Enclosure

U.S. DEPARTMENT OF COMMERCE
NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY
Gaithersburg, MD 20899

REPORT OF TEST
FR 3987

April 29, 1992

TOXICOLOGICAL EVALUATION OF THE COMBUSTION PRODUCTS FROM A THERMAL BARRIER MATERIAL DECOMPOSED UNDER FLAMING AND NONFLAMING CONDITIONS

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Submitted to:

Office of Nuclear Reactor Regulation
United States Nuclear Regulatory Commission
Washington, DC 20555

9208280254 XA

TOXICOLOGICAL EVALUATION OF THE COMBUSTION PRODUCTS FROM A THERMAL BARRIER MATERIAL DECOMPOSED UNDER FLAMING AND NONFLAMING CONDITIONS[1]

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ABSTRACT

The toxicity of a sample of the material used in nuclear power plants as a fire protection barrier for cable trays, was examined under both flaming and non-flaming conditions in the radiant heat smoke toxicity apparatus. The procedure was modified slightly to account for the long burning and decomposition time of this material. Carbon monoxide, CO_2, HCN, and O_2 concentrations were monitored in each test. Hydrogen chloride, HBr, HF and NO_x were measured initially and determined to be produced in insufficient quantities to warrant further monitoring. A total of eight LC_{50} values (based on animal tests) and their equivalent N-Gas values were determined for the various combinations of flaming or non-flaming conditions, for loaded or consumed masses, and for the deaths that occurred during the 30 minute exposures or for those that occurred during the 30 minute exposures plus the 14 day post-exposure observation periods. A comparison of the LC_{50} values based on consumed mass and within plus post-exposure deaths for the flaming or non-flaming modes showed the material sample to be about as toxic as Douglas fir or flexible polyurethane foam which were tested previously in the same apparatus. In the flaming mode, the N-Gas values indicate that the toxic gases monitored were probably responsible for the deaths that occurred. In the non-flaming mode, it appears that one or more additional gases or other factors are contributing to the toxicity. The intumescent char layer that remains following the 30 minute exposures was removed from the non-flaming test residues and heated at 50 kW/m^2 in a separate non-flaming test. Compared to the gas yields from the other non-flaming tests, the intumescent char generated more CO and CO_2 and an amount of HCN which fell within the mean and one standard deviation of the HCN generated from the complete samples.

Keywords: combustion products; flaming; inhalation; LC_{50}; N-Gas model; non-flaming; radiant heat; toxicology.

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1.0 INTRODUCTION

A sample of a material used in nuclear plants as a fire protection barrier for cable trays was provided to the National Institute of Standards and Technology (NIST) by the Office of Nuclear Reactor Regulation of the United States Nuclear Regulatory Commission (NRC) to determine the toxicity of the fumes emitted during thermal decomposition. The Fire Hazard Analysis group at NIST evaluated the toxicity of the material under both flaming and nonflaming laboratory conditions using a bench-scale radiant heat smoke toxicity procedure [1].[2]

2.0 MATERIALS AND METHODS

2.1 Materials

The material was designated by NRC as Exhibit #3, prefabricated subliming material approximately 25 mm (1 inch) thick and identified by invoice #3-91-006.

2.2. Gases

In all tests, chemical analyses were conducted to determine the concentrations of carbon monoxide (CO), carbon dioxide (CO_2), hydrogen cyanide (HCN), and oxygen (O_2). In some tests, hydrogen chloride (HCl), hydrogen fluoride (HF), hydrogen bromide (HBr) and total nitrogen oxides (NO_x) were also measured to determine if sufficient quantities would be generated to warrant further monitoring. Calibration gases (CO, CO_2, HCN) were commercially supplied in various concentrations in nitrogen. The concentrations of HCN in the commercially supplied cylinders were routinely checked by silver nitrate titration [2], since it is known that the concentration of HCN stored under these conditions will decrease with time. Nitric oxide (NO) in nitrogen, a standard reference material, was obtained from the Gas and Particulate Science Division, NIST.

Carbon monoxide and CO_2 were measured continuously during each test by non-dispersive infrared analyzers. Oxygen concentrations were measured continuously with a paramagnetic analyzer. Syringe samples (100 μL) of the chamber atmosphere were analyzed for HCN approximately every three minutes with a gas chromatograph equipped with a thermionic detector [3]. The concentration of NO_x was measured continuously by a chemiluminescent NO_x analyzer equipped with a molybdenum converter (set at 375°C) and a sampling rate of 25 mL/min. The change from a stainless steel converter to a molybdenum converter prevented interference from HCN. All combustion products and gases (except HCN, NO_x, and the halogen gases) that were removed for chemical analysis were returned to the chamber. The CO, CO_2, O_2 and NO_x data were recorded by an on-line computer every 15 seconds.

The halogen gases, HF, HCl, and HBr, were analyzed by ion chromatography. The combustion products were bubbled into 30 mL impingers containing 25 mL of 5 mM KOH at a rate of approximately 30 mL/min for the 30 minute tests. The flow was monitored every five minutes and averaged over the 30 minute run to determine the amount of gases collected. The resulting solution was analyzed for F^-, Cl^-, and Br^- by the modified method A-106 as described in reference [4]. In this modified method, the eluent was changed from a 2.5 mM lithium hydroxide solution to a 5 mM KOH

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[2] Numbers in brackets refer to references listed at the end of this report.

solution, a manual injector was used instead of an automatic injector, and a 590 programmable pump was employed instead of the 510 solvent delivery module.

For each test, the reported gas concentrations are the time-integrated average exposure values which were calculated by integrating the area under the instrument response curve and dividing by the exposure time [i.e., (ppm x min)/min or, in the case of O_2, (% x min)/min]. The calculated CO and CO_2 concentrations are accurate to within 100 ppm and 500 ppm, respectively. The calculated HCN concentrations are accurate to 10% of the HCN concentration. The calculated NO_x concentrations are accurate to 10% of the NO_x concentration.

2.3. Animals

Fischer 344 male rats, weighing 200-300 grams, obtained from Taconic Farms (Germantown, NY),[3] were used in these tests. They were allowed to acclimate to our laboratory conditions for at least 7 days prior to testing. Animal care and maintenance were performed in accordance with the procedures outlined in the National Institutes of Health's "Guide for the Care and Use of Laboratory Animals." Each rat was housed individually in suspended stainless steel cages and provided with food (Ralston Purina Rat Chow 5012) and water *ad libitum*. Twelve hours of fluorescent lighting per day were provided using an automatic timer. All animals (including the controls) were weighed daily from the day of arrival until the end of the 14 day post-exposure observation period.

2.4. Radiant Heat Smoke Toxicity Procedure

All exposures were conducted using the combustion system, the chemical analysis system, and the animal exposure system that were designed for the radiant heat smoke toxicity method [1]. Figures 1 and 2 are a diagram and schematic drawing of the experimental arrangement, respectively. To prepare the test samples, the sheet was cut into pieces of predetermined weight to obtain the desired test concentrations (defined as grams of material loaded or consumed in the furnace divided by the exposure chamber volume in cubic meters, i.e., g/m^3).

Tests were conducted in both flaming and non-flaming modes. The flaming mode tests were conducted at a flux of 50 kW/m^2 with a spark ignitor kept on until the flaming ceased. Tests to determine a non-flaming flux showed that this material would not flame even at 50 kW/m^2 as long as the spark ignitor was off. Therefore, the only difference between the flaming and non-flaming tests is that the spark ignitor was only used in the flaming mode.

The radiant heat smoke toxicity method is a closed design in which all the gases and smoke are kept in a 200 liter rectangular chamber for the duration of the test. The samples are decomposed in the furnace located directly below the animal exposure chamber such that all the combustion products from the test sample evolve directly into the chamber. Six rats are exposed in each test. Each animal

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[3] Certain commercial equipment, instruments, materials or companies are identified in this paper to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

is placed in a restrainer and inserted into one of six portholes located along the front of the exposure chamber such that only the heads of the animals are exposed. In the tests conducted to determine LC_{50} values, the weighed sample was placed onto a load cell in the combustion chamber and animal exposures started when the radiant lamps were turned on. Animal exposures continued for 30 minutes. In the first flaming test, it was noted that the material was still vigorously flaming at 15 minutes, the time at which the lamps would usually be turned off, since the thermal decomposition of most previously tested materials was complete by 15 minutes. Since the material was obviously still being decomposed, the decision was made to leave the radiant heat on until the end of the animal exposures to assure that the underlying layers would also be exposed. In addition to the continuous mass loss data from the load cell, the test specimens were weighed before and after the exposure to determine the total mass of material consumed.

The toxicological endpoint was the LC_{50} values, which were calculated based on the deaths that occurred either during the 30 minute exposures or the 30 minute exposure plus 14 day post-exposure observation period. The percentage of animals dying at each fire effluent concentration was plotted to produce a concentration-response curve from which the LC_{50} values were calculated. The LC_{50} in these cases is defined as the mass of material loaded in the furnace or consumed by the exposure divided by the animal exposure chamber volume (g/m^3) which caused 50% of the animals to die during the exposure only or during the exposure plus the 14-day post-exposure observation period. It is important to note that the lower the LC_{50} value, the greater the toxicity. The LC_{50} values and their 95% confidence limits were calculated by the statistical method of Litchfield and Wilcoxon [5].

For this study, eight LC_{50} values were determined for the conditions shown in Table 1. The N-Gas values (determined as shown in Section 2.5) that were equivalent to these LC_{50} values were also calculated.

Table 1. Test Conditions for LC_{50} Determinations

LC_{50} number	Conditions					
	Flaming	Non-Flaming	Mass Loaded	Mass Consumed	WE	WE & PE
1	X		X		X	
2	X		X			X
3	X			X	X	
4	X			X		X
5		X	X		X	
6		X	X			X
7		X		X	X	
8		X		X		X

WE. Deaths occurring within the 30 min exposure.
WE & PE. Deaths occurring during the 30 min exposure and the 14 day post-exposure period.

2.5. Determination of Unusual Toxicity

In previous studies, NIST has examined the toxicological interactions of six gases, CO, CO_2, HCN, reduced O_2, HCl and HBr, to provide enough data to predict the toxic potency (based on mass) and determine whether that toxicity is usual (i.e., the toxicity can be explained by the measured gases) or is unusual (i.e., additional gases are needed to explain the toxicity). These studies have resulted in the empirically derived N-Gas Model [6-9] shown in equation (1).

$$N\text{-}Gas\ Value = \frac{m[CO]}{[CO_2]-b} + \frac{[HCN]}{LC_{50}\ HCN} + \frac{21-[O_2]}{21-LC_{50}\ O_2} + \frac{[HCl]}{LC_{50}\ HCl} + \frac{[HBr]}{LC_{50}\ HBr} \quad (1)$$

where the numbers in brackets are the time-integrated average atmospheric concentrations during a 30 minute exposure period [(ppm x min)/min or for O_2 (% x min)/min]. If the N-Gas value equivalent to the LC_{50} value is approximately 1 ± 0.2 (95% Confidence interval), then the gases monitored are probably responsible for the deaths that occurred. If the N-Gas value equivalent to the LC_{50} value is below 0.8, then additional gases or toxicological factors are probably contributing to the toxicity and the combustion products from the material would be considered unusually toxic.

The N-Gas approach has been shown to work well in different combustion systems (radiant as well as convective heat sources; bench-scale as well as full-scale room tests) [11-14].

3.0 RESULTS AND DISCUSSION

3.1 Flaming Tests

3.1.1 Determination of Best Test Conditions

The one inch thick material was exposed to a radiant flux of 50 kW/m^2 with the spark ignitor on. In the first test (Table 2, Expt. A-1), the material began emitting smoke at 35 seconds, started flaming intermittently about 1.25 minutes, began burning intensely and consistently about 7 minutes, and continued burning until the radiant heat was turned off and the shutter between the combustion chamber and animal chamber was closed at 15 minutes. Analytical sampling continued for another 15 minutes. Examination of the sample at the end of the 30 minute exposure showed that the material had intumesced approximately 0.75 inches above the original height.

Since the material was still burning vigorously at 15 minutes and only 30% of the sample had decomposed by this time, a decision was made to allow the radiant heat to continue beyond the 15 minutes in future tests to permit as much of the material to decompose as possible during the 30 minute exposure. In this way, lower layers of the material would also be exposed to the heat. We considered the test sample fully decomposed when the CO concentrations had reached equilibrium. Table 2 indicates the times at which the samples experienced the various stages of smoke and flaming. Comparison of test A-1 with test A-3 in which the same amount of material was loaded into the furnace shows that in the first case (where the sample was exposed to 15 minutes of heat), only 30% of the sample was consumed; whereas, in the second case (where the sample was exposed to 30 minutes of heat), 53% was consumed. In all the other tests, between 53 and 56% of the sample was consumed. As would be expected from the increased mass consumed, the time-integrated concentrations of CO, CO_2, and HCN all increased and O_2 decreased. In most cases, the rate of CO generation was rapid during the flaming stage, slowed significantly after the flaming stopped and reached equilibrium shortly thereafter. The CO generation in the test in which the radiant heat was turned off and the shutter was closed at 15 minutes (Expt. A-1) and in an test where the radiant heat was kept on and the shutter was kept open for the full 30 minutes (Expt. R-3) is illustrated in Figure 3. Table 3 provides the time-integrated average concentrations. In these two tests, approximately the same amount of material was consumed, although almost twice as much of the material was loaded into the furnace in the 15 minute heat exposure. The results show that the CO generation was significantly greater when the radiant heat was kept on for the full 30 minutes. Comparison of the HCN generation in Expt. A-1 (radiant heat off and shutter closed at 15 minutes) and other tests (radiant heat on and shutter open for 30 minutes) shows that Expt. A-1 generated the lowest concentration of HCN even though the amount of mass consumed was similar to that of many of the other tests (Fig. 4 and Table 3).

To confirm that we were exposing the complete sample to the radiant heat, we also compared a thinner sample with a larger surface area (the thinner sample was prepared in our laboratory by shaving the thick sample) and a thicker sample with a smaller surface area (Fig. 5). The same amount was loaded in the furnace and exposed to the radiant heat for the full 30 minutes; about the same amount was consumed. The time-integrated average gas concentrations were about equal

(Table 4). Examination of the production of the gases over time indicated that the thinner sample started to generate the gases earlier (O_2 concentrations dropped earlier), but, eventually, they reached the same equilibrium levels; the one exception was the HCN concentration where the thicker sample seemed to generate a higher maximum level of HCN (Fig. 5).

Since we decided to leave the radiant heat on for the full 30 minutes, a control test without any material was conducted to examine the effects of just the heat from the radiant lamps and any stress that the animals may have experienced from undergoing the test conditions (Table 3, Expt. RC-1) The animals were exposed to the same conditions as the other flaming tests (except A-1), i.e., a radiant flux of 50 kW/m^2 with the shutter open for the full 30 minutes and the ignitor on for 20 minutes. In this control exposure, the average 30 minute temperature measured at animal positions 1, 3, and 6 was 26.5°C and the highest temperature was 28.8°C. These temperatures were slightly lower than those observed in some of the flaming material tests in which the average animal exposure temperatures ranged from 24.5 to 33°C and the highest temperatures ranged from 26.2 to 42.9°C. This heat control test appeared to have little or no effect on the animals. Their appearance and activity levels were fine following the exposure and their post-exposure weight gain was similar to the control animals which were kept in their cages and weighed daily (Fig. 6). The analytical chemical results from this control heat exposure show the increased CO_2 which comes from the animals' respiration and a small amount of NO_x which comes from the spark ignitor. These results indicate that keeping the heat on for the full 30 minutes did not add any undue stress on the animals.

These results supported our decision that leaving the radiant heat on for the full 30 minutes would provide a more realistic toxicological profile of the material's behavior in an actual fire. It would also allow us to use smaller sample sizes to produce a toxic atmosphere and prevent the possibility of overloading the system.

3.1.2 Determination of LC_{50} Values and Equivalent N-Gas Values

Table 3 presents the chemical and toxicological data for all the flaming tests except the thin shaved sample. Three tests were conducted for chemical analytical data only and five tests were conducted to determine the toxicological as well as the chemical data. Hydrogen chloride, HBr, HF, and NO_x were not routinely measured, since their concentrations were relatively low or not detectable.

Table 2. Smoke and Flaming Data from Flaming Tests

Mass		Test Type - number	Smoke noted	Flame intermittent	Flame steady	Flame out	Ignitor off	CO equilibrium
loaded (g/m^3)	consumed (g/m^3)		(min:sec)	(min:sec)	(min:sec)	(min:sec)	(min:sec)	(min)
225[a]	68	A-1	0:35	1:15	7:00	15:00	15:00	SGU @ 15 min
129	70	A-2	0:13	1:20	1:30	17:30	18:00	22
223	118	A-3	immediately	1:20	NR	16:40	17:05	SGU @ 30 min
94	53	R-2	NR	NR	1:45	17:10	17:40	SGU @ 30 min
114	63	R-3	NR	1:50	2:15	14:55	21:35	21
129[b]	69	R-4	0:13	0:40	1:30	7:25	9:20	23
129	71	R-5	0:15	0:58	1:55	21:20	20:50	22

a. In this test, the radiant lamps were shut off at 15 minutes. In all other tests, the radiant lamps were left on for the full 30 minutes.
b. Some of gases leaked out of chamber during test.
A. Analytical chemical test; no animals exposed.
NR. Not recorded.
R. Rat test; animals exposed and chemical analyses conducted.
SGU. Carbon monoxide concentrations were still increasing at time noted.

Table 3

Chemical and Toxicological Data from Material Sample Decomposed in the Flaming Mode at 50 kW/m^2 in Radiant Heat Smoke Toxicity System

Test type-number	Mass		Chemical Analytical Data[a]								Toxicological Data				
											# died / # tested		N-Gas Value		Day of death
	loaded (g/m^3)	consumed (g/m^3)	CO (ppm)	CO_2 (ppm)	HCN (ppm)	O_2 (%)	NO_x (ppm)	HCl (ppm)	HBr (ppm)	HF (ppm)	WE	WE & PE	WE	WE & PE	
A-1[b]	22[illegible]	68	770	17900	60	18.3	NM	10	ND	30	NA	NA	0.63	0.74	-
A-2	129	70	1530	22300	130	17.8	NM	10	ND	16	NA	NA	1.14	1.36	-
A-3	223	118	1790	26700	120	16.9	NM	trace	ND	30	NA	NA	1.23	1.43	-
RC-1	0	0	0	5000	6	20.4	30	NM	NM	NM	0/6	0/6	0.07	0.08	-
R-2	94	53	1100	20400	90	18.1	NM	NM	NM	NM	3/6	3/6	0.83	0.98	-
R-3	114	63	1230	19400	120	18.3	5	NM	NM	NM	5/6	6/6	0.98	1.17	1
R-4[d]	129	69	490	8700	80	19.9	NM	NM	NM	NM	4/6	6/6	0.56	0.69	2,11
R-5	129	71	1110	23400	100	17.7	10	NM	NM	NM	5/6	5/6	0.92	1.08	-

a. Time-integrated average concentrations.
A. Analytical chemical test, no animals exposed.
b. Shutter on combustion system, radiant heat and ignitor were turned off at 15 minutes even though material was still flaming vigorously.
R. Test in which both analytical chemical and animal exposure data were collected.
C. Control Test with animals to determine effect of heat; no sample was decomposed.
d. Gases leaked from exposure chamber; sample flamed only until 7:25 min:sec; whereas, in all other tests, the shortest time at which the material stopped flaming was 1[illegible]:55 min:sec.
NA. Not applicable.
ND. Not detected.
NM. Not measured.
WE. Within exposure
WE&PE Within exposure plus post-exposure.

Table 3

Chemical and Toxicological Data from Material Sample Decomposed in the Flaming Mode at 50 kW/m^2 in Radiant Heat Smoke Toxicity System

Test type-number	Mass		Chemical Analytical Data[a]								Toxicological Data				
	loaded (g/m^3)	consumed (g/m^3)	CO (ppm)	CO_2 (ppm)	HCN (ppm)	O_2 (%)	NO_x (ppm)	HCl (ppm)	HBr (ppm)	HF (ppm)	# died / # tested		N-Gas Value		Day of death
											WE	WE & PE	WE	WE & PE	
A-1[b]	225	68	770	17900	60	18.3	NM	10	ND	30	NA	NA	0.63	0.74	-
A-2	129	70	1530	22300	130	17.8	NM	10	ND	16	NA	NA	1.14	1.36	-
A-3	223	118	1790	26700	120	16.9	NM	trace	ND	30	NA	NA	1.23	1.43	-
RC-1	0	0	0	5000	6	20.4	30	NM	NM	NM	0/6	0/6	0.07	0.08	-
R-2	94	53	1100	20400	90	18.1	NM	NM	NM	NM	3/6	3/6	0.83	0.98	-
R-3	114	63	1230	19400	120	18.3	5	NM	NM	NM	5/6	6/6	0.98	1.17	1
R-4[d]	129	69	490	8700	80	19.9	NM	NM	NM	NM	4/6	6/6	0.56	0.69	2,11
R-5	129	71	1110	23400	100	17.7	10	NM	NM	NM	5/6	5/6	0.92	1.08	-

a. Time-integrated average concentrations.
A. Analytical chemical test, no animals exposed.
b. Shutter on combustion system, radiant heat and ignitor were turned off at 15 minutes even though material was still flaming vigorously.
R. Test in which both analytical chemical and animal exposure data were collected.
C. Control Test with animals to determine effect of heat; no sample was decomposed.
d. Gases leaked from exposure chamber; sample flamed only until 7:25 min:sec; whereas, in all other tests, the shortest time at which the material stopped flaming was 12:55 min:sec.
NA. Not applicable.
ND. Not detected.
NM. Not measured.
WE. Within exposure
WE&PE Within exposure plus post-exposure.

Table 4

Comparison of Chemical and Toxicological Data from the Material Sample Cut into Thick, Smaller Surface Areas and Thin, Larger Surface Areas and Decomposed in the Flaming Mode

Test type-number	Mass		Size		Chemical Analytical Data[a]								N-Gas Value	
	loaded (g/m^3)	consumed (g/m^3)	thickness (cm)	surface area (cm^2)	CO (ppm)	CO_2 (ppm)	HCN (ppm)	O_2 (%)	NO_x (ppm)	HCl (ppm)	HBr (ppm)	HF (ppm)	WE	WE & PE
Thin Sample	130	72	0.6	34	1700	28600	120	16.8	NM	NM	NM	NM	1.19	1.38
A-2	129	70	3.0-3.2	8.6	1530	22300	130	17.8	NM	10	ND	16	1.14	1.35

a. Time-integrated average concentrations.

Table 5 gives the LC_{50} values and their equivalent N-Gas values based on tests in Table 3. Animals that survived the exposures experienced difficulty breathing, were gasping loudly, and had extensive mucus discharges from their noses and mouths. Some exhibited tremors. Since there were few post-exposure deaths, the LC_{50} values were essentially the same for the deaths that occurred during the 30 minutes and those that included both within and post-exposure deaths. One death occurred as late as 11 days post-exposure. The LC_{50} value based on the mass loaded in the furnace was 94 g/m^3 for the within and within plus post-exposure and the LC_{50} value based on mass consumed was 53 g/m^3. At this mass (either loaded or consumed), the N-Gas values were 0.90 for the within exposure deaths and 1.07 for the within plus post-exposure deaths. Both of these values are in the range where one would expect some deaths to occur; an indication that the gases monitored are probably the gases responsible for the deaths. The slightly lower N-Gas value for the within exposure deaths may be due to the high levels of HCN which occur during the latter half of the exposures (Fig. 4) and which are not obvious from the time-integrated average concentrations. Table 6 lists both the time-integrated average and the maximum HCN concentrations.

The N-Gas values equivalent to the LC_{50} values were calculated a second time excluding Expt. A-3 which looked as though this large sample loading could have overloaded the system (compare HCN generation of Expt. A-3 with A-2 in Table 6). The results of the N-Gas calculations without this point are shown in Table 5 and indicate that the N-Gas values are about the same as when the calculation included Expt. A-3.

Table 5

LC$_{50}$ Values, Confidence Limits and Equivalent N-Gas Values for the Material Sample Decomposed in the Flaming Mode

Conditions	LC$_{50}$ (g/m^3)	95% Confidence Limits (g/m^3)	N-Gas Value[a]	N-Gas Value[b]
Mass loaded WE	94	77 - 114	0.90	0.84
Mass loaded WE & PE	94	78 - 113	1.07	1.00
Mass consumed WE	53	45 - 63	0.90	0.85
Mass consumed WE & PE	53	45 - 63	1.07	1.00

a. N-Gas value at the LC$_{50}$ based on a least squares linear regression analysis of mass (loaded or consumed) vs. N-Gas value for tests A-2, A-3, R-2, R-3, and R-5 in Table 3. Other tests not used for reasons listed in legend of Table 3.

b. N-Gas value at the LC$_{50}$ based on a least squares linear regression analysis of the mass (loaded or consumed) vs. the N-Gas value for all tests used in a. except A-3 which was eliminated from the calculation due to a possible overload condition.

WE: Values based on animals that died during the 30 minute exposures.

WE & PE: Values based on animals that died during the 30 minute exposures plus the 14 day post-exposure observation period.

Table 6. Hydrogen Cyanide Concentrations in Flaming Tests

Test type-Number	Mass		HCN	
	loaded (g/m^3)	consumed (g/m^3)	time-integrated average (ppm)	maximum (ppm)
A-1	225	68	60	90
A-2	129	70	130	300
A-3	223	118	120	300
RC-1	0	0	6	7
R-2	94	53	90	150
R-3	114	63	120	290
R-4	129	69	80	160
R-5	129	71	100	190

3.2 Non-Flaming Tests

3.2.1 Determination of the Non-Flaming Flux

To determine the flux at which the non-flaming tests should be conducted, we started by examining a flux of 25 kW/m^2 without the spark ignitor (Table 7, Expt. A-1). No flaming occurred and only 26% of the mass loaded (151 g/m^3) was consumed in the 30 minute exposure. As in the flaming mode, the material also intumesced. The concentrations of the gases were low providing N-Gas values of 0.09 (within exposure) or 0.11 (within exposure plus post-exposure). These extremely low N-Gas values indicated that we were not close to a fire effluent concentration that would be lethal to the rats.

The next flux tested was 35 kW/m^2 (Table 7, Expt. A-2). No flaming was observed, 45% of the mass loaded (154 g/m^3) was decomposed, and the N-Gas values were 0.27 (within exposure) and 0.35 (within exposure plus post-exposure). Again, these values indicated that these fire atmospheres would not be very toxic.

We then tested a flux of 50 kW/m^2, which is the same as that used for the flaming combustion mode, except without the spark ignitor (Table 7, Expt. A-3). No flaming occurred, 52% of the mass loaded (159 g/m^3) decomposed, and the N-Gas values were 0.56 and 0.72 for the within exposure and the within exposure plus post-exposure, respectively. As expected, the highest flux (50 kW/m^2) generated the greatest concentrations of gases. The effect of flux on the evolution of HCN over time is illustrated in Fig. 7.

Two more analytical tests at higher mass loadings were conducted to try to achieve higher N-Gas values. However, even though the amount loaded into the furnace was doubled, the concentrations of the gases did not change very much and the final N-Gas values were about the same or lower (Table 7, compare Expt. A-4 and A-5 with A-3). In these tests, it appeared that mass loadings above 200 g/m^3 or consumed masses above 100 g/m^3 overload the system.

3.2.2 Determination of LC$_{50}$ Values and Equivalent N-Gas Values

The first animal exposure (Table 7, Expt. R-9) was conducted with a mass loading of 607 g/m^3 in an effort to achieve higher N-Gas values. At this loading, about 30% of the material was consumed and we obtained N-Gas values of 0.77 (within exposure) and 0.96 (within plus post-exposure). At these N-Gas values, we would expect no deaths within exposure and only some deaths post-exposure. However, all of the animals died during the 30 minute exposure at times ranging from 16.5 to 27 min; an indication that the material is probably generating a toxic gas that we are not taking into account with our N-Gas equation.

The non-flaming LC$_{50}$ values, their 95% confidence limits and their equivalent N-Gas values are given in Table 8. The N-Gas values equivalent to the LC$_{50}$ values are calculated from a least squares linear regression analyses of individual test N-Gas values vs. mass (loaded or consumed) from Expts. R-1 through R-9. To determine if there was any difference due to a possible overload of the system from sample sizes above 200 g/m^3, these values were also calculated from a least squares linear regression analyses of individual test N-Gas values vs. mass (loaded or consumed) from Expts. R-1 through R-6 in Table 7. These results show that in the non-flaming mode, the N-Gas values which are equivalent to the LC_{50} values (regardless of whether the possible overload was considered) are lower than those expected if the gases in the model were the only gases contributing to the toxicity.

Many of the animals that survived the 30 minute exposures had difficulty breathing (were gasping for breath) and had brownish, watery discharges from their mouths. Some exhibited convulsions or tremors. Eight animals died beyond 24 hours following the exposures and three died as late as 8 days post-exposure (Figs. 8 and 9). These post-exposure deaths beyond 24 hours also indicate that gases other than those considered in the N-Gas Model or additional factors are probably contributing to the toxicity.

As in the flaming tests, the HCN continued to increase during the last 15 minutes of exposure (Fig. 10). The time-integrated average HCN concentrations do not reflect the high maximum levels reached towards the end of the exposures (Table 9). Although not specifically examined, the possibility exists that the animal deaths are resulting from the high levels achieved during the latter half of the exposures. The N-Gas model is based on steady-state pure and mixed gas exposures. Additional research may be needed to examine the effects of continuously increasing concentrations.

Table 7. Chemical and Toxicological Data from the Material Sample Decomposed in the Non Flaming Mode in Radiant Heat Smoke Toxicity System

Test type - number	Flux (kW/m^2)	Mass		Chemical Analytical Data[a]					Toxicological Data				
		Loaded (g/m^3)	Consumed (g/m^3)	CO (ppm)	CO_2 (ppm)	HCN (ppm)	O_2 (%)	NO_x (ppm)	# died / # tested		N-Gas Value		Day of death
									WE	WE & PE	WE	WE & PE	
A-1	25	151	39	45	1350	15	21.1	4	NA	NA	0.09	0.11	NA
A-2	35	154	69	130	2050	45	20.7	2	NA	NA	0.27	0.35	NA
A-3	50	159	83	490	4210	90	20.5	3	NA	NA	0.56	0.72	NA
A-4	50	299	120	660	3400	80	20.4	NM	NA	NA	0.55	0.68	NA
A-5	50	313	130	480	3090	55	20.5	3	NA	NA	0.38	0.47	NA
R-1	50	52	30	370	4940	70	20.4	NM	1/6	3/6	0.44	0.55	8,8
R-2	50	55	31	290	5100	55	20.3	NM	0/6	1/6	0.36	0.44	8
R-3	50	56	33	280	5110	60	20.4	NM	0/6	2/6	0.37	0.46	1,2
R-4	50	76	43	410	5530	60	20.2	NM	0/6	6/6	0.42	0.52	1,1,1,2,2,3
R-5	50	102	56	410	5340	100	20.5	NM	2/6	6/6	0.60	0.77	1,1,1,6
R-6	50	152	81	520	6840	125	20.1	NM	2/6	6/6	0.76	0.96	1,1,1,1
R-7	50	203	107	580	7420	120	20.2	NM	5/6	6/6	0.75	0.96	0
R-8	50	229	110	470	6850	60	20.2	NM	4/6	6/6	0.41	0.51	1,1
R-9	50	607	178	880	6930	115	20.0	NM	6/6	6/6	0.77	0.96	-

a. Time-integrated average concentrations; HCl, HBr, and HF were not measured in these tests.
A. Analytical chemical test, no animals exposed.
R. Test in which both analytical chemical and animal exposure data were collected.
NA. Not applicable.
NM. Not measured.
WE. Within exposure.
WE&PE. Within exposure plus post-exposure.

Table 8

LC_{50} Values, Confidence Limits and Equivalent N-Gas Values for the Material Sample Decomposed in the Non-Flaming Mode

Conditions	LC_{50} (g/m^3)	95% Confidence Limits (g/m^3)	N-Gas Value[a]	N-Gas Value[b]
Mass loaded WE	138	99 - 193	0.52	0.71
Mass loaded WE & PE	69	55 - 87	0.60	0.55
Mass consumed WE	72	54 - 96	0.54	0.68
Mass consumed WE & PE	42	32 - 55	0.58	0.58

a. N-Gas value at the LC_{50} based on a least squares linear regression analysis of mass (loaded or consumed) vs. N-Gas value for tests R-1 through R-9 in Table 7.

b. N-Gas value at the LC_{50} based on a least squares linear regression analysis of the mass (loaded or consumed) vs. the N-Gas value for tests R-1 through R-6 in Table 7. Tests R-7, R-8, and R-9 were eliminated from calculation due to possible overload condition.

WE: Values based on animals that died during the 30 minute exposures.

WE & PE: Values based on animals that died during the 30 minute exposures plus the 14 day post-exposure observation period.

Table 9. Hydrogen Cyanide Concentrations in Non-Flaming Tests

Test type - number	Mass		HCN	
	loaded (g/m^3)	consumed (g/m^3)	time-integrated average (ppm)	maximum (ppm)
A-1[a]	151	39	15	28
A-2[b]	154	69	45	86
A-3	159	83	90	175
A-4	299	120	80	196
A-5	313	130	55	227
R-1	52	30	70	126
R-2	55	31	55	88
R-3	56	33	60	109
R-4	76	43	60	124
R-5	102	56	100	206
R-6	152	81	125	254
R-7	203	107	120	337
R-8	229	110	60	186
R-9	607	178	115	277

Flux level was 50 kW/m^2 except where noted. Flaming tests had the spark ignitor on; whereas, non-flaming tests were conducted without the spark ignitor.

a. Flux level was 25 kW/m^2

b. Flux level was 35 kW/m^2

3.2.3 Examination of the Intumescent Material

In 1985, we found that heating the charred residues from a flexible polyurethane foam that had been thermally decomposed in the non-flaming mode generated significant quantities of HCN [15]. Since the intumescent char layer from the NRC material sample increased as the HCN was generated, the question arose as to whether the HCN was produced by the intumescent char layer. A test was conducted in which 194 g/m^3 of the intumescent char layers (including the imbedded mesh) that remained following a number of 30 minute non-flaming tests were combined and exposed to the non-flaming conditions (radiant heat of 50 kW/m^2 for 30 minutes, no ignitor). The amount consumed was 29 g/m^3. Fig. 11 shows the generation of CO, CO_2, HCN, and the reduction in O_2 over time (two of the HCN points appear to be the result of the obstruction of the sampling syringe and are, therefore, not connected to the main curve). The yields of the gases from this test of the intumescent material and from the other tests on the complete material are given in Table 10. These results show that the intumescent char layer produces yields of CO and CO_2 which are greater than those produced by the whole material. Yields of HCN are within one standard deviation of the mean ($x = 0.0029 \pm 0.0010$ g/g) of the yields from the whole material.

Table 10
Comparison of Gas Yields from the Intumescent Char Layer and the Whole Sample Decomposed in the Non-Flaming Mode.

Test	Gas Yields (g/g)		
	CO	CO_2	HCN
Intumescent Char	0.088	0.868	0.0023
A-3	0.017	0.174	0.0022
A-4	0.018	0.121	0.0017
A-5	0.011	0.094	0.0019
R-1	0.028	0.548	0.0046
R-2	0.021	0.510	0.0030
R-3	0.021	0.500	0.0036
R-4	0.021	0.399	0.0031
R-5	0.018	0.307	0.0039
R-6	0.019	0.288	0.0033
R-7	0.019	0.240	0.0034
R-8	0.014	0.221	0.0018
R-9	0.014	0.146	0.0017

3.3 Comparison of Toxicity of NRC Material Sample and Other Materials

A number of materials have been examined by the radiant heat smoke toxicity methodology [1]. These materials (other than the material tested for this report) have been examined in the flaming mode in which they were exposed to a radiant heat flux of 50 kW/m^2 for 15 minutes. For most of these materials, 15 minutes was sufficient to decompose the sample and heating the material any longer would not have generated any additional gases. For the NRC sample material to be toxic in the 15 minute exposure time, we would have had to increase the sample size and we ran the risk of overloading the system. A larger sample size and a shorter exposure time would have generated a larger LC_{50} value and make the material appear less toxic than with a smaller sample size and longer exposure time as used in these tests. The lower the LC_{50} value, the more toxic the material. Comparison of the values in Table 11 indicates that the sample material is one of the least toxic of the materials examined.

Table 11. Comparison of LC_{50} Values for Various Materials

Material	LC_{50}[a] (g/m^3)	
	Value	95% Confidence Limits
NRC Sample	53	45 - 63
NRC Sample - (Non-flaming)	42	32 - 55
Douglas fir	56	54 - 57
Rigid Polyurethane Foam	22	21.6 - 22.2
PVC	26	21 - 31
Flexible Polyurethane Foam	52	46 - 59
Melamine Polyurethane Foam	13	10 - 16
Vinyl Fabric	32	28 - 37
Vinyl Fabric over Melamine Polyurethane Foam	26	24 - 28

a. LC_{50} values in this table are based on the mass of consumed material (radiant heat flux was 50 kW/m^2 and the mode was flaming except where noted) that caused 50% of the rats to die during the exposures and the 14 day post-exposure observation period (WE & PE).

4.0 CONCLUSIONS

1. The LC_{50} value of the sample material decomposed in the flaming mode was compared to the LC_{50} values of other materials tested in the radiant heat smoke toxicity apparatus and appears to be among the least toxic.

2. The LC_{50} value of the sample material decomposed in the non-flaming mode also indicates a relatively low toxicity compared to materials decomposed in the flaming mode.

3. The monitored gases (CO, CO_2, HCN, and reduced O_2) generated in the flaming mode appear to account for the toxicity produced.

4. The monitored gases (CO, CO_2, HCN, and reduced O_2) generated in the non-flaming mode appear to account for only 55 to 70% of the toxicity. Therefore, one or more additional gases or other factors may need to be considered when determining the gases or factors responsible for the toxicity.

5. The animal deaths occurring beyond 24 hours following the non-flaming exposures also indicate an additional toxic factor which acts during the post-exposure period.

6. When heated in the non-flaming mode, the intumescent char layer generates higher yields of CO and CO_2 and about the same amount of HCN as the whole material.

5.0 ACKNOWLEDGEMENTS

The authors are grateful for the help of Ms. Maya Paabo who performed the analytical chemical measurements in some of the tests and Mr. Ronald McCombs who assisted in the tests, prepared the animal weight graphs, and cared for the animals.

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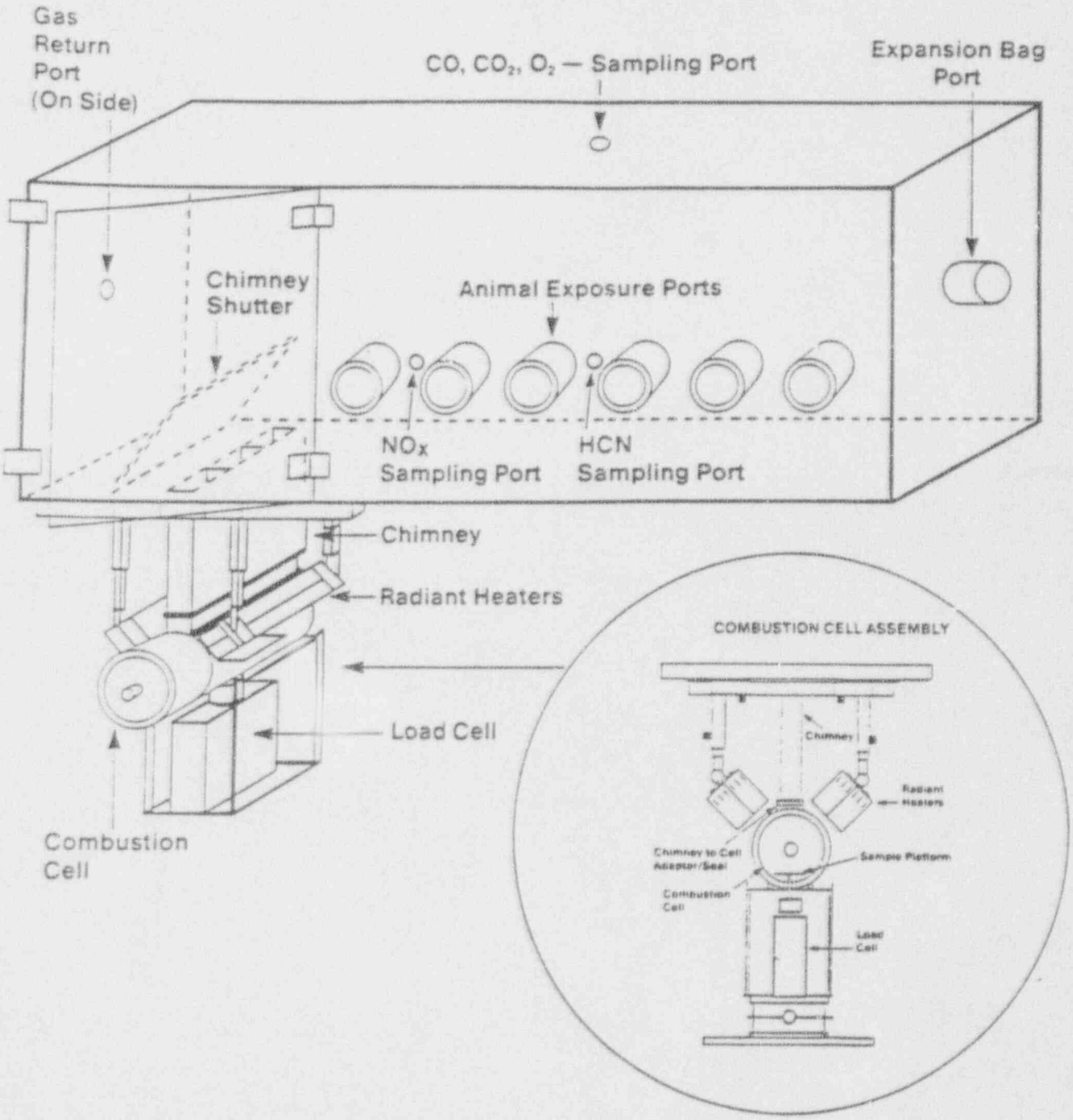

Figure 1. Radiant Smoke Toxicity Apparatus with insert showing radiant furnace.

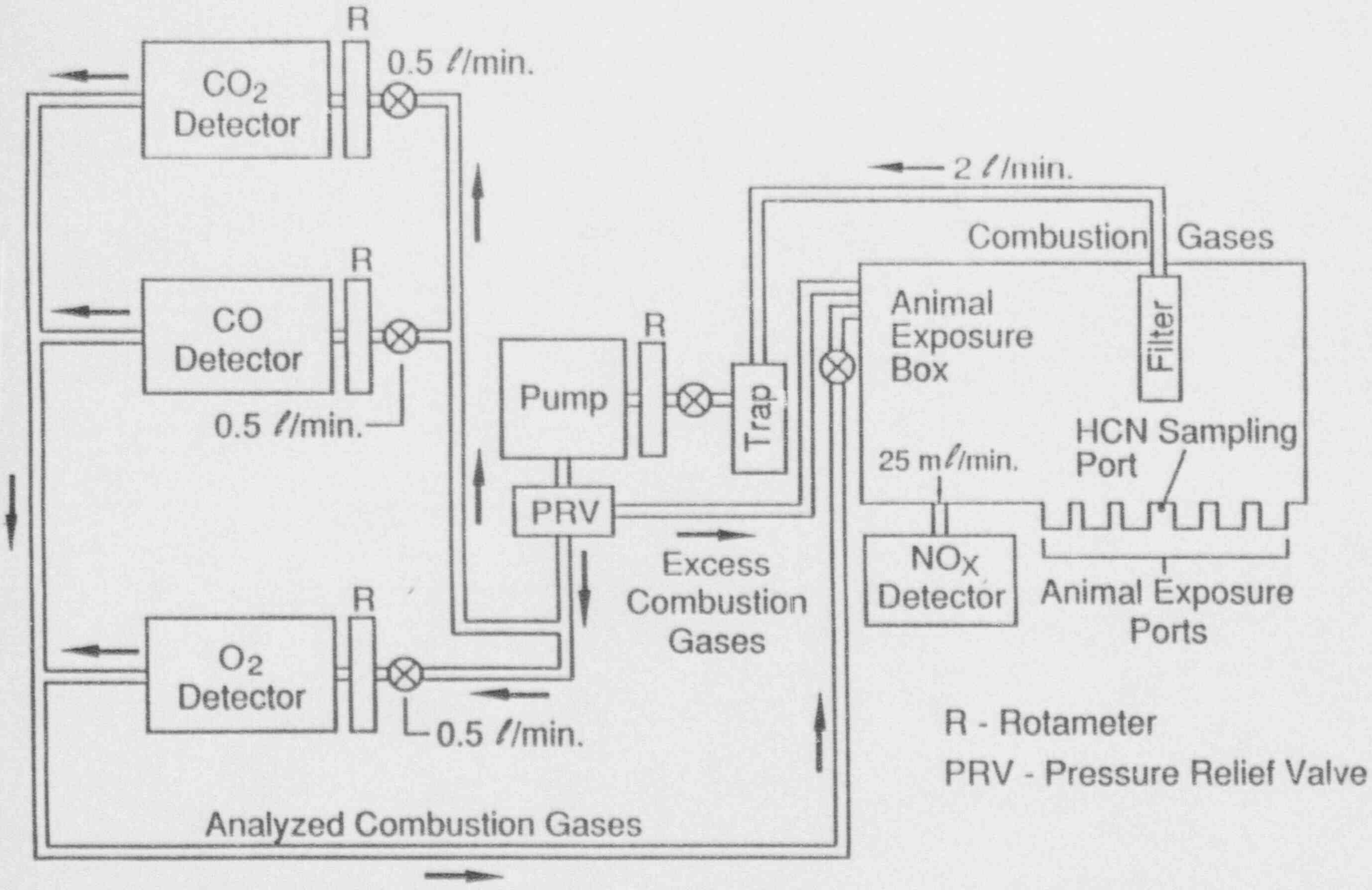

Figure 2. Schematic of Radiant Smoke Toxicity Apparatus showing chemical analytical instrumentation.

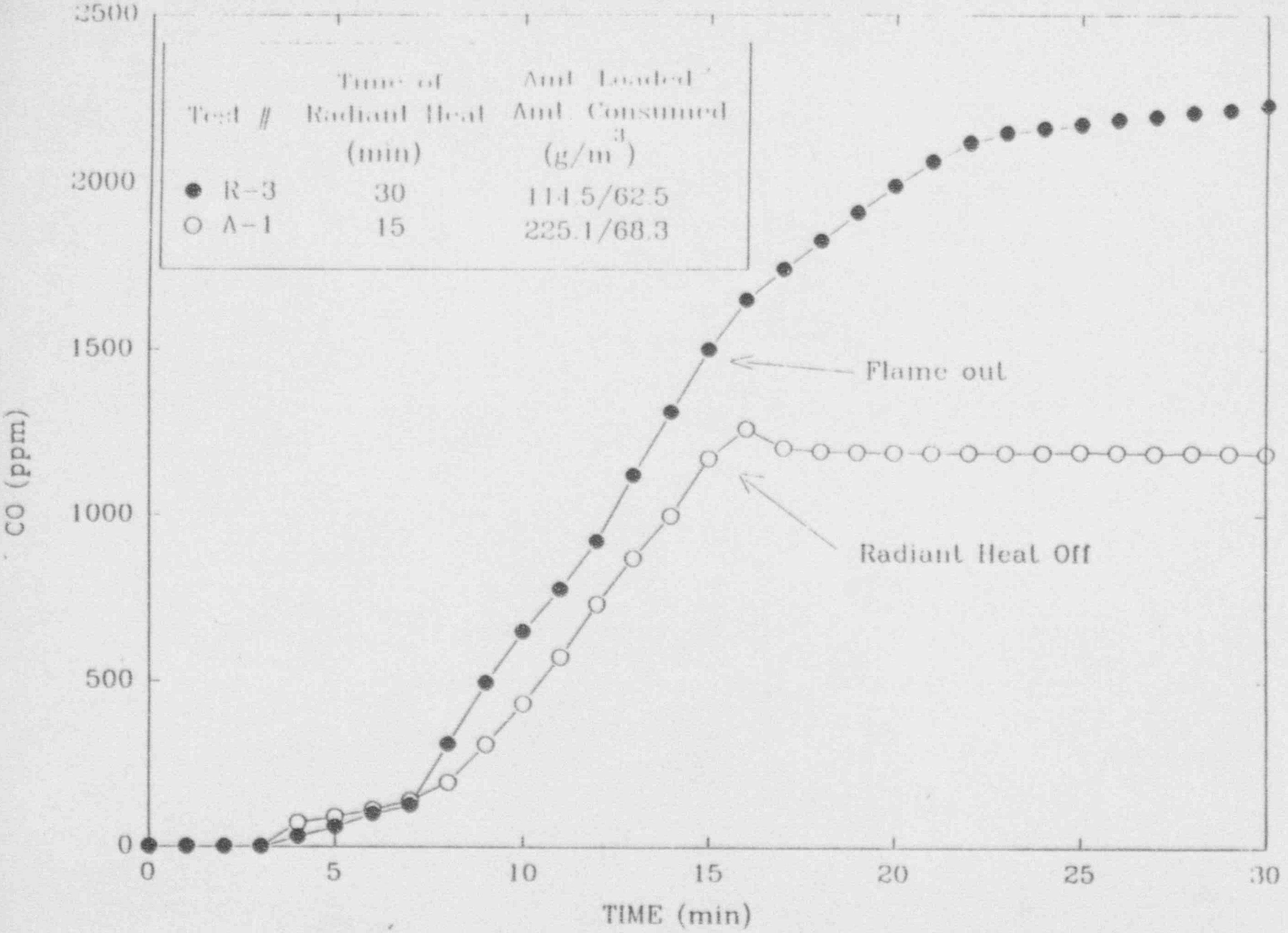

Figure 3. Effect of increased heating time on monoxide generation from sample decomposed in flaming mode.

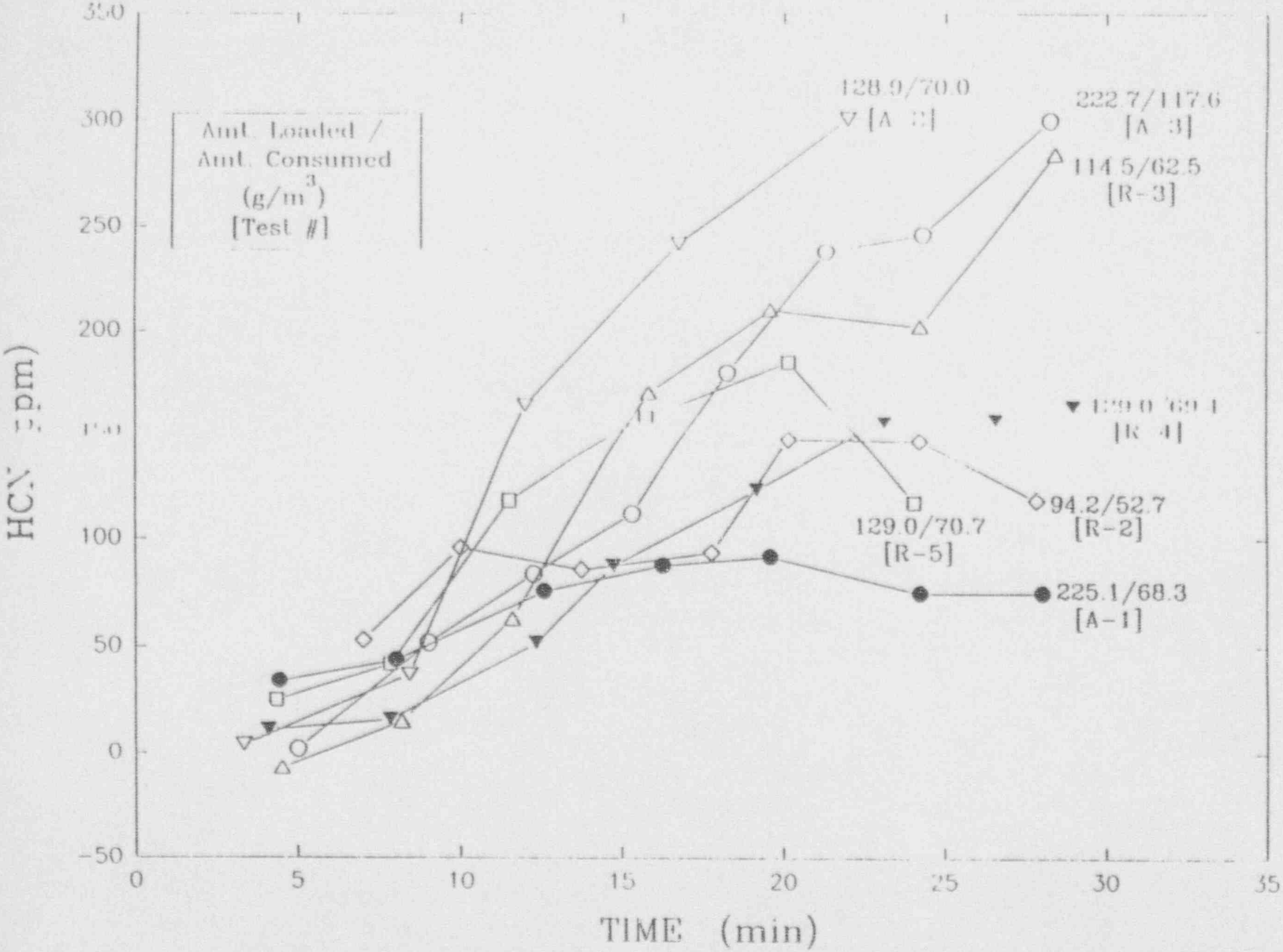

Figure 4. Hydrogen cyanide generation from samples decomposed in flaming mode.

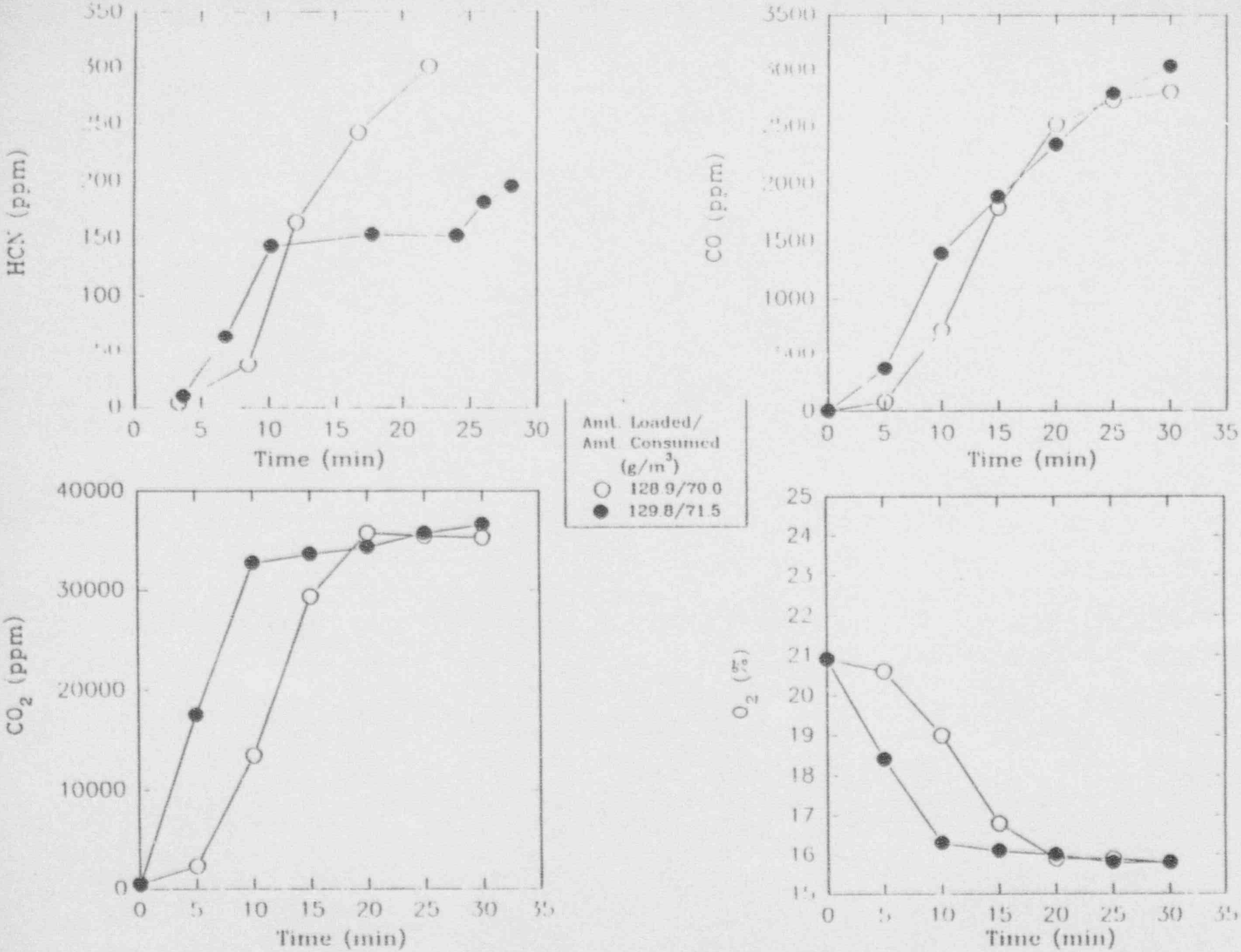

Figure 5. Comparison of gas generation from a thick, smaller surface area and a thin, larger surface area sample decomposed in the flaming mode.

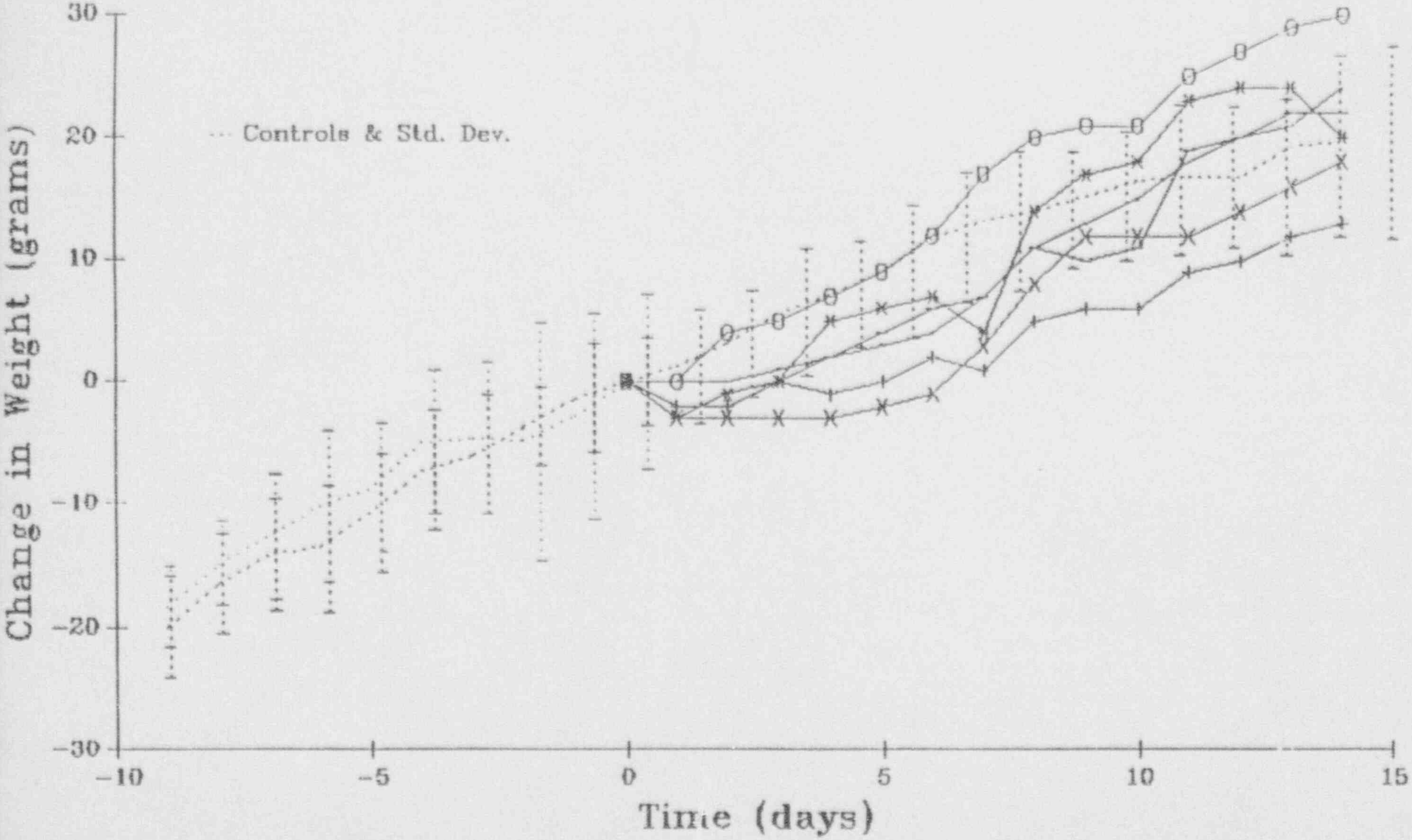

Figure 6. Control test indicating effect of radiant heat and experimental stress on weight gain of the rats. Day 0 is the day of exposure. The lines prior to Day 0 show the mean and standard deviation of the weight gain of animals who have not been exposed and the six animals who were used in this test. The rats were exposed in the head-only mode for 30 minutes while the furnace was heated by the radiant lamps set at a flux level of 50 kW/m^2. All the animals lived 14 days and gained weight normally.

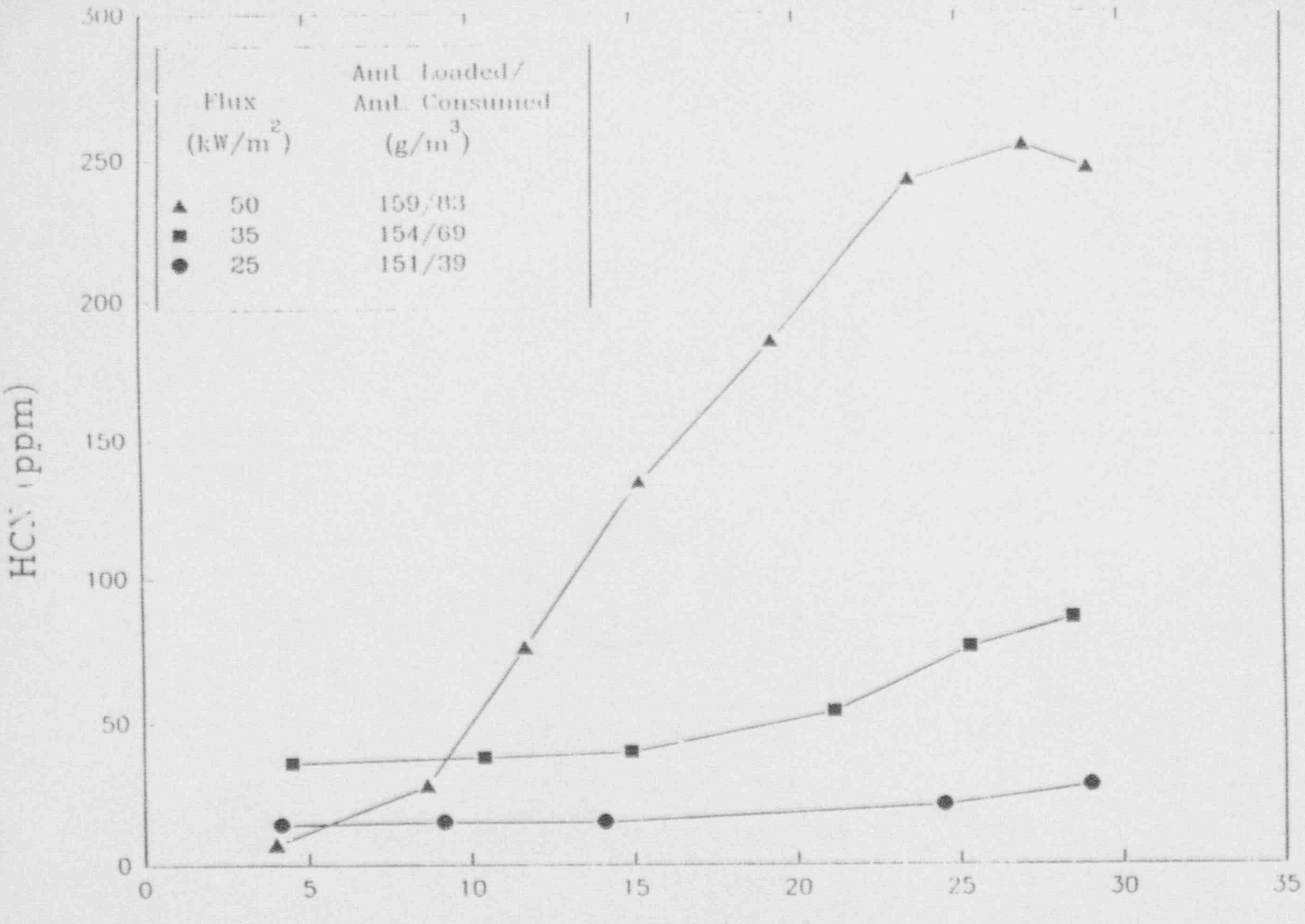

Figure 7. Effect of changing the radiant heat flux on the generation of hydrogen cyanide from samples decomposed in the non-flaming mode

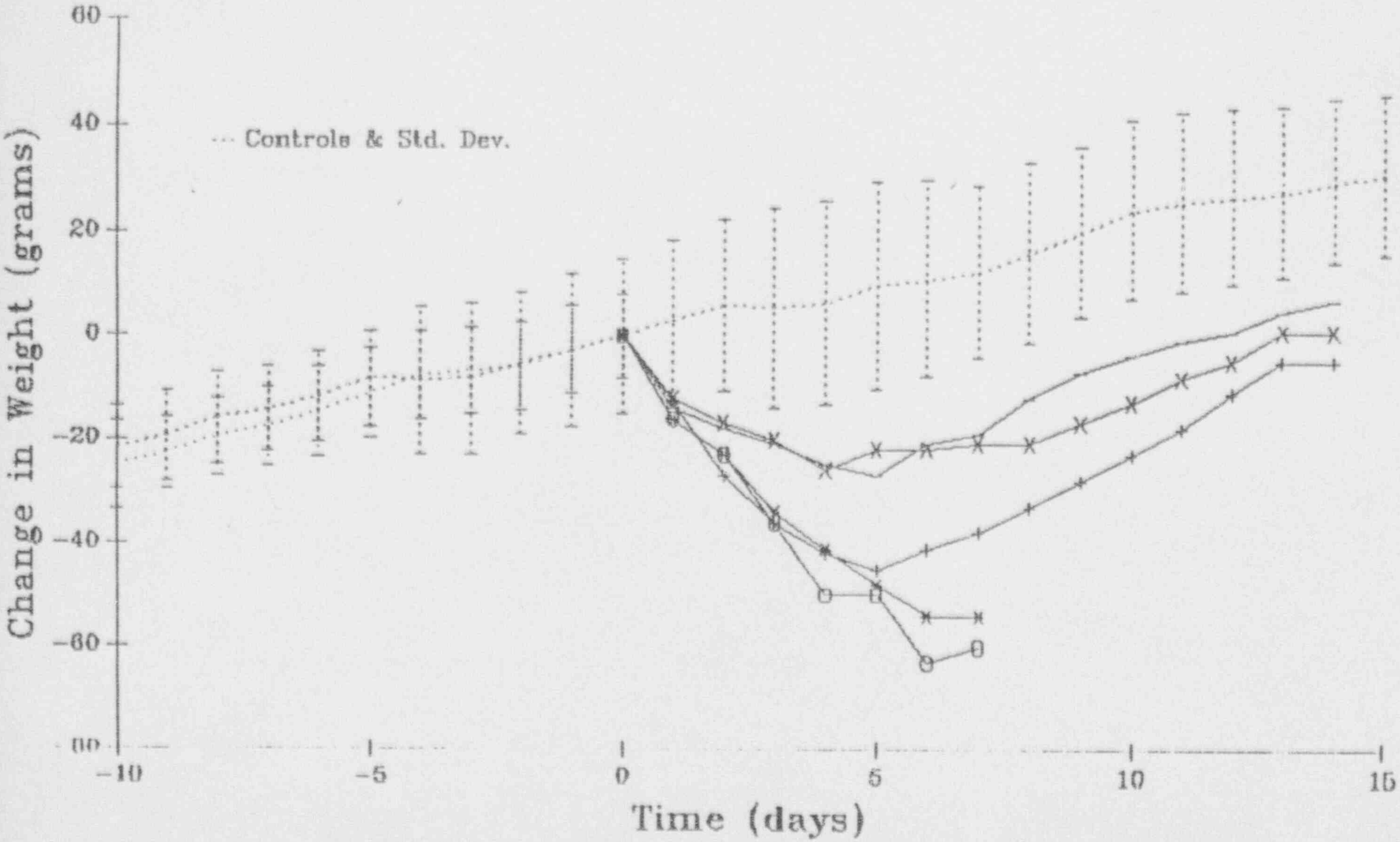

Figure 8. Change in weight of test animals following exposure to a sample decomposed in the non-flaming mode. The amount loaded in the furnace was 52 g/m^3 and the amount consumed was 30 g/m^3. Day 0 is the day of exposure. The lines prior to Day 0 indicate the mean and standard deviation of the weight gain of animals who have not been exposed and the six animals who were used in this test. In this test, one animal died at the end of the 30 minute exposure and two animals died on day 8.

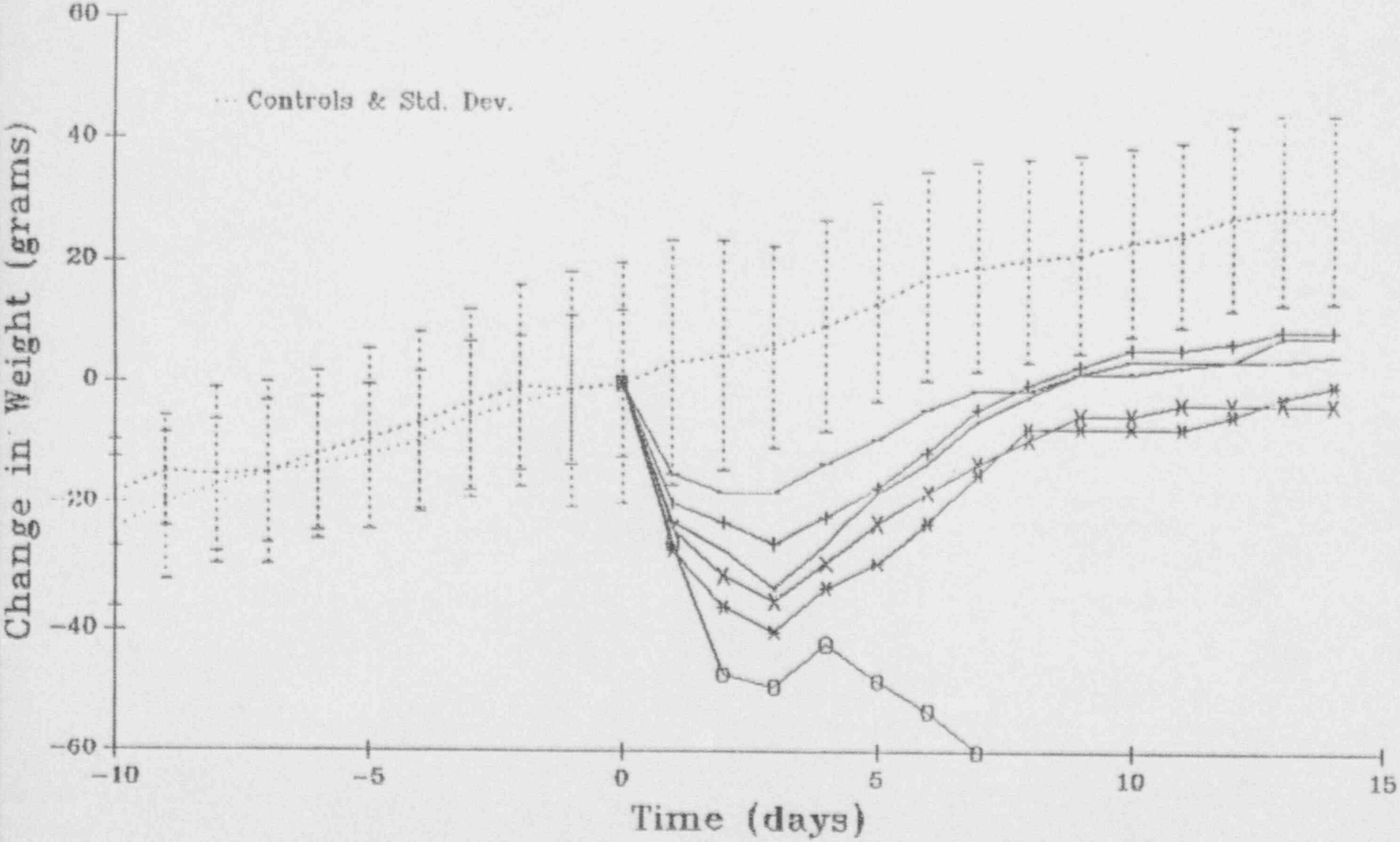

Figure 9. Change in weight of test animals following exposure to a sample decomposed in the non-flaming mode. The amount loaded in the furnace was 55 g/m^3 and the amount consumed was 31 g/m^3. Day 0 is the day of exposure. The lines prior to Day 0 indicate the mean and standard deviation of the weight gain of animals who have not been exposed and the six animals who were used in this test. In this

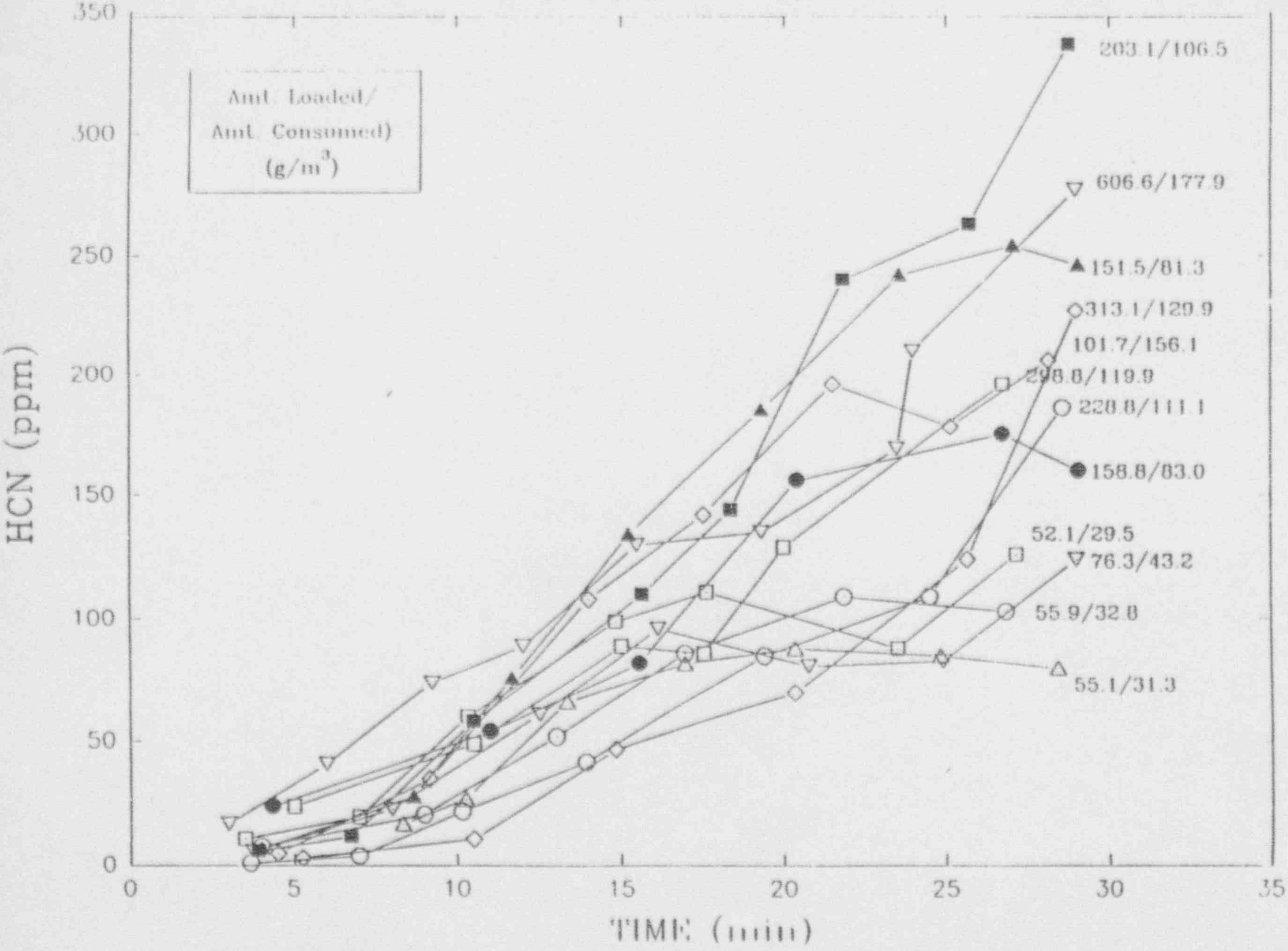

Figure 10. Hydrogen cyanide generation from samples decomposed in non-flaming mode.

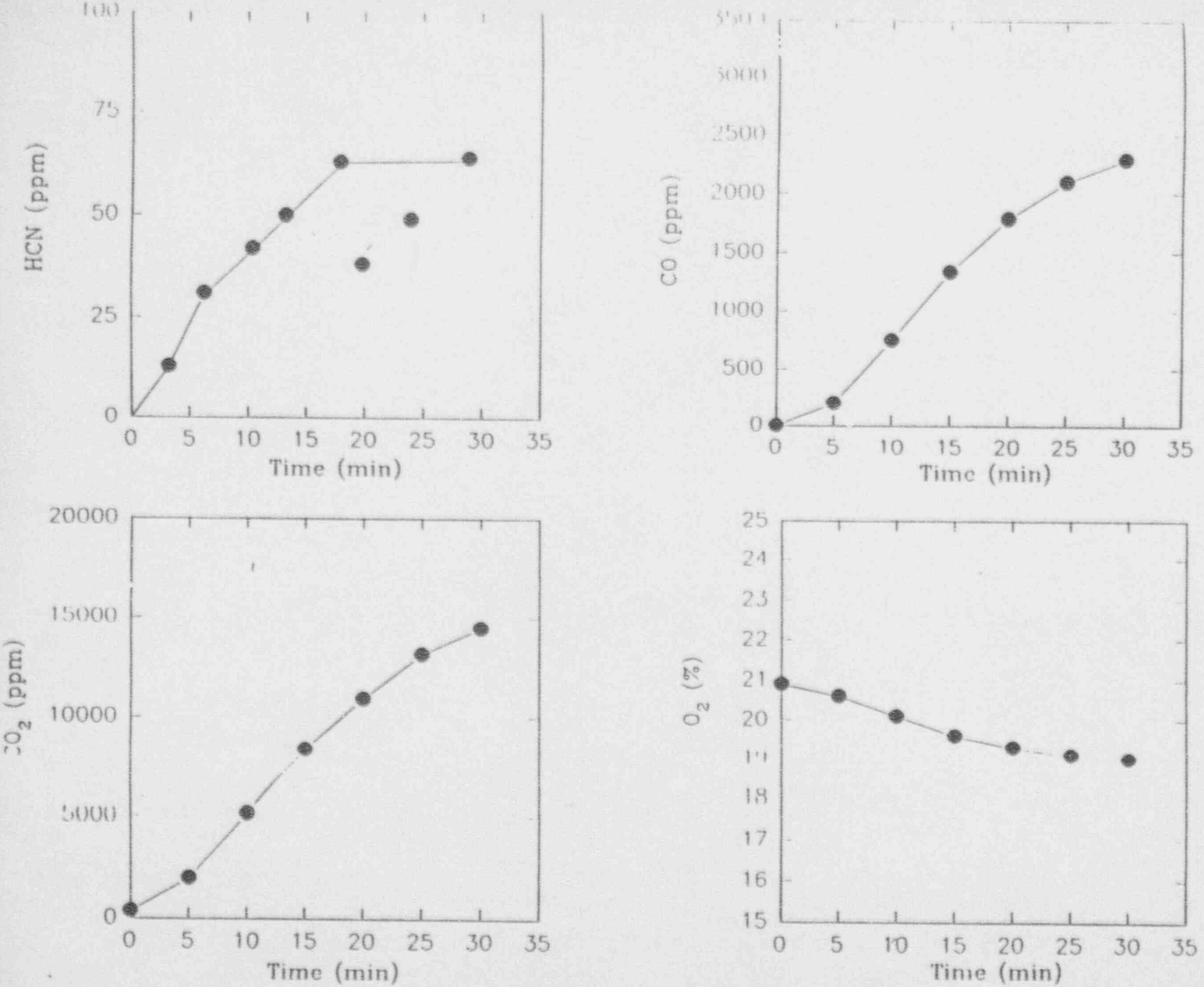

Figure 11. Gas generation from the intumescent char layer formed during the non-flaming tests. The amount of material loaded in the furnace was 101 [illegible]^3 [illegible] ^{3}