Carbon Monoxide, Nitric Oxide, and Nitrogen Dioxide Levels in Gas Ovens Related to Surface Pinking of Cooked Beef and Turkey

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Carbon monoxide (CO) and total nitrogen oxide (NO_x) levels were monitored during meat cookery with a standard Ovenpak and a new ultralow-NO_x (ULN) cyclonic gas burner. With the standard burner, CO varied from 103 to 152 ppm, NO_x was 1.3–10.7 ppm, and surface pinking was observed on both beef and turkey. The ULN burner at optimal efficiency produced only 6.7 ppm of CO and 1 ppm of NO_x, insufficient to cause surface pinking. To determine the relative contribution of CO and NO_x to pinking, trials were also conducted in an electric oven with various pure gases. Pinking was not observed with up to 149 ppm of CO or 5 ppm of NO. However, as little as 0.4 ppm of nitrogen dioxide (NO_2) caused pinking of turkey rolls. Beef roasts were pink at >2.5 ppm of NO_2. Thus, pinking previously attributed to CO and NO in gas ovens is instead due to NO_2, which has much greater reactivity than NO with moisture at meat surfaces.

Keywords: *Carbon monoxide; nitric oxide; nitrogen dioxide; meat; pinking*

INTRODUCTION

Meat cooked in a gas oven or heavily smoked frequently develops surface pinking. Upon slicing, a pink ring is observed to a depth of ~8–10 mm from the surface. Pink ring is a traditional and desirable attribute of "Texas BBQ" beef roasts (Cornforth et al., 1991). In most cases, however, the surface pinking is undesirable, since consumers may associate pinking with undercooking and increased risk for trichinosis in pork (Kotula et al., 1982), salmonellosis in rare roast beef (Anonymous, 1978), or *Escherichia coli* O157 H7 in rare hamburger (Frost et al., 1995). A recent joint effort by the Institute of Gas Technology (IGT, Des Plaines, IL) and Maxon Corp. (Muncie, IN) led to the development of an ultralow-emission, gas-fired burner for direct air heating applications (Xiong et al., 1991, 1992). In their tests, emissions of carbon monoxide (CO) were <3 ppm, and total nitrogen oxides (NO_x, where $NO_x = NO + NO_2$) were <1 ppm. The objective of this study was to monitor emission gas levels (CO, NO, NO_x) and meat surface pinking in ovens equipped with either a standard Ovenpak (Model 400; Maxon Corp., Muncie, IN) or new ultralow-NO_x (ULN) cyclonic burner. Additional cooking trials were also conducted in an electric oven with pure gases (CO, NO, NO_2) to determine their relative contribution to meat surface pinking.

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MATERIALS AND METHODS

Apparatus. The following equipment was used: Alkar Model 1000 gas-fired oven (Alkar, Lodi, WI); Alkar Model 700 electric oven (Alkar); Model 400 Ovenpak gas burner (Maxon Corp.); ultralow-NO_x cyclonic burner (IGT; Maxon Corp.); gas flow control and distribution panel (IGT); Model 14A chemiluminescent gas analyzer (Thermo Electron Corp., Franklyn, MA); Model 755R paramagnetic oxygen measurement system (Beckman Industrial Corp., La Habra, CA); Model 880 nondispersive infrared detector (Rosemount Analytical, La Habra, CA); Model 864 nondispersive infrared detector (Beckman Industrial Corp.); Model 400A hydrocarbon analyzer (Beckman Industrial Corp.); Rotameter (flow meter; King Instruments, Huntington Beach, CA); Model D25D2 Hunter color meter (Hunter Associates Laboratory, Inc., Reston, VA).

Reagents. Experiment 1 calibration gases (Matheson Gas Products, Newark, NJ) were nitrogen, nitric oxide (4.8 and 47.5 ppm in nitrogen), oxygen (20.98% in nitrogen, where 1% = 10 000 ppm), carbon monoxide (81.8 ppm in nitrogen), carbon dioxide (18.5% in nitrogen), and methane (10.4 ppm in nitrogen). Experiment 2 gases (Matheson Gas Products, Newark, NJ) were nitric oxide (1.48% in nitrogen), nitric oxide (738 ppm in nitrogen), nitrogen dioxide (1.44% in nitrogen), and carbon monoxide (3.98% in nitrogen).

Experiment 1. *Comparison of Gas Burners.* Cooking trials were conducted in the laboratories at Alkar (Division of DEC International, Lodi, WI), using a gas-fired Alkar Model 1000 one-truck oven (160 kg capacity). The oven system included a chamber behind the oven where the air was heated by a conventional Ovenpak 400 gas burner (Maxon Corp.). The heated air was then ducted into the oven. A small portion (<15%) of the process air was exhausted from the oven, and the remaining air was recirculated to the burner chamber along with some fresh makeup air. The circulation rate in the oven was typically 12 volume changes/min. The rear chamber was modified by addition of a new ULN cyclonic burner (IGT; Maxon Corp.). Thus, either burner could be used to heat the oven. Stainless steel probes (6.4 mm diameter; IGT) were installed at six sites to sample the exhaust gases. Two probes were placed at the exit of each burner (center and side). Probes were also installed at the top center and the

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middle side of the oven and in the middle of the recirculation and fresh air ducts. From the probes, the sampled gases entered two coalescing filters followed by a membrane dryer to remove water vapor. After drying, the sample was sent via Teflon tubing to a sample flow control and distribution panel (IGT) for channeling to the appropriate gas analyzers. The flow control panel also allowed for calibration gases to be channeled to the analyzers as desired. Ahuja et al. (1996) provide a complete description of the ULN burner, including piping and gas flow regulation diagrams, available on request from IGT main offices (Chicago, IL).

Gas Analysis. Samples were analyzed for nitric oxide (NO), nitrogen oxides (NO_x = NO + NO_2), oxygen (O_2), carbon monoxide (CO), carbon dioxide (CO_2), and total unburned hydrocarbons (THC). Nitric oxide and NO_x were determined with a Model 14A chemiluminescent gas analyzer (Thermo Electron Corp.). For NO measurements, the gas sample was blended with ozone (O_3) in a flow reactor, where NO + O_3 → NO_2 + O_2 + h_v. Light emission occurred when the excited NO_2 molecules decayed to lower energy levels and was measured spectrophotometrically. To measure NO_x (NO + NO_2), the sample gas was first diverted through a NO_2-to-NO catalytic converter. Nitric oxide was then measured as previously described.

Oxygen was measured with a Model 755R paramagnetic oxygen measurement system (Beckman Industrial Corp.). Paramagnetic oxygen has the capability of becoming a temporary magnet when placed in a magnetic field. Most other gases are diamagnetic and therefore not affected. The Model 755R measured the volume magnetic susceptibility of oxygen in the gas sample.

Carbon monoxide was measured with a Model 880 nondispersive infrared (NDIR) analyzer (Rosemount Analytical). The instrument produced infrared radiation from two separate energy sources. This radiation was modulated by a chopper into 5 Hz pulses, which passed through optical filters to reduce background interference from other infrared-absorbing components. Each infrared beam passed through a separate cell, one of which was sealed and contained the reference gas (CO). The other cell contained the continuously flowing sample gas. The quantity of infrared radiation absorbed was proportional to the CO concentration. The detector was a "gas microphone" based on the Luft principle, converting the difference in energy between sample and reference cells to a change in capacitance, which was amplified and displayed (Rosemount Analytical, 1995). Carbon dioxide was measured with a Beckman 864 NDIR detector (Beckman Industrial Corp.), using the same principle as described for CO but with CO_2 in the reference cell.

THC were measured by flame ionization with a Model 400A hydrocarbon analyzer (Beckman Industrial Corp.). In this method, a regulated flow of sample gas was passed through a hydrogen flame, where hydrocarbon components were ionized. Polarized electrodes collected the ions, causing current to flow through electronic measuring circuitry. Current flow was proportional to the rate at which carbon atoms entered the burner.

Instrument grade nitrogen gas was used to zero the instruments and to purge the sampling lines between samples. Signals from the O_2, NO/NO_x, and CO analyzers were connected to strip chart recorders to monitor their mole fractions during the tests. All of the gas analyzers were zeroed and calibrated at the beginning of each day and rechecked at least twice a day. Calibration gases (Matheson Gas Products) were 4.8 and 47.5 ppm of NO, 20.98% O_2, 81.8 ppm of CO, 18.15% CO_2, and 10.4 ppm of methane.

Meat Cookery. Precooked turkey breasts (3.6 kg) were steam conditioned in an Alkar Model 1000 oven for 10 min (82 °C wet bulb and dry bulb), to keep the surface moist during the early stages of cooking, and then browned for 60 min (turkey breast sample T1) or 90 min at 199 °C (T2–T9). Raw beef top round roasts (2 kg; samples B5 and B6) were dry cooked to 71 °C internal temperature using the following cooking steps: 30 min at 88 °C dry bulb; 2 h at 88 °C dry bulb, 60 °C wet bulb; 60 min at 82 °C dry bulb, 65 °C wet bulb; and

then sufficient time at 77 °C dry bulb, 71 °C wet bulb, to reach 71 °C internal temperature. The damper was set to automatic throughout, and wet bulb, dry bulb, and internal meat temperatures were recorded continuously during each test. Cooking times for beef samples B5 and B6 were 290 and 342 min, respectively. Oven gas concentrations were measured every 18 min during turkey browning or beef cookery. For turkey samples T1 and T2 and beef sample B5, relatively high concentrations of CO and NO_x were obtained during heating with the standard Ovenpak burner. For samples T3, T4, and B6, low levels of NO_x were obtained using the ULN burner at optimal settings. For samples T5 and T6, higher CO and NO_x levels were obtained with the ULN burner by closing the oven damper during heating and by purposely adjusting the burner flame to achieve incomplete combustion. Low CO levels were also achieved during heating by use of the ULN burner set for complete combustion and with the dampers open (T7–T9).

Half of each roast was then vacuum packaged, labeled, packed with Blue Ice in a Styrofoam container, and shipped to Utah State University for photography, panel color evaluation, instrumental evaluation of color using the Hunter color meter, and nitrosoheme pigment concentration. Upon delivery, samples were stored at 2 °C, and all further measurements were completed within 3 days.

Color Measurements. *Panel Evaluation of Color.* Panelists (12) rated slices (1 cm thick) for pink color intensity on a scale of 1–5, where 1 = no pink color, 2 = slightly pink, 3 = moderately pink, 4 = very pink, and 5 = extremely pink. Fresh slices of cooked turkey breast and beef pastrami served as controls with color scores of 1 and 5, respectively.

Instrumental Color Measurement. Hunter color lightness (L), redness (a), and yellowness (b) values were measured by first obtaining thin (3 mm) slices from the meat surface, so that the exposed surface was within the pink ring area. The slices were placed with the freshly cut surface toward the bottom of the sample cup (7 cm diameter). Color measurements were obtained on a Hunter Lab Digital Color Difference Meter D25D2 (Hunter Associates Laboratory, Inc.), standardized with a pink plate (L = 66.8, a = 21.4, and b = 12.0). Triplicate readings were taken for each sample. The sample cup was rotated 90° between readings.

Nitrosoheme Pigment Concentration. Concentration of nitrosylhemochrome, the cured meat pigment, was determined spectrophotometrically at 540 nm on acetone extracts of meat samples. Total pigment was determined at 640 nm on acidified acetone extracts (Hornsey, 1956). The browned meat surface was trimmed, and duplicate samples (10 g each) from the potentially pink area (within 7 mm of the original surface) were used. Acetone pigment extraction was done in the dark, and measurements were conducted under subdued light to minimize pigment fading.

Experiment 2. *Pure Gases.* To determine the relative contribution of various gases to meat surface pinking, tests were conducted using a Model 700 electric oven (2.2 m high × 1.2 m wide × 1.3 m deep; Alkar), modified to allow the introduction of controlled levels of pure CO, NO, or NO_2 (Matheson Gas Products). Gas flow rate from the pure gas canister was controlled with rotameters (King Instruments), which were in turn connected to the oven external water pipe. Thus, the gas was introduced into the oven via the water system normally used to spray and cool products after cooking. Two spray nozzles at the top of the oven were replaced with a T-connector to two short copper tubes (100 mm long × 3.2 mm diameter), so the desired gas was actually introduced at four sites in the top of the oven, just above the fan. The copper tubes were flattened at the end to produce a "jet effect".

Extensive preliminary tests were conducted for each pure gas, to determine the flow rates needed to maintain the desired oven gas level and to measure the uniformity of gas distribution. Gas samples were withdrawn via Teflon tubes at six sites in the oven: center and side at 0.3 m from the top, middle (center and side), and 0.3 m from the bottom of the oven (center and side). Using 1.48% NO, for example, at a flow rate of 3.5 cm³/h and with dampers open, a very uniform NO distribution was achieved in the oven. The mean of two runs, six samples

Oven Gases Related to Meat Pinking

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Table 1. Gas Oven Cooking Conditions[a] and Level of Various Oven Gases in Relation to Pink Ring Intensity, Hunter Color Values, and Nitrosylhemochrome Concentration on the Surface of Cooked Turkey (T) or Beef (B)

sample	burner/ damper[b]	NO (ppm)	CO (ppm)	NO_x (ppm)	pink ring[c]	Hunter color[d]			NO-hemo- chrome (ppm)
						L	a	b	
T1, high CO, NO_x	STD/O		151.7	10.7	2.4	56.9	5.7	11.8	9.0
T2, high CO, NO_x	STD/O		130.0	9.2	2.1	56.8	6.7	9.9	7.8
T3, low NO_x	ULN/O	0.5	24.3	0.5	1.7	60.0	2.4	12.9	3.8
T4, low NO_x	ULN/O	0.5	17.8	0.8	1.7	60.1	4.0	12.9	4.4
T5, high CO, NO_x	ULN/C	0.6	57.8	1.2	2.8	59.2	3.2	12.5	5.8
T6, high CO, NO_x	ULN/C	0.5	175.6	1.4	3.2	56.8	8.3	9.2	7.8
T7, low CO	ULN/O	0.9	10.4	1.2	2.7	57.1	6.2	10.6	9.0
T8, low CO	ULN/O		19.4	0.8	1.9	57.6	4.6	12.6	14.2
T9, low CO	ULN/O		13.2	0.8	2.0	62.0	5.6	11.7	16.0
B5, high CO, NO_x	STD/C		102.9	1.3	3.7	43.1	11.4	9.3	240.1
B6, low CO, NO_x	ULN/C		6.7	1.0	1.0	44.7	6.3	10.9	17.1
$LSD_{0.05}$[e]		0.5	27.4	1.1	0.2	1.7	2.7	2.7	21.1

[a] Precooked turkey breast rolls were steam conditioned (100% RH) at 82 °C for 10 min. T1 was then browned for 60 min at 199 °C. Other turkey samples were browned for 90 min. Raw beef top round roasts were dry cooked to 71 °C internal temperature. [b] STD, standard Ovenpak burner; ULN, ultralow-NO_x burner; O, open damper; C, closed damper. [c] Pink ring intensity: 1 = no pink ring; 5 = extremely pink ring. [d] L, lightness, where 100 = pure white and 0 = pure black; a, redness; b, yellowness. [e] Fisher's least significant difference ($p < 0.05$) among means within columns.

per run, was 2.7 ± 0.08 ppm of NO. With dampers closed or on automatic (partially open), values were 15.0 ± 0.32 and 7.1 ± 0.08 ppm of NO, respectively. Similar uniformity was achieved with CO and NO_2. Since damper position changed during cooking, gas flow rates also were changed as needed, to maintain constant gas levels during cooking. Gas concentrations were determined as described for experiment 1 and were recorded during each test using strip chart recorders.

In most cases, only pure gases were introduced into the oven during cooking. However, for turkey trial T8, a two-way mixture (NO_2 + NO) was used. For run T9 a two-way mixture (NO_2 + CO) was also used. Gases were merged into a single line using T-connectors. To ensure complete gas mixing before injection into the oven, 4.3 m long Teflon tubing was used.

Cooking. Commercial cooking procedures were also used for experiment 2. Precooked turkey rolls (3.6 kg) were reheated for 2 h at 71 °C dry bulb, 0 °C wet bulb, dampers on automatic; for 1 h at the same temperature settings with damper closed; and then for 1 h at 79 °C dry bulb, 0 °C wet bulb (dampers closed). At these wet and dry bulb settings, relative humidity was very low throughout the cook cycle. Raw beef roasts (2 kg) were cooked for 30 min at 88 °C dry bulb, 0 °C wet bulb, dampers on automatic; for 1 h at 88 °C, with wet bulb at 60 °C to obtain 26% relative humidity; and then for sufficient time at 90 °C dry bulb, 71 °C wet bulb (43% relative humidity), to reach an internal temperature of 71 °C. Total cooking time for beef roasts was ~6 h. When damper position was changed during cooking, gas flow rates were manually adjusted as needed to maintain the desired gas concentration. Oven gas concentrations were measured at 10 min intervals during cooking. Cooked samples were packaged, shipped, and analyzed as described for experiment 1.

Statistical Analysis. Experimental data were analyzed by one-way ANOVA, using Statistica for the Macintosh (StatSoft, Inc., 1994). Differences between means were determined using Fisher's least significant difference (LSD) test. Significance was accepted at the 95% confidence level.

RESULTS

Cooking conditions and gas levels during cooking with a standard Maxon Ovenpak or new ULN burner are shown in Table 1. Oven gas levels were affected by burner type (standard or ULN), oven damper position (open or closed), and oven temperature (199 °C for browning of precooked turkey or 88 °C for beef cookery). The standard burner produced higher levels of CO and NO_x than the ULN burner (Table 1). However, higher CO and NO_x levels were also observed with the ULN burner, if the damper was closed (sample T6, Table 1).

Nitric oxide levels were always <1 ppm in the ULN oven, even if the damper was closed (Table 1). With the standard burner, CO varied from 103 to 152 ppm and NO_x was 1.3−10.7 ppm. The ULN burner at optimal efficiency produced only 6.7 ppm of CO and 1 ppm of NO_x (B6, Table 1). For turkey sample T4 with the ULN burner (Table 1), the NO_x level was only 0.8 ppm, with 0.5 ppm of NO, and, by difference, 0.3 ppm of NO_2.

CO and THC levels were closely associated. As with CO, THC levels were highest (115 ppm) for sample T6. Samples T1, T2, and B5, heated with the standard burner, had mean THC values of 63, 47, and 35 ppm, respectively. Other samples had THC values from a low of 7 ppm (T4) to 23 ppm (T5). CO_2 concentration was highest for samples T5 and T6, using the ULN burner but with dampers closed (3.9 and 3.0% CO_2, respectively). For other samples, CO_2 concentration varied from a low of 0.8% for B5 to 2.3% for T1. Predictably, O_2 concentrations tended to be lower for samples with high CO, CO_2, and THC. Samples T5 and T6, with the highest CO_2, had the lowest O_2 levels (14 and 15% O_2, respectively). Other samples had O_2 levels ranging from 17% (T1) to 19% (B5).

A definite pink ring was observed on turkey breasts T1 and T2 heated with the standard burner. Panel scores for pink ring intensity were 2.1−2.4, where 2 = slight and 3 = moderate pink color (Table 1). Pink ring intensity and Hunter color redness values were significantly lower ($p < 0.05$) for turkey heated with the ULN burner (T3 and T4; Table 1). However, pink ring intensity could be increased substantially ($p < 0.05$) with the ULN burner if the dampers were closed, increasing the levels of CO and NO_x in the oven (T5 and T6, Table 2). The most intense pink ring and the highest Hunter color redness values were observed on the beef roast (B5; see Figure 1) heated with the standard burner and with dampers closed. However, pink ring was completely eliminated using the ULN burner at optimum efficiency (6.7 ppm of CO, 1 ppm of NO_x, B6; Table 1), even if dampers were closed.

No significant differences were observed in nitrosylhemochrome content of turkey surface samples. However, nitrosylhemochrome content was very high (240 ppm) in beef sample B5, which had a very prominent ring. The meat pigments were essentially 100% ni-

Table 2. Effect of Various Pure Gases on Surface Pinking of Beef (B) or Turkey (T) Cooked in an Electric Oven

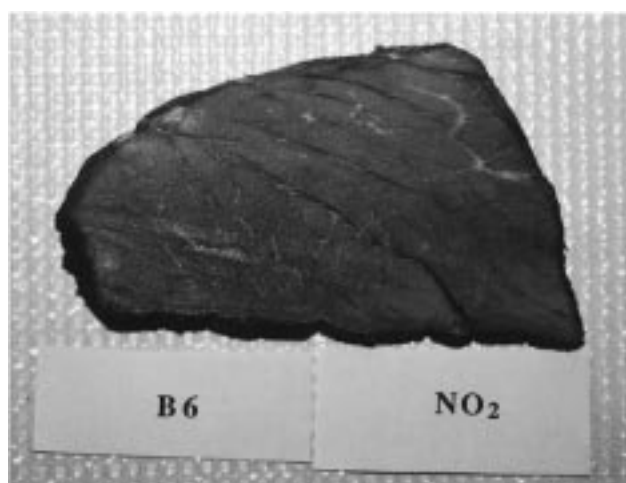| sample	added gas	CO (ppm)	NO (ppm)	NO_2 (ppm)	NO_x (ppm)	pink ring	pink ring score[a]	Hunter color[b]			NO-hemo-chrome (ppm)
								L	a	b	
control	none	1.4	0.1	0.0	0.1	no	1.0	38.6	7.8	9.5	5.1
B1	NO	0.6	2.0	0.0	2.0	no	1.1	37.6	6.4	9.3	7.0
B2	NO	0.3	4.5	0.0	4.5	no	1.2	42.1	7.4	10.1	3.9
B3	CO	149.3	0.1	0.0	0.1	no	1.2	38.1	8.5	9.1	3.6
B4	NO_2	2.5	0.6	0.4	1.0	no	1.4	41.6	8.4	9.7	6.2
B5	NO_2	2.3	0.8	1.2	2.0	no	1.1	43.2	10.1	9.7	5.2
B6	NO_2	1.6	1.0	4.2	5.2	yes	4.7	42.1	12.2	8.9	174.3
B7	NO_2	0.9	0.7	2.5	3.2	yes	4.3	43.0	9.1	9.3	18.4
control	none	0.4	0.1	0.0	0.1	no	1.2	57.8	5.6	9.2	0.9
T1	NO	1.4	5.0	0.0	5.0	no	1.4	59.9	7.1	9.1	1.3
T2	NO	0.6	1.9	0.0	1.9	no	1.4	59.3	6.6	9.4	1.7
T3	CO	15.0	0.1	0.1	0.2	no	1.0	68.2	7.3	11.1	1.2
T4	CO	30.3	0.1	0.0	0.1	no	1.0	67.4	8.6	10.7	1.0
T5	NO_2	1.5	0.9	4.4	5.3	yes	3.1	65.6	6.8	10.1	3.2
T6	NO_2	0.9	0.3	0.6	1.0	yes	2.9	66.5	7.1	11.0	3.6
T7	NO_2	1.9	0.2	0.4	0.7	yes	2.6	64.7	6.8	11.0	6.1
T8	NO_2, NO	3.2	7.4	0.9	8.4	yes	3.1	58.7	7.6	9.8	4.9
T9	NO_2, CO	33.5	0.3	0.8	1.1	yes	1.9	64.4	5.9	11.5	5.5
$LSD_{0.05}$[c]		1.9	0.3	0.1	0.3		0.5	1.3	2.8	1.1	13.8

[a] Pink ring intensity: 1 = no pink ring; 5 = extremely pink ring. [b] *L*, lightness, where 100 = pure white and 0 = pure black; *a*, redness; *b*, yellowness. [c] Fisher's least significant difference (*p* < 0.05) among means within columns.

Figure 1. Pink ring development on a beef top round roast heated in a gas oven equipped with a standard Ovenpak burner (sample B5, experiment 1). Mean concentrations of CO and NO_x during cooking were 102.9 and 1.3 ppm, respectively (Table 1).

Figure 2. Pink ring development on a beef top round roast heated in an electric oven in the presence of 4.2 ppm of NO_2 (sample B6, Table 2).

trosylated, since total pigment content was 232 ppm. For comparison, a retail sample of beef pastrami analyzed according to the same acetone extraction procedure had 94.5 ppm of nitrosylhemochrome and 153 ppm of total pigment (62% pigment nitrosylation).

In experiment 1, it was not possible to determine the relative contribution of the various emission gases (CO, NO, or NO_2) to pinking. Thus, a second set of cooking trials was conducted using pure gases in an electric oven. Meat surface pinking has previously been associated with both CO (Pool, 1956; Tappel, 1957; Livingston and Brown, 1981) and NO (McBrady, 1968; Braddock and Dugan, 1969; Ranken, 1973). In contrast to these previous papers, neither pure CO nor pure NO in this study caused meat surface pinking at concentrations typical of gas oven cookery (Table 2). For example, 103 ppm of CO and 1.3 ppm of NO_x were associated with a prominent pink ring on sample B5, experiment 1 (Table 1). However, pink ring was not observed on beef surfaces in the presence of either 149 ppm of pure CO (B3) or 4.5 ppm of pure NO (B2, Table 2). Similarly,

surface pinking was not observed on turkey breast in the presence of 30 ppm of CO (T4) or 5 ppm of NO (T1, Table 2). Pinking was observed only in the presence of NO_2. As little as 0.4 ppm of NO_2 was associated with pinking of turkey breast (T7), but higher levels were required for beef. Beef treated with 0.4 or 1.2 ppm of NO_2 was not pink, but roasts exposed to 2.5 or 4.2 ppm of NO_2 had a definite pink ring (Table 2). Panel scores for pink color intensity generally increased with increasing exposure to NO_2. Beef sample B6 (Figure 2) exposed to 4.2 ppm of NO_2 had the highest pink color score (4.7, very to extremely pink; Table 2).

The panelists were more sensitive to pink ring than was the Hunter color meter, probably because of the large (7 cm diameter) aperture of the meter. Multiple surface slices, each of slightly variable pinkness, were required to cover the large aperture. Beef samples B6 and B7 both had distinct pink rings, but only B6 had a significantly higher Hunter color *a* value than the control (Table 2). Beef samples sometimes had both surface and interior pinkness. The interior pinkness was not due to gas treatment, but rather to globin hemochromes that typically form in well-cooked meats

during anaerobic refrigerated storage (Ghorpade and Cornforth, 1993). However, the interior pinking faded rapidly after slicing, and panelists were able to easily distinguish between surface and interior pinking in samples that exhibited both.

All of the turkey samples treated with NO_2 (T5−T9) had noticeable pink ring (Table 2). Sample B6, treated with the highest level of NO_2, was the only sample to have significantly higher nitrosylhemochrome (cured meat pigment) than controls (Table 2).

DISCUSSION

In addition to CO and CO_2, burner exhaust is well-known to contain both NO and NO_2 (Miller and Bowman, 1989). In a flame, NO_2 is produced mainly from the reaction of NO with the hydroperoxy radical, HO_2, as follows, where atmospheric nitrogen is the source of nitrogen atoms:

$$NO + HO_2 \rightarrow NO_2 + OH^{\bullet} \qquad (1)$$
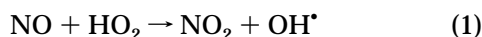
In natural gas burners, the primary paths for production of NO are via the *thermal* or *prompt* mechanisms (Miller and Bowman, 1989; Ahuja, 1994). Nitric oxide formed in the flame or postflame zone may diffuse back into the preflame zone. Relatively higher concentrations of HO_2 also exist in the preflame region, because it is at a relatively lower temperature than other regions of the flame. This favors production of NO_2 via eq 1. Generally, NO_2 is a transient species that is rapidly converted back to NO by reactions with hydrogen and oxygen radicals. However, due to quenching of these reactions in turbulent flames, NO_2 can be present in the burner exhaust (Miller and Bowman, 1989).

Of the burner emission gases, CO and NO are well documented as meat color reactive. Carbon monoxide (1−2%) imparts a bright red color to fresh meat surfaces, and thus its use has been proposed to increase color stability of fresh beef in retail display (El-Badawi et al., 1964; Gee and Brown, 1978a,b). A U.S. patent has been issued for use of NO as a meat curing agent (McBrady, 1968). Bacon slices exposed to 0.1% nitric oxide develop excellent cured color, with no nitrite residue (Ranken, 1973). Thus, it was initially surprising that neither CO nor NO caused surface pinking in experiment 2 of this study.
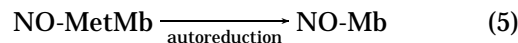
However, specific conditions are needed for these gases to act as meat pinking agents. Rather high CO concentrations (10 000−20 000 ppm) have been applied to fresh meats in color stability studies (El-Badawi et al., 1964; Gee and Brown, 1978a,b). Also, CO reacts primarily with fresh meat pigments. CO has little or no affinity for denatured globin hemichrome, the brown cooked meat pigment. Reduction of cooked meat surfaces with sodium hydrosulfite was required for binding of CO as denatured globin carbon monoxide hemochrome (Tappel, 1957). In fact, bright red, CO-treated fresh meat turns brown with cooking (Vahabzadeh et al., 1983), with release of up to 85% of ^{14}CO (Watts et al., 1978).

Nitric oxide has very low water solubility (Windholz et al., 1976). In a chamber initially containing only NO(g) and water at atmospheric pressure and 25 °C, only 56.3 ppm of NO dissolved in the water phase (Shank et al., 1962). Tidona et al. (1988) also found relatively high water solubility for NO_2 in sampling lines of combustion systems but almost no solubility of NO in liquid water. On the basis of this consideration alone, NO would be an unlikely candidate to cause pink ring, since at the low levels typical of gas ovens or smokehouses, NO would be unable to enter the aqueous meat system in sufficient quantity to cause pink ring at depths up to 1 cm from the surface. Nitrogen dioxide, however, reacts readily with water to produce nitrous and nitric acid (Shank et al., 1962):

$$2NO_2 + H_2O \rightarrow HNO_2 + HNO_3 \qquad (2)$$
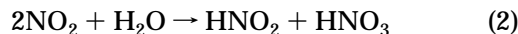
Nitric acid (HNO_3) or the nitrate ion produced via eq 2 probably has no influence on meat color, since muscle tissue is incapable of nitrate reduction to either nitrous acid (HNO_2) or NO, thus precluding the possibility of nitrosylmyoglobin (NO-Mb) formation (Walters and Taylor, 1964). However, nitrous acid produced at meat surfaces (eq 2) would be free to diffuse inward, where endogenous meat reductants, including myoglobin itself, may regenerate NO [Koizumi and Brown, 1971; review by Cornforth (1996)]. Nitric oxide binds to metmyoglobin, followed by rapid autoreduction to nitrosylmyoglobin, as follows (Killday et al., 1988):

$$Mb + HNO_2 \rightarrow MetMb + NO + H_2O \qquad (3)$$

$$NO + MetMb \rightarrow NO\text{-}MetMb \qquad (4)$$

$$NO\text{-}MetMb \xrightarrow{\text{autoreduction}} NO\text{-}Mb \qquad (5)$$

Given the relative inability of atmospheric NO to react with meat pigments, the effectiveness of gaseous NO for meat curing (McBrady, 1968; Ranken, 1973) may be explained by the fact that at high concentration in the presence of oxygen, NO rapidly reacts to form NO_2, along with the orange-brown color characteristic of this gas (Beckman, 1996):

$$2NO + O_2 \rightarrow 2NO_2 \qquad (6)$$
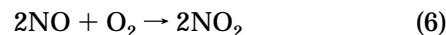
However, at very low NO concentrations, as in polluted air (or in the atmosphere of a gas oven), the reaction is much slower. NO may persist for hours in a polluted urban atmosphere. In atmospheric processes, the reaction of oxygen with two nitric oxides is considered to be a negligible source of NO_2 (Beckman, 1996). NO_2 is a deadly poison due to the rapid formation of nitric acid in the lung (eq 2). The resultant inflammation and edema are often fatal (Windholz et al., 1976). However, low concentrations of NO can be safely administered in the breathing circuit for patients with pulmonary hypertension, with only trace conversion to NO_2 (Frostell et al., 1991). Another example of the relatively benign nature of atmospheric NO is its lack of inhibitory effects on various bacteria, even at elevated pressure (40 psi). However, when 0.5−1.0% air was injected into the NO chamber, resulting in formation of 0.18−0.36% NO_2, a very significant reduction was observed in numbers of all bacteria (Shank et al., 1962).

Thus, it is apparent that gaseous NO, due to its low water solubility, has restricted entry into aqueous biological systems such as meat or vegetative bacteria. To affect meat color, NO must be present at a relatively high concentration in the presence of oxygen, allowing formation of NO_2 (eq 6), which enters the aqueous meat system as nitrous acid (eq 2). NO may then be regenerated within the meat system (eq 3), leading to formation of nitrosylmyoglobin (eqs 4 and 5) and then nitrosyl-

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hemochrome, the pink, cured meat pigment, upon application of heat (eq 7).

$$\text{NO-Mb} \xrightarrow{\Delta} \text{denatured NO-Mb} \qquad (7)$$

There has been only one previous study relating emission gases to meat pinking in gas ovens. Pool (1956) reported that turkeys developed distinctly pink surfaces when roasted while a vigorous stream of air mixed with either CO or NO was forced through an electric oven chamber. The CO or NO concentrations were estimated to be <1%. Even 0.1%, however, is equivalent to 1000 ppm, which is much higher than would normally occur in gas ovens (<150 ppm of CO, <10 ppm of NO). Also, the turkeys used by Pool (1956) were not skinless. The dehydrated skin may have excluded oxygen, preventing the pigment oxidation and browning that normally occurs during cooking of CO-treated meats (Vahabzadeh et al., 1983; Watts et al., 1978). The level of NO used by Pool (1956) was probably sufficiently high for reaction with oxygen to form NO_2 (eq 6), permitting reaction with meat pigments via nitrous acid as previously described (eqs 2−5).

CONCLUSIONS

Although both CO and NO are well-known meat color-reactive gases, their concentrations in modern gas ovens (<150 and <10 ppm, respectively) are too low to cause meat surface pinking. NO_2 was found to be the most potent pinking gas in gas ovens. Even though it is also present at very low levels (<10 ppm) in gas oven atmospheres, it caused pinking at <1 ppm on precooked turkey and at 2.5 ppm on beef roasts. NO_2 reacts with moist meat surfaces, producing nitrous acid, which diffuses inward, producing pink ring via the classic meat curing reactions of brines containing sodium nitrite. Meat surface pinking in gas ovens could be eliminated using the ULN burner, which, when operated at optimal efficiency, had NO_x emissions <1 ppm and NO_2 emissions <0.3 ppm.

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