Polycyclic Aromatic Hydrocarbons in Smoke Used to Smoke Cheese Produced by the Combustion of Rock Rose (*Cistus monspeliensis*) and Tree Heather (*Erica arborea*) Wood

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In this work, the polycyclic aromatic hydrocarbons (PAHs) and their methyl derivatives concentrations have been determined in smoke from the rock rose and tree heather wood combustion. The combustion is done in two types of smokers, kiln and drum, commonly used in the Canary Islands (Spain) to smoke cheese. The low control of the operational conditions justify the great variability of the PAHs concentration in the emissions, with values between 251.8 and 2547 μg/m^{3}N. In general, the lowest concentrations correspond to the tree heather wood combustion in the drum, while the highest concentrations are usually reached in the rock rose wood combustion in the kiln. However, the relative contributions of each PAH to the total concentration are independently similar to the type of smoker and wood used. In the combustion conditions, the equilibrium is not reached during the PAHs distribution process between the gas and aerosol phases. Therefore, while naphthalene and their 1- and 2-methyl derivatives remain in the gas phase, phenanthrene and PAHs with higher molecular weight remain mainly in the aerosol phase. In this phase, the PAHs concentration represents 39.9% of the total PAHs produced by burning rock rose wood and 29.1% of the total PAHs when tree heather wood is used. To establish the carcinogenic potential in both phases, the percentages of some PAHs were calculated. These values are significantly higher in the aerosol phase and, at the same time, higher when rock rose wood is used.

KEYWORDS: Cistus monspeliensis (rock rose); Erica arborea (tree heather); polycyclic aromatic hydrocarbons (PAHs); smoked cheese

INTRODUCTION

Smoking cheese is a traditional activity in different parts of the Canary Islands. It is prepared in rural areas using as fuel vegetation common to the region that over the years has been chosen because of the organoleptic characteristics that the smoke it produces gives the cheese. Different kinds of vegetation are used for this activity, including those common to arid regions, such as prickly pear (*Opuntia ficus índica*), and others that come from more humid areas, such as rock rose (*Cistus monspeliensis*) and tree heather (*Erica arborea*).

The combustion is usually done in rudimentary artisanal devices. As for the process, once the type of fuel is decided upon, the rest of the variables are not rigorously supervised. To achieve the best results in the smoking process, Canarian artisans use two basic criteria. First, maintain the densest smoke possible, and second, avoid flames during the smoking process to avoid the negative effects that excessively high temperatures can cause on smoked foods. Obviously, whether these goals

are met and the way that the process is done significantly condition the physical and chemical characteristics of the smoke that is produced.

The regulating councils of the different "*Denominaciones de Origen*" (PDO, Protected Designation of Origin created by the European Union) of cheese that exist in the Canary Islands, organizations responsible for ensuring the quality and characteristics of artisanal smoked cheese, must accept and respect traditional practices regarding the type of material and the operating conditions used for combustion and smoking. Besides guaranteeing that the smoked products maintain their traditional characteristics, the regulating councils also make sure that the level of pollutants in smoked food products is as low as possible.

Smoking is used not only to give foods a particular organoleptic profile but also as way to inactivate the actions of enzymes and microorganisms. It is known that the smoke produced from wood burning in low oxygen content conditions not only contains active sensorial components, such as phenols, carboxylic compounds, etc. (*1–3*), but also considerable amounts of polycyclic aromatic hydrocarbons (PAHs), some of which are known for their carcinogenic and mutagenic properties (*4, 5*).

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Food products that are directly exposed to smoke carry high concentrations of PAHs on their surfaces. Decomposition phenomenon caused by light and by interaction with other products present causes the concentration of PAHs to diminish (*6*, *7*). Nevertheless, the PAHs can also penetrate into the smoked products, thus being protected from light and oxygen, stabilizing their concentrations after a period of time (*8*). Some countries, like Germany, have established a maximum acceptable concentration of 1 μg/kg of B(a)Py in smoked foods. The European Union and the United States permit maximum limits of 0.03 μg/kg of B(a)Py in foods aromatized with smoke flavoring additives (SFA).

This work focuses on the emission of PAHs in smoke from combustion of rock rose and tree heather wood, habitually used in El Hierro and La Gomera, islands belonging to the Canary Island archipelago, to smoke cheese. The artisanal process of smoke production was respected as far as possible, practically without controlling the operating variables, using the devices and production techniques used by Canarian farmers. The smoke samples were collected with a sampling system made from an aspiration pump, a quartz fiber filter followed by a PUF/XAD-2/PUF cartridge, with the objective of retaining the particle-bound PAHs fraction, as well as the volatile and semivolatile fraction. The analytic procedure used for the extraction, cleanup, and quantification by gas chromatography–mass spectrometry (GC–MS) of PAHs has been developed in an earlier work (*9*).

One of the principal objectives of this work has been to establish the nonsubstituted and methyl derivatives PAH content in the smoke produced by the combustion of rock rose (*Cistus monspeliensis*) and tree heather (*Erica arborea*) wood and its relation with the type of smoker and combustible, as well as the characteristics of the smoke in the area where the cheese is smoked. Moreover, this work provides information about the distribution of individual PAHs in aerosol and gas phases of the smoke, relating the concentrations of the PAHs with the potential carcinogenicity provided by the samples.

MATERIALS AND METHODS

Reagents and Materials. Deuterated internal standards mixture 25 (500 μg/mL in acetone), PAH mixture 9 (100 μg/mL in acetonitrile), and PAH mixture 112 (100 μg/mL in acetonitrile) were supplied by Dr. Ehrenstorfer, Reference Materials (Augsburg, Germany). These standards were stored at 4 °C and used for the preparation of working standard solutions (10 μg/mL in dichloromethane).

Decafluorobiphenyl (DFB) (2000 μg/mL in dichloromethane) was provided by Accustandard (New Haven, CT), stored at 4 °C, and diluted to 12 μg/mL in dichloromethane.

For smoke sampling, quartz fiber filter, PUF of 22 mm outside diameter × 7.6 cm length and a density of 0.022 g/cm^3, XAD-2 resin, glass holder for PUF, and filter cartridges were supplied by Supelco (Bellefonte, PA).

Dichloromethane (DCM), diethyl ether, and hexane of GC grade and pentane of organic trace analysis grade were provided by Merck (Darmstadt, Germany), and silica gel type 60, 70–230 mesh was supplied by Aldrich (Steinheim, Germany). All other reagents were of an analytical-reagent grade.

The biofuels used in the combustion were pine needles (precursor to the combustion), pieces of rock rose and tree heather wood exposed for a variable time period to atmospheric conditions. The dimensions of the pieces of wood varied between a length of 30 and 45 cm and a diameter between 5 and 20 cm.

Smoker and Operating Conditions. The two types of smokers used most frequently by the Canary Island farmers were used. The drum type consists of a metallic cylinder 90 cm high and 63 cm in diameter, without a lid on the upper part, where the available cheese is placed

on a wood grill. Through a hole made in the lower part, the biofuel to be burned is introduced. The kiln type is formed by two metallic chambers, one for combustion and the other for smoking, connected by a duct, between which the smoke circulates without control mechanisms.

In both smokers, the combustion process of the wood is similar. The combustion is started with the help of a small amount of pine needles. During the process, fire is avoided by manually applying small amounts of water.

Determination of the Temperature and Carbon Monoxide. The determination of these parameters in the smoke is performed in the place where the food to be smoked is placed. The measurements are taken at 5 min intervals during the sampling with a portable combustion efficiency analyzer (MRU 89/5 Vario, Hamburg, Germany).

Sampling. The PAHs sampling system consists of a quartz fiber filter followed by a polyurethane foam (PUF) 3 cm length/XAD-2 (2 g)/PUF (3 cm length) cartridge sandwich, which were coupled to a Bravo H air sampler (TCR Tecora, Milan, Italy), with the objective of retaining the particle-bound PAHs fraction, as well as the volatile and semivolatile fraction. Sampling conditions were described in a previous work (*9*). The filters and adsorbents that contain the samples were transported in an icebox to the analytical laboratory where they were conserved at less than or equal to 4 °C in absence of light for up 7 days prior to extraction.

Extraction and Cleanup. The filter and glass holder with the PUF/XAD-2/PUF cartridge were extracted directly for 18 h in a Soxhlet apparatus (4 cycles/hour) with 300 mL of 1:9 diethyl ether/hexane (v/v). The extract was dried, concentrated, and cleaned as previously described (*9*).

GC–MS Analysis. The aromatic fraction obtained after cleanup was concentrated to less than 1 mL, spiked with 100 μL of deuterated internal standards, and diluted with dichloromethane to 1 mL for their analysis within 30 days.

The PAHs extracts were analyzed using GC–MS on a 3800-Varian Saturn 2000 GC–MS system (Varian Inc., Palo Alto, CA), equipped with a 30 m × 0.25 mm inside diameter WCOT CP-SIL-8 CB column (Chrompack, The Netherlands) and an Autosampler Varian model 8200 CX. The Saturn GC–MS Workstation 5.52 software was used for data acquisition.

The GC–MS was operated under the following conditions: injection volume of 1 μL, splitless injection at 300 °C, GC column temperature began at 60 °C, 2 min of isothermal, 8 °C/min to 290 °C, and held for 12 min. The carrier gas was helium, with a constant flow of 0.9 mL/min and a linear velocity of 35.0 cm/s. The temperature of the transfer line was maintained at 290 °C. The ionization was performed with a kinetic energy of the impacting electrons of 70 eV. The temperature of the ion trap was 200 °C. The MS analysis was carried out in scan mode with a range of mass between 50 and 350 amu.

PAHs were identified by their retention times and confirmed by comparing their mass spectra with the mass spectra of the NIST library version 1.7a (Varian, Inc.).

The selected ion-monitoring mode (SIM) was used for quantification by means of the deuterated internal standards. The quantification conditions and the characteristics of standards calibration curves were previously described and obtained (*9*).

RESULTS AND DISCUSSION

As the introduction made clear, while interpreting the following results, one should keep in mind that they are probably affected by considerable variability, not only between different experiments completed without any apparent modification of the operating variables but also during a single smoking process. Moreover, analysis of the data obtained from the different determinations has verified that the results do not usually obey a normal distribution. Consequently, nonparametric methods were used for statistical treatment of the results (*10*).

Chemical–Physical Characteristics of the Smoke. Before establishing the PAHs content in the smoke resulting from the combustion, some of the principal characteristics of the emis-

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Table 1. Temperature and Carbon Monoxide Values of Smoke from Combustion in Kiln and Drum of Rock Rose and Tree Heather Wood

biomass	temperature (°C)	CO (mg/m³)
kiln[a]		
rock rose wood	35.6 (30.1–59.5)	5148 (2334–10487)
tree heather wood	36.9 (31.6–51.3)	5711 (2409–9654)
drum[b]		
rock rose wood	45.7 (40.9–62.4)	1115 (894–1648)
tree heather wood	46.5 (35.8–53.5)	885 (643–1162)

[a] 22 samples. [b] 8 samples.

sions were established, such as the temperature and carbon monoxide concentration. The results shown in **Table 1** correspond to the median and range values determined at 5 min intervals.

The temperatures reached in the smoke are more or less similar. The maximum values oscillate between 51.3 and 62.4 °C, while the minimum values are between 30.1 and 40.9 °C. Evidently, the medians are much closer. The results obtained in the kiln were slightly lower, possibly because of the fact that the distance between the position where the combustion takes place and the position where the sample is taken is greater than in the drum. In any case, the smokes obtained in the smoking processes are known as "cold smoke".

The results of the carbon monoxide concentrations show that even in the position where the food is smoked there is an oxygen deficit (reducing conditions).

The CO concentrations obtained when either of the two types of wood selected is used are very similar. The results seem to indicate that, in the conditions used by the different operators, the carbon monoxide concentration in the smoke depends on the type of smoker and not on the type of fuel. In general, the concentrations obtained in the kiln are significantly higher.

There is an inverse relationship between the temperature and the concentration of carbon monoxide measurements in the position of the smoker where the smoking process takes place. Actually, the obtained results, for 26 determinations, show a correlation coefficient value of 0.60 and a negative slope.

PAHs Content. PAHs content of the smoke is dependent on the analyte recoveries of the sampling system with possible lost PAHs during processing each sample. In one of our earlier works (*9*), it was shown that the lightest PAHs, naphthalene, acenaphthene, and acenaphthylene, as well as the methyl derivatives of naphthalene, show analyte recoveries between 44.3 and 63.8%, with an average value of 57.3%. However, the rest of the hydrocarbons had analyte recoveries between 59.9 and 105%, with the average value rising to 75%. In any case, the present work has established that the recovery of decafluorobiphenyl, the internal standard recommended by the regulations UNE 77250 and USEPA TO-13A, is 86.0% (*11, 12*), a value considered acceptable.

Table 2 shows the medians of the results obtained. The four dimethyl derivatives of naphthalene and the two benzo derivatives of fluorene included in the standard solution that was used have been quantified, but it was not possible to establish the connection between the respective chromatographic signals and the chemical nature of the isomer.

Among the concentrations measured for the total of the PAHs, there are statistically significant differences between the results obtained from the smoke produced by tree heather wood in the drum and the one produced by the rock rose wood in the kiln and between the smokes produced by the tree heather wood in the kiln and in the drum, at a 95% confidence level. The values in the inferior and superior quartiles prove that only the PAHs

concentration in the tree heather wood smoke produced in the drum is significantly different.

It is difficult to compare our results with those obtained by other authors. There are many differences in the manner in which the combustion processes were carried out and also in the type and number of PAHs that were taken into consideration. Even so, as an example, the results obtained by Kakareka et al. (*13*) and Hattula et al. (*14*) can be cited, who found average values for the concentrations of total PAHs in the smoke produced by the combustion of agricultural debris and alder chips of wood, of 550.4 and 2300 μg/m³, respectively. These results are comparable to the medians that we obtained, 1604 and 2547 μg/m³, for rock rose smoke, and 252 and 1898 μg/ m³, for tree heather smoke, in both cases referring to combustion produced in the drum and kiln, respectively.

The results reveal that both the device used for the combustion and fuel can greatly influence the total concentration of PAHs. Higher concentrations of hydrocarbons are found in the smoke produced using rock rose wood as fuel. At the same time, when using the same material, kiln combustion produces a higher total PAHs content.

It is generally accepted that experimental conditions that allow a complete combustion favor the formation of smaller quantities of organic compounds (*15−18*). Although this conclusion refers to the area where the combustion is produced, it can be extended to the experiments that we executed to explain why the kiln combustion of rock rose and tree heather wood, carried out in a less oxidized atmosphere than in the drum, produce larger concentrations of PAHs. This conclusion is corroborated by the correlation that exists ($r = 0.63$) between the carbon monoxide concentration and the total concentration of PAHs in the smoke samples ($n = 27$), **Figure 1**.

The PAHs contents in each of the types of smokes studied show considerable differences. In the first place, it is notable that, in the 28 hydrocarbons analyzed, only the PAHs lighter than anthracene, one benzofluorene (BFl-1), and methyl derivatives of naphthalene except one of the dimethylnaphthalene (diMNph-4) were detected in all of the smoke samples studied. Moreover, considering the smoker and fuel as a unit, neither 3,6-dimethylphenantrene for rock rose wood smoke in the kiln nor dibenz[*a,h*]anthracene, 1-methylphenanthrene, and 3,6-dimethylphenantrene for tree heather wood smoke in the kiln were detected in any of the smoke samples produced. In the rest of the not detected median values in **Table 2**, the PAH considered has a lower number of detected smoke samples than the undetected ones.

In every case, the naphthalene concentrations in the different kinds of smoke are considerably higher than the rest of the PAHs. Its contribution oscillated between 28.6 and 36.3% of the total PAHs content. Similar results were obtained by Gulyurtlu et al. (*19*) in the combustion of coconut shell in a fluidized bed. In any case, the naphthalene has been indicated as the largest byproduct of pyrolysis and incomplete combustion processes (*20, 21*).

The results for the four smoking systems that we used show that the five most abundant PAHs are naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, acenaphthylene, and phenanthrene. For both the kiln- and drum-produced smoke, the content for these five PAHs represent, in relation to the total PAHs content, 68.3 and 73.0%, respectively, in the case of rock rose smoke, and 62.5 and 65.8%, respectively, when the fuel was tree heather wood.

To compare the PAHs distribution in the samples studied, the median values in **Table 2** have been related to the

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Table 2. PAHs Concentrations Values ($\mu g/m^3N$) of Smoke from Combustion in Kiln and Drum of Rock Rose and Tree Heather Wood

compound	kiln[a]		drum[b]	
	rock rose	tree heather	rock rose	tree heather
PAHs				
naphthalene (Nph)	764.3	542.8	582.8	78.1
acenaphthylene (Aci)	185.6	122.1	219.4	19.9
acenaphthene (Ace)	23.5	17.5	13.2	2.2
fluorene (Fl)	134.3	110.8	74.9	10.0
phenanthrene (Phe)	232.5	143.6	122.2	19.0
anthracene (A)	63.5	41.7	31.2	4.7
fluoranthene (Ft)	24.3	14.9	25.5	5.9
pyrene (Py)	19.9	13.4	24.1	6.0
benzofluorene-1 (BFl-1)	42.2	25.6	16.9	4.1
benzofluorene-2 (BFl-2)	32.9	17.2	12.9	2.5
benz[*a*]anthracene (B(a)A)	18.1	14.5	15.0	8.7
chrysene (Ch)	13.5	7.8	9.8	nd[c]
benzo[*b*]fluoranthene (B(b)Ft)	18.8	11.6	20.5	nd
benzo[*k*]fluoranthene (B(k)Ft)	nd	nd	11.4	nd
benzo[*a*]pyrene (B(a)Py)	10.0	6.6	18.3	nd
indene(1,2,3-cd)pyrene (I(1,2,3-cd)Py)	6.9	3.4	10.8	nd
dibenz[*a,h*]anthracene (diB(a,h)A)	nd	nd	6.4	nd
benzo[*g,h,i*]perylene (B(g,h,i)Per)	6.7	3.9	11.8	nd
methyl-PAHs				
2-methylnaphthalene (2-MNph)	337.9	228.3	142.4	29.6
1-methylnaphthalene (1-MNph)	220.1	150.3	103.2	19.1
dimethylnaphthalene (diMNph-1)	95.5	82.7	26.9	7.9
dimethylnaphthalene (diMNph-2)	107.5	83.1	31.1	7.2
dimethylnaphthalene (diMNph-3)	60.2	32.1	18.0	4.1
dimethylnaphthalene (diMNph-4)	nd	nd	nd	nd
2,3,5-trimethylnaphthalene (2,3,5-triMNph)	36.1	70.4	9.3	6.9
1-methylphenanthrene (1-MPhe)	nd	nd	nd	nd
1-methylanthracene (1-MA)	23.9	11.8	8.2	nd
3,6-dimethylphenanthrene (3,6-diMPhe)	nd	nd	nd	nd
(total PAHs)$_{medians}$	2547	1898	1604	251.8
quartiles	1713–4189	1346–2771	1054–2303	177–373

[a] median values of 28 samples (14 for rock rose and 14 for tree heather). [b] median values of 10 samples (4 for rock rose and 6 for tree heather). [c] nd = not detected.
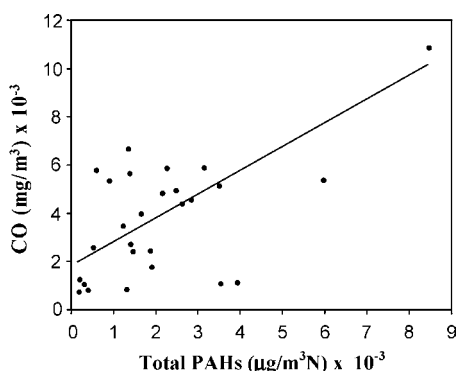

Figure 1. Correlation between CO concentrations and the total concentration of PAHs in the smoke samples ($n = 27$) from rock rose and tree heather wood combustion in each smoker studied.

naphthalene concentration, the most common compound in all of the smoke samples. **Figure 2** represents the relations between the concentration of each of the PAHs and the concentration of naphthalene, except that which corresponds to naphthalene. In general, the distribution is similar in the different smoke samples. However, a few differences can be highlighted. For instance, the rock rose and tree heather wood smoke produced by kiln combustion is differentiated primarily by the lower proportion of methyl naphthalene derivatives in the rock rose smoke. The results from drum combustion show a higher proportion of fluoranthene, pyrene, benzofluorene-1, and benz[*a*]anthracene in the tree heather wood smoke and, just as before, a lower proportion of methyl derivatives in the rock rose smoke.

PAHs Distribution between the Gas Phase and the Aerosol Phase. Different processes intervene in the formation of PAHs during the combustion process of the biomass. Subsequently, during the cooling of the emissions, the PAHs condense, producing an oil that can form small droplets or be adsorbed on the surface of solid particles produced by the combustion of the wood. Some authors (*22*) have affirmed that the distribution of the PAHs between the gas phase and the particulated phase depends on the temperature, air humidity, and the properties of the adsorbent surfaces, as well as the characteristics of the PAHs, such as the molecular weight and vapor pressure.

Under the conditions in which cheese is smoked in the Canary Islands, the surface of the cheese can retain large quantities of the aerosol made of small oil drops and solid particles. Consequently, to know the possible retention of PAHs by the cheese to be smoked, it is important to establish the distribution of the PAHs produced in the combustion systems employed between the gas and aerosol phase.

For this purpose, simultaneous smoke samples were taken with two similar sample pumps from near points in the smoker. One of them used the same sampling system described in the Materials and Methods to establish the total PAHs content, while the other sampling system only uses a quartz fiber filter to retain the fraction of PAHs contained in the aerosol. The determinations were done 3 times, in the kiln, with tree heather and rock rose wood as fuel.

Figure 3 illustrates the distributions that are present in the PAHs contained in the smokes produced by the combustion of rock rose and tree heather wood. It shows that, except for exceptions, the behavior is somewhat similar. In general, the
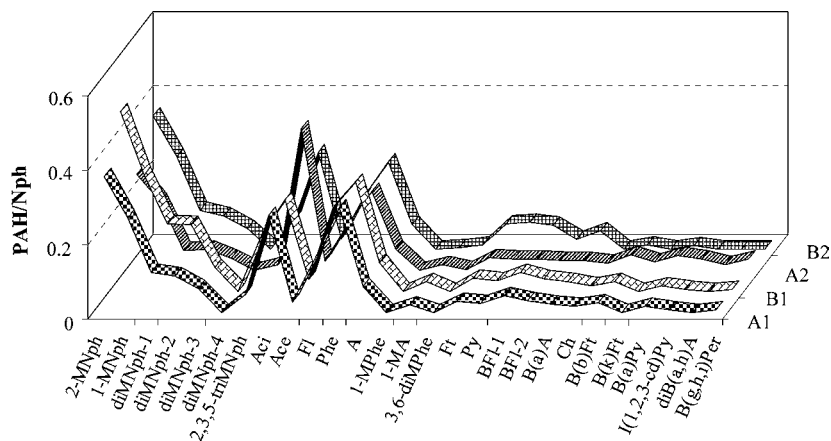
Figure 2. Emission profiles of PAHs normalized to naphthalene for rock rose wood (A) and tree heather wood (B) combustion in a kiln (1) and drum (2). Abbreviations of PAHs and methyl-PAHs are in **Table 2**.
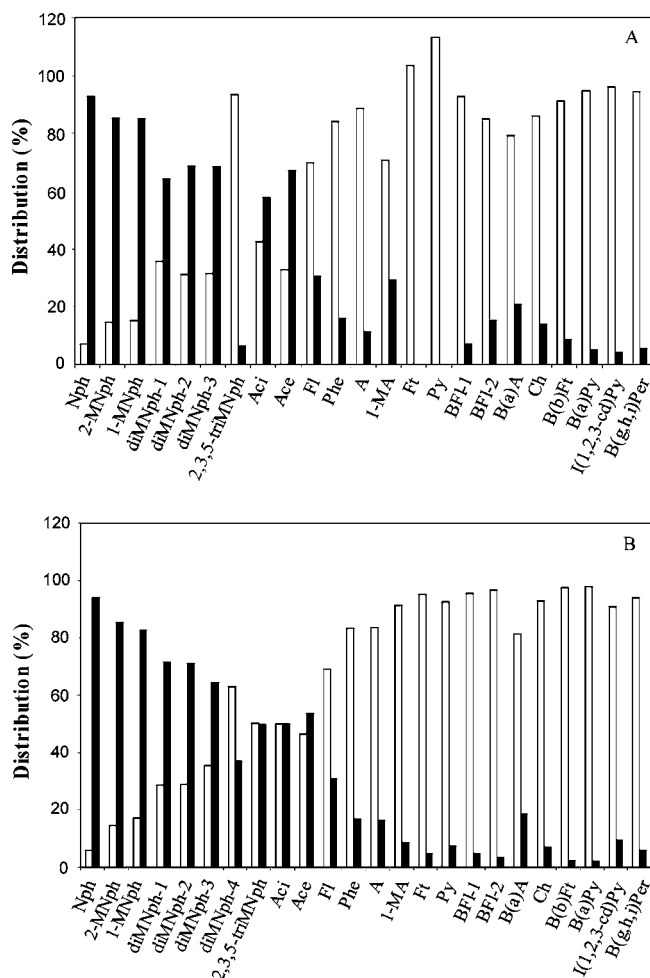

Figure 3. Representative distribution of individual PAHs between gas (■) and aerosol (□) phases in the smoke from combustion of rock rose wood (A) and tree heather wood (B) combustion. Abbreviations of PAHs and methyl-PAHs are in **Table 2**.

PAHs can be separated into three groups: (i) in both cases, naphthalene and its 1-methyl and 2-mehtyl derivatives remain in percentages higher than 83% in the gas phase; (ii) conversely, the phenanthrene and all of the PAHs that have a higher molecular weight than phenanthrene are found in percentages higher than 83% in the aerosol phase, with the exception of benz[*a*]anthracene and 1-methylanthracene, whose percentage in this phase does not reach 80%; and (iii) in the aerosol phase,

the PAHs with intermediate molecular weights have percentages between 28 and 70%, with the exception of 2,3,4-trimethyl-naphfthalene that, at 93.4% in the aerosol phase for rock rose wood smoke, should be classified in group ii. In any case, it should be indicated that, globally considered, the largest quantity of PAHs emitted from the combustion of rock rose and tree heather wood, in the described conditions, are found in the gas phase.

As with the earlier data, the distribution of PAHs in the two phases should also be interpreted within certain limitations, among other reasons, because of the difficulties in obtaining the equilibrium conditions during the distribution process. For the equilibrium,

$$(PAHs)_{gas} \rightleftarrows (PAHs)_{aerosol}$$

a constant distribution can be defined that would represent the relation of concentrations expressed in $\mu g/m^3$ of every PAH in both phases (C_a and C_g for gas and aerosol, respectively), and this constant can also be expressed by the relation

$$K_D = [C_a/C_g](V/W) \qquad (1)$$

in which V is the total smoke volume taken in the sample, expressed as cubic meters, and W is the weight, expressed in micrograms, in the aerosol phase of the sample.

The constant distribution defined in eq 1 relates to the subcooled liquid pressure P_L° (Pa) by the expression

$$\log K_D = m \log P_L^\circ + b \qquad (2)$$

Assuming (*23, 24*) that for a specific sample and under equilibrium conditions, the slope of the regression line (*m*) must be −1.

As a model to establish if equilibrium in the distribution of the PAHs is reached between the gas and aerosol phases, a group of PAHs was selected that included naphthalene, 2-methyl-naphthalene, 1-methylnaphthalene, acenaphthylene, acenaph-thene, fluorene, phenanthrene, and anthracene. When eq 2 was applied, the regression lines that present acceptable correlation coefficients were obtained (*r* = 0.96 and 0.98, for rock rose and tree heather smoke, respectively) as well as slopes with values of −0.78 and −0.77, for the distributions of rock rose and tree heather wood, respectively. These results, which are similar to those obtained by Chen et al. (*25*), show that equilibrium is not reached between the gas and aerosol phases during the PAHs distribution process.

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Table 3. Minimum and Maximum Percentage Contribution of 11 PAHs to B(a)Py Equivalents for Rock Rose and Tree Heather Smoke in the Two Smokers Studied[a]

| | | B(a)P$_{eq}$ (%)[b] | | | |
| | | kiln | | drum | |
compounds	TEF[c]	rock rose	tree heather	rock rose	tree heather
Phe	0.0005	0.5–2.6	0.5–1.8	0.1–0.7	nq[d]–0.5
A	0.0005	0.1–0.8	0.1–0.4	0.0–0.2	nq–0.1
Ft	0.05	5.4–22.5	5.9–24.8	1.5–16.2	nq–12.8
Py	0.001	0.1–0.4	0.1–0.4	0.0–0.3	nq–0.3
B(a)A	0.005	0.6–1.6	0.6–1.5	0.2–0.7	nq–1.3
Ch	0.03	2.4–7.3	0.0–4.9	0.9–3.1	nq–3.6
B(b)Ft	0.05	6.6–11.8	5.4–14.8	4.6–6.4	nq–5.9
B(k)Ft	0.1	0.0–4.2	0.0–5.2	4.8–10.5	nq–7.1
B(a)Py	1	100–100	100–100	100–100	nq–100
I(1,2,3-cd)Py	0.1	0.0–7.2	0.0–10.8	4.3–10.6	nq–10.2
B(g,h,i)Per	0.02	0.7–1.7	0.0–5.1	0.9–2.5	nq–2.1

[a] Abbreviations of PAHs and methyl-PAHs are in **Table 2**. [b] B(a)P$_{eq}$ (%) = (PAH$_{TEF}$PAH$_{MC}$/B(a)Py$_{TEF}$B(a)Py$_{MC}$)100, where MC is the median concentration. [c] Toxic equivalence factors. [d] nq = not quantified because B(a)Py$_{MC}$ is not detected.

One of the most important reasons to study PAHs emissions in the smoke used to smoke foods is to determine its potential toxicity. To accomplish this, the percentages of a group of PAHs were calculated, expressed as benzo[*a*]pyrene equivalents [B(a)-P$_{eq}$ (%)], using the toxic equivalence factors (TEF) introduced by J. Larsen and P. Larsen (*26*).

Table 3 shows minimum and maximum B(a)P$_{eq}$ (%) values of the 11 PAHs normally selected for their carcinogenic characteristics. For the calculation, the PAHs concentrations for each smoke sample were used. Because of its toxicity, the most important PAH in the all of the samples is the benzo[*a*]pyrene, but the following PAHs that are more important depend on the combustion system used. Considering the maximum contributions to the toxicity in the kiln, the rest of the more important PAHs are fluoranthene and benzo[*b*]fluoranthene and, in lower percentage, indene(1,2,3-cd)pyrene and chrysene. However, in the drum, the rest of the more important PAHs are fluoranthene, indene(1,2,3-cd)pyrene, and benzo[*k*]fluoranthene and, in lower percentage, benzo[*b*]fluoranthene. In general, the B(a)P$_{eq}$ (%) values are higher in the kiln than in the drum, while for the same smoker, there are no important differences between the biomass used. These values are considerably lower than those obtained by other authors (*27*, *28*) for pine, oak, eucalyptus, and birch wood burned in other conditions, where fluoranthene reaches between 41 and 115% of B(a)P$_{eq}$.

The distribution of individual PAHs contents is considerably different in the aerosol and gas phases. The distribution of percentages of the PAHs present in the aerosol phase is dominated by compounds that have a molecular weight heavier than that of fluorene, and although they represent 54% of the measured PAHs, their concentrations represent 39.9% of the total PAHs produced by burning rock rose wood, while only 29.1% of the PAHs content is in the aerosol phase when using tree heather wood.

To establish the comparisons between the possible carcinogenicity of the smokes that were studied, it is preferable to use the index introduced by Cecinato (*29*).

By calculating this index in the gas and aerosol phases, expressing the PAHs concentrations in μg/m³, the values found in **Table 4** are obtained.

When the potential carcinogenicity associated with each of the phases is compared, one can see that the BaPE values related

Table 4. Benzo[*a*]pyrene-Equivalent (BaPE) Carcinogenic Power Values, According to the Cecinato Index, for the Gas and Aerosol Phases of Smoke Produced from Rock Rose and Tree Heather Wood in Kiln

| | BaPE[a] | |
phase	rock rose	tree heather
gas phase (μg/m³)	0.8	0.4
aerosol phase (μg/m³)	10.5	9.6
aerosol phase (mg/Kg aerosol)	20.2	4.4

[a] Cecinato et al. index (*29*): BaPE = 0.06B(a)A + 0.07B(b)Ft + 0.07B(k)Ft + 1B(a)Py + 0.6diB(a,h)A + 0.08I(1,2,3-cd)Py.

with the aerosol phase, in the smoke produced by both types of wood, are considerably higher than those from the gas phase. Without a doubt, although the PAHs content in the aerosol phase is considerably lower than that found in the gas phase, the higher toxicity associated with hydrocarbons with a high molecular weight, which have less volatility, justify the finding.

Moreover, concerning the possible depositing of PAHs on the surface of the food to be smoked, it may be of interest to establish the BaPE values that concern the aerosol phase. The results obtained, referred to as aerosol mass, are found in **Table 4** and show that the toxicity of the aerosol produced by rock rose wood smoke is considerably higher than that produced by tree heather wood.

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