ELSEVIER

PII: S0308-8146(97)00191-X

Food Chemistry, Vol. 62, No. 2, pp. 201–205, 1998

Printed in Great Britain
0308-8146/98 $19.00+0.00

Effect of adding smoke-flavouring to frankfurters on nitrite and nitrate levels

M. L. Pérez-Rodríguez,* M. García-Mata & N. Bosch-Bosch

Departamento de Nutrición y Bromatología II: Bromatología. Facultad de Farmacia, Universidad Complutense de Madrid, 28040-Madrid, Spain

(Received 15 February 1997; accepted 1 August 1997)

Different concentrations of sodium nitrite, potassium nitrate or both together were used to prepare four standard solutions and four frankfurter formulations. These were elaborated with and without the addition of 2 g/kg of a commercial solid smoke-flavouring preparation. Monitoring of nitrite and nitrate residual levels in standard solutions stored at 3°C showed that smoke-flavouring addition results in a depletion of nitrite levels and/or reduction of nitrate to nitrite. In a much more complex system such as meat products, nitrite and nitrate, incorporated in the formulation separately or combined, were also rapidly depleted when smoke-flavouring was added. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

For centuries, natural wood smoke has been applied to products in traditional smokehouses. It imparts flavour, colour and aroma to foods, as well as preserving them (Pszczola, 1995). According to Müller (1992), today flavouring instead of preservation is the main purpose of smoking.

On the other hand, a liquid version of wood smoke is gaining increasing use in a variety of food products. It can be processed into three forms: aqueous, vegetable oil-based and dry-powdered. The use of smoke condensates virtually eliminates smoke as a source of polycyclic aromatic hydrocarbon (PAH) compounds (Pszczola, 1995). However, recent studies have detected PAH concentrations higher than allowed in some commercial smoke flavourings (Gomaa *et al.*, 1993; Yabiku *et al.*, 1993).

The main components of liquid smoke are acids, phenols, and carbonyls. Added to a meat product they provide an acidic and antioxidant medium that favours the transformation of nitrite in nitrous acid and, as a consequence, the formation of red nitrosomyoglobin, with a lower residual nitrite level in the final product (Girard, 1991). Present-day objections to the use of smoke-flavourings are based on the possibility that they could enhance reactions between smoke constituents and additives or ingredients of the meat product. The reaction of nitrous acid and phenols is noteworthy. Because the products of the condensation are usually acids, there are enough hydrogen ions to transform nitrite to nitrous acid. Knowles *et al.* (1975) have noted the presence of nitrophenols in the smoke condensate that results from the oxidation of nitrosophenols. The toxicological importance of both compounds is related to their role in the catalysis of nitrosamine formation (Walker *et al.*, 1982).

In this paper the influence of a solid smoke-flavouring preparation, used in the Spanish food industry, has been tested on nitrite and nitrate depletion during storage of standard aqueous solutions and Frankfurter-type sausages prepared in a pilot plant. Results obtained could contribute to a better understanding of additive behaviour. The need for this can be inferred from a recently published review (Cassens, 1995) in which recently found associations between childhood consumption of hot dogs and brain tumour or leukaemia risks is indicated, and it has emerged that nitrite from cured meats, rather than total nitrite, is important.

MATERIALS AND METHODS

Samples preparation

Frankfurters were prepared from lean pork trim and pork backfat in the pilot plant at Escuela de la Carne (Madrid, Spain) on two different occasions, giving a

---

*To whom correspondence should be addressed. Fax: 34-1-3941798.

total of two replicates. In both, eight batches were performed—four test ones (system 2) with 2 g/kg of a commercial solid smoke flavouring preparation (SSFP), used in the Spanish food industry, and four control batches (system 1) without SSFP. Formulation and processing of frankfurters have been described in a previous paper (Pérez-Rodríguez *et al.*, 1996). In brief, the composition of the curing agents added to each formulation was as follows: sodium chloride (2.2%), sodium ascorbate (0.05%), sodium nitrite (75 mg/kg in batches 1 and 4; 250 mg/kg in batch 2) and/or potassium nitrate (200 mg/kg in batches 3 and 4). Day P was designated as the day on which curing agents were mixed with the meat; day PN was the day just before heating and day 0 was the day on which the product was vacuum-packaged. After packaging they were labelled and stored in a refrigerator until needed for analysis. Both the experimental (smoked) and the control (non-smoked) frankfurters, in each formulation, underwent comparative tests (proximate analysis, pH, nitrite and nitrate). Determinations were carried out periodically, in triplicate, during a 4-month period.

Standard $NaNO_2$ and KNO_3 (Merck) solutions were also prepared at the same concentrations that they had been included in frankfurter formulations, with and without addition of 2 g/l of SSFP. The pH value of the resulting aqueous solutions ranged from 6.2 to 6.4. Addition of the SSFP resulted in a pH value of 5.5 in all the solutions. In order to obtain a pH value comparable to the pH of the batters (Table 1), another series of four standard solutions was prepared in citrate–phosphate buffer at pH 6.4. All these solutions were stored at 3°C until needed for analysis.

Nitrite and nitrate determination

Nitrite and nitrate were determined following the Normes AFNOR N.F.V. 04.409 (1974) and AFNOR N.F.V. 04.410 (1974), respectively. Nitrate content was therefore calculated from the nitrite values before and after cadmium reduction. Corrections for the Cd column efficiency are described elsewhere (García-Mata *et al.*, 1995). This method has been proved to be perfectly correlated to the HPLC UV/VIS one (Alonso *et al.*, 1992).

Results were expressed as mg $NaNO_2$/kg and mg KNO_3/kg fresh weight.

RESULTS AND DISCUSSION

Figures 1–4 show the changes of nitrite and nitrate in batches 1–4 of frankfurter formulations, respectively. The different behaviour observed in system 1 and 2, free of smoke-flavouring formulations and their smoked counterparts, is represented in each of them.

Proximate analysis and pH are shown in Table 1.

Percent recoveries of nitrite and nitrate obtained during storage of standard solutions are displayed in Table 2.

Endogenous reducing agents of the muscle tissue are responsible for the nitrate formation in meat products,

Table 1. Frankfurter proximate analysis and pH

System	Batch[a]	pH[b]	Moisture[b] (%)	Protein[b] (%)	Fat[b] (%)	Salt[b] (%)
1	1	6.3 ± 0.1	63.6 ± 0.7	13.8 ± 0.0	19.2 ± 0.9	1.6 ± 0.1
1	2	6.3 ± 0.1	61.3 ± 0.9	13.8 ± 0.3	21.4 ± 0.9	2.1 ± 0.1
1	3	6.1 ± 0.2	62.1 ± 0.9	12.5 ± 0.1	21.7 ± 0.6	1.7 ± 0.1
1	4	6.5 ± 0.2	61.1 ± 0.8	14.1 ± 0.2	21.4 ± 0.9	2.1 ± 0.0
2	1	6.3 ± 0.2	65.4 ± 0.4	14.8 ± 0.2	15.7 ± 0.4	1.7 ± 0.0
2	2	6.4 ± 0.2	65.0 ± 0.4	14.6 ± 0.4	16.6 ± 0.5	2.4 ± 0.1
2	3	6.4 ± 0.2	63.3 ± 0.3	15.2 ± 0.6	18.1 ± 0.4	1.8 ± 0.1
2	4	6.3 ± 0.2	64.6 ± 0.2	15.6 ± 0.5	16.2 ± 0.5	1.7 ± 0.0

[a]See 'Samples preparation' for description of batches.
[b]Average values ($n = 9$) and standard deviations over the storage length.

Table 2. Nitrite and nitrate recoveries during storage of standard solutions.(*2g/l of SSFP added, [b]buffered solution at pH 6.4)

Standard solutions	TIME (days)	Recovery (%)											
		(75 ppm $NaNO_2$)			(250 ppm $NaNO_2$)			(200 ppm KNO_3)			(75 ppm $NaNO_2$ 200 ppm KNO_3)		
		A	A*	A*b	B	B*	B*b	C	C*	C*b	D	D*	D*b
NITRITE	6	98	99	101	99	102	99				78	78	76
	18	96	94	96	100	97	97		Tr	Tr	74	70	74
	26	97	96	96	97	98	97		6	Tr	79	72	75
	46	98	77	82	97	98	96		52	Tr	80	54	48
	75	98	59	46	97	97	90		51	Tr	80	205	200
NITRATE	6							98	98	97	104	104	102
	18							97	82	88	105	105	102
	26							95	60	78	100	101	100
	31							97	30	67	100	96	98
	35							96	0	55	100	85	98
	46							96	0	0	100	78	99
	75							99	0	0	104	0	10

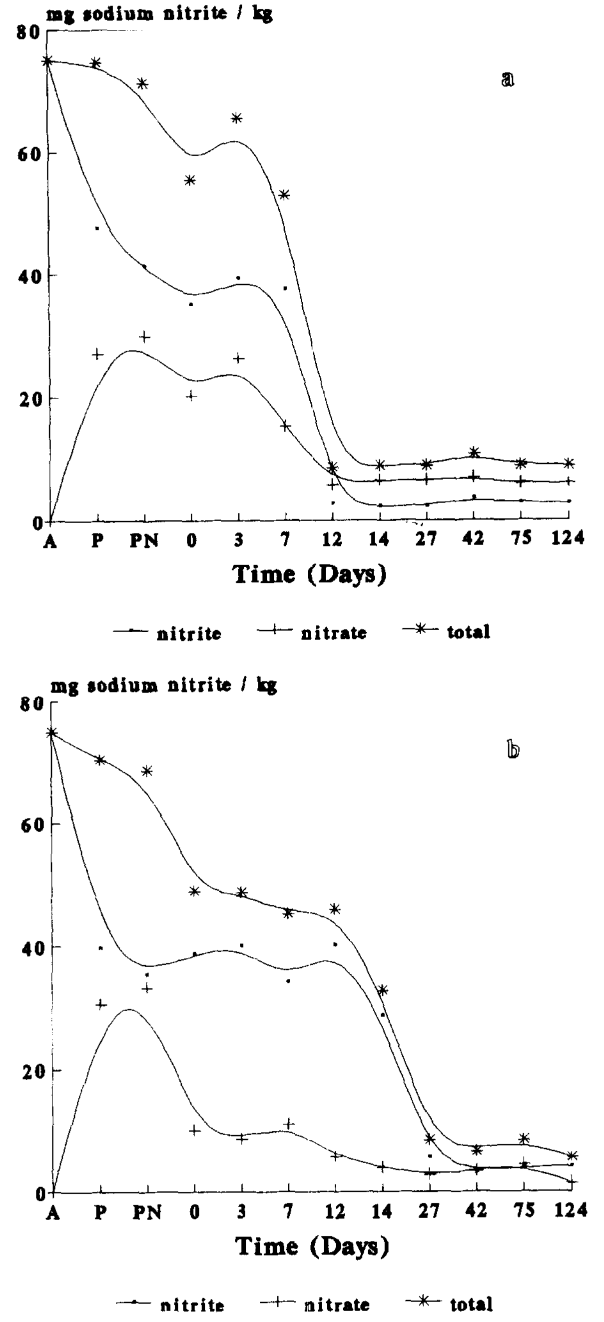

Fig. 1. Changes of nitrite, nitrate and total of both (calculated as mg $NaNO_2$/kg fresh weight) during frankfurter processing and storage at 3°C. (a) With 2 g/kg smoke-flavouring; (b) unsmoked A = added (75 mg/kg $NaNO_2$).

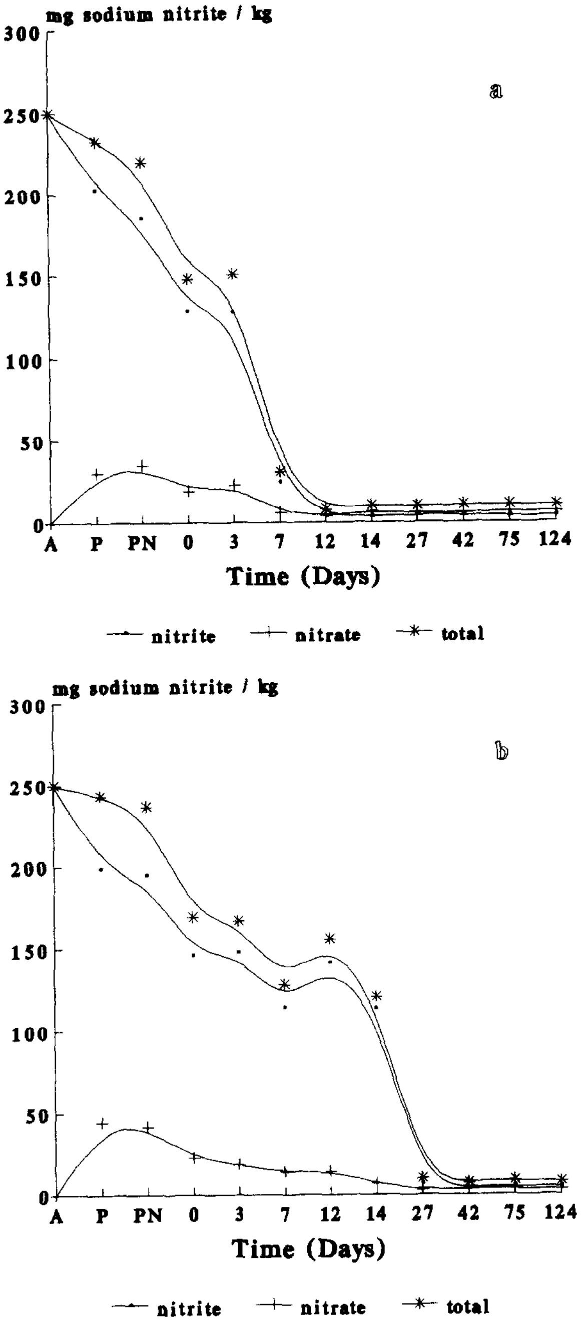

Fig. 2. Changes of nitrite, nitrate and total of both (calculated as mg $NaNO_2$/kg fresh weight) during frankfurter processing and storage at 3°C. (a) With 2 g/kg smoke-flavouring; (b) unsmoked. A = added (250 mg/kg $NaNO_2$).

which is sometimes enhanced by the addition of reductants such as ascorbic acid (Lee *et al.*, 1978; O'Boyle *et al.*, 1990). The well-known alkyl derivatives of syringol and guaiacol have been considered as key compounds responsible for the antioxidant properties of liquid smoke (Maga, 1988). They have been found to constitute approximately 25% of the volatile fraction of a Spanish SSFP (Guillen and Manzanos, 1996). Another group of compounds, which are interesting because of their strong antioxidant effects, are dihidroxybenzene derivatives (Guillén *et al.*, 1995). These antioxidant properties of some smoke components could explain that a slightly minor transformation of nitrite to nitrate was observed in frankfurters of system 2 in contrast to their system 1 counterparts: 36.2% versus 43.5% of the 75 mg $NaNO_2$/kg incorporated in batch 1, and 13.9% versus 18.3% of the 250 mg $NaNO_2$/kg added in batch 2. However, the main difference observed among batches from both systems was the rapid depletion of residual nitrite after a few days in storage when SSFP had been initially added to the formulation. Only about 8 mg/kg residual nitrite (sum of nitrite and nitrate forms, expressed as $NaNO_2$) could be detected after 12 days storage in batches 1 and 2 from system 2 (Figs 1a and 2a), while

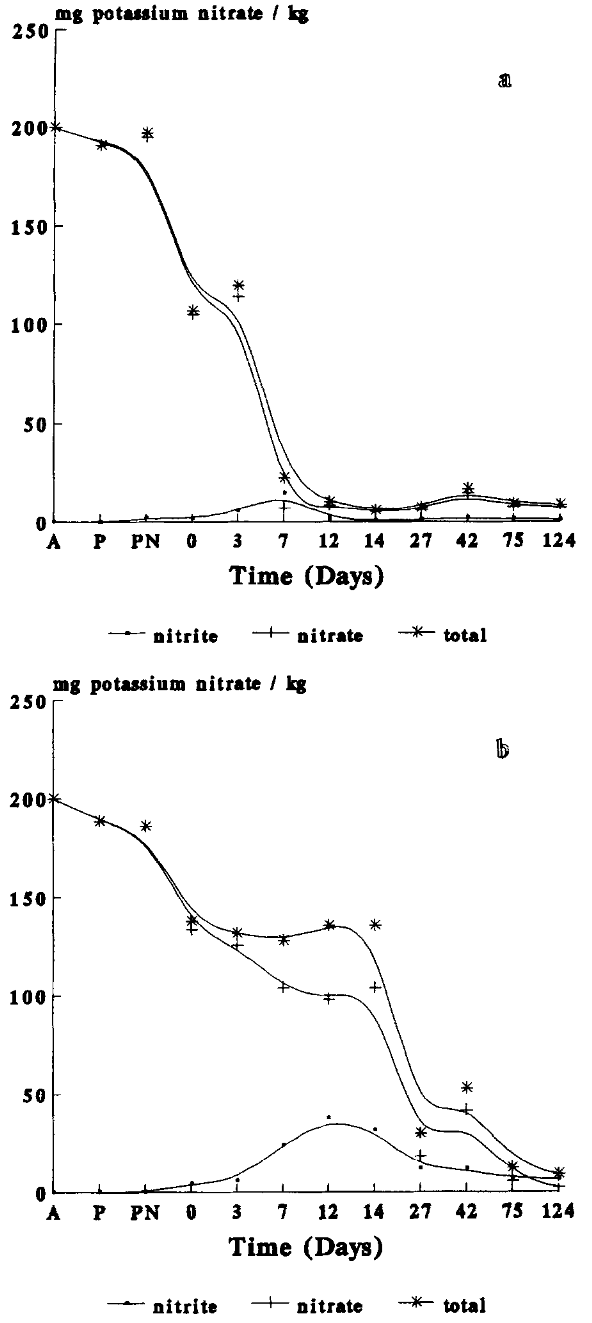

Fig. 3. Changes of nitrite, nitrate and the total of both (calculated as mg KNO_3/kg fresh weight) during frankfurter processing and storage at 3°C. (a) With 2 g/kg smoke-flavouring; (b) unsmoked. A = added (200 mg/kg KNO_3).

the concentrations found by that time in system 1 were 46 and 156 mg $NaNO_2$/kg, respectively (Figs 1b and 2b).

Nitrite recovery after 75 days storage of standard solutions A (spiked with 75 mg $NaNO_2$/kg) was less than 60% if SSFP had been initially included (A^*, A^{*b}) while it was nearly 100% for the control solution prepared without smoke-flavouring (Table 2). The pH value of aqueous solution A^*, initially more acidic than the control and citrate–phosphate buffered ones, increased until 6.5 was reached by this time. However, no significant losses of nitrite or pH variations were observed during storage of standard solutions B (spiked with 250 mg $NaNO_2$/kg). As expected, no nitrate forms could be detected in these solutions.

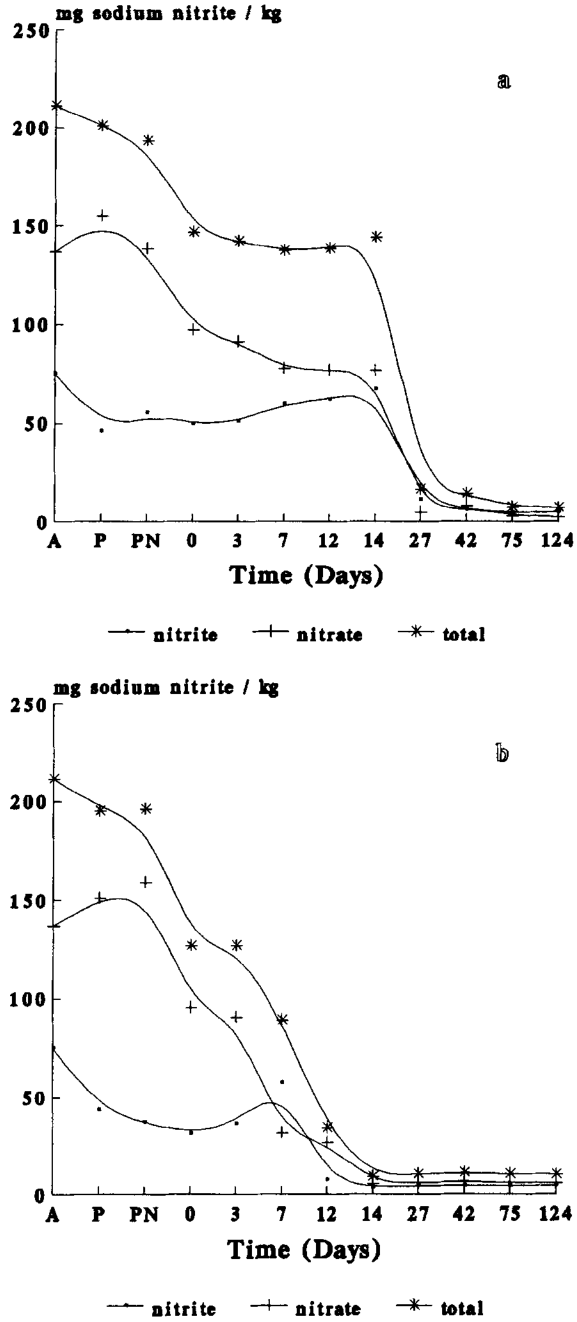

Fig. 4. Changes of nitrite, nitrate and the total of both (calculated as mg $NaNO_2$/kg fresh weight) during frankfurter processing and storage at 3°C. (a) With 2 g/kg smoke-flavouring; (b) unsmoked. A = added (75 mg/kg $NaNO_2$ plus 200 mg/kg KNO_3).

Even more remarkable were the effects initiated by the presence of the SSFP on frankfurters and standard solutions formulated only with nitrate. Only about 10% of the nitrate added to batch 3 in system 2 could be detected after 7 days storage (Fig. 3a), while by the same time more than 60% remained in system 1 (Fig. 3b). In aqueous solution C the concentration of nitrate remained relatively constant over the storage length, as did the pH value. However, SSFP addition (C^*) resulted in a significant nitrate reduction to nitrite, especially after 26 days storage. By this time, pH had increased up to 6.7. Twenty days later, the nitrite formed accounted for more than 50% of the initially added nitrate and this form could not be found any more. In the previously buffered solution (C^{*b}) nitrate was also lost but only traces of nitrite could be detected. In standard solution D^*, in which the same concentration of nitrate and smoke-flavouring had been incorporated but 75 mg $NaNO_2$/kg were also present, a similar pattern was observed except that nitrate depletion was retarded.

Nitrate and nitrite behaviour during storage of frankfurters formulated with both curing additives was also different in systems 1 and 2 (Fig. 4). Concentrations of 114 versus 53 mg KNO_3/kg were obtained in both systems, respectively, after 7 days storage. For $NaNO_2$, concentrations of 62 versus 7.5 mg/kg were found.

In view of these results it may be concluded that the antioxidant properties of some smoke-flavouring components influence nitrite and nitrate solution stability. In a much more complex system, such as a meat product, the addition of the smoke-flavouring preparation results in a more rapid depletion of nitrite and nitrate when they are incorporated in the formulation either separately or combined.

ACKNOWLEDGEMENTS

M.L. Pérez-Rodríguez thanks the Ministerio de Educación y Ciencia for a predoctoral fellowship. The authors also thank staff from the Escuela de la Carne de Madrid for their technical assistance in the meat systems preparation done in their installations.

REFERENCES

AFNOR NF V 04.410 (1974) *Association Française* de Normalisation, **12** Paris-La Défense.

AFNOR NF V 04.409 (1974) *Association Française* de Normalisation, **12** Paris-La Défense.

Alonso, A., Etxaniz, B. and Martínez, M. D. (1992) The determination of nitrate in cured meat products. A comparison of the HPLC UV/VIS and Cd/spectrophotometric methods. *Food Additives and Contaminants* **9**, 111–117.

Cassens, R. G. (1995) Use of sodium nitrite in cured meats today. *Food Technol.* **115**, 72–79.

García-Mata, M., Bosch-Bosch, N. and Pérez-Rodríguez, Mª. L. (1995) Effect of cooking on nitrate in dehydrated soups. *Int. J. Food Sci.and Technol.* **30**, 45–48..

Girard, J. P. (1991) El ahumado. In *Tecnología de la carne y de los productos cárnicos*, ed. J. P. Girard, pp. 183–229. Acribia, Zaragoza.

Gomaa, E. A., Gray, J. I., Rabie, S., López-Bote, C. and Booren, A. M. (1993) Polycyclic aromatic hydrocarbons in smoked food products and commercial liquid smoke flavouring. *Food Addit. Contam.* **10**, 503–521.

Guillen, M. D. and Manzanos, M. J. (1996) Study of the components of a solid smoke flavouring preparation. *Food Chem.* **55**, 251–257.

Guillén, M. D., Manzanos, M. J. and Zabala, L. (1995) Study of a commercial liquid smoke flavoring by means of gas chormatography/mass spectrometry and Fourier transform infrared spectroscopy. *J. Agric. Food Chem.* **43**, 463–468.

Knowles, M. E., Gilbert, J. and McWeeny, D. J. (1975) Phenols in smoked, cured meats: nitrosation of phenols in liquid smokes and in smoked bacon. *J. Sci. Food Agric.* **26**, 267–276.

Lee, S. H., Cassens, R. G., Winder, W. C. and Fennema, O. R. (1978) Factors affecting the formation of nitrate from added nitrite in model systems and cured meat products. *J. Food Sci.* **43**, 673–676.

Maga, J. A. (1988) *Smoky in Food Processing*. CRC Press, Boca Raton, Florida.

Müller, W. D. (1992) Embutir y ahumar. In *Tecnología de los embutidos escaldados*, ed. F. Wirth, pp. 149–169. Acribia, Zaragoza.

O'Boyle, A. R., Rubin, L. J., Diosady, L. L., Aladin-Kassam, N., Comer, F. and Brightwell, W. (1990) A nitrite-free curing system and its application to the production of wieners. *Food Technol.* **44**, 88–104.

Pérez-Rodríguez, Mª. L., Bosch-Bosch, N. and García-Mata, M. (1996) Monitoring nitrite and nitrate residues in frankfurters during processing and storage. *Meat Sci.* **44**, 65–73.

Pszczola, D. E. (1995) Tour highlights production and uses of smoke-based flavors. *Food Technology* **49**, 70–74.

Walker, E. A., Pignatelli, B. and Friesen, M. (1982) The role of phenol in catalysis of nitrosamine formation. *J. Sci. Food Agric.* **33**, 81–84.

Yabiku, Y. H., Martius, S. M. and Takahashi, M.Y. (1993) Levels of benzo(*a*)pyrene and other polycyclic aromatic hydrocarbons in liquid smoke flavour and some smoked foods. *Food Addit. Contam.* **10**, 399–405.