#1563

2159

J H BROMLY CEng MInstE ARACI MIEAust,* F J BARNES MIEAust,*
R C R JOHNSTON BE MEngSc MIEAust† and L H LITTLE PhD‡

Nitrogen oxide emissions from unflued space-heaters

The levels of nitric oxide and nitrogen dioxide emitted by radiant and convective space heaters were measured. It was found that the NO_x emitted by the former was mainly NO_2. In the case of the convective heater, when operating in fresh air, the NO_x was mostly NO; however, when the air became vitiated, this changed radically

This short practical paper describes what has been considered worthy of attention in everyday practice. Publications and Conferences Committee will welcome short, practical papers on other topics to consider for publication.

1. Introduction

In recent years, as an energy saving measure, there has been a tendency to reduce air infiltration rates in dwellings and other buildings.[1,2] In view of this and increasing concern about the role of NO_2 in indoor pollution,[3–6] it was decided to investigate levels of NO_x ($NO + NO_2$) produced by typical unflued natural gas burning space-heaters.

It is recognized that a certain level of air vitiation (reduction of the oxygen content and corresponding increase in the nitrogen, carbon dioxide and water vapour concentrations) necessarily occurs when an unflued space-heater operates in a partially enclosed area. For this reason, some tests were conducted in a vitiation room to simulate such operation.

2. Experimental

2.1. Appliances

2.1.1. Radiant (infra-red) type heaters

Two different makes (three heaters in all) of this type were used in the tests. In this type of heater, which is widely utilized in domestic situations, the gas/primary air mixture enters at the back of a perforated ceramic tile and burns at or near the front surface.

2.1.1.1. Radiant heater A

Flueless fan-assisted heater, input rating 18 MJ/h.

2.1.1.2. Radiant heaters B1 and B2

Two flueless space-heaters of same make and model, not fan-assisted, input rating 11 MJ/h.

2.1.2. Convective type

This heater consists essentially of a bar burner, that is a tube into which the gas/primary air mixture is fed to burn as a series of premixed flames at ports along the length of the burner. In these tests a flueless convective fan-assisted heater of input rating 18 MJ/h was used.

*State Energy Commission of Western Australia.
†Department of Mechanical Engineering, University of Western Australia.
‡Department of Physical and Inorganic Chemistry, University of Western Australia.

2.2. Monitoring equipment

2.2.1. Carbon oxides

ADC** infra-red type 511 CO/CO_2 analyser.

2.2.2. Nitrogen oxides

CSI§ 1600 chemiluminescence analyser.

2.2.3. Calibration

The CO/CO_2 analyser was calibrated with primary gravimetric standard gas.[7] The NO_x meter was calibrated by standard gas for NO and by permeation tube for NO_2. Its accuracy was crosschecked using the Saltzman method.[8]

2.3. Sampling

2.3.1. Heater exit gases

In almost all cases, samples were initially drawn through stainless steel tubing followed by teflon tubing to the nitrogen oxides analyser and by PVC laboratory tubing to the carbon oxides analyser. When hot gases were being sampled directly from the heaters, the stainless steel tubing served to cool these sufficiently before entry into the other lines. In all cases, however, the hottest gases (approximately 250°C) were below temperatures at which stainless steel probes are reported[9] to distort results significantly and far below temperatures encountered in flame-probing experiments.[10,11] There was generally enough air dilution to overcome the problem of unwanted condensation in sampling lines, which is known to cause errors in nitrogen dioxide determinations.[9]

In one instance an all teflon sampling system was used briefly to confirm that contact with the stainless steel did not appreciably affect the results obtained from one of the radiant heaters.

2.3.2. Room atmosphere

In the case of room atmosphere gases, which were relatively cool, the samples were drawn directly into the teflon and PVC lines to the NO_x and CO/CO_2 analysers respectively.

2.4. Vitiation room

The room used for vitiation testing of the heaters has dimensions of 2.5 m × 3.1 m × 2.3 m (19 cubic metres volume). The door is fitted with a glass panel so that an appliance under test can be observed. Two movable

**The Analytical Development Company, Hoddesdon, England.
§Columbia Scientific Industries, Austin, Texas, USA.

TABLE 1 Fuel gas composition

Analysis by gas chromatography	
Component	**Mol percentage**
Nitrogen	0.77
Carbon dioxide	1.63
Methane	95.2
Ethane	1.7
Propane	0.39
iso-Butane	0.053
n-Butane	0.094
iso-Pentane	0.032
n-Pentane	0.032
Hexanes	0.043
Heptanes	0.046
Octanes	0.035
Calculated data	
Specific gravity	0.593 (relative to air)
Gross heating value	38.0 MJ/m³
Net heating value	34.3 MJ/m³
Wobbe index	49.3

TABLE 2 Radiant heater A (operated in fresh air)

Fan on

	Sampled exit gases				
Time from ignition (min)	**NO (ppm)**	**NO_2 (ppm)**	**CO (ppm)**	**CO_2 (%)**	**Ratios × 10^4 NO_2/CO_2**
5	<0.05	0.65	33	0.44	1.5
10	<0.05	0.7	29	0.45	1.6
15	<0.05	0.7	25	0.44	1.6

Fan off

	Sampled exit gases				
Time from ignition (min)	**NO (ppm)**	**NO_2 (ppm)**	**CO (ppm)**	**CO_2 (%)**	**Ratios × 10^4 NO_2/CO_2**
20	<0.05	1.4	58	0.88	1.6
25	<0.05	1.3	56	0.89	1.5
30	<0.05	1.3	59	0.94	1.4
35	<0.05	1.4	57	0.93	1.5
40	<0.05	1.4	56	0.95	1.5
45	<0.05	1.4	53	0.94	1.5
50	<0.05	1.45	53	0.92	1.6
55	<0.05	1.45	52	0.93	1.6
60	<0.05	1.4	51	0.90	1.6

vents are fitted, one in the ceiling and one 300 mm above the floor, which can be used to provide variable degrees of vitiation.

2.5. Reporting

All concentrations are reported on a volume/volume basis.

The carbon monoxide and carbon dioxide figures are always 'waterfree', as water vapour must be removed before the analyser.

As the vitiation room was not completely gas tight, ratios of the concentrations of minor components to carbon dioxide are used in some instances. It is assumed that there was no preferential diffusion of any species present. On this basis and because of their independence of dilution influences, the ratios of the concentrations of the nitrogen oxides components to carbon dioxide are taken as a quantifying measure in vitiation and other tests.

2.6. Fuel gas

In most of this test series, natural gas of a composition shown in Table 1 was used. The composition and calorific value of the gas did not vary appreciably over the duration of the tests.

In one test, high-purity methane and high-purity methane with nitric oxide added were used as fuel gases.

3. Results and discussion

3.1. Radiant heaters

3.1.1. Nonvitiated operation

3.1.1.1. Radiant heater A

Typical results of operation of this model with the heater's fan on and off are presented in Table 2.

With the fan on there is greater dilution of the combustion products. The ratios of the minor components to carbon dioxide remain practically unchanged.

The NO_x is seen to be mainly the more toxic NO_2.[12]

Essentially similar results were obtained when the exit gases of this heater, which were at approximately 150°C, were drawn directly into a teflon sampling line.

3.1.1.2. Radiant heaters B1 and B2

Tables 3 and 4 show typical results of running two of these heaters under nonvitiated conditions. From these tables, it is seen that the second type of radiant heater, like the first, produced a NO_x which consisted mainly of NO_2.

3.1.2. Radiant heaters operating in vitiated conditions

In these tests the vitiation room was sealed, as far as possible, and the heaters were allowed to operate under conditions of falling oxygen levels and increasing concentrations of inerts. From Tables 5 and 6, which respectively give the results of running the different types of

TABLE 3 Radiant heater B1 (operated in fresh air)

	Sampled exit gases						
Time from ignition (min)	**NO (ppm)**	**NO_2 (ppm)**	**CO (ppm)**	**CO_2 (%)**	**Ratios × 10^4 NO/CO_2**	**NO_2/CO_2**	**Ratio NO_2/NO**
0	0.09	0.73	9	0.75	0.12	0.97	8.1
5	0.12	0.80	9	0.82	0.15	0.98	6.7
10	0.16	0.73	7	0.79	0.20	0.92	4.6
15	0.15	0.74	7	0.81	0.19	0.91	4.9
20	0.10	0.69	7	0.78	0.13	0.88	6.9
25	0.10	0.70	7	0.76	0.13	0.92	7.0
30	0.12	0.72	9	0.80	0.15	0.90	6.0

TABLE 4 Radiant heater B2 (operated in fresh air)

	Sampled exit gases						
Time from ignition (min)	**NO (ppm)**	**NO_2 (ppm)**	**CO (ppm)**	**CO_2 (%)**	**Ratios × 10^4 NO/CO_2**	**NO_2/CO_2**	**Ratio NO_2/NO**
0	0.11	0.89	37	0.70	0.16	1.27	8.1
5	0.10	0.88	43	0.72	0.14	1.22	8.8
10	0.07	0.84	44	0.70	0.10	1.20	12.0
15	0.09	0.86	43	0.66	0.14	1.30	9.6

TABLE 5 Radiant heater A (in vitiation room)

Time from ignition	Sampled exit gases							Room atmosphere						
	NO	NO_2	CO	CO_2	Ratios × 10^4		Ratio	NO	NO_2	CO	CO_2	Ratios × 10^4		Ratio
(min)	(ppm)	(ppm)	(ppm)	(%)	NO/CO_2	NO_2/CO_2	NO_2/NO	(ppm)	(ppm)	(ppm)	(%)	NO/CO_2	NO_2/CO_2	NO_2/NO
15	0.11	1.75	105	1.33	0.08	1.3	16.0							
20								0.10	0.74	61	0.93	0.11	0.80	7.4
25	0.15	2.40	142	1.90	0.08	1.3	16.0							
30								0.12	1.15	82	1.23	0.10	0.93	9.6
35	0.16	2.75	175	2.28	0.07	1.2	17.2							
40								0.16	1.65	114	1.65	0.10	1.00	10.3
45	0.19	3.15	234	2.72	0.07	1.2	16.6							
50								0.20	2.07	155	2.10	0.10	0.99	10.4
55	0.21	3.45	320	3.17	0.07	1.1	16.4							
60								0.21	2.60	213	2.52	0.08	1.03	12.4
65	0.23	3.75	462	3.59	0.06	1.0	16.3							
70								0.24	2.85	286	2.95	0.08	0.97	11.9
75	0.25	3.95	1000	3.96	0.06	1.0	15.8							
80								0.26	3.15	440	3.37	0.08	0.93	12.1
85	0.35	4.00	1610	4.16	0.08	1.0	11.4							
Heater self extinguished														

TABLE 6 Radiant heater B1 (in vitiation room)

Time from ignition	Sampled exit gases							Room atmosphere						
	NO	NO_2	CO	CO_2	Ratios × 10^4		Ratio	NO	NO_2	CO	CO_2	Ratios × 10^4		Ratio
(min)	(ppm)	(ppm)	(ppm)	(%)	NO/CO_2	NO_2/CO_2	NO_2/NO	(ppm)	(ppm)	(ppm)	(%)	NO/CO_2	NO_2/CO_2	NO_2/NO
5	0.08	1.10	82	1.09	0.07	1.01	13.8	0.05	0.24	21	0.34	0.15	0.71	4.8
15	0.10	1.50	114	1.41	0.07	1.06	15.0	0.07	0.51	44	0.63	0.11	0.81	7.3
25	0.13	1.83	140	1.71	0.08	1.07	14.1	0.09	0.81	71	0.93	0.10	0.87	9.0
35	0.15	2.15	163	1.97	0.08	1.09	14.3	0.12	1.06	95	1.22	0.10	0.87	8.8
45	0.20	2.35	180	2.28	0.09	1.03	11.8	0.14	1.30	117	1.52	0.09	0.86	9.3
55	0.20	2.6	193	2.57	0.08	1.01	13.0	0.15	1.56	138	1.82	0.08	0.86	10.4
65	0.20	2.9	224	2.89	0.07	1.00	14.5	0.16	1.82	161	2.09	0.08	0.86	11.4
75	0.20	3.2	250	3.20	0.06	1.00	16.0	0.20	2.06	186	2.39	0.08	0.86	10.3
85	0.22	3.5	258	3.46	0.06	1.01	15.9	0.20	2.30	206	2.68	0.07	0.86	11.5
95	0.20	3.75	295	3.75	0.05	1.00	18.8	0.20	2.55	250	2.98	0.07	0.86	12.8
105	0.22	3.9	660	4.01	0.05	0.97	17.7	0.21	2.75	340	3.26	0.06	0.84	13.1
Heater self extinguished														

radiant heaters, it is seen that the predominance of nitrogen dioxide over nitric oxide continues under these conditions.

The samples from the room atmosphere were drawn through an all-teflon system, which eliminates the possibility of metal-catalysed conversion of NO to NO_2. This provided further evidence that the observed generation of NO_2 from radiant heaters was real and not a sampling probe artifact.

3.2. Convective heater

Only one convective heater was used in the tests. Unlike the radiant heaters, which are surface combustors, the flames in the convective heater are essentially 'free standing' and without significant impingement.

3.2.1. Nonvitiated operation

Table 7 gives the results of operating the convective heater in fresh air. It is seen that, in this case, NO is the predominant nitrogen oxide.

3.2.2. Operation of convective heater under vitiated conditions

Table 8 shows the effect of the vitiation level, expressed as the carbon dioxide content (which is common in the gas industry[13,14]), in the intake air.

TABLE 7 Convective space-heater (operating under nonvitiated conditions)

Fan off

Time from ignition	Sampled exit gases						
	NO	NO_2	CO	CO_2	Ratios × 10^4		Ratio
(min)	(ppm)	(ppm)	(ppm)	(%)	NO/CO_2	NO_2/CO_2	NO_2/NO
1	*	*	3	0.80	*	*	*
2	*	*	3	0.70	*	*	*
3	5	0.40	1	0.76	6.5	0.53	0.08
10	5	0.26	1	0.75	6.5	0.35	0.05

Fan on low

Time from ignition	Sampled exit gases						
	NO	NO_2	CO	CO_2	Ratios × 10^4		Ratio
(min)	(ppm)	(ppm)	(ppm)	(%)	NO/CO_2	NO_2/CO_2	NO_2/NO
10	1.8	0.08	1	0.23	7.9	0.35	0.04

*Instrument not stabilized.

TABLE 8 Effect of vitiation on the convective space-heater

Time from ignition	Intake air	Sampled exit gases						
	CO_2	NO	NO_2	CO	CO_2	Ratios × 10^4		Ratio
(min)	(%)	(ppm)	(ppm)	(ppm)	(%)	NO/CO_2	NO_2/CO_2	NO_2/NO
2	0.06	1.6	0.4					0.3
4	0.15	2.3	0.4					0.2
6	0.27	3.0	0.6					0.2
8	0.33	3.4	0.8					0.2
10	0.42	3.9	0.7					0.2
12	0.49	4.2	0.7					0.2
14	0.56	4.6	0.6					0.1
16	0.62	4.9	0.6					0.1
18	0.68	5.2	0.5					0.1
20	0.71	5.4	0.5					0.1
22	0.79	5.5	0.5					0.1
24	0.84	5.6	0.6					0.1
26	0.85	5.5	0.8					0.1
28	0.91	5.3	1.1					0.2
30	0.94	4.9	1.5					0.3
32	0.97	4.3	1.8	48	1.35	3.19	1.33	0.4
34	1.01	3.9	2.2					0.6
36	1.02	3.4	2.6					0.8
38	1.04	3.1	2.9					0.9
40	1.08	2.7	3.3					1.2
42	1.07	2.5	3.6					1.4
44	1.12	2.1	3.8	102	1.49	1.41	2.55	1.8
46	1.11	1.8	4.0					2.2
48	1.12	1.5	4.3					2.9
50	1.14	1.1	4.4					4.0
52	1.13	1.1	4.6					4.2

TABLE 9 Comparison of analysis methods (heaters operated under nonvitiated conditions)

	Saltzman		Analyser	
	NO (ppm)	NO_2 (ppm)	NO (ppm)	NO_2 (ppm)
Radiant heater A	Nil	1.0	0.03	0.74
Convective heater	3.2	1.5	3.2	1.2

It is seen from Table 8 that as the level of vitiation approaches 1% CO_2 there is a significant change in the nature of the NO_x. The initial increase in NO concentration over the first 24 minutes is considered to result from recycling of combustion gases. The subsequent change in the nature of the NO_x is attributed to the reduced intensity of the flame due to vitiation.

3.3. Tests on chemiluminescence analyser

The appearance of high levels of nitrogen dioxide in the combustion products was not expected. It was, therefore, decided to check the results obtained with the chemiluminescence analyser using an alternative method.

Table 9 shows the results obtained using the radiant heater A and the convective heater with the analyser and with the Saltzman method.[8] The tests were conducted simultaneously with exit gases initially passing through a common sampling line.

The results shown in Table 9 are regarded as representing acceptable agreement and confirming the presence of nitrogen dioxide. It is seen that, in this test, the level of nitrogen dioxide from the convective heater was considerably higher than the results reported in Table 7 where it operated under similar conditions. In other tests in which the convective heater operated in fresh air, it was found that the NO_2/NO ratio varied from essentially zero to 0.31. The result in Table 9, however, represents an unusually high excursion of the NO_2/NO ratio, which may have been due to an unintended recirculation of exit gases.

3.4. Tests burning methane spiked with nitric oxide

A mixture of approximately 400 ppm nitric oxide in high-purity methane was prepared and used to fuel the radiant heater A. The level of nitrogen dioxide in this mixture was less than 10 ppm.

It is evident from Table 10 that, while a large proportion of the NO was converted to NO_2, there was a big increase in the nitric oxide emitted by the heater, in comparison with the very low levels found when pure methane was used as the fuel.

The relationship between NO and NO_2 in radiant heaters is being further investigated.

4. Conclusion

From the results presented above, it is seen that the rate of generation of total nitrogen oxides by the radiant heaters was lower than that by convective heaters. This finding is consistent with other reports[15] and is attributed to lower combustion temperatures.

However, it was also found that the NO_x produced by the radiant heaters was quite different in nature from that produced by the convective heater. The former contained a greater proportion of the more toxic nitrogen dioxide.

The chemical nature of the nitrogen oxides produced by the radiant heaters was found to be essentially invariant with vitiation. In the case of the convective heater, however, vitiation was accompanied by a radical change from a predominance of nitric oxide over nitrogen dioxide to the reverse.

It seems that the cooler burning conditions which are present in surface combustors[15,16] favour the escape of

TABLE 10 Comparison of nitrogen oxides produced by radiant heater A burning high-purity methane and high-purity methane spiked with nitric oxide

Time from ignition	Sampled exit gases									
	High-purity methane fuel					Spiked high-purity methane fuel				
	NO	NO_2	CO_2	Ratios × 10^4		NO	NO_2	CO_2	Ratios × 10^4	
(min)	(ppm)	(ppm)	(%)	NO/CO_2	NO_2/CO_2	(ppm)	(ppm)	(%)	NO/CO_2	NO_2/CO_2
5	<0.05	0.96	0.59	<0.08	1.63	0.85	1.73	0.59	1.44	2.93
10	<0.05	0.96	0.59	<0.08	1.63	0.86	1.70	0.59	1.46	2.88
15						0.88	1.69	0.58	1.52	2.91

nitrogen dioxide. This appears to concur with the findings reported elsewhere[11,17,18] and may indicate that much of the early formed NO is converted to NO_2 by reaction with HO_2 radicals, which are present in the relatively cool combustion gases.[11,18] Conditions which are induced by higher levels of vitiation appear to have a similar effect.

It is evident that the nature of the NO_x produced by an unflued space-heater is strongly dependent on the type of heater and the conditions under which it operates. This is a significant feature of these appliances in respect to ventilation and requires further investigation.

5. Acknowledgments

The work described in this paper was conducted at the State Energy Commission of Western Australia's East Perth Gas Depot. The authors wish to thank the SEC (WA) for permission to publish these results and acknowledge the technical assistance of W D McClintock and R Rowland.

6. References

1. Prepared by BARNES F J. Review of rules for unflued room heaters. State Energy Commission of Western Australia Report ES16, 1982 (Feb).
2. Prepared by BROMLY J H and BARNES F J. Indoor pollution by oxides of nitrogen from unflued gas room heaters. State Energy Commission of Western Australia Report ES36, 1983 (Aug).
3. MELIA R J W, FLOREY C DU V, DARBY S C, PALMER E D and GOLDSTEIN B D. Differences in NO_2 levels in kitchens with gas or electric cookers. *Atmos Environ*, 1978, **12**, 1379–1381.
4. KELLER M D. Population studies of the health effects of atmosphere NO_2 exposure. *AGA Month*, 1981 (Jan) (American Gas Association).
5. JOHNSON D O and KURZYNSKE F R. Indoor air quality. *Gas Res Inst Dig*, 1982, **5**, 4–6.
6. ROTH H D and POST E. NO_2 and health effects: analysis of selected studies. Annu Rep (Nov 1980–Oct 1981), H Daniel Roth Associates Inc, Rockville MD, Oct 1982. GRI - 80/0112.
7. MILLER J E, CARROLL A J and EMERSON D E. Preparation of primary gravimetric standard gas mixtures for analytical instruments. US Bur Mines RI 6674, 1965.
8. Selected methods of measuring air pollutants. WHO Offset Publication No 24, 1976.
9. HILLIARD J C and WHEELER R W. Catalysed oxidation of nitric oxide to nitrogen dioxide. *Combust Flame*, 1977, **29**, 15–19.
10. DUTERQUE J, AVEZARD N and BORGHI R. Further results of nitrogen oxides production in combustion zones. *Combust Sci Technol*, 1981, **25**, 85–95.
11. JOHNSON G M, SMITH M Y and MULCAHY M F R. The presence of NO_2 in premixed flames. 17th symp. (int) on *Combustion*. Combustion Institute, 1979.
12. SMITH I. Nitrogen oxides from coal combustion—environmental effects. Report No ICTIS/TR10, Oct 1980. IEA Coal Research, London.
13. REED S B and WAKEFIELD R P. Vitiation of combustion air. *J Inst Gas Eng*, 1970, **10**, 77–92.
14. HARRIS J A and SOUTH R. Flame stability—principles and practice. *Gas Eng Manage*, 1978 (May), pp 153–74.
15. HARRIS M E, ROWE V R, COOK E B and GRUMER J. Reduction of air pollutants from gas burner flames. US Bur Mines Bull 653, 1970.
16. COLES K F and BAGGE L P. New developments in radiating heating systems. Inst Gas Eng, communication 839, 1970.
17. SCHEFER R W and SAWYER R F. Lean premixed recirculating flow combustion for control of oxides of nitrogen. 16th symp (int) on *Combustion*. Combustion Institute, 1977.
18. HARDGRAVES K J A, HARVEY R, ROPER F G and SMITH D B. Formation of NO_2 by laminar flames. 18th symp (int) on *Combustion*. Combustion Institute, 1981.

(*Paper received April 1984*)