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Effects of use of modified traditional driers in making smoked paprika "Pimentón de La Vera", on pepper quality and mitigation of PAH contamination

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ABSTRACT

"Pimentón de La Vera" is a smoked paprika regulated by a Protected Designation of Origin. The smoking process confers highly-valued sensorial properties to paprika. However, this particular drying process also increases the levels of polycyclic aromatic hydrocarbons to concerning concentrations. In this work, two modified dryers were compared to a traditional dryer as a strategy to mitigate PAH contamination. Drying parameters (temperature and humidity of the dryers, days of drying required), quality of the peppers (moisture, reflected colour parameters, ASTA (American Spice Trade Association) units, PACI ($[1000a^*/(L^* + H^*)]$) index, and colour stability), and the content of benzo(a)pyrene, chrysene, benzo(b)fluoranthene, and benzo(a)anthracene were evaluated during four different seasons. The moisture of the fresh peppers varied among the seasons (ranging from 69.4% to 81.4%), and was positively related with lower drying times. There were no differences in the final moisture of the peppers on the basis of dryer type used. Different seasons influenced the colour values of the dried peppers. Peppers obtained from dryer type 2 presented the highest values of extractable colour (133 ASTA units). Differences in PAH4 levels were observed between seasons (ranging from 277 to 1208 μg/kg) and between the types of dryer used (ranging from 432 to 932 μg/kg). Dryer type 2, characterized by combustion of firewood in a closed chamber and forced convection with a fan, diminished the levels of PAHs contamination and maintained the quality of the smoked paprika.

1. Introduction

"Pimentón de La Vera" is a type of paprika recognised under a Protected Designation of Origin (PDO) (Commission Regulation, 2007). This form of paprika has unique sensorial and compositional characteristics relating to its origin (north of the Extremadura, Spain), varieties (*Capsicum annuum* L. varieties Jaranda, Jariza and Bola), and the particular drying process achieved by smoking the pepper (Hernández al., 2006; 2007; 2010; Velázquez et al., 2019). Smoke confers a special colour and flavour and improves the quality and hygienic stability by dehydration and given antimicrobial and antioxidant compounds (Goulas and Kontominas, 2005; Lingbeck et al., 2014). Wood smoke is a complex mix of phenols, ketones, aldehydes, alkanes, acids, furan, organic acids, esthers, alcohols, hydrocarbons, heterocyclic compounds, etc. influenced by factors as time-temperature profile, atmosphere composition, and type of wood (Stolihwo and Sikorski 2005). Health hazards of smoke is mainly associated to carcinogenic PAH and PAH derivates, which their formation are enhanced to temperature higher than 425 °C (Zhang et al., 2020).

The drying process used for peppers in La Vera involves traditional dryers containing two plants, with the fire (containing oak or holm oak wood) and peppers located on the ground and the first floors, respectively. The particular climatic conditions in the La Vera region prompted the use of smoking as a method of dehydrating the peppers.

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Processes used in food production, such as drying and smoking, can produce polycyclic aromatic hydrocarbons (PAHs) (Singhet al., 2016). The European Food Safety Authority (EFSA) has suggested that the four PAHs (benzo(a)pyrene [B(a)P], chrysene [CHR], benzo(b)fluoranthene [B(b)F], and benzo(a)anthracene [B(a)A]), are among the top 15 priority PAHs most suitable for indicators of PAH levels in foods (Commission Regulation, 2006; Commission Regulation, 2011). Therefore, starting April 1st 2016, dried culinary herbs and spices sold on the EU market must not exceed a maximum level (mL) of 10 μg/kg for B(a)P or 50 μg/kg for the sum of B(a)A, CHR, B(b)F, and B(a)P. Nevertheless, smoked fruits of *Capsicum* species are exempt from the MLs required of other smoked products to remain on the market, and because the consumption of these spices is low (Commission Regulation (EU) 2015/1933).

In this case, the literature on the PAH content of dried red pepper and paprika powder is very limited. Overall, paprikas and dried peppers dehydrated by methods different from smoking present PAH contains lower than legal limits. Rozentale et al., (2018) reported concentrations ranged from 0.33 to 2.21 μg/kg of B(a)P and 2.86 and 14.0 μg/kg of the sum of four designated PAHs in samples of paprika and chilli originating from Brazil and China. Similar values were reported for dried red peppers (Ishizaki et al; 2010), and paprikas dehydrated by air-drying at 50–80 °C for 12–36 h and heat pump-assisted drying at 50–80 °C for 7–31 h (Hwange et al., 2019). Conversely, smoked paprika exceed by far referenced values. Fasano et al., (2016) evaluated PAH concentrations in seven samples of smoked paprika ("Pimentón de La Vera") purchased from different north Spanish markets. The mean B(a)P concentration was 104 μg/kg and the concentration of four PAH4 was 1600 μg/kg. Similar results were obtained by Monago-Marañ̃a et al., (2016), who demonstrated high concentrations of PAHs in smoked paprika samples. The average concentration (21 samples) of B(a)P and the PAH4 were 67 μg/kg and 1780 μg/kg, respectively.

Smoked paprika producers are working on methods of PAH reduction that do not diminish the peppers remarkable sensorial properties, antioxidant activity, and colour stability (Martín et al., 2017; Velázquez et al., 2014). In particular, "Pimentón de La Vera" is a spice consumed in small quantities in order to provide flavour and colour to Iberian pork sausages (Spanish dry-fermented sausage), as well as other dishes (or cuisine recipes). PAHs contamination levels of smoked products may be influenced by modification of the smoking chamber (Onopiuk et al., 2021); Separating combustion chamber of grilled chamber (Assogba et al., 2020) did no reduced PAH contain in grilled pork; however using of physical barriers to provide an indirect smoking (Gomes et al., 2013) reduced on PAH contains in dry fermented sausages. Therefore, the aim of the current work was to analyse the effects of certain modifications to the traditional drying method of smoking the paprika "Pimentón de La Vera" on mitigating the levels of PAHs while maintaining quality of colour.

2. Material and methods

2.1. Experimental design and sampling

In the traditional manufacturing of paprika in La Vera, the drying process requires approximately 10 days, during which the peppers change from a moisture content of 80% to less than 15%. In order to achieve uniformity in the drying process, the peppers are turned daily. As this process is completely unmechanised, the drying conditions including temperature and humidity are not controlled with any precision and the temperatures reached during the process are unknown.

In this work, the drying process of peppers was conducted according to traditional method of La Vera region. The experiment was conducted by using three different types of dryers for smoking the peppers: a traditional dryer (dryer 1) and two traditional dryers with modifications (dryers 2 and 3), across four consecutive years from 2015 to 2018 in the "La Vera" region, north of Extremadura (Spain). A total of 38 dryers were evaluated in this work. Twelve dryers belonged to dryers type 1 (2 dryers in 2015, 4 dryers in 2016, 4 dryers in 2017, and 2 dryers in 2018); 8 to dryers type 2 (2 dryers in 2015, 4 dryers in 2016, 1 dryer in 2017, and 1 dryer in 2018), and finally 18 to dryers type 3 (6 dryers in 2015, 3 dryers in 2016, 4 dryers in 2017, and 5 dryers in 2018).

In this work, the paprika was manufactured according to the regulations of P.D.O. "Pimentón de La Vera". In the La Vera region, the dryers are located together in the fields where the peppers are grown. Farmers are responsible for managing and harvesting the fresh peppers, transporting the peppers to the dryers, and managing the peppers during the drying process.

2.2. Description of traditional and modified dryers and management of the drying process

In this work, the fresh peppers came from three different plots of peppers that were cultivated by three different farmers. The three dryers are described below (Fig. 1).

Dryer 1 (Traditional dryer): The drying process used for peppers in La Vera involves traditional dryers containing two plants, with the fire and peppers located on the ground and the first floors, respectively. The peppers are introduced into the upper floor through a loading window, as represented in Fig. 1. The combustion chamber is located on the lower floor and the fire is kept burning until the peppers are completely dried.

Dryer 2: Modified dryer with a wood-fire in a closed chamber with only one exit for smoke. The chamber was located lateral to the ground floor and an air-fan was used (forced convection drying method).

Dryer 3: Modified dryer with a wood-fire in a closed barrel kiln with four nozzles for smoke. The barrel kiln was located in the middle of the ground floor and an air-fan was used (forced convection drying method).

The management of the fire and peppers was common for the three types of dryers accoding to D.O.P "Pimentón de La Vera" directions (Regulation of PDO "Pimentón de La Vera"). The fire was made with wood of holm oak (*Quercus ilex* L.) and/or oak (*Quercus robur* L.). The peppers were spread out over a latticework of wood that separated the two floors. The latticework allowed contact between the peppers and the hot air and smoke. The capacity of these dryers was 3200 kg, corresponding to an 80–100 cm layer of fresh peppers. The peppers were dug over daily. The drying process was considered finalised when the moisture level of the peppers was under 15% according to regulations of PDO "Pimentón de La Vera".

2.2.1. Determination of temperature and relative humidity in the dryers

A data logger (model 176 H1; Instrumentos Testo S.A., Cabrils, Barcelona) was placed in the ground floor of each of the dryers to determine and control the drying conditions. Each logger was fitted with probes for recording temperature, with a measurement range between − 20 and 70 °C, and humidity, from 0% to 100%.

2.3. Sampling

Each year, samples of fresh pepper were taken from each farmer in triplicate. These samples were collected just before the dryers were filled, resulting in nine fresh pepper samples from each farmer each season.

During the drying process, samples were collected on the initial day, the the intermediate day (depending on the duration of drying), and the last day of the drying process in triplicate. Each time, dried peppers were sampled from 3 points of the dryer, away from each other. Thus, 9 dried pepper samples were analysed from each dryer during drying process.

A sample consisted of 50 fruits of fresh pepper or dried peppers. Immediately after being obtained, the peppers were transported in paper bags to the laboratory (Escuela de Ingenierías Agrarias, University of Extremadura, Badajoz, Spain) and analysed.

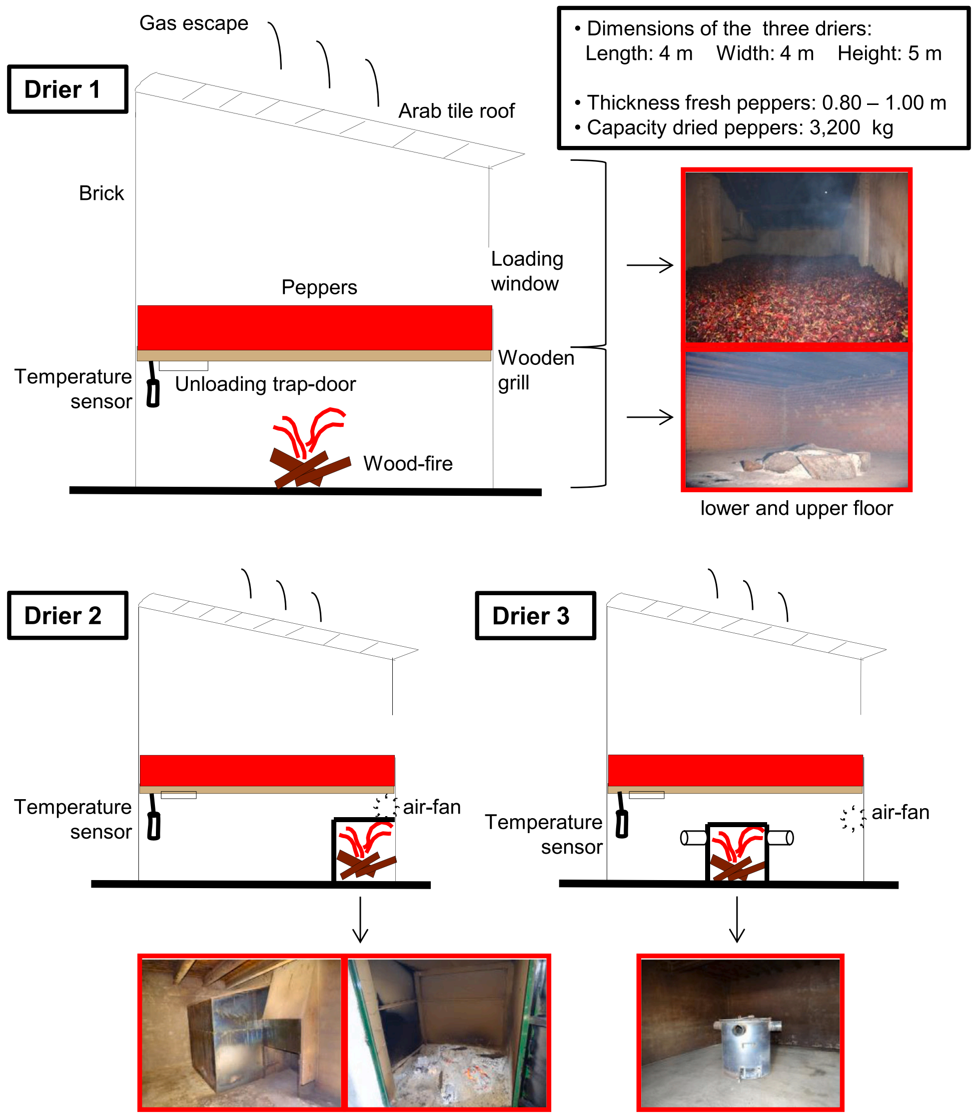

Fig. 1. Graphical representation of the three dryers studied: Dryer 1: Traditional dryer with wood-fire on the ground floor and no air-fan; Dryer 2: modified dryer with wood-fire in a closed chamber with only one exit for smoke with an air-fan; Dryer 3: modified dryer with wood-fire in a barrel kiln with four nozzles for smoke with an air-fan.

2.4. *Physicochemical analysis and colour*

After samples were received by the laboratory, the fresh and dried pepper samples were crushed using a mincer (model A327R1 700; Moulinex, Barcelona, Spain) and stored at − 80 °C until analysis. The samples were analysed in triplicate to evaluate the quality and safety characteristics.

2.4.1. *Moisture*

Moisture was determined by drying the samples at 105 °C until a constant weight was achieved. The determination was based on the Official Methods of Analysis, Association of Official Analytical Chemists (AOAC, 2005).

2.4.2. *Determination of colour*

2.4.2.1. Reflected colour. The reflected colour (CIELab space) of the samples, described as coordinates L^*(darkness/whiteness), a^*(greenness/redness), and b^*(blueness/yellowness), was measured using a colourimeter (model CR-300; Minolta, Osaka, Japan). The instrument was pre-calibrated with a calibration plate ($L^* = 97.26$, $a^* = 0.08$, and $b^* = 1.81$). The hue angle (H^*), chroma (C^*) and PACI index ($[1000a^*/(L^* + H^*)]$) values of the samples were calculated as derived colour parameters. These determinations were made on fresh pepper and dried pepper samples on the initial, middle, and last days of the drying process.

2.5. *Extractable colour*

The American Spice Trade Association (ASTA) colour of the samples was determined according to the Association of Official Analytical Chemists' International method (AOAC, 2002), with the modification introduced by Topuz et al., (2009). Crushed fresh and dried peppers (0.10 g) were extracted with 20 mL of acetone. Next, the samples were incubated for 4 h in a water bath (axially shaken at 140 rpm) maintained at 25 °C in total darkness. The extract was diluted to one-fifth of its original concentration with acetone. The absorbance of the diluted extract was measured against acetone at 460 nm using a spectrophotometer (Biomate 3, Thermo Fisher Scientific, Hudson, NH, USA). The extractable colour of the samples was expressed in ASTA units, as defined below:

$$ASTA = (A_{460} \times 164 \times If)/w.$$

where A is the absorbance of the extract, If is the deviation factor of the spectrophotometer, which was calculated by dividing the theoretical absorbance (0.600) by the real absorbance of a standard colour solution (0.001 M $K_2Cr_2O_7$ and 0.09 M $(NH_4)_2Co(SO_4)_2.6\ H_2O$ in 1.8 M H_2SO_4) at 460 nm, and w is the sample weight (g) on a dry basis.

2.6. Determination of colour stability

To determine the stability of the colour, dried peppers from the final day of the drying process were exposed to the action of ultraviolet (UV) light. Thin layers of crushed peppers were prepared in Petri dishes by weighing out 8 g in each dish. The dishes were placed in a laminar air flow (Telstar AH-100, SP) with UV light switched on for 6 days at 25 °C. Samples were placed perpendicularly to the light source at 0.75 m of distance. The UV light source consisted of a 15 W UV-C germicidal lamp (TUV 36 W/G36 T8, Philips, Holland). The total energy flux was about 0.74 W m^{-2}. According to results of Velázquez et al. (2014), triplicate samples were collected and the reflected colour were analysed on day 2 and day 6 of UV exposure, as described above.

The results of the reflected colour analysis are presented in terms of a^*_i/a^*_0, where a^*_0 represents the initial value of the sample before its exposure to UV light and a^*_i represents the value during the exposure to UV light for i days.

2.7. Determination of PAHs

The 4PAHs were extracted using the QuEChERS process (Pule et al., 2012). For extraction, 5 g of pepper and 10 mL acetonitrile (HPLC grade) were placed in a 50 mL polypropylene tube. The samples were analysed in quadruplet; in one of the samples, 10 μL of 4PAHs mixture (1000 μg L^{-1}) was added. The samples were vortexed for 1 min and then introduced into an ultrasonic bath for 20 min at 45 °C. Next, the samples were centrifuged at 3824 g for 1 min and 1 mL of the concentrated extract was passed through 50 mg sodium acetate anhydrous and 200 g magnesium sulphate in a 1.5 mL tube. The resultant mixture was vortexed for 30 s and centrifuged at 15294 g for 1 min. After centrifugation, 600 μL of the supernatant were transferred to a 1.5 mL polypropylene tube containing 75 mg magnesium sulfate, 25 mg PSA (Primary Secundary Amine; Supelco, Bellefonte, PA, USA), and 25 mg C18ES sorbent (Scharlab; Barcelona, Spain). Then, the sample was vortexed for 30 s and centrifuged at 15294 g for a further 1 min. Next, 400 μL of the supernatant were transferred to a vial and this volume was injected and analysed by HPLC (Pule et al., 2012).

HPLC analysis was carried out in a Hewlett-Packard 1100 series instrument (Palo Alto, CA, USA) equipped with a fluorescence detector (260 ex/420 em) and a SUPELCOSIL™ LC-PAH HPLC Column (Supelco, Inc., Bellefonte, PA, USA) (5 μm particle size, 250.0 × 4.6 mm i.d.; 25 °C). The mobile phase was composed of deionized water (channel A) and acetonitrile (channel B), with a flow rate of 0.8 mL/min. Five microlitres of sample were injected, and a gradient flow was applied with 60% of channel B from 0 to 1.5 min, 90% of channel B from 1.5 min to 7 min, and, finally, 100% of channel B from 7 to 13 min. For peak identification, the retention time (RT) and absorption spectra were compared with those of standard material obtained from Sigma Chemical Co. (St. Louis, MO, USA) for B(a)P, B(a)A, CHR, and B(b)F. The quantification of these compounds was expressed in μg·kg^{-1} of product. The limits of detection and quantification were 0.08 and 0.28 μg·kg^{-1} for B(a)P, 0.5 and 1.72 μg·kg^{-1} for B(a)A, 0.5 and 1.76 μg·kg^{-1} for CHR, and 0.1 and 0.3 μg·kg^{-1} for B(b)F.

2.8. Data analyses

Values of drying parameters, quality attributes, and PAHs were analysed by one- and two-way analyses of variance (ANOVA). Groups with statistically different mean values were separated by Tukey test ($p < 0.050$). Relationships among variables and determinations were established by principal component analyses. Finally, a simple linear regression analyses was performed to relate colour stability (a_f/a_0) with predicted stability colour values based on mean temperatures of the dryers.

3. Results and discussion

3.1. Drying parameters

Table 1 shows the initial moisture of the fresh peppers used as raw material for the manufacture of "Pimentón de La Vera" and the parameters of drying for the three types of dryer and the different seasons studied. The initial mean values of moisture levels ranged from 81% to 69% for fresh peppers, depending on the season. This significant difference is associated with the climatic conditions of the La Vera region, which underwent an especially dry summer in the 2017 season (Supplementary data). Regarding the different types of dryers studied, no significant differences were found in the moisture levels of the fresh peppers in each type of dryer, with mean values ranging from 75% to 79%.

With respect to the dryer parameters, the mean values for dryer humidity were around 30% during all seasons except for 2015, which showed a mean value of 50% attributable to several dryers with remarkably high humidity during this season (Table 1). Significant differences for humidity were also found between the different types of dryers, with the lowest values (20%) found using the traditional dryer (Dryer 1). Traditional dryers also presented the lowest drying temperatures, with mean values of 43.4 °C compared to 46.9 and 46.2 °C for dryers 2 and 3, respectively. Regarding the seasons, mean temperature values ranged from 43.6 to 45.6 °C except during the 2018 season, which showed the highest mean value of 47.6 °C. Finally, no significant differences were found in the mean number of days required for drying between the different types of driers studied. Meanwhile, the differences presented for mean number of drying days between the seasons can be explain by the initial humidity level of the fresh peppers. As such, the 2017 season, which had the lowest values of pepper humidity, presented a mean of 5.6 days required for drying while the 2016 season, which had the highest values of pepper humidity, showed a mean of 9.0 days (Table 1).

The evolution of moisture during the drying of peppers for the different seasons and type of dryer is shown in Fig. 2. No significant differences were found in the final values of moisture for either season or the type of dryer used, with mean values ranging between 10.3% and 13.4% depending on season, and between 11.9% and 12.8% for the different types of dryers. Carbonell et al., (1986) determined an optimum residual moisture content of 7.5% in order to provide a film around the pepper particles that protects against oxidation reactions. However, the 2017 and 2018 seasons demonstrated lower mean values of moistures in samples taken during the middle of the drying process than samples from the 2015 and 2016 seasons. This fact can be attributed to lower initial moistures in the case of peppers in the 2017 season, and by a higher drying temperature in the 2018 season (Table 1).

3.2. Quality parameters of paprika

The parameters related to apparent and extractable colour showed significant differences between paprika obtained from different seasons and dryers (Table 2). Total carotenoid contents are measured as extractable colour, generally expressed as an ASTA value. Additionally, we used PACI index because it has been proposed as a rapid predictive and non-destructive way for determining the ASTA units of unsmoked paprika samples (Nieto-Sandoval et al., 1999).

The samples from the 2016 season and dryer 2 presented the highest values for ASTA and PACI, which were related to high values for the CIELAB coordinate a* and low values for L*. On the contrary, paprika from the 2017 and 2015 seasons, which had the shortest drying times,

Table 1
Moisture of the fresh pepper and the dryer parameters for the three types of dryer and the four different seasons studied.

	Fresh pepper				Drying parameters								
	n	Moisture (%)			Humidity (%)			Temperature (ºC)			Days		
		Mean		SD	Mean		SD	Mean		SD	Mean		SD
Season													
2015	27	78^{b}	±	3.4	51^{b}	±	12	45.6^{ab}	±	4.5	6.7^{ba}	±	0.9
2016	27	81^{b}	±	3.0	31^{a}	±	13	43.6^{a}	±	2.9	9.0^{c}	±	1.1
2017	27	69^{a}	±	11	30^{a}	±	12	43.9^{ab}	±	3.2	5.6^{a}	±	1.6
2018	27	79^{b}	±	3.5	31^{a}	±	14	47.6^{b}	±	3.4	7.2^{b}	±	0.8
Type of Dryer													
Dryer_1	36	75	±	11	20^{a}	±	2.4	43.4^{a}	±	3.9	7.3	±	2.1
Dryer_2	36	79	±	2.5	38^{b}	±	21	46.9^{b}	±	2.0	7.6	±	0.8
Dryer_3	36	79	±	3.6	45^{c}	±	5.2	46.2^{b}	±	3.7	6.9	±	1.5
Global mean		77	±	7.1	35	±	15	45.3	±	3.8	7.2	±	1.6
P values													
P_y		*0.006*			*<0.001*			*0.021*			*<0.001*		
P_d		*0.252*			*<0.001*			*0.001*			*0.131*		
$P_y{*}P_d$		*0.001*			*<0.001*			*0.009*			*0.030*		

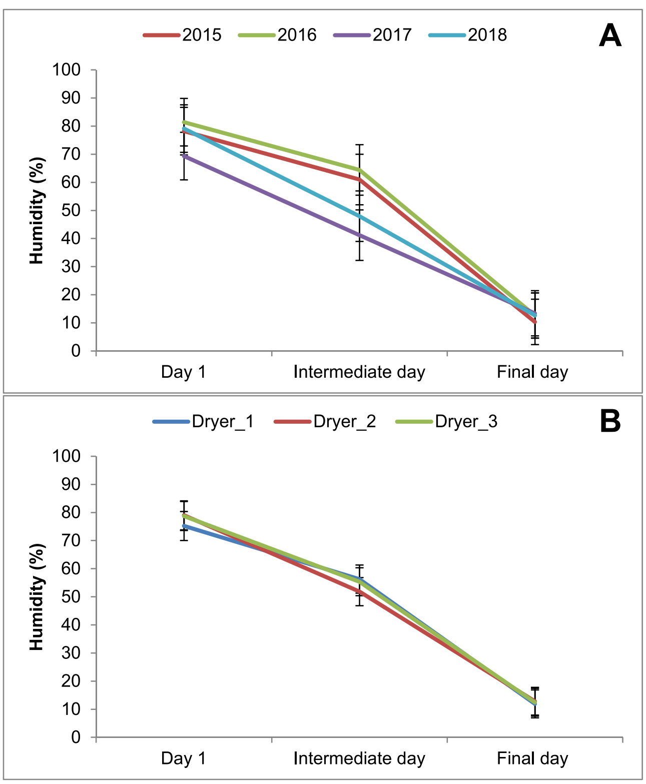

Fig. 2. Evolution of humidity levels (%) of the peppers across the four seasons (A) and the three types of dryers studied (B). Samples, depending on the duration of drying, were taken on the first day, the intermediate day (between day 3 and day 6), and the final day (between day 6 and day 11).

showed the lowest values for PACI index (Table 2). Oxidation of the pigments during the drying of peppers accounts for the colour loss observed in the final product (Carbonell et al., 1986; Topuz et al., 2009). On the other hand, an additional biosynthesis of carotenoids has been reported in living tissues in previous research during slow and long drying processes (Mínguez-Mosquera and Hornero-Méndez, 1994; Mínguez-Mosquera et al., 1994; Topuz et al., 2011).

3.3. Polycyclic aromatic hydrocarbons (PAHs)

Alexander et al. (2008) described PAH4 as a good indicator of the occurrence of total PAHs in paprika. Table 3 shows the values of these PAHs in the dried peppers at the final day of the drying process for each season and dryer. According to the p values and standard deviations, a high variability was observed, both inter and intra group, for the different seasons and type of dryer studied, showing how variable the smoking process can be in paprika smokehouses. In general, anthracene was the major PAH with a mean value of 461 µg/kg, followed by CHR, B(b)F, and B(a)P, with a mean value for total PAHs of 780 µg/kg (Table 3). The high variability found in our work has also been described by Fasano et al. (2016), who reported values of PAHs in commercial samples of "Pimentón de La Vera" ranging from 593 to 3200 µg/kg, underlining the importance of controlling the smoking process. In this case, fluoranthene and pyrene were reported as the highest contributors. Within the seasons, 2015 (with the highest values for humidity of the dryers) and 2018 (with the highest values for temperature of the dryers) showed the highest levels of total PAHs, with 1210 and 941 µg/kg, respectively. In the same way, the samples from dryer 3, which presented high values in the dryer parameters of humidity and temperature, showed higher values for total PAHs than the others types of dryer studied (Table 3). The composition of smoke is dependent on the temperature, as PAHs are easily formed in the temperature range between 660 and 740 °C (Hokkanen et al., 2018). In contrast, the 2017 season (with the lowest moisture level in the fresh peppers and the shortest drying times) presented total PAH levels of only 277 µg/kg (Table 3).

Interestingly, this significant increase of 4HAPs in dryer type 3 was due to the increase of [B(a)A], while [CHR], [B(b)F], and [B(a)P] did not differ between dryer types. In the same sense, the results obtained by Gomes et al. (2013) showed an unequal effect of direct or indirect smoking on the concentration of different PAH, such as fluoranthene, which was not affected, or the 4HAPs which showed a very significant reduction by used physical barriers to the smoke. Asamoah at al. (2021) and Nunoo et al. (2019) confirmed the differences on profile of PAH based on the differences on smoke method (kilns).

3.4. Multivariate analysis

Principal component analysis was carried out using the whole data set in order to obtain an interpretable overview of the main information. Fig. 3 shows the three-way loading and score space, where the principal component 1 (PC1 = 39.61%), principal component 2 (PC2 = 21.68%), and principal component 3 (PC3 = 9.89%) explained 71.18% of the total variability. High values for colour parameters such as the PACI index, a*, b*, as well as the fresh pepper humidity, B(b)F, and CHR levels, were explained by the positive axis of PC1 and were related to longer drying times and the use of dryer 2. Low temperature of drying, associated to longer drying time, has been recommended to maintaining colour quality of paprika and reducing the formation of browning compounds

Table 2
Colour parameters on the final day of drying for the three types of dryer and the four different seasons studied in the production of "Pimentón de La Vera".

	n	CIELAB colour space									PACI_f[a]			ASTA_f[b]		
		L_f			a_f			b_f								
		Mean		SD	Mean		SD	Mean		SD	Mean		SD	Mean		SD
Season																
2015	30	41.0^{cc}	±	6.3	16.3^{a}	±	4.0	19.1^{b}	±	7.2	188^{a}	±	50	130^{bc}	±	21
2016	33	34.4^{b}	±	1.8	24.0^{b}	±	3.2	26.7^{c}	±	5.0	292^{b}	±	36	101^{abc}	±	18
2017	27	49.0^{d}	±	5.5	15.3^{a}	±	5.9	13.4^{a}	±	7.3	173^{a}	±	77	96^{ab}	±	38
2018	24	38.9^{bc}	±	3.8	18.6^{a}	±	3.5	22.4^{bc}	±	3.6	210^{a}	±	47	88^{a}	±	34
Type of Dryer																
Dryer_1	36	41.7^{b}	±	8.2	18.0^{a}	±	4.2	19.3^{a}	±	7.1	211^{a}	±	57	91^{a}	±	32
Dryer_2	27	34.6^{a}	±	4.2	22.1^{b}	±	7.7	23.0^{b}	±	11.6	281^{b}	±	87	133^{b}	±	31
Dryer_3	54	40.1^{b}	±	7.4	17.1^{a}	±	4.9	19.2^{a}	±	6.6	199^{a}	±	64	108^{a}	±	34
Global mean		39.7	±	7.5	18.3	±	5.4	19.9	±	7.7	217		70	106	±	35
P values																
P_y		*< 0.001*			*< 0.001*			*< 0.001*			*< 0.001*			*0.040*		
P_d		*0.020*			*< 0.001*			*< 0.020*			*< 0.001*			*0.001*		
P_y*P_d		*0.353*			*< 0.001*			*< 0.001*			*0.005*			*0.004*		

[a] PACI index = [1000$a^*/(L^* + H^*)$]
[b] American Spice Trade Association
[c] Mean values with different letters indicating statistical differences (p<0.050).

Table 3
Mean contains on polycyclic aromatic hydrocarbons (benzo(a)pyrene, chrysene, benzo(b)fluoranthene, benzo(a)anthracene) of peppers respect to seasons and type of dryer.

	n	Polycyclic Aromatic Hydrocarbons (µg/kg)												PAH4		
		[B(a)A] [a]			[CHR]			[B(b)F]			[B(a)P]					
		Mean		SD	Mean		SD	Mean		SD	Mean		SD	Mean		SD
Season																
2015	30	841^{bb}	±	340	221	±	140	124^{bc}	±	49	22^{a}	±	8	1210^{c}	±	490
2016	33	215^{a}	±	100	228	±	110	151^{c}	±	52	40^{a}	±	14	634^{b}	±	270
2017	27	115^{a}	±	90	44	±	71	34^{a}	±	45	85^{b}	±	48	277^{a}	±	130
2018	24	623^{b}	±	410	180	±	160	85^{b}	±	39	53^{ab}	±	22	941^{bc}	±	350
Dryer																
Dryer_1	36	269^{a}	±	220	198	±	160	77	±	73	55	±	31	602^{a}	±	340
Dryer_2	27	271^{a}	±	200	97	±	52	101	±	32	23	±	11	492^{a}	±	170
Dryer_3	54	611^{b}	±	470	160	±	140	110	±	61	51	±	41	932^{b}	±	570
Global mean		461	±	400	166	±	140	97	±	63	49	±	36	780	±	490
P values																
P_{year}		*< 0.001*			*0.209*			*0.013*			*0.027*			*< 0.001*		
P_{dryer}		*0.004*			*0.378*			*0.374*			*0.264*			*0.017*		
$P_{year*dryer}$		*0.006*			*0.052*			*0.002*			*0.677*			*0.003*		

[a] [B(a)P] benzo(a)pyrene, [CHR] chrysene, [B(b)F] benzo(b) fluoranthene, [B(a)A] benzo(a)anthracene [B(a)A]
[b] Mean values with different letters indicated statistical differences (p<0.050).

(Ibrahim et al., 1997; Gupta etal., 2002). PC2 was mainly explained by the total PAH levels located at the extreme of the positive axis, relating high PAH values to high drying temperatures and, to a lesser extent, high humidities. These drying parameters were highlighted when using dryer 3, unlike dryer 1. Finally, variability of the ASTA values was mainly explained by the positive axis of PC3, not showing a clear correlation with any drying parameters or apparent colour parameter. A very poor linear correlation between CIELab colour parameters and ASTA values of paprika had been previously described (Nieto-Sandoval et al., 1999). However, ASTA values did not show a significant correlation with PACI index in our study, suggesting a relevant impact of the smoking process on this non-destructive index for determining the ASTA units in unsmoked paprika.

With respect to the stability of the dry pepper colour after exposure under UV-light for two days, the a_i/a_0 ratios ranged from 0.94 to 0.57 in the samples studied and did not show a relationship to the initial ASTA values. However, the colour degradation capacity of the dry peppers showed a significant negative correlation (p < 0.010) with the mean drying temperature.

A simple linear regression (SLR) was used to model the relationship between the a_i/a_0 ratio and the mean drying temperature. The model (r = 0.693) indicated that up to 45% of the variation in the a_i/a_0 ratio could be predicted from the mean values of drying temperatures. The biplot of the predicted versus measured a_i/a_0 ratio values showed two groupings of samples according to dryer type (Fig. 4). In agreement with other authors, these results confirm that the stability of the main carotenoids in the peppers is dependent on the drying conditions, with the degradation rate increasing as drying temperatures increase (Malchev et al., 1982; Carbonell et al., 1986). Additionally, previous findings have shown that the smoking process confers high colour stability to the peppers (Velazquez et al., 2014) with respect to sun drying and oven drying.

4. Conclusions

The results of this work have proven that the moisture level of fresh peppers is a crucial factor in diminishing the time of the smoking process and, hence, reduced PAH contamination. Moreover, maintenance of dryer temperatures as low as possible ensures good quality in terms of colour stability and control of PAH generation. The confinement of the

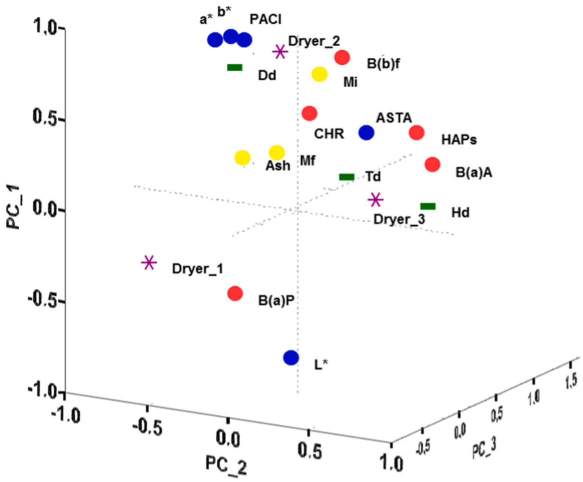

Fig. 3. Loading and score plot after principal component analysis of the drying parameters, quality parameters of dry smoke peppers, and PAHs in the space defined by the three principal components (PC1, PC2, and PC3). In blue: CIELab parameters (luminosity (L*), red-green exe (a*), blue-yellow exe (b*)), ASTA units, and PACI index; in red: benzo(a)pyrene [B(a)P], chrysene [CHR], benzo (b)fluoranthene [B(b)F], and benzo(a)anthracene [B(a)A], and total PAHs (PAHs); in yellow: mean initial moisture of dryers (Mi) and mean final moisture of dryers (Mf); in green: mean days of drying (Dd), mean temperature of drying (Td), and mean humidity of drying (Hd); and in purple: type of dryers (dryer_1; dryer_2, and dryer_3).(For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

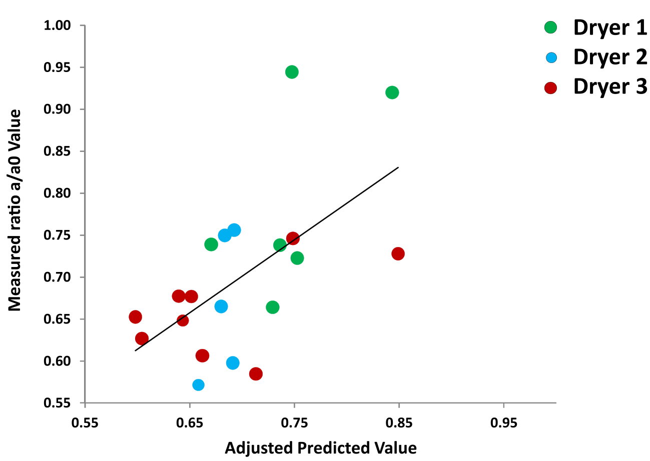

Fig. 4. Simple linear regression (SLR) plot for the relationship between the experimental values vs. predictive values (r = 0.693) of the a_i/a_0 ratio on the basis of mean drying temperature.

fire in a closed chamber, with smoke exposure controlled through the use of a fan (dryer 2), improved quality and stability of colour compared to traditional drying (dryer 1), with direct exposure of smoke; and reduced PAH contamination compared to the use of barrel kilns with four nozzles (dryer 3), which an indirect smoked happened.

CRediT authorship contribution statement

Rocio Velázquez: Investigation. **María de Guía Córdoba:** Conceptualization, Resources. **Alejandro Hernández:** Conceptualization, Writing – original draft, Writing – review & editing. **Rocio Casquete:** Methodology, Investigation. **Emilio Aranda:** Data curation. **Teresa Bartolomé:** Funding acquisition. **Alberto Martín:** Writing – original draft, Formal analysis, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jfca.2022.104566.

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