

# Emission of air pollutants from burning candles with different composition in indoor environments

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## Introduction

Both indoor and outdoor sources affect the concentration and composition of pollutants in indoor air. There is usually more information available on emission characteristics, such as

emission factors or emission rates, of outdoor pollutants sources (Ravindra et al. 2008; Estrellan and Iino 2010) than of indoor ones. However, quantification of emissions from indoor sources is very important for assessing the human exposure to pollutants (Ott and Siegmann 2006; Sarigiannis et al. 2011). The most significant sources, for indoor environments, include tobacco smoking, cooking, kerosene heating and wood burning (Tuckett et al. 1998; Long et al. 2000; Fan and Zhang 2001; Destailats et al. 2008). Combustion processes are the main indoor sources of smaller particles, being the vast majority of them in the submicrometer range and containing a host of organic and inorganic material (Morawska and Zhang 2002). However, gaseous pollutants from combustion play also 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).

The increase of candle use improved the public concern about potential health effects because of the exposure to candle emissions; burning of candles in indoor environments can release a large number of toxic chemicals, including carbon monoxide, nitrogen oxides, aldehydes and unburnt hydrocarbons, such as polycyclic aromatic hydrocarbons (Lau et al. 1997; USEPA 2001; Lee and Wang 2006; Orecchio 2011; Manoukian et al. 2013). It is believed that regular burning of several candles in indoor environments can expose people to harmful amounts of organic chemicals (USEPA 2001; Chuang et al. 2012).

Only few studies are available in literature concerning the emissions from burning candles; in particular emissions of lead (van Alphen 1999; Wasson et al. 2002), zinc (Nriagu and Kim 2000) or soot (Guo et al. 2000; He et al. 2004; Zai et al. 2006; Pagels et al. 2009; Stabile et al. 2012), produced by the heating of candles wick cores or by the wax combustion/evaporation were evaluated, while less researches have been focused on the presence of volatile organic compounds or

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polycyclic aromatic hydrocarbons (PAHs) in candle emissions (Lau et al. 1997; Fine et al. 1999; Lee and Wang 2006; Maupetit and Squinazi 2009; Orecchio 2011; Derudi et al. 2012). However, the candle composition is expected to influence the pollutants emissions, possibly leading to important differences in the emissions of volatile organic compounds and PAHs. In this regard, the purity of the raw materials and additives used can play a key role because raw materials which have not been adequately refined can contain some precursors which promote the formation of pollutants once the candle wax is burnt. Paraffin waxes constitute the major bulk of crude oil based crystalline waxes and are really important for industrial applications; more than 50 % of the worldwide wax production is used for candles manufacturing (Kuszlik et al. 2010).

Consequently, the aim of this work has been to investigate the presence of several pollutants both in raw materials and in exhaust gases from the burning of different container candles using a test chamber. In particular, emission factors for some PAHs, aromatic species (BTEX), short-chain aldehydes and particulate matter (PM) have been determined for container candles constituted by paraffin waxes with different degrees of refinement. Among the various pollutants, several EU priority chemicals, such as formaldehyde, benzene, toluene and naphthalene, have been monitored into the raw materials and within the candles exhausts. Then, the obtained results have been compared to identify the possible role of the raw materials composition on the pollutants emissions.

These emission factors could be used, at least at a first glance, to foresee the expected pollutant concentration in a given indoor environment with respect to health safety standards, while the test chamber used for performing the reported results could be useful to perform estimations with any other kind of candles in an easy-to-build standardised environment.

## Materials and methods

### Experimental setup

A fundamental aspect in the determination of the pollutants emissions from burning candles is the simulation of realistic burning conditions. Different approaches have been proposed in the literature, ranging from sampling ambient air close to a candle burning in a real room (Orecchio 2011) or in a fume hood (Shooto and Dikio 2011), to sampling exhaust air from a real-scale ventilated room (Maupetit and Squinazi 2009) or from a ventilated environmental chamber (Lee and Wang 2006) where the burning candle is located. These methods provide some pro and some contra, the latter being mainly related to the cost of a real-size instrumented room or to the lack of reproducibility of a non-controlled environment. To overcome these problems, a laboratory-scale test chamber has

been designed to ensure well defined and reproducible burning conditions as well as the possibility of sampling easily the exhausts. As discussed elsewhere (Derudi et al. 2012), the test chamber has been realised to obtain a smooth air flow around the candle in a large vortex above it, which mixes candle exhausts with the incoming air providing well-mixed conditions and uniform concentration at the inlet of a long stack, from which air is sampled far enough from the stack inlet to avoid entrance effects. The test chamber shown in Fig. 1 is basically constituted by three sections: a cylindrical room (diameter, 0.6 m; height, 0.4 m) covered by a conical cap (height, 0.6 m) and a stack (internal diameter, 0.07 m and height 1.5 m). The cylindrical chamber is equipped with two portholes to observe the candles behaviour during the tests.

The internal walls of the chamber have been blackened to minimise radiation phenomena from the chamber walls to the candle leading to uncontrolled rise of the candle temperature. An air sparger has been located at the bottom of the test chamber to supply air for candles combustion with minimum turbulence and very low velocity. Such an air sparger is constituted by a perforated coil covered by a bed of small glass spheres. For all experiments, pre-cleaned air through a charcoal trap has been used. To verify the trap effectiveness, a blank measure on the air fed to the chamber has been carried out before each test.

The air flow rate to the test chamber has been adjusted to 10–15 NL/min to obtain realistic burning conditions with a burning rate close to the values measured in some preliminary

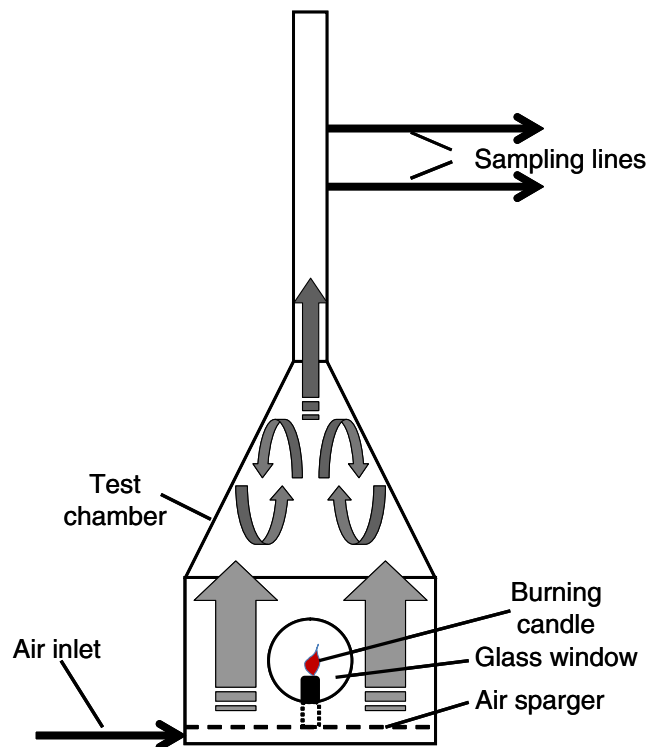


Fig. 1 Sketch of the test chamber (arrows roughly represent air patterns)

burning tests in real rooms. Furthermore, equipment to monitor temperatures into the candle body, at the chamber wall and within the stack, as well as an on-line gas analyser for monitoring main products (O<sub>2</sub>, NO<sub>x</sub>, SO<sub>2</sub>, CO and CO<sub>2</sub>) within the exhausts, complete the experimental setup.

Four candles have been burned simultaneously for each test; they have been placed upright at the centre of the chamber bottom, spaced enough to avoid undesirable thermal influence from one candle to the others. The locations of the individual candles inside the chamber have been recorded and kept equal for all the tests. Burning four candles simultaneously allows for both increasing the pollutant production rate and averaging the possible differences among candles of the same kind, thus reducing the uncertainties in the estimation of the pollutants emission factors.

To determine the candle burning rate, each candle has been weighted before and after the burning experiment and the corresponding burning time has been recorded.

Three different kinds of container candles with a cotton wick, manufactured in Italy, have been tested. The candles had an approximate weight of 100 g and were contained in a glass beaker (70 mm diameter×75 mm height). The main characteristics of the waxes that constitute the investigated candles are summarised in Table 1; each wax sample has been identified by means of two main properties that classify the material, being the first one the wax freezing temperature and the other one the oil content of the raw material. The investigated materials contain some oil since paraffin waxes are separated from crude oil during the production of distillate lubricating oils (Kuszlik et al. 2010), and they are classified by oil content and degree of refinement. The crudest versions belong to the slack wax category and contain usually between 5 and 20 % by weight of oil-like, low melting components; candles B and C fall into this category even if they have quite different melting points. With reference to the data summarised in Table 1, the B sample can be considered as a macrocrystalline light slack wax, while the C sample showed freezing point, viscosity and color index typical of semimicrocrystalline heavy slack waxes (Zaky et al. 2010). Scale

waxes are more refined and contain between 1 and 5 % oil. They can be produced by a deoiling or wax fractionation process, which selectively remove oil and low melting waxes from the slack waxes (Zaky et al. 2007). The highest grade of refinement is the fully refined wax. Fully refined paraffin waxes, as the candle A, contain less than 0.5 % oil and have been hydrotreated or clay treated to remove impurities and colour. Therefore, the resulting waxes are water clear, odour free and normally food grade.

#### Raw materials characterisation

Different analytical techniques have been used to investigate the composition and the presence of pollutants precursors into the paraffin samples. A given amount of each wax (about 0.4–0.5 g) has been sampled from the candles and mineralised with strong acids in a microwave oven, so as to obtain (at the end of the process) a homogeneous aqueous solutions. This solution, after a further dilution, has been quantitatively analysed by means of an ICP-OES technique to determine the content of sulphur and several metals, as reported in Table 2. Apart from a slight content of barium into the B and C samples, very low amount of other metals have been detected. Conversely, the sulphur content of the raw materials was really different. The A sample evidenced the lowest sulphur content (about 20 µg/g), which is from 20 to 100 times lower than the sulphur concentrations found in B and C waxes. As the latter belong to the slack waxes category, a non-negligible sulphur content was expected (Zaky et al. 2010). Clearly, this could affect the propensity of these candles to produce sulphur-containing pollutants during the combustion process.

Raw materials have been also solubilised in high-grade n-dodecane and analysed with a gas chromatography coupled with a mass-spectrometry (GC-MS), equipped with Restek Rxi-5Sil-MS chromatographic column, to determine the concentration of BTEX; none of the investigated samples evidenced the presence of BTEX, being their content always less than 0.2 µg/g of wax. However, the GC plots of the raw

**Table 1** Properties of the waxes constituting the investigated container candles

Parameter	Method	Candle A	Candle B	Candle C
Color	ASTM D1500	0.5	0.5	2.5
Density (kg/m <sup>3</sup> )	ASTM D1298	0.81	0.82	0.86
Freezing point (°C)	ASTM D87	50	55	65
Penetration at 25 °C (0.1 mm)	ASTM D1321	16	22	51
Viscosity at 100 °C (mm <sup>2</sup> /s)	ASTM D445	–	3.69	6.7
Oil content (wt.%)	ASTM D721	<0.5	8.7	5.9
Flash point (°C)	ASTM D92	>220	>220	>220
Soot Index	EN 15426	0.063	0.157	3.324
Burn rate (g/h)		2.8±0.1	1.9±0.2	2.7±0.1

**Table 2** Concentrations (in microgrammes per gramme) of several elements in the waxes constituting the investigated container candles

Element	Candle A	Candle B	Candle C
S	20	430	2700
Ba	50	260	110
Ca	30	30	30
Al	50	n.d.	n.d.
Si	6	25	10
Fe	1	2	7
Zn	3	n.d.	n.d.
Cu	2	n.d.	n.d.
B	n.d.	10	3
K	n.d.	7	7
P	n.d.	4	2
Na	n.d.	n.d.	4

*n.d.* concentrations below the limit of quantification

materials, reported in Fig. 2, help to qualitative define the composition of the investigated waxes. In particular, considering that the waxes are largely constituted by linear and branched paraffins, with a small amount of naphthenes, the retention times of the chromatographic peaks can be roughly related to the molecular weight of the corresponding species. Hence it is possible to notice that the average molecular weight of the long-chain paraffins that constitute the raw materials increases from the A to the C samples, as expected from the different melting temperatures of the waxes. More in detail, the most abundant paraffins should be C24 (retention time of about 34 min) and C28 hydrocarbons (retention time of about 40 min) for the A and B samples, respectively, while C35 and C36 species are the highest molecular weight components. The GC plot of the C sample evidenced the presence of a bimodal distribution of the chromatographic peaks; the main fraction should be constituted by C35 hydrocarbons, while the highest molecular weight components are probably species containing more than 45 carbon atoms (C45+ species), which is consistent with the heavy slack wax classification proposed for this sample.

Finally, raw material samples have been analysed to determine their PAHs content; about 100 mg of wax has been solubilised in 10 mL of dichloromethane and, after dilution, a CG-MS analysis has been performed. A summary of these results is shown in Table 3; the B sample evidenced levels of total PAHs of about 46 µg/g which are mainly due to 3-ring PAHs, as shown in Fig. 3, and particularly to high levels of phenanthrene. Conversely, less than 3 µg/g of total PAHs have been found for the other samples. Considering three- and four-ring PAHs, phenanthrene and pyrene were always the main species detected, but the fraction of four-ring PAHs was quite high in the C sample (see Fig. 3). Some naphthalene was also found in the slack waxes (B and C candles), evidencing that

poorly refined raw materials could contain small amounts of volatile and semi-volatile PAHs. No carcinogenic PAHs were found in the analysed samples.

#### Emissions sampling and analysis

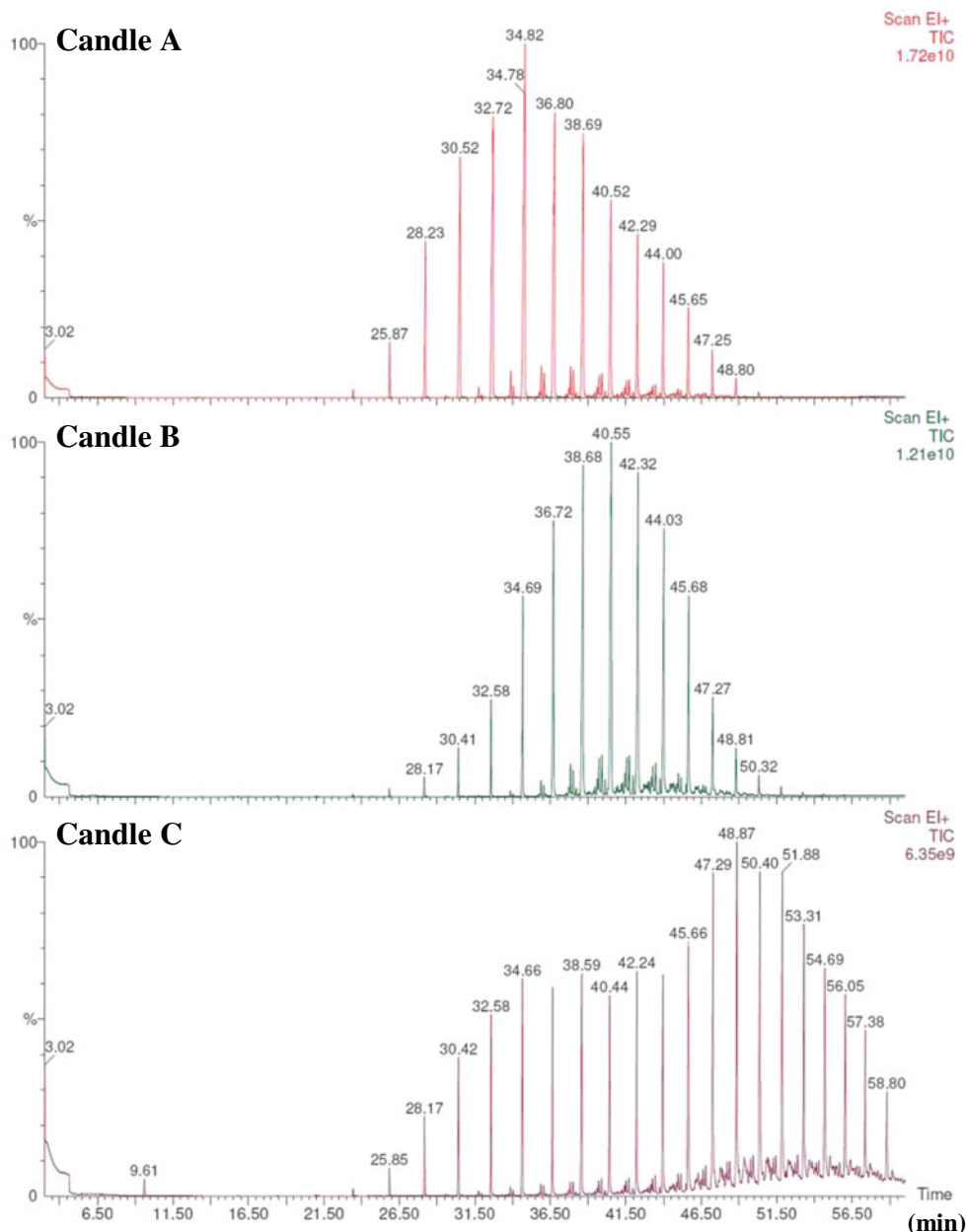
At the beginning of each experimental run the candles were burnt for about 15 min before to start the exhaust sampling. This initial burning period was used to check that individual candles reached proper burning conditions, with an established fuel pool and a stable flame (according to ASTM F-2326), and to ensure that steady conditions are obtained within the chamber, as verified by on-line measurements of the residual oxygen concentration within the stack. Once a steady state oxygen concentration was measured, the sampling was started. Then, exhaust gases were sampled and analysed to evaluate the concentrations of light gases, PAHs, BTEX, PM, as well as short-chain aldehydes such as formaldehyde, acetaldehyde, propionaldehyde and benzaldehyde. Considering both the initial transient phase and the sampling period, the overall duration of each experiment was less than 4.5 h.

For the short-chain aldehydes, the 2,4-dinitrophenylhydrazine (DNPH) method was used (Sesana et al. 1991). By means of a gas sampling pump a well defined volume of exhaust is passed through a cartridge containing the DNPH sorbent (LpDNPH S10 cartridge). The aldehydes react quantitatively with DNPH to give the corresponding hydrazone compounds which can be measured through HPLC. According to the sampling capacity of the DNPH cartridge, a sampling flow of about 1.5 L/min allows for collecting a total volume of about 45 L in 30 min. The DNPH cartridge can be desorbed using acetonitrile, and aldehydes analysed using HPLC (C18 column, 5 µm 250 mm, detector UV at 360 nm). The extraction yield of the aldehydes has been always close to 100 % and the relative standard deviations on the corresponding concentrations were less than 5 %. The detection limit for the various aldehydes has been estimated equal to about 0.1 µg/g of candle burnt.

For the determination of the concentrations of benzene, toluene, ethyl-benzene and xylenes, a well-defined volume of exhaust gas was sampled by means of a gas pump and passed through a charcoal cartridge (Carbotrap 349). According to the sampling capacity of the charcoal cartridge, a sampling flow of about 0.05 L/min allows for collecting a total volume of about 12 L in 4 h. After sampling, the charcoal cartridge was thermally desorbed and analysed with CG/MS. The average extraction yields of the BTEX ranged from 86 to 100 % and the relative standard deviations of the corresponding concentrations were less than 10 %. The detection limit for the various BTEX has been estimated equal to about 0.01 µg/g of candle burnt.

PAHs were sampled with a combined particle/gas phase system: a well defined volume of exhaust gas was sampled by

**Fig. 2** GC plots of the candles waxes



means of a gas pump and passed through a PTFE filter (TE, 35; pore size of 0.2  $\mu\text{m}$ ) and an adsorption Tenax cartridge (Supelco XAD Orbo Tube). Particles were collected on the PTFE filter surface, while gas phase PAHs were sampled on the XAD2 sorbent. Both filter and cartridge were extracted with dichloromethane coupled with a sonication treatment of 30 min. According to the sampling capacity of both the filter and the cartridge, a sampling flow of about 0.5 L/min allows for collect a total volume of about 120 L in 4 h. After vacuum concentration, the desorbed solution was analysed using a GC/MS. Considering the measurements of all the samples, extraction yields of the PAHs were never less than 85 % and in most cases almost 100 %, while the relative standard

deviations of the corresponding concentrations were less than 15 %. The detection limit for the various PAHs has been estimated equal to about 0.01 ng/g of candle burnt.

PM emitted during the candles combustion has been also measured; different PM fractions (50 % cutoff at 10, 2.5, 1.0, 0.5 and 0.25  $\mu\text{m}$ ) have been collected using a personal cascade impactor sampler (PCIS) at 9 NI/min.  $\text{PM}_{0.25}$  was collected on a 37 mm, 2.0  $\mu\text{m}$  PTFE filter with polymethylpentene support ring and PCIS impaction stages were constituted via 25 mm, 0.5  $\mu\text{m}$  PTFE membranes. PM mass has been determined by gravimetric analysis; the net PM mass on filters has been determined by weighing the conditioned filters before and after sampling with a micro-balance

**Table 3** Concentration (in microgrammes per gramme) of PAHs in the waxes constituting the investigated container candles

Pollutant	Candle A	Candle B	Candle C
Naphthalene	n.d.	0.33	0.15
Acenaphthylene	0.08	0.85	0.08
Acenaphthene	0.04	1.62	0.08
Fluorene	0.53	7.65	0.35
Phenanthrene	1.16	19.34	0.36
Anthracene	n.d.	5.64	n.d.
Fluoranthene	0.26	4.81	0.26
Pyrene	0.60	5.92	0.49
Total PAHs	2.67	46.16	1.77
Carcinogenic PAHs	<0.01	<0.01	<0.01

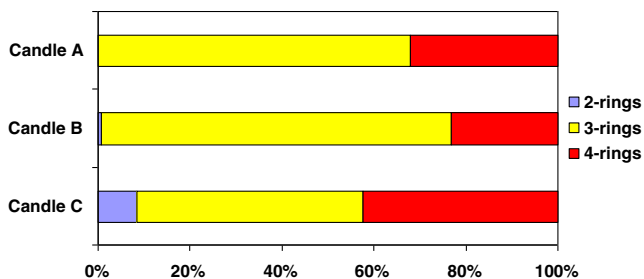
*n.d.* concentrations below the limit of quantification

in a temperature ( $20 \pm 1$  °C) and relative humidity ( $50 \pm 5$  %) controlled cabinet. The quality of the weighing procedure has been assessed using the ASTM D 6552 standard. The weighing accuracy was 18 µg for 37 mm filters and 10 µg for 25 mm filters.

Sampling was always stopped before the blow out of the candles so as to avoid the collection of pollutants produced during the last transient stage of the burning process.

## Results and discussion

Several preliminary thermogravimetric analyses (TG/DT) have been performed on raw materials to highlight the behaviour of the waxes once they are heated up by the flame. TG/DT runs with about 30 mg of wax have been performed (from 30 up to 600 °C, heating rate of 10 °C/min) using air as carrier gas. The fully refined paraffin wax (candle A) showed about 97 % weight loss in the range 165–315 °C; the light slack wax (candle B) evidenced a similar trend, with a 98 % weight loss in the range 190–330 °C. On the other hand, the heavy slack wax (candle C) produced a somewhat different TG curve, characterised by two separated weight losses; the sample lost about 90 % of its weight in the range 210–360 °C, while the remaining residue was slowly burnt until 550 °C as shown in

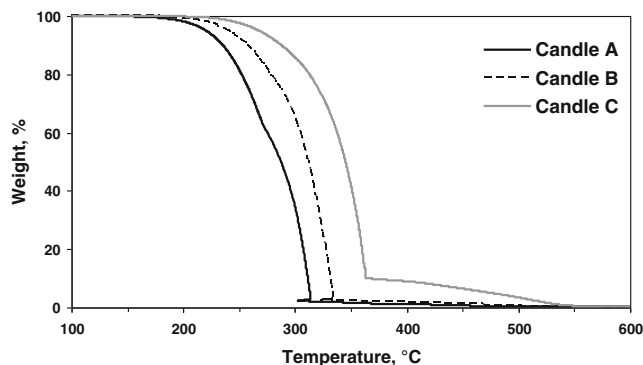


**Fig. 3** PAHs fractions in the candles waxes

Fig. 4. These results are in agreement with the qualitative molecular weight distributions evidenced with the GC-MS analyses (see Fig. 2), being the fully refined paraffin candle the one with the lowest average molecular weight and confirming the presence of a bimodal distribution of the constituents into the heavy slack candle.

As previously mentioned, four container candles have been burnt in the test chamber for each test, leading to an average candle burning rate of about 1.9 g/h for the candle B and 2.7 g/h for the other ones (see Table 1). In particular, container candles have been burnt in a single step, but to verify if the emissions were constantly released few experiments have been also carried out in different burning cycles of about 4 h, followed by a 1 h stop between the cycles. No significant differences were found between the two procedures. Moreover, temperatures inside the enclosed combustion chamber used for the experiments have been monitored to avoid an excessive wax melting and consumption. For this reason, three thermocouples allowed for measuring the temperatures of the candle container, at the chamber wall, and within the stack; Fig. 5 reports typical temperature profiles detected during an experimental run performed burning four C candles simultaneously. It can be noticed that the candle container never reached a temperature close to the melting temperature of the analysed wax, preventing the formation of an excessive liquid pool around the candle wick and ensuring realistic candle burning conditions. The detection of main combustion products and pollutants allowed to determine the proper inlet air flow-rate that must be used to ensure a combustion environment similar to the real room conditions as well as the duration of the initial start up in which steady state conditions were achieved within the test chamber. After about 15 min, as indicated by the dotted line of Fig. 6, all the main combustion products and the residual oxygen reach a steady state into the stack. This evidences that combustion conditions, both in terms of wax burning rate and emission of pollutants, do not change over the whole sampling period.

Measured emissions have been recast into specific emission factors with reference to 1 g of candle burnt. These values allow a direct comparison between different types of candles;



**Fig. 4** Thermogravimetric analysis of the candles waxes

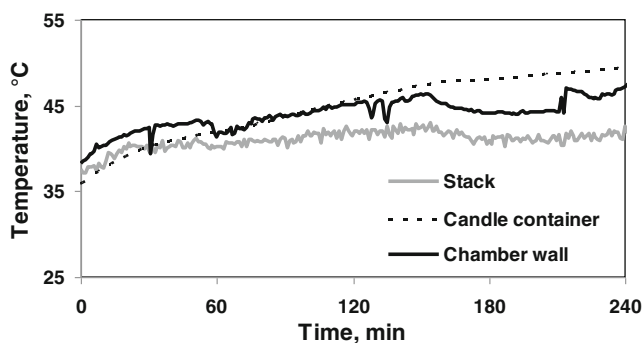


Fig. 5 Typical temperature profiles while burning four candles simultaneously

as shown in Tables 4, 5, and 6, emission factors change significantly from one candle type to another one: variation as large as one order of magnitude have been recorded. However, all the investigated candles evidenced very similar NO<sub>x</sub> emission factors and negligible aldehydes emissions. NO<sub>x</sub> production is strongly dependent from the flame temperature and no significant differences can be expected for different paraffin candles. Concerning aldehydes, whose emission factors were below 0.1 µg/g, their formation is not affected by the degree of wax refinement of the paraffin used for the candle production or, in other words, by the paraffin oil content. These results confirm the findings of previous works (Lau et al. 1997; Derudi et al. 2012), where aldehydes emissions were mainly ascribed to the presence of dyes or fragrances in the candle rather than to the wax composition.

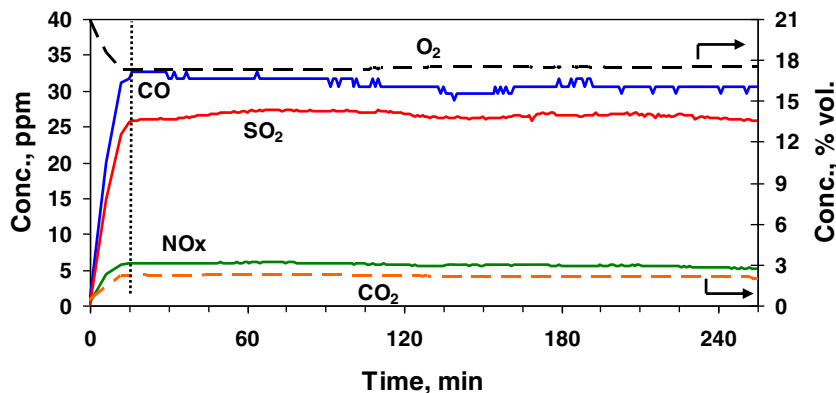
As previously mentioned, the sulphur content of the studied raw materials (reported in Table 2) can be directly related to their SO<sub>2</sub> emission factors (see Table 4); no SO<sub>2</sub> emissions were basically determined for the A candles, while all the sulphur contained in the B and C waxes was released as SO<sub>2</sub> during the corresponding combustion experiments.

A correlation can be deduced among CO, BTEX and PAHs emissions and the composition of the investigated waxes. It should be noted that BTEX were not present in the raw materials but they are formed by the incomplete combustion of the waxes; moreover, they are typical precursors of the PM.

It is possible to notice that the candle A showed the lowest emission factors for all the pollutants considered, including total PM (see Table 6). About the individual pollutants, in most cases the A sample evidenced the lowest emission factors, apart from the 5-ring PAHs whose emission factors are at an intermediate levels. The combustion of heavy slack candles (sample C) led to intermediate levels of CO, BTEX and PAHs but their CO emission factor is only 33 % higher than the corresponding one of the sample A, while the total BTEX and PAHs emissions are two and three times higher, respectively. Light slack candles (sample B) always showed the worst performances in terms of emission of harmful compounds; CO emission is about 64 % by weight larger than those of the sample A, while total BTEX and PAHs are about 10- and 6-fold higher, respectively.

The determined emission factors clearly point out that the oil content of the raw material can strongly affect the pollutants production; an increase of the oil amount into the paraffin lead to an overall worsening of the combustion process, producing high level of BTEX and PAHs. With reference to BTEX, it seemed that less refined paraffin candles promoted the formation of toluene and some xylenes; similarly, emissions of naphthalene and three-ring PAHs, are significantly increased. The propensity of the oil-containing waxes to produce high levels of aromatic and polyaromatic emissions can be reasonably ascribed to the oil percentage, but it is difficult to find a relationship between the PAHs presence into the waxes and their concentration within the exhausts. As an example, the lowest PAHs content was found for the sample C (see Table 3), while the lowest PAHs emissions were obtained from the combustion of the A candles (see Table 5); PAHs were the highest both into the wax and within the emissions for the sample B but no clear relation exists between them. First of all, it is worth noticed that most of the PAHs emission factors are orders of magnitude lower than the corresponding values detected in the raw materials; therefore, it can be assumed that PAHs found in the wax are burnt in flame, similarly to other hydrocarbons, during the candles combustion. This means that the relative composition of the PAHs

Fig. 6 Typical trends for main combustion products and residual oxygen concentrations determined into the stack



**Table 4** Permanent gases and BTEX emission factors estimated for the investigated container candles

Pollutants	Candle A	Candle B	Candle C
Permanent gases			
CO (mg/g)	2.44±0.07	3.99±0.05	3.24±0.03
NO <sub>x</sub> (mg/g)	0.89±0.03	0.87±0.03	0.92±0.02
SO <sub>2</sub> (mg/g)	<0.01	1.07±0.24	5.52±0.30
BTEX			
Benzene (µg/g)	0.02±0.01	0.37±0.07	0.03±0.02
Toluene (µg/g)	0.03±0.01	0.46±0.12	0.08±0.07
Ethylbenzene (µg/g)	0.02±0.01	0.11±0.04	0.02±0.01
( <i>m+p</i> )-xylenes (µg/g)	0.02±0.01	0.11±0.02	0.07±0.05
<i>o</i> -xylene (µg/g)	0.03±0.01	0.05±0.01	0.04±0.01
Total BTEX (µg/g)	0.12	1.10	0.24

emitted by the candles combustion does not reflect the distribution of PAHs in the equivalent wax. Figure 7 reports the PAHs fractions that contribute to the overall PAHs measured for the investigated candles; naphthalene was always the most abundant fraction, while in the raw materials two-ring PAHs were the lowest fraction, as shown in Fig. 3. Moreover, 3-ring and 4-ring PAHs constitute more than 90 % of total PAHs in the waxes; conversely, no 4-ring PAHs were practically found within the exhausts and 5-ring PAHs contributed for more than 10 % to the overall PAHs emissions, confirming that there is no relation between raw materials and emissions for this kind of pollutants.

**Table 5** PAHs emission factors (in nanogrammes per gramme) from burning container candles

Pollutant	Candle A	Candle B	Candle C
Naphthalene	16.7±2.5	123±45.3	55.3±2.2
Acenaphthylene	0.51±0.06	1.50±0.13	0.68±0.60
Acenaphthene	0.15±0.01	5.99±5.10	1.47±1.45
Fluorene	0.06±0.05	6.09±5.16	0.43±0.34
Phenanthrene	0.77±0.27	6.04±1.91	4.19±3.06
Anthracene	3.12±2.62	8.72±8.70	10.2±0.77
Fluoranthene	0.09±0.08	0.23±0.22	0.13±0.12
Pyrene	<0.01	<0.01	0.23±0.22
Benzo[a]anthracene	<0.01	<0.01	<0.01
Chrysene	<0.01	0.10±0.08	0.53±0.51
Benzo[b]fluoranthene	<0.01	<0.01	3.46±3.45
Benzo[k]fluoranthene	3.78±2.83	<0.01	3.50±3.49
Benzo[a]pyrene	1.41±1.00	<0.01	3.44±3.40
Indeno[1,2,3-cd]pyrene	<0.01	<0.01	<0.01
Dibenzo[a,h]anthracene	<0.01	<0.01	<0.01
Benzo[g,h,i]perylene	<0.01	<0.01	<0.01
Total PAHs	26.6	152	83.6
Carcinogenic PAHs	5.19	0.1	10.9

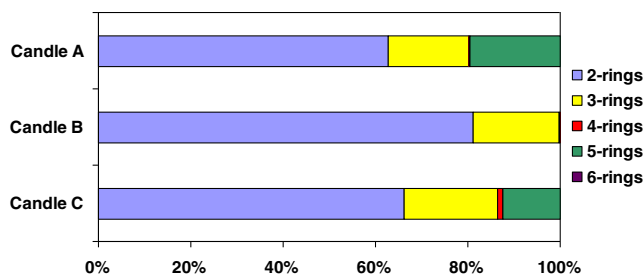
**Table 6** Particulate matter emission factors (in microgrammes per gramme) from burning container candles

Size fraction	Candle A	Candle B	Candle C
<0.25 µm	2.51	96.2	238.7
0.25–0.5 µm	0.39	3.55	26.2
0.5–1 µm	1.89	3.84	3.65
1–2.5 µm	1.01	0.93	3.14
2.5–10 µm	1.17	1.31	0.16
Total PM <sub>x</sub>	6.97	105.8	271.9

Then, the distribution of different PAHs isomers into the exhausts was studied to define if they are released by evaporation and pyrolysis phenomena at relatively low temperature, due to the overheating of the candles constituents, or produced by an incomplete combustion (Yunker et al. 2002; Orecchio 2010). Usually, values of anthracene to anthracene plus phenanthrene Ant/(Ant+Phe) ratio of <0.10 are an index of low temperature sources while values larger than 0.10 indicates a dominance of combustion (Yunker et al. 2002). All the investigated samples evidenced high values of this index, ranging from about 0.6 of the sample B to about 0.8 of the A high-grade paraffin candles. Concerning the Fla/(Fla+Pyr) ratio, a value of 0.4 can be assumed as threshold between low temperature sources and intermediate conditions or combustion sources (liquid and solid fossil fuels). For the candles studied in this paper, the sample C exhibited a Fla/(Fla+Pyr) index that is slightly lower than 0.4, while a value equal to 1 has been found for the other two candles, thus confirming that PAHs are mainly emitted by combustion. To solve the problem of the discordant average values obtained for the candles C, as suggested by Mannino and Orecchio (2008) and Orecchio (2010), a total index, defined as the sum of the above mentioned isomeric ratios, normalised to the limit values reported in literature (Yunker et al. 2002; Derudi et al. 2012), has been evaluated as follows:

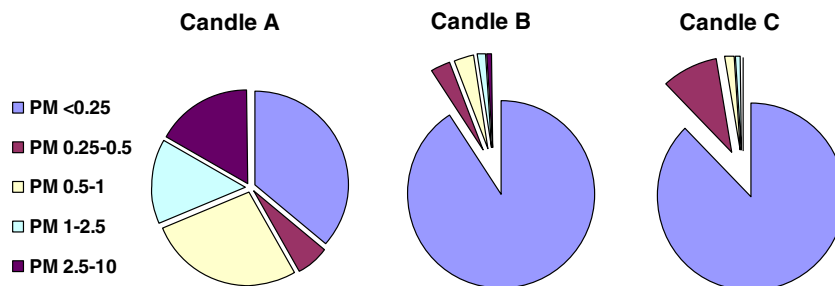
$$\text{Totalindex} = \frac{\text{Ant}}{(\text{Ant} + \text{Phe}) \times 0.1} + \frac{\text{Fla}}{(\text{Fla} + \text{Pyr}) \times 0.4} \quad (1)$$

With respect to the formula commonly reported in the literature, the expression of Eq. (1) includes only two isomeric ratios because the other terms, which refers to high molecular

**Fig. 7** PAHs fractions determined from burning the investigated candles



**Fig. 8** PM fractions determined from burning the investigated candles



weight PAHs isomers, are negligible because of the fact that the emission factors determined in this study for PAHs such as benzo[a]anthracene (B[a]A) and indeno[1,2,3-cd]pyrene were below the limit of quantification. When the total index is  $>4$ , PAHs are mainly originated from combustion processes while lower values indicate prevalently low temperature emissions. In this study, the average total index is equal to about 8 for candles B and C, and to about 10 for the sample A, thus confirming that PAHs are only emitted by high temperature processes.

Finally, the PM emission factors, obtained for different size fractions, have been reported in Table 6. The sample A shows the lowest emission factor for total  $PM_x$  ( $6.97 \mu\text{g/g}$  of burnt wax), confirming the trends obtained for the other pollutants; in particular, a very low amount of particles  $<0.25 \mu\text{m}$  was found with respect to the corresponding values determined for the B and C candles. The total  $PM_x$  emissions of the slack candles were about 106 and  $272 \mu\text{g/g}$  for samples B and C, respectively; this means that the candle characterised by the highest BTEX and PAHs emission factors (sample B) did not produce also the highest amount of PM. As shown in Fig. 8, the  $<0.25 \mu\text{m}$  fraction was the most abundant for all the studied candles but its contribution is below 50 % for sample A while it represents about 90 % of the emitted PM for the other two candles; this highlights the fact that the oil presence into the candle wax influenced not only the PM emission factors but also the particles size formation and growth mechanisms. Moreover, these results are in agreement with the findings of Afshari et al. (2005) and Shooto and Dikio (2011) which evidenced that candle wax flame soot particles are extremely small, with a majority of them about  $0.3 \mu\text{m}$  in diameter. The high PM production rate of sample C basically confirms the qualitative information available from the soot index of this candle (reported in Table 1), which is particularly high; the soot

index can be considered as characteristic of the sooting behaviour of the type of candle tested. However, it gives only a qualitative information of the soot propensity of a given candle because this measurement is strongly dependent on the optical properties of the particles produced by the combustion reaction; these properties are usually considered constants for different materials, thus leading sometimes to a misrepresentation of the sample behaviour as it happened for the B candles. Samples B and A had similar soot index but they are characterised by really different PM emission factors. This clearly evidences the need for simple and cheap methodologies to measure the emission factors of commercial candles to foresee the expected pollutant concentration in a given indoor environment and compare it with health safety standards. In this regard, the laboratory-scale test chamber used in this study could be useful to perform estimations in an easy-to-build standardised environment.

Emissions of few high priority pollutants have been compared, for the sake of example, to the corresponding ambient air quality standards; on the basis of the determined emission rates of the candles, a simple and typical indoor air scenario was considered to determine resulting indoor air levels when two container candles are burnt simultaneously in a  $30 \text{ m}^3$  room, considering an air exchange rate of  $0.5 \text{ h}^{-1}$ . Considering a well-mixed environment, the steady-state concentration of the  $i$ th pollutant ( $C_{ss}$ ) can be computed as follows:

$$C_{ss,i} = \frac{n \cdot m \cdot EF_i}{V \cdot AER} \quad (2)$$

with  $n$ =number of candles,  $m$ =candle burning rate,  $EF_i$ =emission factor of the  $i$ th pollutant,  $V$ =room volume, and  $AER$ =air exchange rate.

**Table 7** Airborne concentrations of pollutants determined for the considered exposure scenario

Pollutant	Candle A	Candle B	Candle C	Threshold limit	Reference
$\text{SO}_2$ ( $\mu\text{g}/\text{m}^3$ )	3.73	271	1,987	350	WHO (2010)
Benzene ( $\mu\text{g}/\text{m}^3$ )	0.01	0.09	0.01	5	EU (2000)
Naphthalene ( $\text{ng}/\text{m}^3$ )	6.23	31.2	19.9	3,000	USEPA (1998)
Benzo(a)pyrene ( $\text{ng}/\text{m}^3$ )	0.53	0.00	1.24	1	EU (2004)
$PM_{2.5}$ ( $\mu\text{g}/\text{m}^3$ )	2.17	26.4	97.8	25	WHO (2006)

The resulting indoor air concentrations, computed for the emission factors found for SO<sub>2</sub>, benzene, naphthalene, benzo[a]pyrene and PM<sub>2.5</sub>, respectively, are summarised in Table 7, together with the corresponding air quality standards. It can be seen that benzene and naphthalene concentrations are well below the standards considered; therefore, it seems that candles burning has a negligible contribution with respect to other sources (Batterman et al. 2012) to the usually measured indoor levels of these pollutants. Conversely, SO<sub>2</sub> and benzo[a]pyrene concentrations exceed the recommended values for candles C; for the considered ventilation rate, it is worth noting that even the use of only one C candle will lead to a severe overexposure to SO<sub>2</sub>, as its threshold level (350 µg/m<sup>3</sup>) is largely exceeded. Similar conclusions can be drawn also for PM<sub>2.5</sub> emissions; PM<sub>2.5</sub> concentration slightly exceeds the threshold value for B candles, while a significant overexposure can be estimated for C candles. In this case, estimated PM concentrations were compared with PM<sub>2.5</sub> WHO air quality guidelines (Apple et al. 2010; WHO 2006), as no threshold values are recommended at present for PM size fractions with cut-off diameters below 2.5 µm. For this reason, a much more detailed toxicological study should be required to critically evaluate the obtained data.

## Conclusions

The main aim of this work has been to characterise pollutants emission factors from the burning of container candles, with particular reference to their relations with the waxes composition. Two different slack waxes and a fully refined paraffin one have been burnt using a laboratory-scale test chamber, which allows for performing the pollutants measurements in a controlled environment avoiding the large investments required by a full-scale environmental room.

Almost no emissions of aldehydes have been found for all the candles, leading to the conclusion that such emissions could be mainly related to the presence of a fragrance rather than to the other candle parameters, in agreement with previous findings concerning scented candles (Derudi et al. 2012).

Conversely, it has been found that CO, SO<sub>2</sub>, BTEX, PAHs and PM emissions are more related (at least for the container candles investigated in this work) to the corresponding wax quality rather than to the wax additives. Moreover, for the container candles investigated it has been highlighted that the presence of oil into the candle wax influences not only PM emission factors but also the particles size formation and growth mechanisms.

Several pollutants emission factors for three different wax-based container candles have been determined in a laboratory-scale test chamber. Such results could be used, at least at a first glance, to foresee the expected pollutant concentration in a given indoor environment with respect to health safety

standards, while the test chamber used for performing the reported measurements could be useful to measure the emission factors of any other candle in an easy-to-build standardised environment.

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