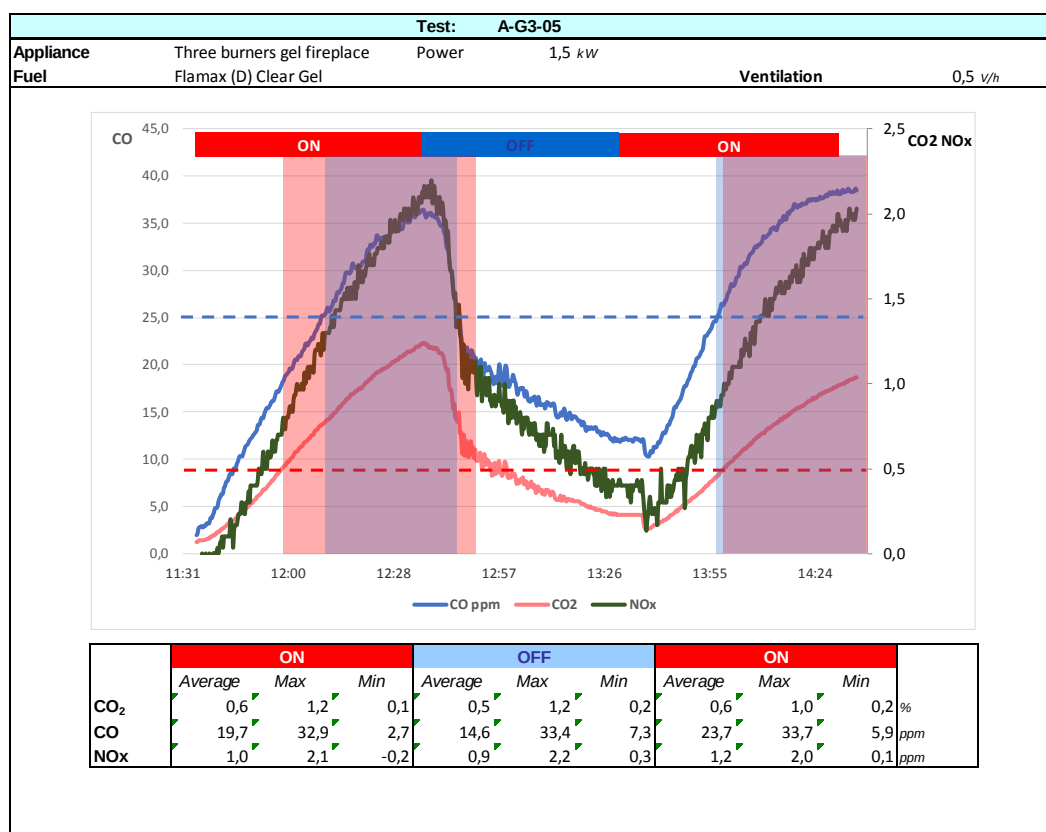


Figure-A 7 Gas concentration in ventilated chamber test, for appliance A

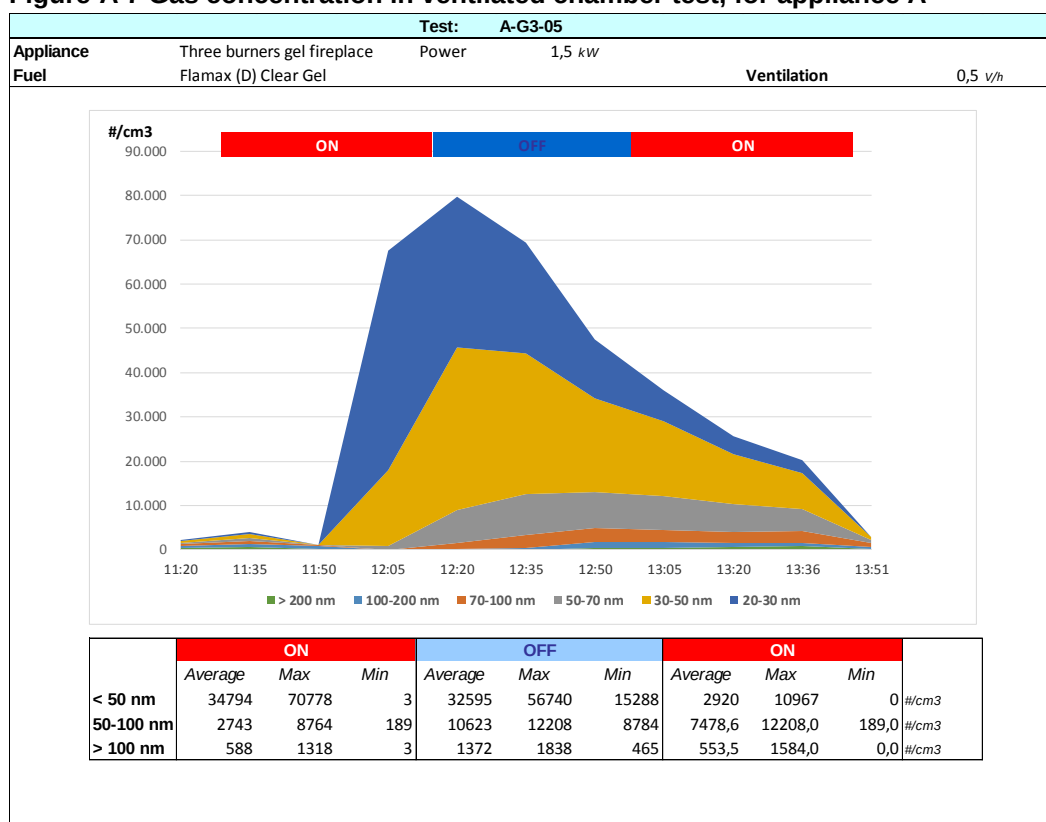


Figure-A 8 Ultrafine particles concentration in ventilated chamber test, for appliance A

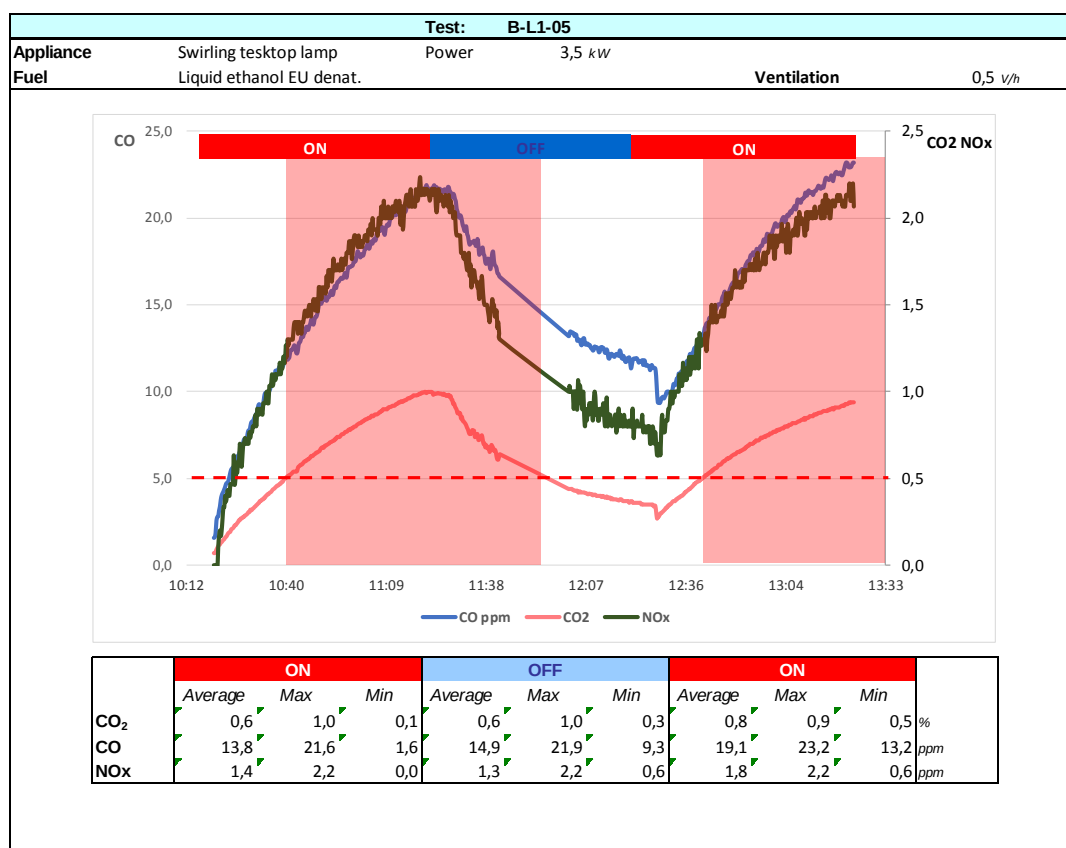


Figure-A 9 Gas concentration in ventilated chamber test, for appliance B

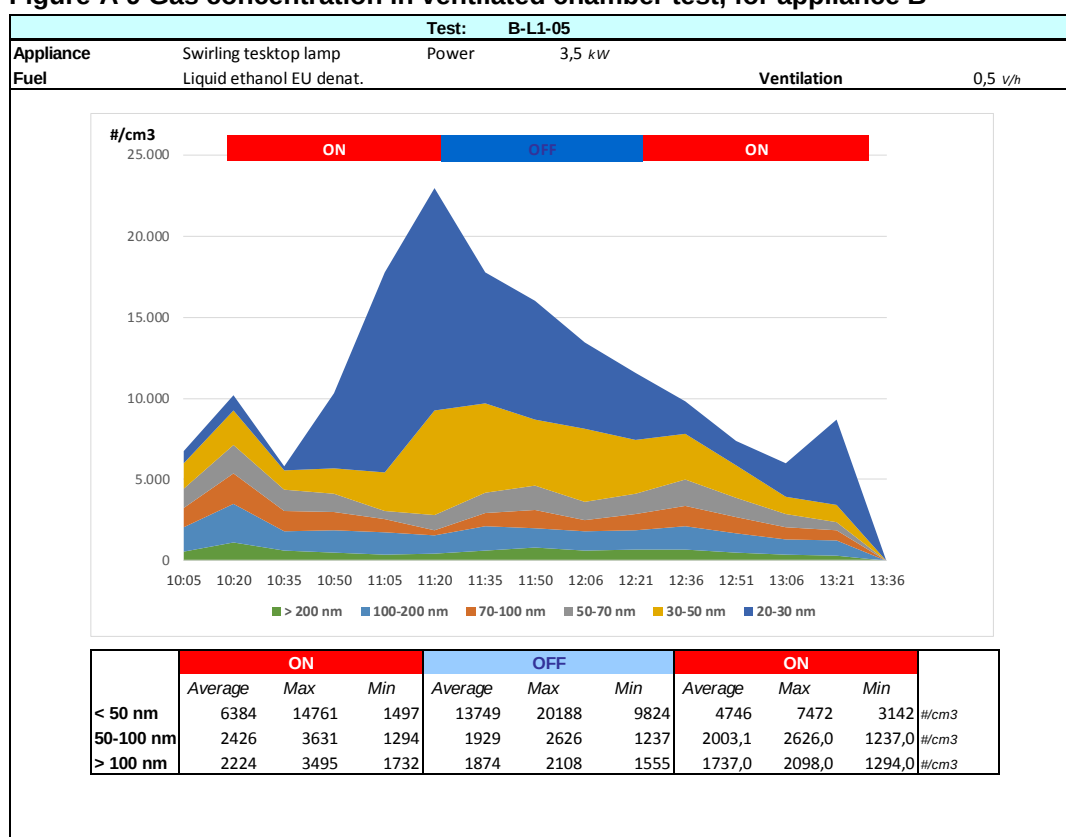


Figure-A 10 Ultrafine particles concentration in ventilated chamber test, for appliance B

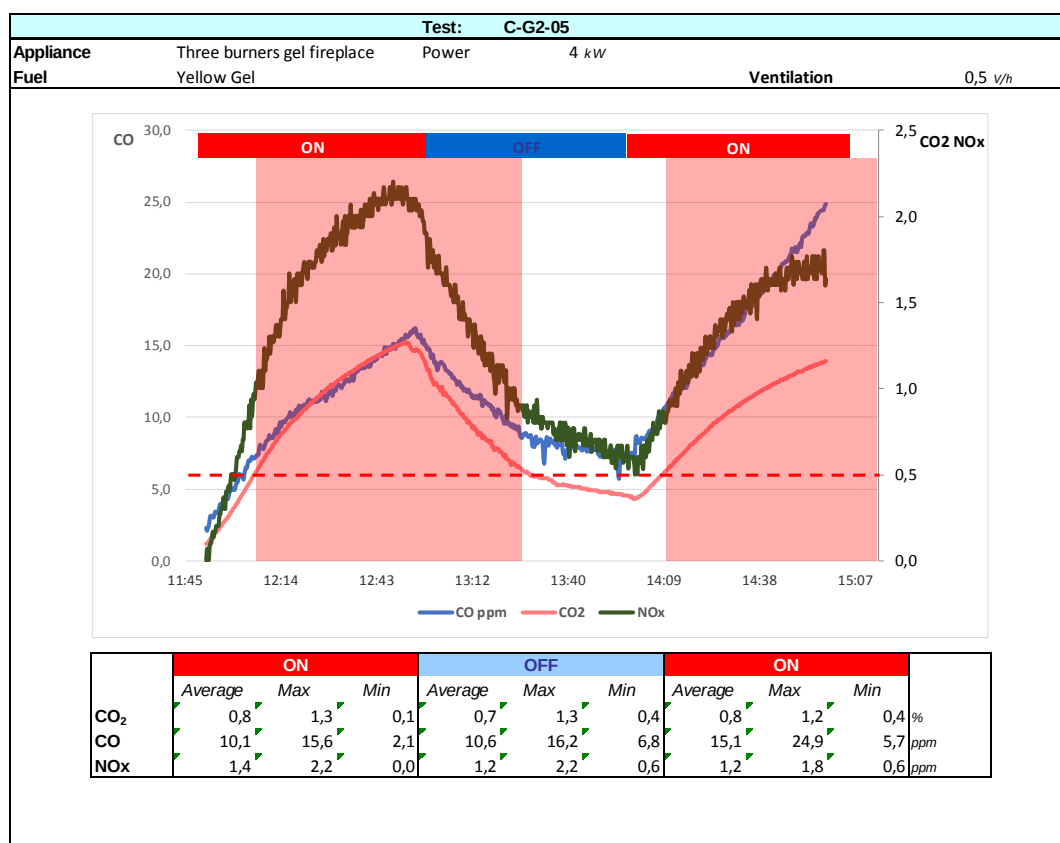


Figure-A 11 Gas concentration in ventilated chamber test, for appliance C

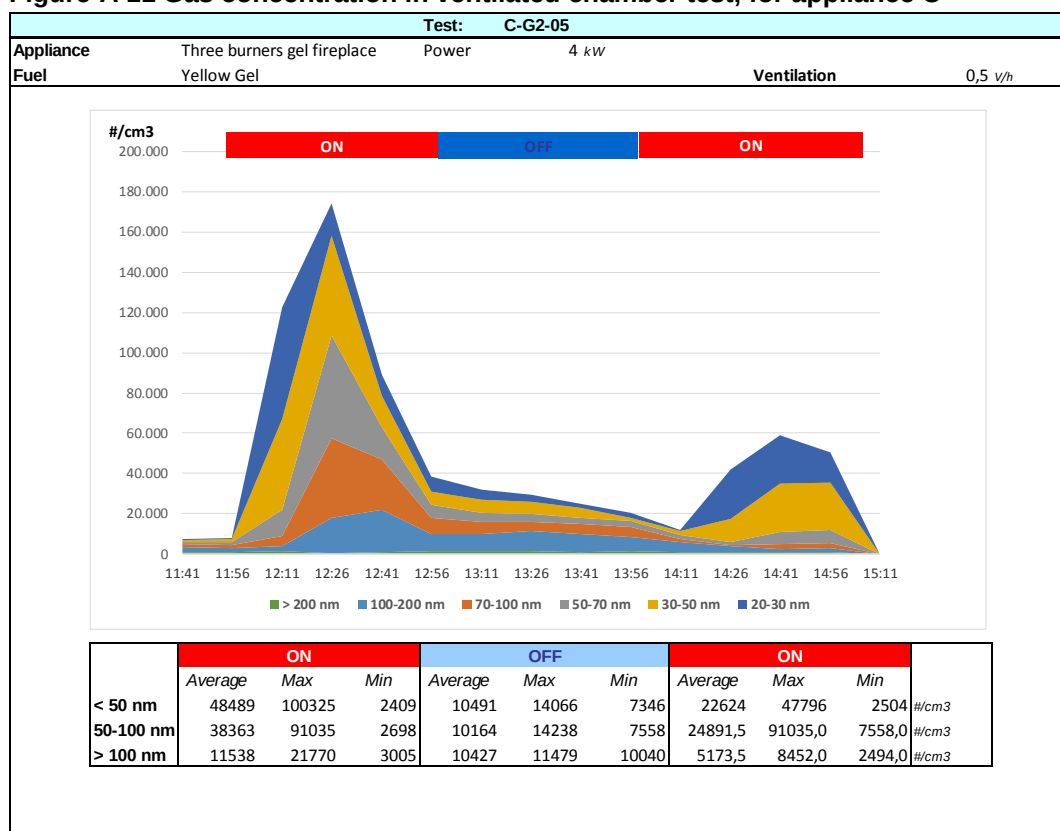


Figure-A 12 Ultrafine particles concentration in ventilated chamber test, for appliance C

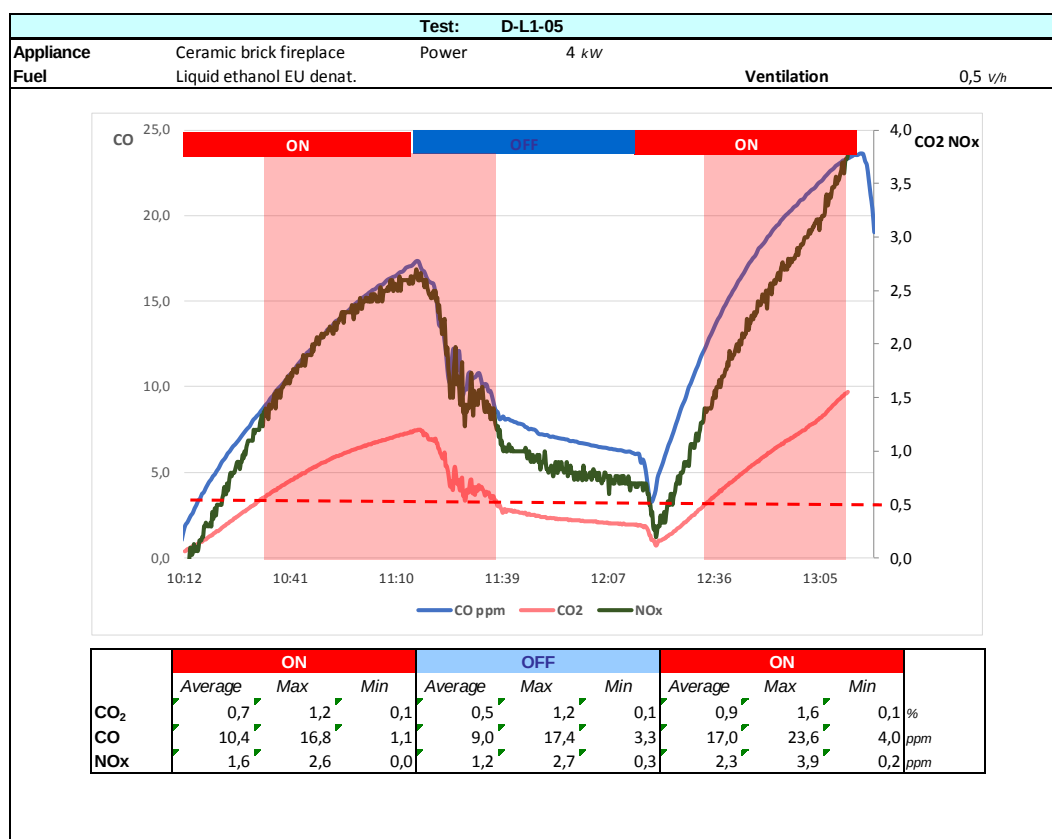


Figure-A 13 Gas concentration in ventilated chamber test, for appliance D

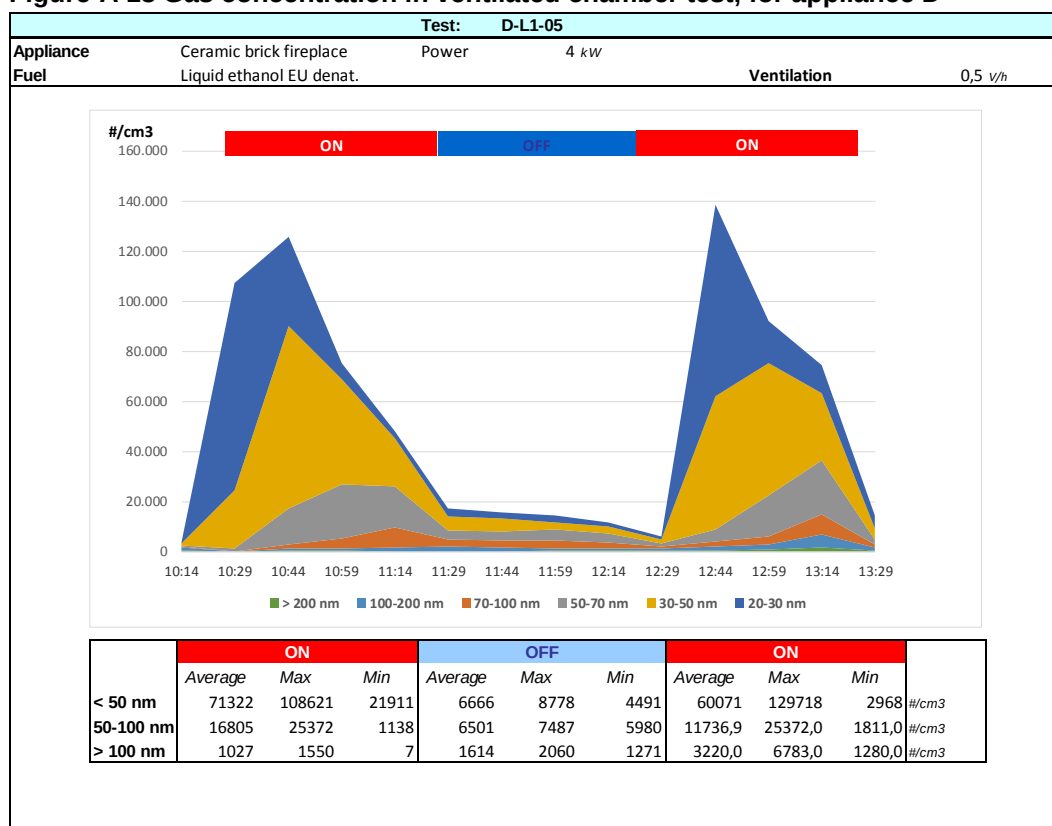


Figure-A 14 Ultrafine particles concentration in ventilated chamber test, for appliance D

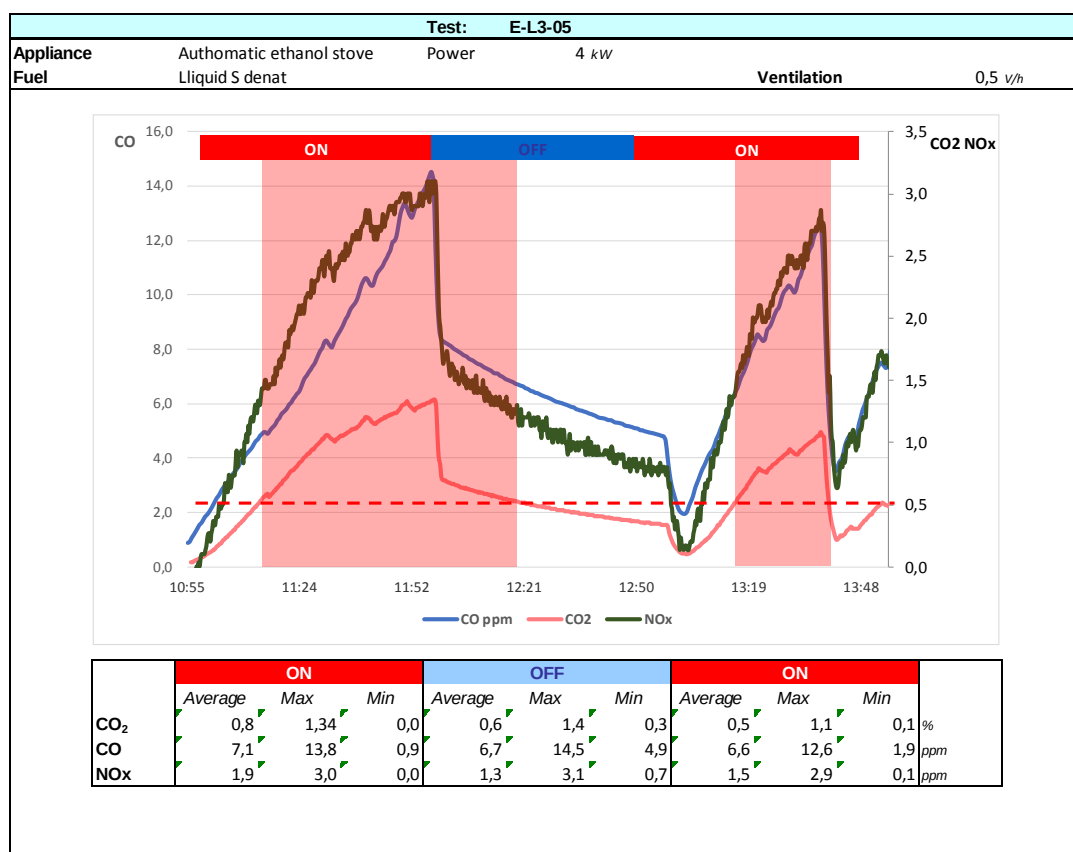


Figure-A 15 Gas concentration in ventilated chamber test, for appliance E

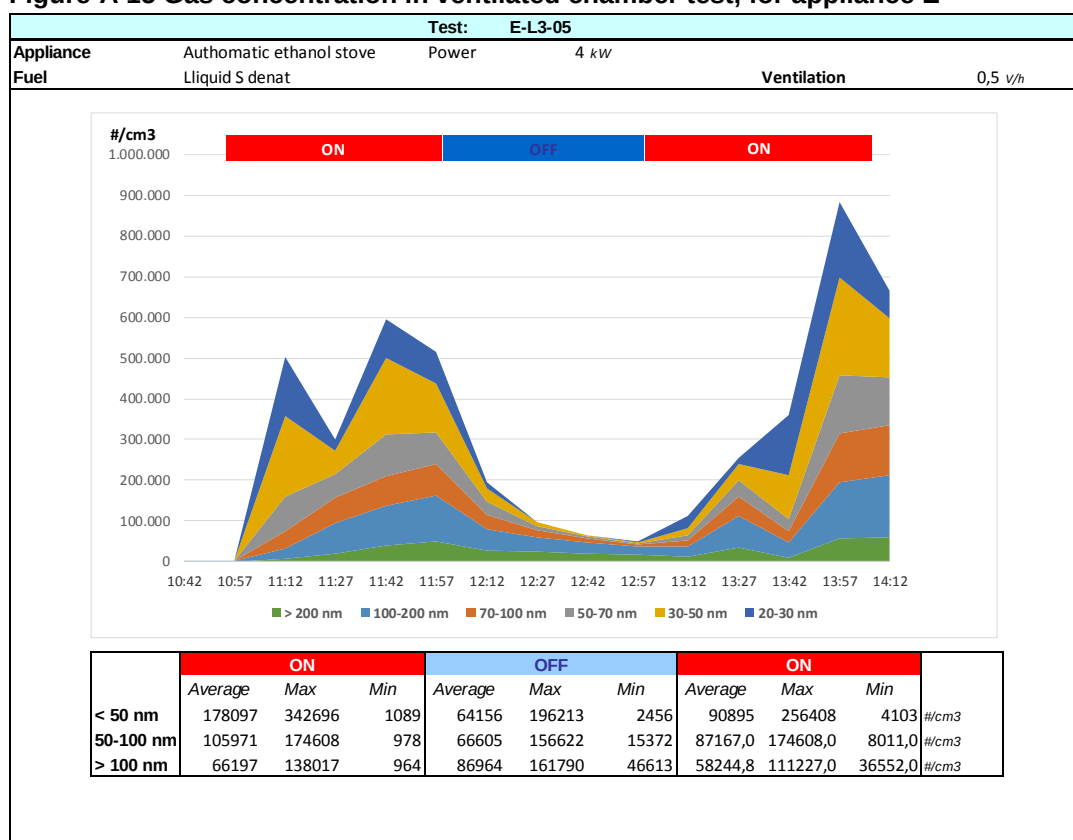


Figure-A 16 Ultrafine particles concentration in ventilated chamber test, for appliance E

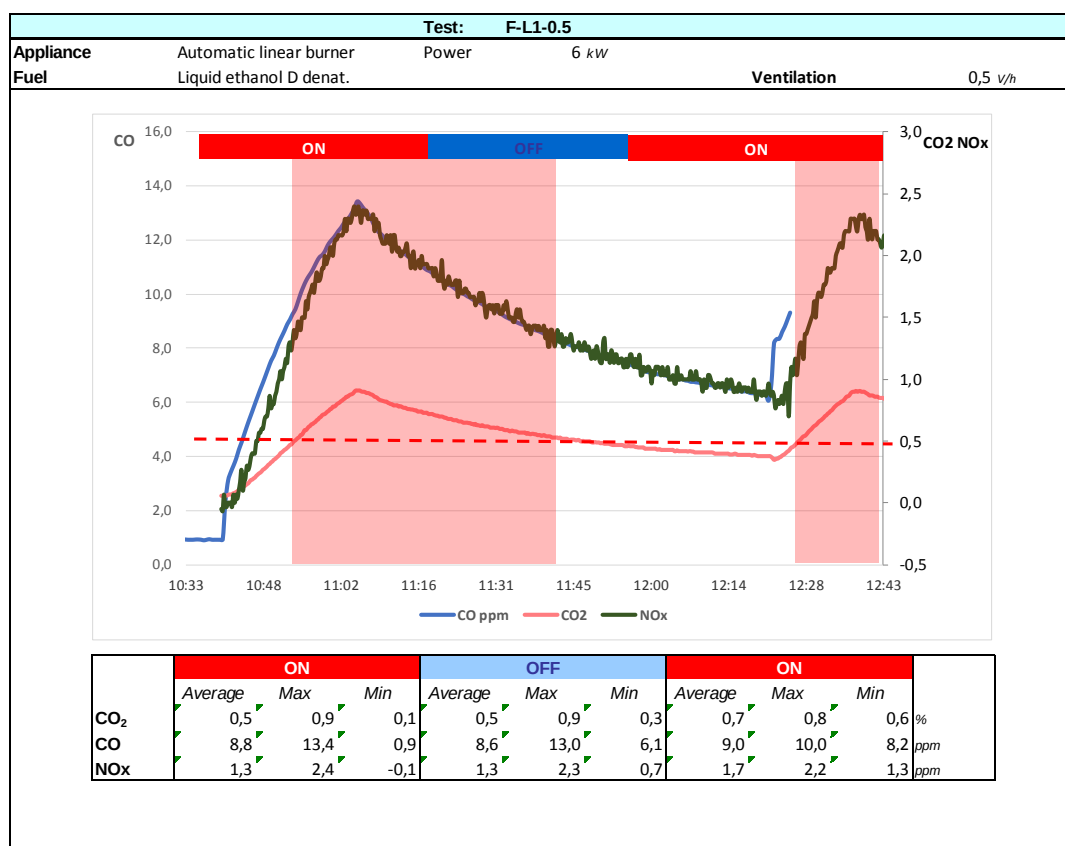


Figure-A 17 Gas concentration in ventilated chamber test, for appliance F

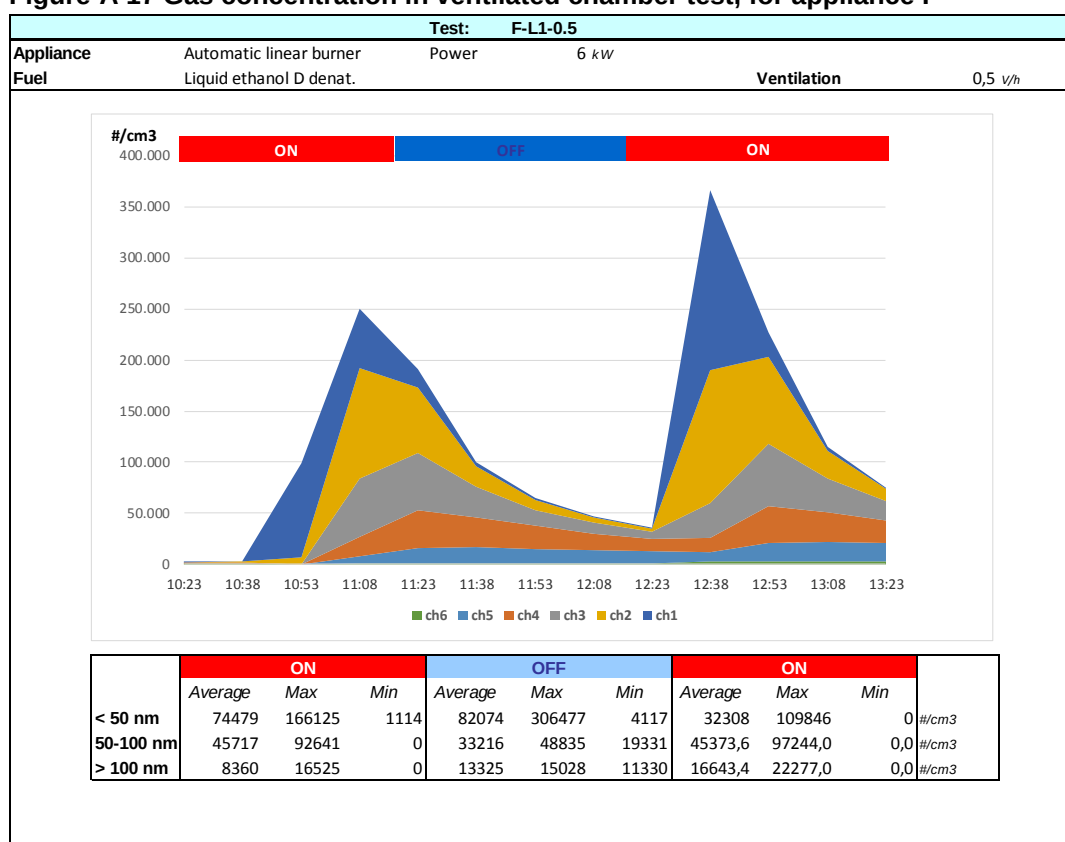


Figure-A 18 Ultrafine particles concentration in ventilated chamber test, for appliance F

ANNEX B - SUMMARY OF INTERNATIONAL AIR QUALITY STANDARDS AND GUIDELINES

^aHCHO: formaldehyde

Std	CO	CO ₂	NO _x	HCHO ^a	C ₂ H ₄ O ^b	Acrolein	Benzene	Toluene	PM _{2.5}	Ethanol	2-propanol	Naphthalene
DIN 4734-1 [ppm]	30	5000										
TLV-TWA^c [ppm]	25	5000	3				0.5	50		1000	200	10
TLV-STEL^c [ppm]		30000	5	0.3	25	0.1	2.5				400	15
IDLH [ppm] ^d	1200	40000	20	20	2000	2	500	500		3300	2000	250
MAK^e [mg/m ³]	35	9100	0.95	0.37	50			190	4	960		
ERPG-1^f [ppm]	200		1	1	10	0.05	50	50		1800		
ERPG-2^f [ppm]	350		15	10	200	0.15	150	300		3300		
WHO^g [µg/m ³]	35000		200	100			0.17		10			10
US-EPA [µg/m ³]					9		30	5000	12			3
EU [µg/m ³]				30	200		5	300	20			10
AEGL-2^h [ppm]	150		15	14	340	0.03		760				
AEGL-1^h [ppm]			0.5	0.9	45	0.18		67				

^b

C₂H₄O: acetaldehyde

^c2009 Threshold Limit Values & Biological Exposure Indices, by the American Conference of Governmental Industrial Hygienists (ACGIH)

^dNIOSH Pocket Guide to Chemical Hazards, 2004, by the National Institute for Occupational Safety and Health (NIOSH)

^eList of MAK and BAT Values 2014, DFG, Deutsche Forschungsgemeinschaft, Germany

^f2013 ERPG/WEEL Handbook, AIHA Guideline Foundation

^gWHO guidelines for indoor air quality: selected pollutants, 2010

^hAEGL Chemical Data, 2014, <http://www.epa.gov/opptintr/aegl/pubs/humanhealth.htm>

According to the source of the air quality standards and/or guidelines the reference concentration values can be expressed in ppm or in mg/m³ (remembering that 1 mg/m³ = 1000 µg/m³). At standard conditions (25°C and atmospheric pressure) it is possible to use this conversion equation:

$$\text{Conc} \left(\frac{\text{mg}}{\text{m}^3} \right) = \frac{\text{Conc} (\text{ppm}) * \text{MW}}{24.45}$$

where MW is the molecular weight (in g/mol or kg/kmol) of the considered substance.

ANNEX C - PREDICTIVE MODELLING OF INDOOR AIR QUALITY AND ROOM VENTILATION (IN EXCEL FORMAT)



**STUDY ON ALCOHOL-POWERED
FLUELESS FIREPLACE
COMBUSTION AND ITS EFFECTS
ON INDOOR AIR QUALITY**

WELL-MIXED ROOM MODEL

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ANNEX D - WELL MIXED ROOM MODEL: user's guide



STUDY ON ALCOHOL-POWERED FLUELESS FIREPLACE COMBUSTION AND ITS EFFECTS ON INDOOR AIR QUALITY

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