FORMATION OF NO_X DURING FUEL OIL COMBUSTION

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PREFACE

This study is concerned with the formation of NO_x during fuel oil combustion. Specifically to be determined are the effects of fuel nitrogen, choice of inert gas (nitrogen or argon), and amount of excess air on the amount of NO_x formed when fuel oil is burned. Statistical analyses will be applied to the data in an effort to determine whether these effects are significant.

I wish to express my appreciation to my major adviser, Dr. B. L. Crynes, for his guidance and assistance throughout this study. Appreciation is also expressed to the other committee members, Dr. R. L. Robinson, Dr. J. H. Erbar, and Dr. J. R. Norton, for their assistance in the preparation of the final manuscript.

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Finally, special gratitude is expressed to my wife, Judith, and ours sons, Ryan III, David, and Michael, for their understanding, encouragement, and many sacrifices.

The last few details in preparing this thesis were finished after the untimely death of Mr. Ryan D. Moats in November, 1973. The work, however, is essentially as he had prepared it.

All of us in the School of Chemical Engineering found Ryan to be a pleasure to associate and work with. He got along well with his fellow students and his professors, and was always willing to do much more than was required of him. Ryan has been a credit to us and to his profession. We were truly grieved by his untimely death.

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CHAPTER I

INTRODUCTION

Pollution! To see the extent of pollution one need only go outside and look at the hazy sky, sewage laden rivers, or trash cluttered land. Clear skies, clean water and trashless roadsides are an increasingly rare sight. No study of less than book length could possibly cover the whole field of pollution or even of air pollution in depth.

The major air pollutants are particulates, ozone, carbon monoxide and dioxide, sulfur dioxide, hydrocarbons, and the oxides of nitrogen (NO_x). There is a definite need for study of nitrogen oxides emitted from both mobile and stationary sources. The oxides of nitrogen are a problem since they form under combustion conditions thought of as ideal: good gas mixing, high gas temperatures, and excess air. Further, analysis by methods other than wet chemistry is difficult since nitrogen oxides are hard to separate.

This dissertation is concerned with a study of the formation of the oxides of nitrogen during fuel oil combustion in a stationary burner. A research combustor was constructed in the School of Chemical Engineering Laboratories at the Oklahoma State University for use in this and future studies in kinetics, in the control of NO_x emissions by modification of the combustion chamber, and in the cleaning or scrubbing of exhaust gases. Fuel oil, with varying portions of air or of inert gas/oxygen mixtures, was burned in the combustor under controlled conditions. Operating data and samples of the combustion product gases were collected. Finally, procedures for analyzing these collected samples for the nitrogen oxides by gas chromatography at ambient conditions were developed and tested.

CHAPTER II

PREVIOUS REPORTS AND PAPERS

A literature survey was conducted to gather available information on the oxides of nitrogen (NO_x), particularly on their formation during combustion in stationary sources. The results are separated into four sections: Introduction, Chemistry and Kinetics, Industrial Situations, and NO_x Studies (both formation and control). A last section summarizes the highlights of the above.

Introduction

The basic sources of air pollution in the United States are transportation, industry, electrical power utilities, space heating, and refuse disposal. Together these sources produce almost 134 million tons of pollution annually (1970 estimate), with monetary effects which are estimated to cost at least $65 per capita per year in the U. S. The following contaminants are discharged: carbon monoxide, sulfur oxides, hydrocarbons, particulate matter, nitrogen oxides, and traces of other gases and vapors (31). The exact amount of NO_x discharged is not known, as shown in Table I, which indicates that several researchers obtained widely differing estimates (2, 3, 16, 81). One reason for this is pointed out by Gerstle (45): each uses a different basis for emission calculations. No matter what the exact figures are, however, everyone agrees that there are great quantities of NO_x emitted to the air.

TABLE I

NO_x EMISSIONS

	(Million Tons Per Year)			
Source Year:	1966 (81)	1968 (2)	1968 (16)	1970 (3)
Transportation	91.30	8.24	6.40	78.20
Industry	29.20	0.20	4.80	25.60
Electrical Power Generating	41.40	9.98	3.60	17.50
Space Heating	37.70*		1.00	8.20
Refuse Disposal	10.70	2.25	0.02	4.20
Total	210.30	20.67	16.00	133.70

* Listed as miscellaneous.

The importance of the control of nitrogen oxides was first mentioned in 1956 in an article (33) urging chemical engineers to develop feasible methods for reducing nitrogen oxides, especially those from internal combustion engine exhaust and furnace and boiler stack effluents. This article noted that pollutant amounts varied from one installation to another and also gave examples of emission values obtained from Stanford Research Institute.

In 1967, a report (44) was given to the U. S. Senate which discussed the air pollution problem. Basically, this report stated that fossil fuel combustion processes "replace usable air with potentially harmful pollutants, and the capability of the atmosphere to disperse and dilute these pollutants - especially in urban areas where people, vehicles, and industries congregate in ever greater numbers - is strictly limited. The overwhelming burden of emissions of sulfur as well as nitrogen compounds and particulate matter in the U. S. today originates from the burning of coal and fuel oil in stationary combustion sources."

Nitrogen and oxygen combine chemically to form several oxides, see Table II. Some of these are stable at room temperature while others tend to decompose to form higher oxides of nitrogen. As the temperature increases, some of the oxides that are stable at room temperature will decompose into nitrogen and oxygen or lower oxides (60).

In general, the NO_x emitted to the air from combustion sources is NO, which is metastable at ambient temperature. It can be oxidized fairly easily to NO_2, although this requires energy and time (52). NO_2 contributes to the formation of aldehydes, ketones, and organic nitrates and forms nitric acid in the lungs. Recall that in the presence of light, NO_2 forms ozone and NO completing the cycle. NO_2 is the most plentiful nitrogen oxide in the atmosphere, with an average natural concentration of 0.25 ppm (31).

TABLE II

NITROGEN OXIDES

Formula	Chemical Name
NO	Nitric Oxide
NO_2	Nitrogen Dioxide
NO_3	Nitrate
N_2O	Nitrous Oxide
N_2O_3	Anhydride of Nitrous Acid
N_2O_4	Dinitrogen Tetraoxide
N_2O_5	Anhydride of Nitric Acid

No_x emissions from stationary sources commonly range from 50 to 1000 ppm although levels as high as 1500 ppm have been observed under severe conditions of high flame temperature and low heat transfer rates. Combustion accounts for over 95% of the man-made NO_x. Roughly half of this is from the internal combustion engine with the rest coming from power plants, and from commercial, industrial and domestic heating. Of all stationary sources, electrical power generating was estimated to account for 25% of the NO_x emission in 1950, 34% in 1960, 38% in 1970, and expected to be 40% in 1980 (52). Coal and gas combustion each account for 40% of NO_x emission, oil for about 15% and refuse and other minor fuels for the balance (16). About 1% of the total man-made NO_x emitted to the ambient air in the U. S. is from chemical sources mainly related to manufacture and use of nitric acid (2).

Current research is aimed at achieving significant reduction in NO_x emission. Many power plants are reducing emissions by redesigning their burners or switching to natural gas. However, this switch does not show a consistent advantage (1).

The exact effect of NO_x on humans, animals, and plants is not really known and may prove to be something other than first thought (81). Because of the possible health hazards caused by pollution, the Federal govenment and various states have established acceptable emission standards. One of the most active states is California; some automobile emission standards are compared with Federal standards in Table III (81). On January 30, 1971, the Environmental Protection Agency issued "Proposed National Ambient Air Quality Standards" for six pollutants in accordance with the provisions of The Clean Air Act (as amended in 1970). Table IV exhibits these proposed primary standards, about which there has been much discussion (6, 28). One article by Ellis and Mencher supported the national primary standard for NO_x only as a useful interim standard and suggested that after sufficient data have been collected these standards should be reevaluated (28). The difficulty in using only one set of emission standards to cover all polluting sources is emphasized in an article in "The Bulletin From Environmental Division of A.I.Ch.E." (7). It notes that E.P.A. has withdrawn its primary standard for NO_x because some analyses and calculations were in error, making the proposed standard too stringent.

Two studies worth mentioning presented information on hydrocarbon emissions from combustion processes, noting that nonperfect fuel oil combustion would emit some hydrocarbons to the air (98, 99). Hence, nonperfect combustion may reduce NO_x emissions, but it is definitely not the answer to the problem of total reduction of air pollution.

TABLE III

AUTOMOBILE EXHAUST EMISSIONS STANDARDS
(GRAM PER MILE) (81)

	Pollutant		
	Hydro-carbons	CO	NO_x
Prior to Control	11.0	80.0	4.0
California (1966) & Federal (1968)	3.4	34.0	-
California (1970)	2.2	23.0	-
(1971)	2.2	23.0	4.0
(1972)	1.5	23.0	3.0
(1974)	1.5	23.0	1.3
Proposed (1975)			
California	0.5	12.0	1.0
Federal	0.6	11.0	0.95

Chemistry and Kinetics

Chemistry

The seven known oxides of nitrogen are NO, NO_2, NO_3, N_2O, N_2O_3, N_2O_4, and N_2O_5, as shown in Table II, page 6. NO_3 and N_2O_4 are too unstable to exist at atmospheric conditions, N_2O_3 and N_2O_5 are anhydrides of nitrous and nitric acid respectively, and N_2O (the anesthetic known as "laughing gas") is a stable compound and will not support combustion. The remaining two oxides, NO and NO_2, are considered air pollutants (2, 54).

TABLE IV

PROPOSED NATIONAL PRIMARY AMBIENT AIR QUALITY STANDARD (28)

Pollutant	Annual Mean (μg/m^3)	Maximum 24-hour concentration not to be exceeded more than once per year (μg/m^3)
Particulates	75 (geometric mean)	260
SO_2	80 (arithmetic mean)	365
NO_2	100 (arithmetic mean)	250

Nitric oxide, NO, is a colorless, ordorless gas. When fossil fuels (gas, fuel oil and coal) are burned with air, some of the oxygen and nitrogen present combine to form NO according to the following reaction: $N_2 + O_2 \rightleftharpoons 2NO$. This reaction is negligible if the temperature is below 1000° F but is quite substantial for temperatures above 3000°F. Once NO is formed, the rate of decomposition is very slow for NO to dissociate into oxygen and nitrogen under ordinary reaction conditions. Nitric oxide tends to react with oxygen to form nitrogen dioxide: $NO + \frac{1}{2}O_2 \rightleftharpoons NO_2$ (2).

Nitrogen dioxide, NO_2, is a toxic brown gas with a pungent odor. The threshold limit set for ambient air by the American Conference of Government Industrial Hygienists is 5 ppm daily exposure (103). The stability of NO_2 decreases with increasing temperatures. Interestingly, although the absolute concentration of NO_2 increases with temperature, the ratio of its concentration to that of NO decreases (2).

The reaction $NO + \frac{1}{2}O_2 \rightleftharpoons NO_2$ is accelerated at high concentration (greater than 50 ppm NO) and in the presence of hydrocarbons; even at low concentration (1-5 ppm in air), it becomes rapid in the presence of sunlight. NO and NO_2 will be considered as a single pollutant, NO_x, because of this tendency to react photochemically. The same type of reaction results in the formation of ozone and peroxyacetyl nitrates (PAN), the major constitutents of eye irritating smogs (54). A discussion of photochemical reactions is beyond the scope of this paper; while their importance is known, the exact reactions are not defined and can only be theorized (51).

The reaction of atmospheric nitrogen and oxygen is called nitrogen fixation. Table V shows the equilibrium concentration of NO in air for various temperatures (31). This table is based on the reaction $N_2 + O_2 \rightleftharpoons 2NO$ with air of 21% oxygen and 79% nitrogen.

TABLE V

EQUILIBRIUM CONCENTRATIONS
OF NO IN AIR (31)

Temperature ($^\circ$F)	NO Concentration (ppm)
64	0.001
802	0.3
982	2.0
2800	3700.0
4000	25000.0

Experimental evidence indicates that during combustion in air, some nitrogen in the fuel is also converted into NO_x. It seems reasonable that oxygen should attack the weaker carbon-nitrogen bonds of fuel molecules more readily than the very strong $N \equiv N$ bond in molecular nitrogen (14). The actual role of fuel nitrogen in NO_x formation appears to vary from being dominant at low temperatures to being negligible at high temperatures (15). Experimental work of Shaw and Thomas, and Argonne National Laboratory has shown the importance of fuel nitrogen in NO_x formation (14).

Kinetics

The kinetics of the formation and/or decomposition of nitric oxide has been studied extensively (2, 13, 15, 16, 22, 23, 31, 35, 37, 47, 55, 66, 75, 78, 81, 95, 101, 112, 113, 114). One of the first studies by Zeldovich in 1945 (114), was of a nonisothermal case for a temperature range of 2000° to 2900°R. He assumed a chain mechanism for the oxidation of nitrogen with the two main reactions:

$$O + N_2 \underset{k_3}{\overset{k_1}{\rightleftharpoons}} NO + N \quad -47 \text{ kcal.} \qquad (a)$$

$$N + O_2 \underset{k_3}{\overset{k_1}{\rightleftharpoons}} NO + O \quad 4 \text{ kcal.} \qquad (b)$$

This chain mechanism was in complete agreement with the thermal nature of the reaction, the velocity and equilibrium of which depend solely on the temperature and the concentrations of oxygen and nitrogen. Although dependence is more complicated than he first presumed, his chain theory gives an expression for the reaction velocity which differs from that of the bimolecular mechanism ($N + O \rightleftharpoons NO$) only in that the velocity coefficient depends on the oxygen content. The following is a brief summary of the development of his mechanism.

At high temperature, the equilibrium constants, C_1 and C_2, for equations (a) and (b) are:

$$C_1 = (\ (NO)\ (N) / (N_2)\ (O)\ )_e = k_1/k_3 = 32/9 \exp(-47{,}000/RT) \qquad (c)$$

$$C_2 = (\ (NO)\ (O) / (O_2)\ (N)\ )_e = k_2/k_4 = \quad 6 \exp(4{,}000/RT) \qquad (d)$$

$$C^2 = C_1 C_2 = k_1 k_2 / k_3 k_4 = (\ (NO)^2 / (N_2)\ (O_2)\ )_e \qquad (e)$$

$$C = (NO / \sqrt{N_2 O_2})_e = 8/\sqrt{3} \exp(-21{,}500/RT) \qquad (f)$$

where the k_i's are reaction constants, and (NO), (N), (O), (N_2), and (O_2) are the equilibrium concentrations of nitric oxide, atomic nitrogen and oxygen, and molecular nitrogen and oxygen respectively, T is temperature in degrees R, and R is the gas constant.

The general kinetics equations are

$$dNO/dt = -dN/dt = -k_1(O)\ (N_2) + k_2(N)\ (O_2) - k_3(N)\ (NO) - k_4\ (O)\ (NO) \qquad (g)$$

The principle of stationary concentration (commonly known as the Steady-State assumption) states that if the concentration of intermediates present is very small when compared to the concentrations of both the reactants and products, then the rates of time change in the system after a very short time can never be great; hence with negligible error these rates are approximately zero. Applying this principle to the atomic gases (O) and (N), the last expression, (g), is equal to zero and (N) can be expressed in terms of (O). Thus,

$$dNO/dt = 2(O)\ (O)/(k_2(O_2) + k_3(NO)\ )\ \ (k_1 k_2\ (N_2)\ (O_2) - k_3 k_4 (NO)^2\ ) \qquad (h)$$

By neglecting the k_3 (NO) and $k_2(O_2)$ terms, utilizing the relation between the velocity coefficients and equilibrium constants, and assuming that the concentration of atomic oxygen is determined by the dissociation equilibrium of molecular oxygen,

$$O = C_o\ \sqrt{O_2}\ ,\ \text{then}\ dNO/dt = 2C_o k_1/C^2\ \sqrt{O_2}\ \ (\ (NO)_e^2 - (NO^2)\ ) \qquad (i)$$

A summary of important findings by Zeldovich is as follows:

(1) Yield of NO is less than the equilibrium amount at the maximum temperature attained.

(2) When combustion takes place in a stream of gas, NO is formed post flame.

(3) Data set forth prove the thermal nature of the reaction: The formation of NO depends only on the high temperature of the combusting gases and is not formed by the combustion reaction.

(4) The chain mechanism of the reaction by way of oxygen and nitrogen is discussed: $O + N_2 \rightleftharpoons NO + N$; $N + O_2 \rightleftharpoons NO + O$. This mechanism agrees with the absolute value of the reaction velocity and does not contradict the thermal nature of the reaction.

In summary, this early work by Zeldovich was quite significant in establishing a number of the kinetic features of NO_x reactions.

Wise and Frech studied the decomposition of nitric oxide in a quartz vessel over a temperature range of 872° to 1275°K (112). The reaction was reported to follow an overall second-order rate law over this temperature range. Activation energy varied from 21.4 kcal below 1000° K to 82 kcal above 1600° K.

Fenimore and Jones studied the decomposition of nitric oxide at 2200° - 2400° K in 1957 (35). They used flat premixed flames of nitrous oxide and fuel that burnt at controlled temperatures on a water cooled porous burner. Nitrous oxide was decomposed entirely in the flame, partly to nitric oxide, and the subsequent decay of NO in the burnt gas down stream of the flame was observed by probe sampling. Decay was second order in nitric oxide, impeded by oxygen, and can be adequately described by: $(O_2)^{\frac{1}{2}} d(1/NO)/dt = 2 \times 10^{12} \exp(-98{,}000/RT)$ with units of $(\text{moles/liters})^{-\frac{1}{2}} \text{sec}^{-1}$.

Where (O_2) is concentration of oxygen

(NO) is concentration of nitric oxide

T is temperature in degrees K

R is the gas constant

Fenimore and Jones concluded that the Zeldovich mechanism contains a flaw of some nature, but they could not state with certainty what it was. It may be that nitrogen atoms are maintained in equilibrium with nitric oxide and oxygen by some process in addition to the above reaction. In this case, the equation $(O_2)^{\frac{1}{2}}d\ (1/NO)/\ dt = 2Kk_2$ still holds, but the reactions which maintain the equilibrium concentration of nitrogen atoms would be unknown and might even change for different reaction mixtures.

Glick and co-workers used a shock tube to study the kinetics of the reaction $N_2 + O_2 \rightleftharpoons 2NO$ between 2000° and 3000° K (47). They found that the kinetics were consistent with the chain mechanism proposed by Zeldovich. The rate-determining step in the chain is: $O + N_2 \rightleftharpoons NO + N$, with the heat of reaction $\Delta H_{2500^\circ K} = 75.8$ kcal/mole and an activation energy of 74 ± 5 kcal/mole.

Yuan and co-workers studied decomposition of nitric oxide in packed Alundum vessels in the range of 973° to 2073° K (113). Below 1373° K, the reaction was heterogeneous and zero order. Above 1673° K and up to 2073° K, the reaction is a simple homogeneous, bimolecular reaction. Between 1373° and 1673° K both mechanisms are involved. The homogeneous second-order reaction rate was given by the expression: $k_2 = 1.9 \times 10^8 \ \exp(-63{,}100/RT)\ \text{atm}^{-1}\ \text{sec}^{-1}$.

In 1959, Olin and Sage considered the reaction $2NO \rightleftharpoons N_2 + O_2$ with $k_2/k_1 = K = (NO)_e^2/(N_2)_e(O_2)_e$ to study the formation and decomposition of nitric oxide (78). They analyzed samples with mass spectrograph. Their technique proved unsuccessful for product analysis because the gas reactions continued to occur in their sample containers. Some kinetic data were listed in the article.

Freedman and Daiber used shock-heated nitric oxide to study the decomposition rate between 3000° to 4300° K (37). They theorized that there are five important reactions involving NO, N_2 and O_2:

Zeldovich mechanism, $N_2 + O \underset{-1}{\overset{1}{\rightleftharpoons}} N + NO$

$NO + O \underset{-2}{\overset{2}{\rightleftharpoons}} N + O_2$

Dissociation, $NO + M \underset{-3}{\overset{3}{\rightleftharpoons}} N + O + M$, where M is an inert diluent

Bimolecular, $2NO \underset{-4}{\overset{4}{\rightleftharpoons}} N_2 + O_2$

Oxygen equilibrium, $M + O_2 \underset{-5}{\overset{5}{\rightleftharpoons}} 2O + M$

They concluded that the decomposition of NO between 3000° and 4300° K proceeds by at least three mechanisms. Initial rate was found to be the sum of the direct dissociation reaction with $k = 7 \times 10^{12} \exp(-150{,}000/RT)$ liters/mole-sec, and the bimolecular reaction with $k = 4.8 \times 10^{20} T^{-5/2}\text{-}\exp(-85{,}500/RT)$ liters/mole-sec. The initial rate is independent of Zeldovich reaction because it depends on the concentration of oxygen. The bimolecular and the dissociation reactions were separated because they were second and first order, respectively, in NO. The Zeldovich reaction dominates the decomposition kinetics after an induction period which decreased with increasing temperature. However, the rate of Zeldovich's reaction cannot be determined because the oxygen recombination time was long compared to the experimental time, so the simplified rate expression cannot be used.

In 1964, Bahn published a summary of the chemical kinetics involving reactions of N_2, O_2, NO, N, and O (13). He discussed the rate constants for six reactions and presented rate constant expressions for these reactions:

(1) $O_2 + M \rightleftharpoons 2O + M$

(2) $N_2 + M \rightleftharpoons 2N + M$

(3) $N_2 + O_2 \rightleftharpoons 2NO$

(4) $NO + M \rightleftharpoons N + O + M$

(5) $O + N_2 \rightleftharpoons N + NO$

(6) $O + NO \rightleftharpoons N + O_2$

where M is an unknown reactant, possibly O_2.

In 1967, the Bureau of Mines conducted a study entitled Flame Characteristics Causing Air Pollution: Production of Oxides of Nitrogen and Carbon Monoxide (95). Their overall purpose was to obtain information on the formation and decay of air pollutants relative to basic fuel and combustor parameters. Three reaction zones were considered, the primary flame zone, the secondary flame zone and the heat exchange zone. However, their immediate objective was to develop methods for predicting concentrations of nitrogen oxides and carbon monoxide in burned gas of lean, stoichiometric and rich propane-air flames.

The authors noted that NO concentrations predicted on the basis of Zeldovich's data are larger than those predicted by other investigators. For lean propane-air flames, $k' = dX/dt = 610 \times 10^{12}(N_2)$ $(O)^{\frac{1}{2}}(1-X^2)/X_e^2 \exp(-128/RT)$ ppm/sec $= k\ (\ (1-X^2)\ /\ X_e^2)$

where t is time in seconds,

T is temperature in °K,

(N_2) and (O_2) are volume percentages of nitrogen and oxygen,

N_2 and O_2 concentrations are equilibrium combustion values and are assumed to be constant with time and temperature, and

X and X_e are NO concentrations in ppm at time t and the equilibrium value at temperature T.

For rich or stoichiometric propane-air flames, $(O)^{\frac{1}{2}} = 82 \exp(-21/RT)$ and $dX/dt \alpha P^{\frac{1}{2}}$, so $dX/dt = 5 \times 10^{16}\ (N_2)\ (1-X^2)\ /X_e^2)\ \exp(-149/RT)$.

In early 1970, the National Air Pollution Control Administration published information on controlling NO_x emissions (2). The following summarizes the kinetic information in their article. The quantity of NO_x produced clearly indicates that high-temperature fixation of atmospheric nitrogen occurs. Chemically bonded nitrogen in the fuel also contributes to NO_x emission from combustion processes, since it reacts with oxygen more readily than the molecular nitrogen supplied by the combustion air. Note that the dissociation energy for the $N \equiv N$ bond is 225,000 calories per gram-mole of nitrogen, whereas the energy necessary to dissociate carbon-nitrogen bonds in fuel molecules falls in the more modest range of 60,000 to 150,000 calories per gram-mole. Except at very high temperatures, therefore, NO_x is formed more from the oxidation of fuel nitrogen than by nitrogen fixation.

It has been noted that the rate of NO formation is highly temperature dependent, Zeldovich estimated an activation energy of 129 kcal/mole for this reaction. He gave the following expression for the rate of formation of NO, derived on the basis of the chain mechanism of reactions: $dNO/dt = 3.0 \times 10^{14} \exp(-129{,}000/RT)(N_2)(O_2)^{\frac{1}{2}}$ where (NO), (N_2) and (O_2) are concentrations in gram-mole/cm^3; t is time in seconds; T is temperature in °K; and R is gas constant, calories/gram-mole-°K. Below 1100° K NO decomposition is catalyzed by surfaces, while above 1400° K it is strictly a gas-phase reaction. Both NO and NO_2 are formed, but the amount of NO_2 is usually under 0.5% of the total NO_x. A long period of time may be required to oxidize trace quantities of NO by this mechanism, but photochemical reaction in sunlight accomplishes such oxidation in a much shorter time. The most important factor in the NO chemistry of flames is the rate of formation of NO.

Ermenc mentioned that kinetics of the reaction of nitrogen and oxygen in air are characterized by the standard second-order equation, although at temperatures below 2000°F, the reaction is zero order (31). Below 3200°F, the rate of formation will control NO concentration present because time is required for full reaction; above 3200°F, the reverse rate becomes so great that it controls. Therefore, pollution control requires a very rapid quench to 3200°F, and then a slow cooling rate so that NO can decompose into N_2 and O_2.

Harris and co-workers' article contained a summary of kinetic studies of the formation and decomposition of NO; this information is presented in Table VI (55). The differences in the numbers may be attributed to the fact that experimental techniques, temperature ranges, and concentrations of NO varied considerably. Investigators have assumed that the ratio of the rate constant of formation to the rate constant of decomposition equalled the equilibrium constant. Table VII shows rate constants for the formation and decomposition of NO and the time for equilibrium (55).

Bartok and co-workers developed and tested a first-generation kinetic model concerning the formation and decomposition of NO (15, 16). They did not consider NO_2 because NO_2 concentration is negligible under combustion conditions. The model of net NO formation in natural gas combustion is idealized by using premixed, gaseous hydrocarbon fuel/air feed. They assumed equilibrium between oxygen atoms and oxygen molecules, although this assumption is valid only in the presence of excess air. Their rate of NO formation and decomposition is: $dNO/dt = 9 \times 10^{14} \exp (13{,}500/RT)(N_2)(O_2)^{\frac{1}{2}} - 4.1 \times 10^{13} \exp (-91{,}600/RT)(NO)^2 (O_2)^{-\frac{1}{2}}$ gram-mole/cubic centimeter-second. The model was tested with three sets of conditions. The simulation obtained agreed fairly well with actual measured emissions from large, gas-fired power plants.

Lange developed a mathematical model of NO_x formation based on a chemical mechanism which includes twenty-one reactions and fourteen species (66). This mechanism was the result of an extensive literature analysis, which involved prescreening a large number of reactions on the basis of both kinetic and thermodynamic constraints.

TABLE VI

SUMMATION OF KINETIC STUDIES OF FORMATION AND DECOMPOSITION OF NITRIC OXIDE (55)

Experimental Technique	Temperature Range, °K	Rate of Formation of NO at 2030° K (ppm/sec)	Source of Kinetic Data
Explosion in metallic vessels	2000-2900	1053	Zeldovich (114)
Hydrocarbon air flame with added NO	2200-2400	758	Fenimore (35)
Not specified	--	652	Marrone*-Bahm (13)
Single pulse shocks in air	2000-2800	560	Glick (47)-Davidson*
Decomposition of NO in packed alundum vessels	1700-2000	371	Yuan (113)
Decomposition of shock-heated NO	3000-4300	440	Freedman (37)
Air heated in quartz vessels	900-1300	342	Wise (112) Zeldovich (114)
Decomposition of NO in porcelain and metallic vessels	1000-2000	354	Hirschfelder (57) Jellinek*
Do	1800-2200	500	Jellinek*, Nernst*
Decomposition of No in porcelain vessels	1500-1700	90	Kaufman*

* Listed in (55) but not available to the author.

TABLE VII

RATE CONSTANTS FOR FORMATION AND DECOMPOSITION OF NO AND TIME REQUIRED FOR EQUILIBRIUM:*

$$N_2 + O_2 \underset{k_1}{\overset{k_2}{\rightleftarrows}} 2NO \quad (55)$$

T (^oF)	k_1	k_2	Time
1340	4.00×10	1.74×10^{-7}	81.6 years
2240	3.78×10^{4}	2.33×10^{-1}	1.26 days
2960	9.06×10^{6}	1.20×10^{3}	2.08 minutes
3320	1.40×10^{8}	5.55×10^{4}	5.06 seconds
4040	3.37×10^{10}	6.98×10^{7}	0.0106 seconds

* Time for formation from air of one-half the equilibrium concentration.

Lange's model, using kinetic parameters reported in the literature, under predicted the set of experimental data taken on a laboratory scale-combustor. Agreement between model and data was improved by adjustment of some kinetic parameters using a non-linear optimization method. The final fit was reasonably good, but further refinement is desirable. The model was then used to calculate the effects of design and operational variables on NO_x emissions. Variables considered were: fuel composition, air-fuel ratio, air temperature, cooling rate for combustion gas, flue gas recirculation through the burner, and fuel bound nitrogen.

Thompson, Brown and Beer studied NO formation in a tubular combustor with interest in inducing combustion driven oscillations (101). They found that NO formation rate is post flame gases of hydrocarbon flames (temperature greater than 1800° K) may be satisfactorily predicted by the application of the Zeldovich chain mechanism if the local oxygen atom concentration is correctly assessed:

	M	N	E
(1) $N_2 + O \rightleftharpoons N + NO$	1.36	11.0	75.40
(2) $N + O_2 \rightleftharpoons NO + O$	6.40	6.0	6.25
(3) $\frac{1}{2}O_2 \rightleftharpoons O$	5.00	1.5	43.30

where M, N, and E are constants in the equation, $k_i = k_i = M_i \times 10^{Ni}$ $*\exp(-E_i/RT)$. Then, $dNO/dt = 2(k_1k_3(O)^{\frac{1}{2}}(N_2) - k_{-1}k_2^{-1}(NO)^2(O_2)^{-\frac{1}{2}})/$ $(1 + k_{-1}(NO)/k_2(O_2)\ )$ moles/liter-second. With $k_{-1}(NO)/k_2(O_2) \ll 1$ when $(NO) \ll (NO)_e$, $dNO/dt = 2(k_1k_3(N_2)\ (O_2)^{\frac{1}{2}} - k_{-1}k_2^{-1}(O_2)^{-\frac{1}{2}}\ (NO)^2)$ moles/liter-second.

Industrial Situations

The third portion of the literature survey involved articles concerning NO_x in industrial situations. Gilbert and Daniels discussed the formation of NO by heating air to above 2000°C and quickly chilling it, an old process used to produce NO commercially (46). Mordell, Thompson, and Yano reported the successful operation of a pre-pilot plant facility for the thermal fixation of atmospheric nitrogen (72). Gas temperatures exceeding 3000° K are reached and the quenching rates to fix the NO are very important. These articles are of interest because they orient the novice to the mechanisms of NO_x formation.

Austin and Chadwick discussed ways of reducing the formation of NO without chemical processing, such as changes in boiler design or in firing arrangements and configurations (11). These factors would affect flame temperature and hence NO formation. Most furnaces emit between 500 and 700 ppm NO when burning oil and 400 to 600 ppm when burning gas. In tests across the United States, emissions from furnaces fired with coal ranged from 650 to 1460 ppm; natural gas - 190 to 1350 ppm; and oil - 310 to 915 ppm. In all cases the boilers were tested with more than one fuel and were consistently high or low in NO_x emission with all fuels.

The tests further indicated that the flame temperature and NO_x concentration were affected by: the rate of firing in the furnace, the mutual radiation between burners, and the manner in which the combustion air was introduced. Reducing the turbulence of the flame and the pressure drop across the burner throats reduced NO emission and maintained satisfactory combustion. Unsuccessful reduction attempts included gas recirculation, varying combustion air temperatures, burner orifice modification and changes in excess air within a practical operating range.

A two-stage process was tried with 90-95% of theoretical combustion air introduced normally through the burners and 15 to 20% of the air through auxilliary front-wall ports. The two-stage process afforded satisfactory furnace combustion, a substantial reduction in NO formation, and no appreciable change in boiler efficiency. Before modification the boiler produced 685 ppm NO; after, it produced only 350 ppm under the same load conditions.

Peters described some effective methods for removing NO, NO_2, and N_2O_4 from gases containing less than 2% of these oxides (81). Two processes of interest are absorption combined with chemical reaction and adsorption. In the first, NO_2 and N_2O_4 react with water to form HNO_3 and NO. NO can then be oxidized to NO_2, which will again react with the water. Since the absorption rate is controlled primarily by the rate of the chemical reaction involved, removal efficiency (the percent of entering oxides that are removed from the gases) decreases drastically with reductions in oxide concentration. For the adsorption process, silica-gel was indicated as giving good removal efficiencies of nitrogen dioxide at gaseous concentrations as low as 0.1%.

Bartok and co-workers studied fuel type and composition versus NO_x emissions upon combustion, finding that coal firing produced the most NO_x, followed by oil and gas firing (16). This "ranking" of fuel types can be explained completely on the basis of adiabatic flame temperatures reached under identical combustion conditions; coal flames have the highest theoretical adiabatic flame temperature and gas the lowest.

Bartok also postulated that chemically bonded nitrogen in the fuel plays a role in NO_x formation; the higher the fuel nitrogen content, the more NO_x is expected to be formed. He cites experiments by Shaw and Thomas (Reference 16 mentions this work) which showed that the addition of organic nitrogen compounds to fuels enhances NO_x formation with or without molecular nitrogen present. He also mentions that Argonne National Laboratory used a fluidized bed experiment with coal as fuel and substituted argon for the nitrogen in the air. The NO_x

concentration in the flue gas was the same with or without nitrogen present in the combustion gases.

At higher temperatures, it is expected that the contribution of the bonded fuel nitrogen to NO_x formation should be less important. Clearly at higher temperatures the source of nitrogen is unimportant; NO_x will form if any nitrogen is present.

The National Air Pollution Control Administration (NAPCA) found that two-stage combustion reduces NO_x emissions from oil- and gas-fired power plant boilers by 30 to 50% (2). Also, low excess air operation reduced NO_x emissions by 30 to 60%, depending upon the percentage of excess air, the design of the boiler and the type of firing. A modified two-stage combustion technique combined with 15% excess air firing reduced the NO_x concentration in stack gas emitted by two 750-megawatt gas-fired power plant boilers from 1500 to 175 ppm. To see the importance of this reduction, note the average values of NO_x emission from power plant boilers in the last column of Table VIII (2). This shows that NO_x emission can be reduced without a decrease in generating capacity.

A switch to a paraffinic, "low sulfur" fuel oil of low nitrogen content in public utility boilers has resulted in nitrogen oxides emissions approximately 50% less than those obtained when a "high sulfur" fuel oil of relatively high nitrogen content was burned.

Changing to gas can reduce NO_x emissions, although care should be exercised in making a conversion so that emissions will be as low as possible. (Note: Owing to the current natural gas shortage, this change may not be too likely.) Proper location, spacing, and design of burners is important to assure low heat release and minimum excess air operation. Provisions for recirculating a portion of the flue gases back to the flame zone could also be considered.

TABLE VIII

COMPARISON OF COAL, OIL AND GAS ON EQUIVALENT BTU BASIS (2)

	Average NO_x Emissions in Boilers and Power Plants, pound of NO_x/Billion BTU		
Fuel	Household ahd Commercial	Industry	Electric Generation
Natural Gas (1046 Btu/cu.ft.)	111	205	373
Fuel Oil (149,966 Btu/gal)	80 - 480	480	680
Coal (11,867 Btu/lb)	337	842	842

The NAPCA report discusses fuel additiives, substances added to a fuel to change its properties in some way. An additive can be liquid, solid or gas; for liquid fuels, it should preferably be a liquid soluble in all proportions in the fuel and effective in very small concentrations. As far as is known, no fuel additive is yet available which will inhibit the formation of NO_x in combustion systems.

James considered some methods for reducing NO formation (60). Modification of burning equipment so that fuel and air mix at a slower rate will reduce flame and combustion gas temperatures and thereby the amount of NO formed by a factor of 2 to 3. There does appear to be a minimum level of NO formation which cannot be reduced. Unfortunately, incomplete combustion often results; therefore, this method is considered unsuitable for commercial application. Successful methods of lowering NO formation include use of lower temperatures, use of two-stage combustion, and mixing of a portion of cool flue gas (about 650°F) with combustion air. James suggests that a combination of all these methods may give better results than any so far obtained.

Tomany, Koppang and Burge described chemical and physical charateristics of the nitrogen oxides, and reviewed current NO_x emissions control technology with special emphasis on a novel low-NO_x-emissions burner design (103). This article is a major one, and will be discussed at length.

NO_x emissions sources: Major catagories are stationary combustion and transportation. Two primary industrial sources are nitric acid plants and those in nitration processes, since up to 3200 ppm NO_x can be discharged with the tail gas from the final nitric acid absorber. In fact, emissions from these plants are usually comprised almost entirely of nitrogen oxides. However, about half of the stationary combustion emissions are discharged by steam-electric generating stations using coal, oil, or natural gas as the fuel.

Note that gas, usually thought of as "clean" compared to oil or coal, is not with regard to nitrogen oxides. Since emissions are influenced by furnace design, fuel type, amount of excess air, and firing method, they can vary widely. Gas-fired boiler designers commonly estimate NO_x emission at about 600 ppm. This may be because the retention period of the combustion gases contributes to NO_x formation, and gas boilers are usually large. The authors do not believe the use of natural gas as a fuel will reduce NO_x emission. This appears contradictory to the theory normally presented for NO_x formations.

Table IX lists some of the processes being considered for the reduction of nitrogen oxides emissions from stationary combustion sources (103). The sulfur in coal usually occurs in pyrites and as organic complexes. Various wet cleaning processes have been studied for their removal. Catalytic reduction of SO_2 to S and NO to N_2 is being investigated by the Chevron Research Company. The active reducing agent is CO, with reactions as follows: $4CO + 2SO_2 \rightleftharpoons 4CO_2 + 2S$, and $2CO + 2NO \rightleftharpoons 2CO_2 + N_2$. A side reaction which produces carbonyl sulfide is recognized as a serious limitation of this process for application.

NO_x reduction techniques of two-stage combustion, non-stoichiometric combustion, combustion products recycling, and preheat temperature reduction have been used. It appears that NO formation is controlled by the air/fuel ratio in the primary zone, and the latter two processes help change this ratio favorably.

Direct combustion of NO_x and a fuel gas, with NO_x serving partially or wholly as the oxidizing component, is being tested. A burner designed to operate from stoichiometric to excess fuel conditions is necessary to effect this reaction. Encouraging preliminary results of 95% conversion of oxides to nitrogen have been obtained with such a burner.

TABLE IX

AIR POLLUTION CONTROL METHODS FOR STATIONARY COMBUSTION SOURCES (103)

Purpose	Method	Status
Sulfur and nitrogen removal from coal	Chemical extraction	Early development
Removal of NO and SO_2 after furnace	Catalytic reduction	Early development laboratory experiment
Removal of NO and SO_2 after furnace	Wet scrubbing	Early development pilot stage
Reduction of NO_x in furnace	Stoichiometric variation and combustion product recycle	Full-scale testing
Reduction of NO_x in furnace	Combustor design	Development- 10^5 Btu/hour burner tests

The authors mention that NAPCA studies have shown that nitrogen compounds in the fuel contribute to NO_x emissions. Although some development efforts are being undertaken for control of nitrogen oxides by the removal of this combined nitrogen in oil and coal fuels, published results are presently unavailable.

Studies of Formation and Control of NO_x

Mullaney experimented with a shock tube and fuel injection system to study NO formation (74). Analysis was by the Saltzman technique (91); at a pressure of 15 psig, the peak formation occurred around

2350° K. Mullaney attributed the difference in NO formation between fuels to ignition lag.

Richter and co-workers explored NO_x emissions in several studies (85, 86, 87). The first study is most important to the present work. It detailed the combustion tube as a 162 inch copper tube of 3.83 inch diameter and fuel as natural gas and air. Carbon monoxide, carbon dioxide, and oxygen were analyzed by conventional Orsat methods. A phenol-disulphonic acid method was used to determine the quantities of the various nitrogen oxides (105).

For a fuel-oxygen mixture of 17% stiochiometric, a rather regular and stable variation in the mole fraction of nitrogen oxides occurred with longitudinal position. Most oxides were formed near the lower part of the tube, with the mole fraction decreasing rapidly at the centerline as radial diffusion or secondary chemical reaction proceeded.

At approximately 85% stoichiometric, the situation was more complex. Oxides increased with longitudinal position as the result of a much larger region of active combustion. They appeared to be formed about 60 inches from the point of mixing.

At 140% stoichiometric under conditions of shear flow, NO_x increased gradually to a maximum of about 15×10^{-6} mole fraction at the exit of the combustor. The mixture ratio exerted a pronounced influence on NO_x formation, with a ratio of between 80 and 100% corresponding roughly to the maximum such production.

Seagrave and co-workers used Richter's experimental apparatus to measure changes in pressure and in total and monochromatic flame intensity during the oscillatory combustion of natural gas and air at atmospheric pressure (93). There was a significant fluctuation in the mole fractions of water and carbon dioxide produced during each cyclic perturbation.

Wasser, Hangebrauch and Schwartz tested an oil-fired furnace in a configuration simulating a domestic furnace (108). Their purpose was to evaluate fuel additives and equipment design modification in order to reduce air pollutant emissions. They analyzed for carbon monoxide, carbon dioxide, hydrocarbons, and nitrogen oxides (reported as NO since NO is predominant).

A lower concentration of NO at the highest air/fuel ratio (2.5) resulted from a combination of low temperature and short mean gas residence time. This concentration increased to a maximum at a ratio of 1.75. At lower air/fuel ratios, in spite of higher temperatures and longer residence times, the decreasing oxygen concentration lowers the level of NO. A minimum was reached at a ratio of 1.25, and then both oxygen and NO concentrations begin to rise again. The increase in NO seemed odd because in processes where essentially complete combustion is achieved, NO minimum is approached as stoichiometric combustion is approached. However, here incomplete combustion results in an increase in oxygen content as the air/fuel ratio of 1.0 was approached; in addition, flame temperature and mean gas residence time continue to increase.

Concentrations of NO formed were far below equilibrium for the nitrogen-oxygen system at the flame temperatures encountered. (Equilibrium concentration would have been in the range of 150-650 ppm.) The range of gas residence time for this operation was too short for equilibrium to be reached. However, a definite upward trend in weight of NO emitted per unit weight of fuel was shown for increasing air/fuel ratios. This occurred because the variation in ppm of NO was relatively small when compared with the decrease in fuel gas volume.

LaMantia and Field discussed sources of NO_x emissions and methods of prevention (65). They noted that NO_x may be destroyed by catalytic decomposition, or that NO_x formation may be limited or prevented by modifying the combustion process. Possible modifications are (1) change in burner design and method of firing (the example cited was that tangential firing has the advantage of reduced flame temperature resulting from larger flame volume), (2) two-stage combustion (only part of the air required for combustion is supplied in the primary combustion zone; the rest is injected at the flame front), (3) flue gas recycle, and (4) low excess air. Note, however, that decrease in excess air increases peak temperature, thereby tending to increase the rate of NO_x information and maximum concentration attainable.

Harris and co-workers at the Bureau of Mines conducted a study of the formation of nitrogen oxides, the decay of carbon monoxides and the concentrations of residual hydrocarbons in the secondary combustion zone of propane-air and methane-air flames (55). They used three enclosed burners designed to simulate gas appliances such as space and water heaters and found generally higher NO_x concentrations for propane than for methane, with highest concentrations observed for stoichiometric flames of both fuels. With lean flames, the difference between the two flue gases remained constant whether recycling was simulated or not. However, stoichiometric propane flames with recycling produced significantly lower NO_x concentration than did stoichiometric methane flames without recycling.

The core region, near the center of the gas stream, contains fairly constant characteristics. However, analysis showed that within the core zones of lean and stoichiometric flames, there were regions where NO_x concentration increased with time, others where it decreased. and still others where it remained fairly stable. For rich flames, the concentration profiles showed that the relative amounts of nitrogen oxides formed at the primary combustion zone changed very little with time.

Selected data for the core zone were used to determine a minimum temperature of 3050^oF, below which nitrogen oxides did not form in the secondary combustion zone within the system's available reaction time. In fact, NO_x concentration profiles for both propane-air and methane-air stoichiometric flames showed a zone in which nitrogen oxides actually decomposed. Temperatures had been above 3050^oF and considerable quantities of NO_x had formed (although equilibrium concentrations had not been reached); as the temperatures dropped below 3050^oF, equilibrium concentrations of nitric oxide became less than the amounts present, and the formation reaction reversed until the temperature fell below 2140^oF. Below 2140^oF, nitrogen oxides will not decompose. It would thus seem advantageous for pollution abatement purposes to cool slowly between 3050^o and 2140^oF. For sampling, since the concentration of nitrogen oxides will tend to change with time even in sample probes, flame gases should be cooled rapidly to below 2140^oF.

NO_x concentrations did not increase with time if flame temperatures never exceeded 3050^oF, which may explain the constant concentration for rich flames. In addition, concentrations will remain fairly steady even though flame temperatures are initially above 3050^o as long as the actual concentration is about the same as the equilibrium concentration.

Williams, Sarofim and Fine examined the dependence of nitrogen fixation on excess air (109). They found that diffusion flames will show peak NO_x emissions at higher excess air values than premixed flames. Theoretical results of the simplified Burke and Schumann flame model (109) indicated that the NO emission from flames is dominated by the small volume of oxygen on the air side of the flame front. All reactions of importance in NO formation were essentially quenched at temperatures below 2800°F.

Lange (66) conducted experiments to measure NO_x formation in a premix, natural gas combustor. He used a natural gas, 96% methane with the balance of ethane and propane. Both NO and temperature were accurately specified versus residence time of the hot combustion gases. Measurements were made for various feed conditions. His model (as mentioned on page 23) under predicted the data. Agreement between the model and data was improved by adjustment of some kinetic parameters using a nonlinear optimization method. The final fit was reasonably good, but could be further refined.

Summary

Of the major pollutants in the atmosphere, NO_x (NO and NO_2) is one of the least studied. All researchers of NO_x formation have had problems, including inability to quench the reaction in sample bombs (78), problems with ignition lag (74), and inability to separate the effects of different variables (55). Another problem has to do with the size of the experimental apparatus; Wasser (108) circumvented this problem by using a pilot plant size furnace.

Iya discussed the kinetics of NO formation, including a very readable summary of Zeldovich's chain mechanism (59). This mechanism, first published in 1946, remains the best for prediction of laboratory results over a wide range of temperatures and pressures. The final result of Zeldovich's scheme can be written $dNO/dt = 2k_1(N_2)(O)(1 - k_2k_4/k_1k_3 (NO)^2/((N_2)(O_2)))/(1 + k_2(NO)/(k_3(O_2)))$, which simplifies to $dNO/dt = 2k_1(N_2)(O)$ over short time intervals.

Most previous authors of NO_x formation studies have utilized gaseous fuel and have analyzed for NO_x by some method other than gas chromatograph. Two studies using fuel oil are Mullaney's shock tube experiment on the formation of NO (74), and Wasser's simulates domestic type furnace (108). Neither of these, however, used analysis by gas chromatograph.

Crynes and Maddox give good coverage of current (1971) NO_x control methods employed by stationary sources (22). They note that the extent of NO formation within the flame zone has not been determined. Zeldovich (114) and others have investigated NO_x formation after complete combustion. Bartok and Shaw and Thomas (15, 16), and Argonne National Laboratory (61) showed that the amount of NO_x increased as the amount of nitrogen in the fuel did, and thus that bonded nitrogen in the fuel does play a part in NO_x formation. Also, Williams (110), found that the amount of NO_x formed from elementary nitrogen in the flame is small when compared to the amount produced post flame from the nitrogen fixed in the fuel.

Crynes and Maddox (22) also discussed combustion pollution control under the three headings of fuel treatment, stack gas cleanup, and combustion zone treatment or control. Fuel denitrogenation data are sparse and almost all published efforts at stack gas cleaning concern oxides of sulfur removal, so only the last heading was covered in detail. At present, the most favorable schemes for controlling NO_x emissions seem to be those involving combustion modifications. Attempts to predict NO_x emissions were also covered. Harris (55) conducted a laboratory experiment, and Williams (110) and Bartok (15) postulated models for prediction of stack effluents. These attempts have had only limited success.

CHAPTER III

EQUIPMENT DESIGN

Introduction

The design of the experimental facility used in the study depended in part on the type of flames it was intended to contain. Flame studies have been carried out by a number of investigators (20, 36, 39, 40, 41, 42, 43, 58, 106, 107). An overall view of the mechanism of flame combustion is given by Hirschfelder and associates (41). This discussion was limited to processes in premixed laminar flames (The reaction front propagates at a constant rate into a laminar region containing unburned gas.), particularly those of hydrocarbon-air systems, since these are quantitatively understood. However, these flames provide useful tools for studying high-temperature chemistry, since they exhibit fundamental processes characteristic of more complex systems. Hirschfelder developed experimental techniques for studying flame microstructure which have yielded quantitative studies of physical processes in the flame. Several important reaction steps in a number of flame systems have also been identified.

Kydd investigated the formation and decay of non-equilibrium concentrations of hydrocarbon products in the burnt gases of rich hydrocarbon products in the burnt gases of rich hydrocarbon flames (64.) Evidence indicated that excess concentrations of hydrocarbons arise because those fuel molecules which react first in the flame front were oxidized almost completely, consuming all the available oxygen in the process and leaving a non-equilibrium fraction of fuel either unchanged or converted to other hydrocarbons and sometimes carbon. These products were then attacked at a much lower rate by the oxidation products of the burnt fuel, largely water vapor, until equilibrium was approached. Relative rates of primary oxidation of the hydrocarbons methane, ethane, and ethylene were determined, and the rates of disappearance of methane and acetylene, the major unburnt products, were measured.

Most studies have been concerned with flames utilizing gaseous fuels, notably propane. Walker and Wright (106, 107) used methane and propane gases as fuel; Fristrom and co-workers (42) used propane, as did Friedman and Burke (39); Fine (36) used propane and hydrogen.

One study was found on the combustion of fuel oil. T. D. Brown theorized that when considering the possible equilibria that might exist in a boiler system, the combustion process of the residual oil droplet should be kept in mind (20). This process can be simplified into five stages:

(1) atomization of the fuel
(2) vaporization of the volatile fuel components
(3) combustion of the volatile fuel components
(4) combustion of the residual carbon
(5) vaporization of the mineral constituents

Brown's study seems important to mention and may contain an exact and entire mechanism for fuel oil combustion.

Fuel oil similar to that used in the electrical power generating industry was to be used in this study. Several factors play an important role in the selection of fuel oil by the power industry. Reed (83, 84) presented a comprehensive study of oils, listing availability, fuel price, firing efficiency, handling cost, burner-boiler maintenance cost, quality of attendance, and consumption and firing rate as primary considerations.

Oil combustion equipment has been researched extensively (4, 9, 10, 12, 17, 30, 48, 68, 69, 70, 71, 79, 80, 83, 84, 88, 89). Research on fuel oil burners prior to 1963 was summarized by Locklin (72). Many articles discussed oil burners suitable for use in commercial and industrial installations, fundamentals of oil firing, or possible reduction of air pollutants as a function of equipment (4, 9, 10, 12, 17, 68, 69, 70, 80, 89). In a second group of articles, oil preheating was discussed as a method of preventing incomplete combustion of heavy fuel oils (19, 20, 30, 79, 84, 88).

From the above information, it appears that when possible power generating industries burn number 6 fuel oil. On the other hand, number 6 is too heavy to be burned in a laboratory apparatus, so number 2 fuel oil was chosen instead. It is readily available and has properties somewhat similar to those of number 6.

Description of Equipment

An experimental facility which would combust fuel oil for NO_x formation studies was built in the School of Chemical Engineering at Oklahoma State University. This facility includes an oil feed system, a gas feed system, an atomizer-vaporizer, a combustor and an ignition system.

The oil feed system consists of a gear pump, control valve, and metering valve and rotameter, see Figure 1 for schematic. Oil is pumped to and from a storage vessel by the gear pump, while the control valve maintains a constant pressure head in the recirculation line. A stream of approximately 1 cc/minute is allowed through the metering valve and rotameter to the atomizer-vaporizer. This rotameter contains an R-2-15-AA tube with stainless steel ball.

Figure 2 shows the gas feed system. Here there are two avenues of flow, one to the mixing chamber in the combustor and the other to the atomizer-vaporizer. The stream to the mixing chamber can carry air and/or oxygen-inert gas mixtures. Air or inert gas flows from gas cylinders through one line and is measured with an open-end mercury manometer and a rotameter with a #75 tube. Air is supplied at approximately 20 psig and the inert gas is supplied at 80 psig. Oxygen supplied at 80 psig is monitored by an open-end mercury manometer and by a rotameter with a #73 tube. The second stream supplies 20 psig helium to the atomizer at 825 cc/minute (air basis). It is fed directly from the bottle through a metering valve and rotameter containing a #72 tube. Calibration curves for all rotameters are contained in Appendix A, pages 191-210.

At a flowrate of 1.0 milliliter per minute, number 2 fuel oil does not atomize. This is caused partly by the lack of head pressure and partly because one milliliter of fuel oil is approximately twenty drops, so the feed rate is only about one drop every 3 seconds and is pulsing. Various feed systems were tried in an effort to eliminate the problems of pulsing and failure to atomize. Preheating the oil was also tried, as was increasing the flowrate up to twice the designed levels. Finally,

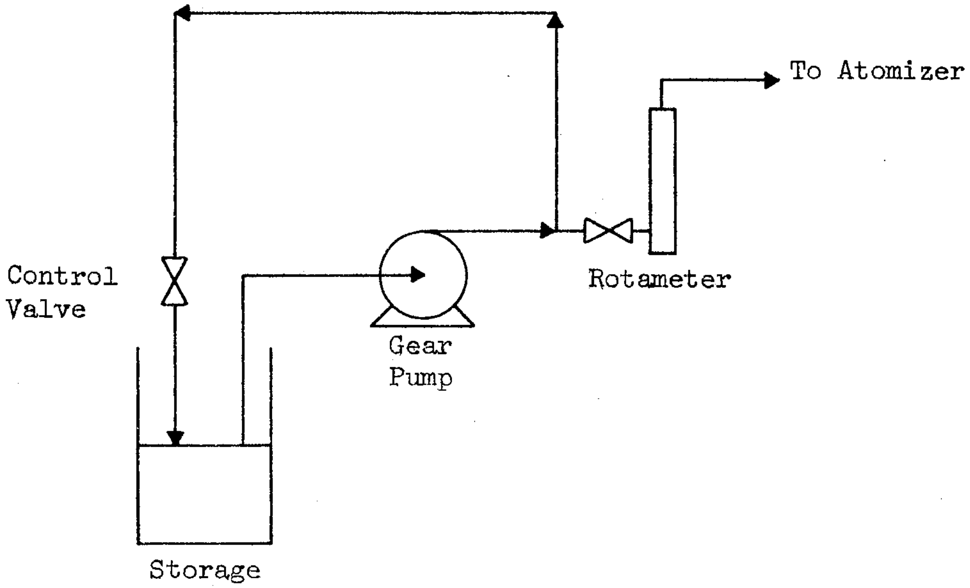
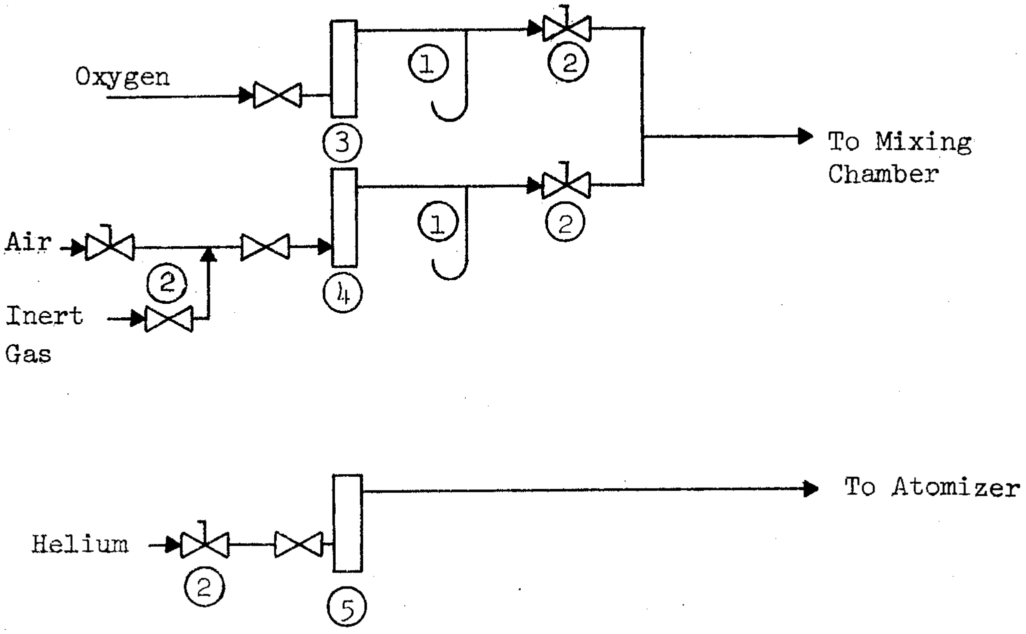


Figure 1. Oil Feed System



LEGEND

1 Open-end mercury manometers
2 "On-off" valves
3 Metering valve with rotameter (#73 tube)
4 Metering valve with rotameter (#75 tube)
5 Metering valve with rotameter (#72 tube)

Figure 2. Gas Feed System

the solution was to use a technique where the feed was vaporized and burned as vapor. The atomizer-vaporizer combines oil and helium and partially atomizes the oil in the atomizer, see Figure 3. The mist enters the vaporizer and is heated until it becomes a gas. The vaporizer consists of two pipe-heaters operated with powerstats connected to the 110 volt line. The 3/8 inch stainless steel tubing through which the oil and vapor passes is packed with glass beads to ensure complete vaporization and turbulence of the oil.

The vapor from the atomizer-vaporizer then enters the combustor; a detailed description of the combustor is shown in Figure 4. The vapor actually enters the mixing changer from the side as the combustible gases enter from the bottom. The mixing chamber is packed with glass beads to assure complete mixing between the two entering streams at a velocity too large to allow immediate combustion. As the mixture leaves the chamber it is burned. The surrounding dead space beside and below the flame is minimized by additional packing of beryl saddles.

The combustor is made of standard 3 inch pipe cut into varying lengths. The first 6 inch section is shown in Figure 5. It contains the mixing chamber, the ignition system, a site glass, three thermocouples (located at 1.5, 2.1 and 3.6 cm above the burner), and two sampling ports (located to take samples at 3.0 and 4.0 cm above the burner). The site glass was included to allow visual inspection of the flame during tests. The next three 9 inch sections are connected and contain three thermocouples (located at 6.0, 12.0 and 36.0 inches above the burner), one sample port at 39.5 cm above the burner, and the thermoswitch. Also, four thermocouples are installed in the wall at flame height and 12, 24 and 36 inches above the flame height. The top three

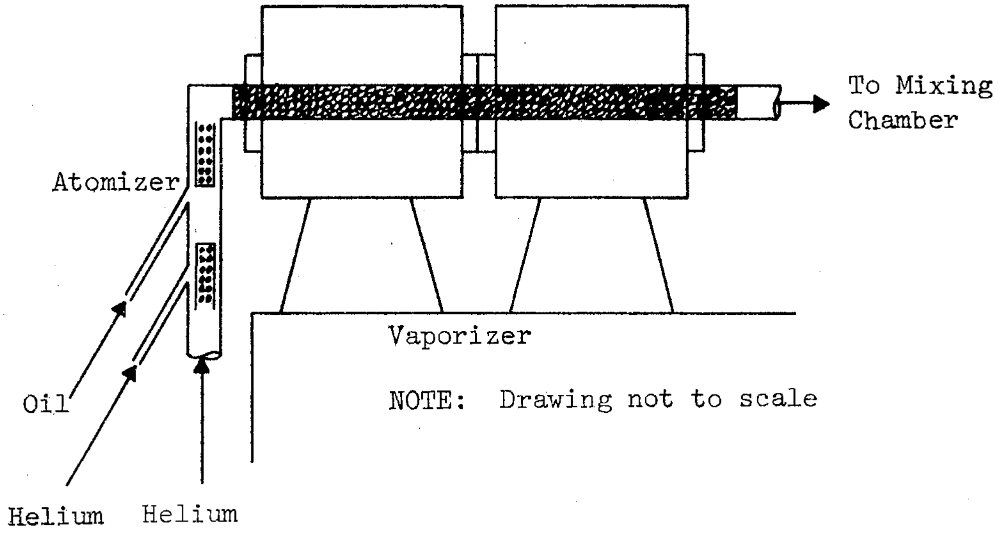


Figure 3. Atomizer - Vaporizer

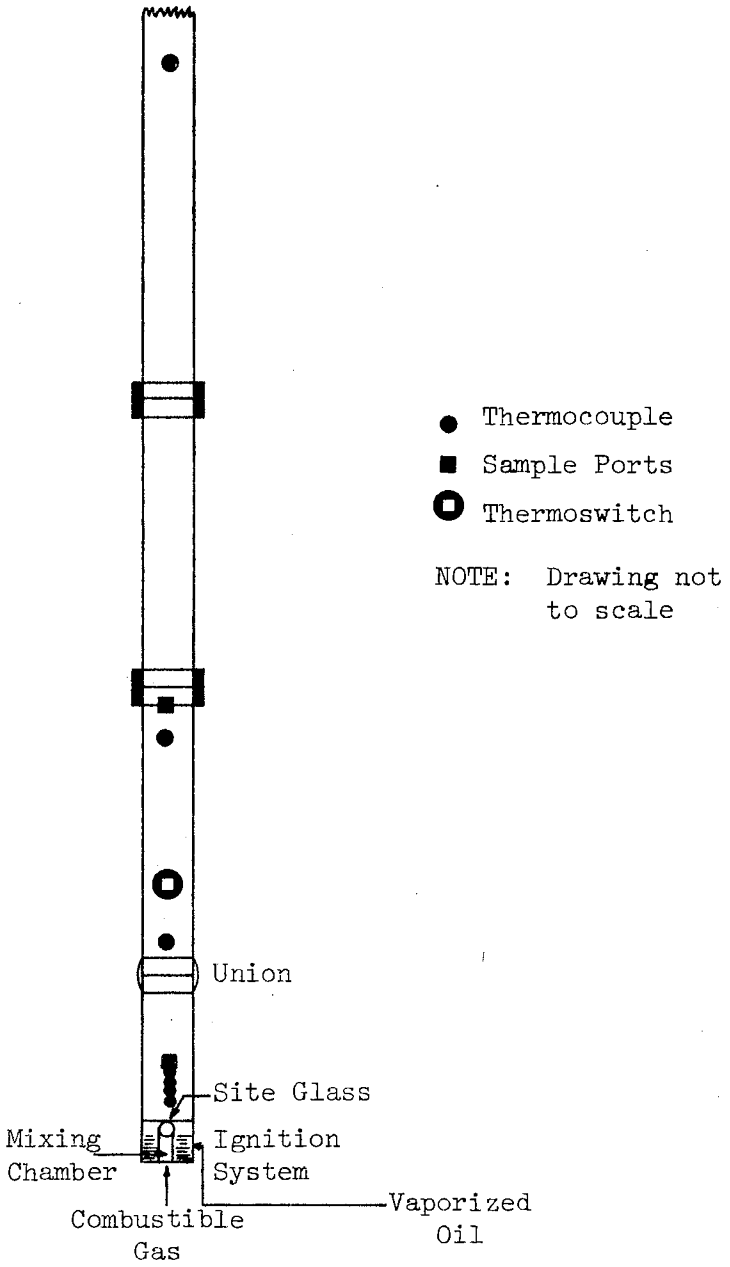


Figure 4. Combustor

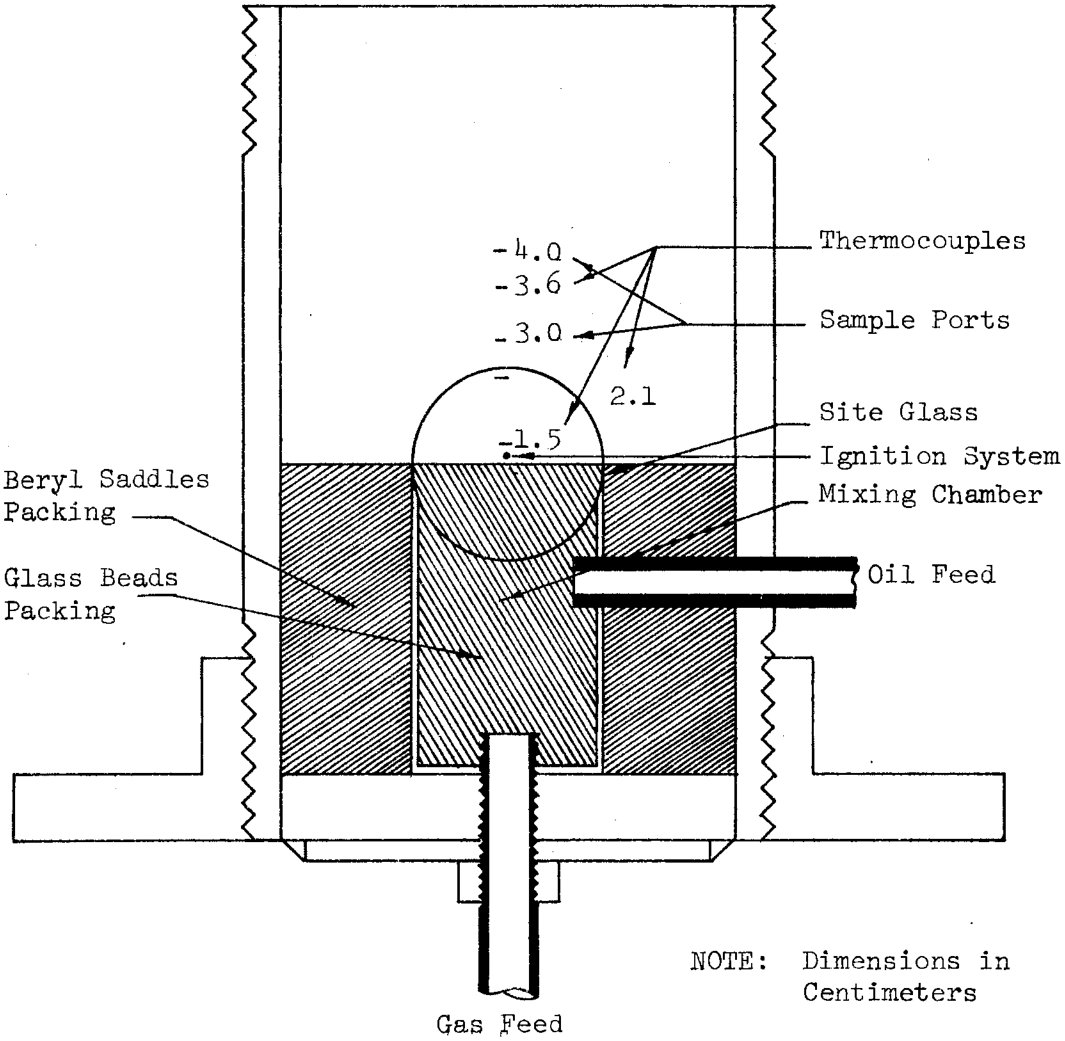


Figure 5. Combustor Chamber

sections are joined to the bottom in a manner which allows access to the inside. To reduce heat loss, the whole chamber is insulated.

The schematic shown in Figure 6 shows the ignition system and the thermoswitch (a safety precaution to eliminate any explosive mixture in the combustor). The ignitor system is a spark gap between the poles of a 2000 volt transformer actuated by an "on-off" switch at operator's control or by the thermoswitch. The thermoswitch is set approximately 5°F below normal operating temperature by adjusting the center set screw. It will then relight the fuel whenever the gas temperature inside the combustor drops 5°F.

The combustion products leave the combustor via a flexible duct or hose and discharge outside the laboratory. Initially the product gases were vented to the laboratory hood, but the air removal capacity of the hood was insufficient to keep fumes out of the laboratory. A supporting rod was added to the end of the flexible hose and was placed outside the laboratory. Gases were then discharged to the atmosphere about 2 feet above the opened window.

Thermocouples used in this study were of various types. Four iron-constantan thermocouples were mounted in the combustor wall at 12 inch intervals (beginning at flame height) to measure wall temperature. Four chromel-alumel thermocouples were used to measure gas temperatures above the flame; they were sheathed and six inches in length. Two tungsten-tungsten/26% rhenium thermocouples, sheathed in 12 inch platinum tubing and capable of measuring temperatures up to 4500°F, measured flame temperature. All thermocouples except those mounted in the wall extended from the combustor into the laboratory. Conductive heat losses resulted; measured temperature was consistently lower than the actual value. These

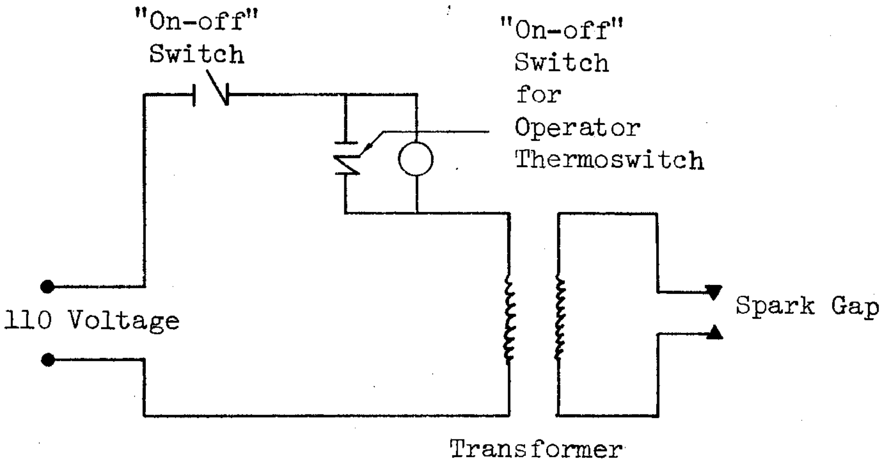


Figure 6. Ignition System

heat losses will be considered in detail during the discussion of results, Chapter VII page 153. Radial temperature profiles require the thermocouples to be moved to a precise location and left there for about a minute to stabilize at the new temperature.

A switching system was installed to facilitate reading all the thermocouples with one Leeds and Northup potentiometer. Calibration curves for the thermocouples and switching system are contained in Appendix A, pages 191-210. Calibrations were done in accordance with ASTM-E207-66 (8).

A summary of the equipment utilized in the research is shown in Table X. Table XI contains a summary of chemicals used.

TABLE X

LIST OF EQUIPMENT UTILIZED

Name	Model or Serial Number	Vendor
1. Thermocouples		
(a) iron-constantan	N/A	Fabricated
(b) chromel-alumel	N/A	Donated by Tom Barnyard Equipment Company
(c) tungsten-tungsten/ 26% rhenium	(Special Order)	Conax Corporation
2. Rotameters		
(a) oil	R-2-15-AA	Matheson
(b) air/argon	75	Matheson
(c) oxygen	73	Matheson
(d) helium	72	Matheson
3. Oil Pump	SN 4-70	Tuthill with Grahams transmission variable model BD4R4-M
4. Pipe Heater	Type 70 Multiple Unit	Hevi-Duty Equipment Company
5. Potentiometer	8686 SN1675446	Leeds & Northrup
6. Powerstats	Input 120 VAC, 7½ AMPS	Superior Electric Company
7. Heating Tapes	Briskheat	W. H. Curtin & Co.
8. Thermoswitch	(unable to determine)	Fenwal
9. Transformer	Model 150 Primary 115 VAC Secondary 10,000 V	Forest Electric Co.
10. Site Glasses	Quartz	Corning Glass
11. Vacuum Pump	SN-12792-2	W. M. Welch Mfg. Co. (Welch Duo-Seal)

TABLE XI

LIST OF CHEMICALS UTILIZED

Name	Purity	Vendor
No. 2 Diesel Oil	Not Available	University Service Station
Pyridine	Certified ACS	Fisher
Oxygen	99.995%	Matheson
Argon	99.96%[2]	Sooner (Linde)
Air	21-22% O_2 78-79% N_2	Sooner
Helium		
(1)	99.9%[1]	Sooner (Linde)
(2)	99.9999%	Matheson
Nitric Oxide in Nitrogen		
(1)	1023 ppm	Matheson
(2)	532 ppm	Matheson
(3)	207 ppm	Matheson

[1] Impurities present: Argon
Neon
Hydrogen
Hydrocarbons (methane)

[2] Impurities present: Oxygen
Nitrogen
Methane

CHAPTER IV

SAMPLING AND EXPERIMENTAL PROCEDURES

Sampling a gas stream without disturbing its streamlines (and thus negating the possibility of obtaining a representative sample) is difficult. Sampling a flame front is even harder. Fristrom pointed out that a principal problem in flame research has been the development of methods of measuring the detailed velocity, temperature, and composition history in a flame front as a function of distance (41). However, local concentrations of a stable species can be measured using quartz sampling probes in the form of miniature supersonic nozzles (10^{-3} to 10^{-4} inch inlet diameter) which freeze the composition of the reacting sample by rapid (10^{-5} second) adiabatic expansion.

Friedman studied flame front sampling (38, 39, 40), finding that a 12-micron wire could measure temperatures without disturbing the streamlines (38). Later, he successfully used probes of simply fused quartz tubes (originally 2 mm o.d. with the end drawn to a capillary tip) to sample the flame front, introducing the probe from above to minimize flow disturbance. He reported that the probe tip had to be located at least 0.7 cm above the luminous zone to keep from disturbing the flame surface (39). This result was duplicated by Longwell and Weiss (69).

Hudson and co-workers investigated flame sampling with tapered fused quartz probes of varying sizes (58). Some had tips as large as 0.1 mm i.d., since the larger probes should cause less pyrolysis of the sample. However, preliminary experiments showed that the larger probes disturbed the streamlines too much; representative samples could not be obtained, and the smaller probes gave better results. Samples were taken with fine probes at various distances to the flame front using the center of the luminous zone as a reference surface.

Halpern and Ruegg sampled flame gases using water-cooled probes of internal diameter of 0.027 to 0.070 cm (53). They were interested in the effects of sampling conditions on concentrations of CO, CO_2, H_2, and H_2O. They found that no probes were able to quench reactions completely and thus to preserve the original composition of the gas, but that smaller size probes were generally more effective. Probe material and configuration had little effect on sample composition, and composition was unaffected by sampling velocity, with one expection. At the higher rates of sampling, quenching effectiveness decreased, possibly because of the large temperature and composition gradients.

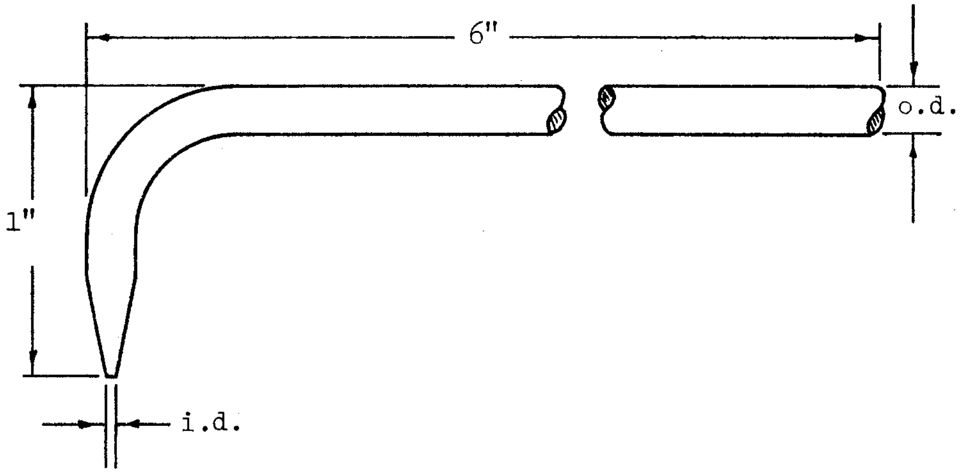
Fine sampled a lean, flat hydrogen/propane flame with uncooled quartz probes (3 mm i.d., drawn to a tip orifice of 25 microns diameter) and analyzed the samples by gas chromatograph (36). Orifice size was adjusted with change in chamber pressure to provide a roughly constant sampling rate. For a given flame at constant pressure, a moderate change in orifice size or shape did not change the slope of the decay profile (fuel concentration versus time). Some changes occurred in duplicate run levels of CO and H_2, possibly because of a systematic error of a few tenths of milliliter in recording the position of the probe relative to the burner.

Consideration of effects of diffusion and of chemical reactions within the probe showed that decay profiles could be converted to time rates of decay in the burned gas. However, because of the complicated shape of the decay profiles, results could be considered only qualitatively.

Lange used a probe made of 0.05 inch i.d. alumina to sample a flame front for NO_x (66). Due to radiative heat loss, probe temperature was well below that of the gas in the stack, and test results showed that the probe provided an adequate quench of the NO forming reactions. Variations in probe internal diameter and sampling rate did not significantly affect NO measurement, leading Lange to conclude that no wall-catalyzed reactions were occurring in the probe.

With the above information in mind, two groups of fused quartz sample probes were fabricated in the Oklahoma State University glass shop. One set of originally 0.60 mm o.d. and the other was 0.40; both were tapered as quickly as possible to a 0.05 mm i.d. Complete specifications are given in Figure 7. A pressure drop of 3 inches (mercury) through the probe tip quenches the hot gases from $3400^{o}F$ to below $2450^{o}F$ (polytropic expansion). Below $2850^{o}F$, the formation and decomposition of NO is frozen.

The sample probes were mounted in the wall of the combustor at 3.0, 4.0 and 39.5 centimeters above the burner, see Figure 8. Mounting glands were shop-modified Swaglock fittings. The fittings with male pipe threads were drilled to hold the sample probes. The metal ferrules were replaced with ones made of Teflon. By adjusting the pressure of the retaining nut on the Teflon ferrules, the probes could be moved from the wall to the chamber centerline; samples could thus be taken to determine radial concentration profiles. Tip location in the chamber was measured from entrance point, and was normally set at the centerline of the chamber (1.5 inches from entrance).

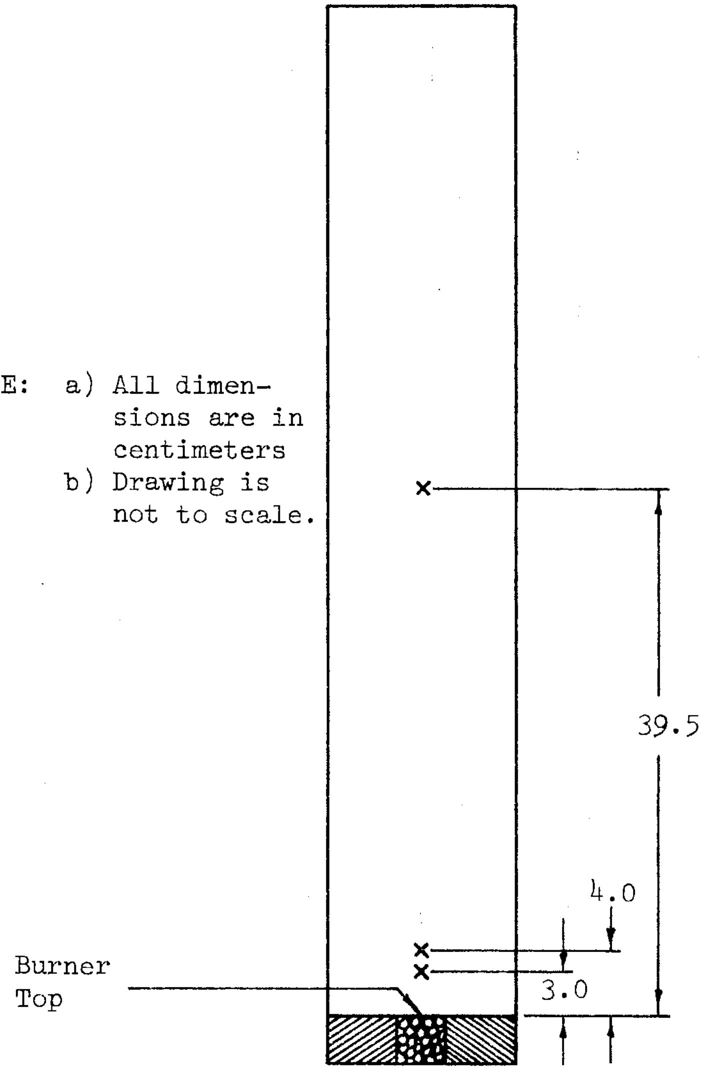


Material: fused quartz

Set Number	o.d.	i.d.
1	0.06	0.05
2	0.04	0.05

NOTE: a) o.d. and i.d. dimensions are in centimeters
b) Drawing is not to scale.

Figure 7. Sample Probes



NOTE: a) All dimensions are in centimeters
b) Drawing is not to scale.

Figure 8. Location of Sample Ports in Combustion Chamber

The exact sampling procedure which was finally used evolved from experimenting with different sampling methods. Initially, samples were taken from three locations, using a vacuum pump and Tygon tubing to pull a sample through the probe into a sample bomb; the connection between probe and bomb was flexible so that an accidental jar would not break the sample probe. The filled sample bombs were set aside for later analysis. Grade 6 helium purged the sample from the bomb and into the sample loop of the gas chromatograph.

Since analysis requires approximately 30 minutes, some of these samples remained in the bombs for over 24 hours. To check on the possibility that adsorption of NO on the walls could have taken place during this time, some bombs were charged with known quantities of NO, stored, and analyzed after specific periods of time. None of these tests indicated adsorption of NO over a long period of time, see Figure 9.

Figure 9 actually contains two sets of data. The upper set was obtained by filling a sample bomb to a pressure of 50 psig with 1023 ppm of nitric oxide in nitrogen gas. Nitrogen was used to pressurize the bomb to 100 psig. The mixture was analyzed with the gas chromatograph at gas storage times of 0, 0.25, 0.5, 1, 2 and 4 hours. After four hours, there was not sufficient gas remaining in the bottle for a representative sample.

The lower set of data was obtained in the same manner. In this case the bomb was filled only to 25 psig with the nitric oxide gas and then pressurized to 100 psig with nitrogen. There was no way in this study to determine the instantaneous adsorption of NO on the walls as NO was charged into the bombs.

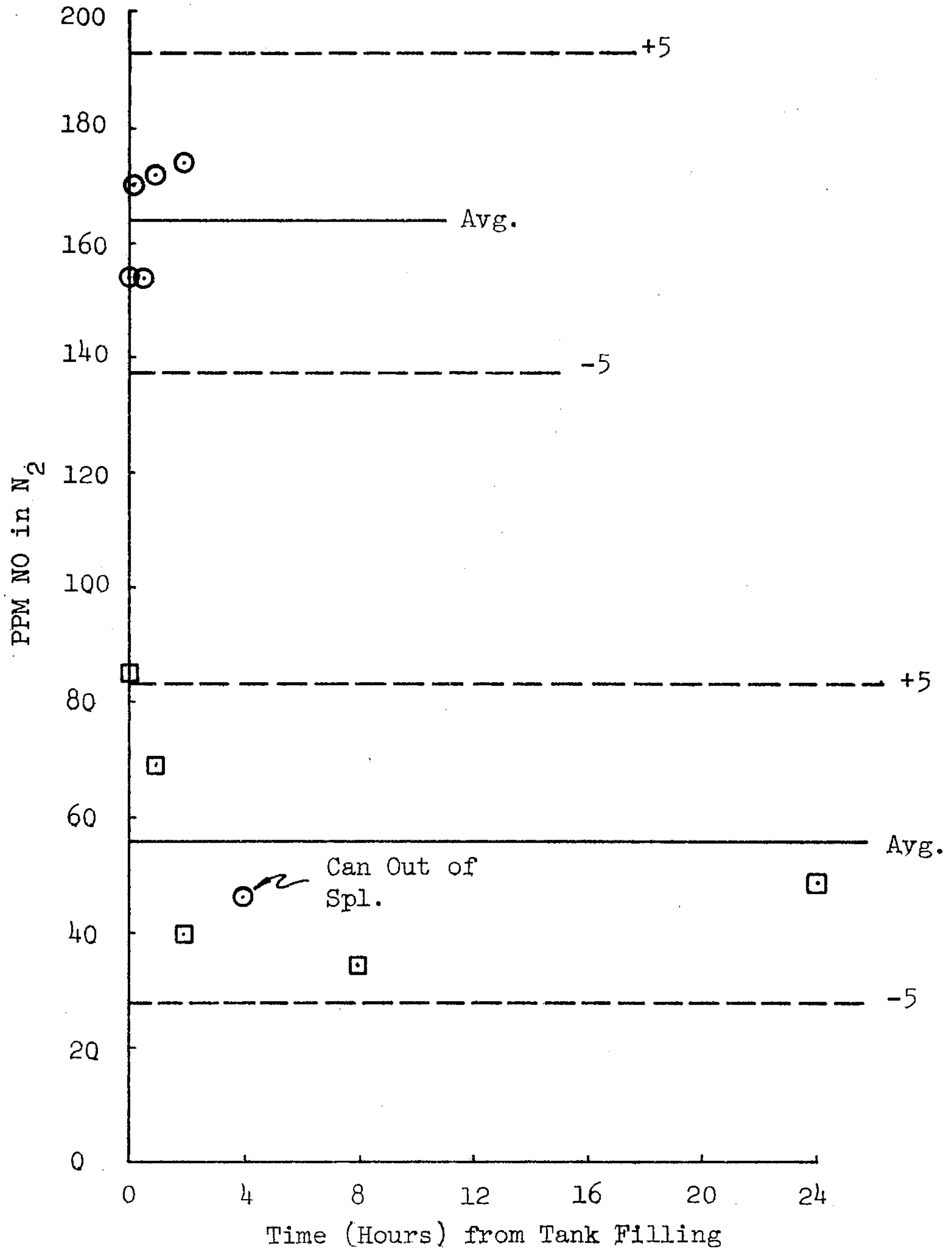


Figure 9. Adsorption Study of NO on Sample Vessel Walls

The second sampling procedure used involved a continuous sampling stream through the probe located 3.0 centimeters above the burner. This reduced the number of samples stored in the bombs but also reduced the number of samples taken through this probe because of the 30 minute analysis time.

Finally, a continuous sampling system was installed, see Figure 10 for schematic. A vacuum pump pulled the sample from the chamber through a probe into the sample loop of the chromatograph at a pressure of 26.2 inches of mercury. A rotameter was placed into the sample line in an effort to measure flow. However, the flow was not sufficient to register on the rotameter. Thus, the only control of the sampling flowrate was by maintaining constant temperature and pressure on the lines.

For this reason the sample lines were heated to approximately 100°C by heating tapes. To further reduce any errors due to varying sample size, all components determined by gas chromatograph were rated to the amount of nitrogen present in the sample.

Samples were taken every 30 minutes, alternating between the two ports located at 3.0 and 39.5 centimeters above the burner. Once a sample had been introduced into the chromatograph, the valve to that port was closed and the other opened. Thus, the sample line was purged 30 minutes before each sampling (approximately 18 minutes was required to purge the lines).

The solubility of NO in water, as cited in Volume 3 of the International Critical Tables, page 256, was used to compute the amount of NO that would be contained in the condensed water vapor present from the combustion of 1 mole of fuel oil. At 100°C, only 4.3×10^{-6} grams

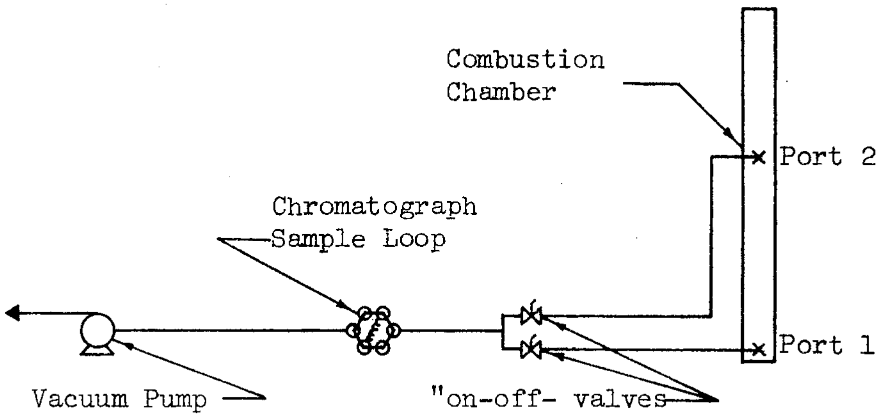


Figure 10. Schematic of Continuous Sampling System

of NO would be dissolved, even if all of the water vapor were condensed. This figure represents only 1.02% of the NO which could be formed from 1 mole of fuel oil.

A detailed operating procedure covering normal startup, running and shutdown of equipment is presented in Appendix B-1, pages 213-214. Normal operating conditions are shown in Table XII. Safety procedures including emergency shutdown, and the instructions posted on the inside of the laboratory door are presented in Appendix B-2, pages 215-217.

Normal startup lasted 5 to 7 minutes. Once startup was complete, the vacuum pump purged the sample lines; the first sample was taken 30 minutes into the experimental run. Operating conditions were usually reached within the first 15 minutes of the run.

Thermocouple temperatures were monitored and recorded every 15 minutes. A complete transverse of the ten thermocouples required about five minutes. Initial transverse of the ten thermocouples required about five minutes. Initial temperature readings (zero time readings) were taken on all thermocouples prior to each startup. Thermocouple locations are shown in Figure 11. The remainder of the time between readings was left for collecting samples and maintaining the gas chromatograph in continuous operation.

TABLE XII

STANDARD OPERATION CONDITIONS

Component	Rate	Pressure[1]	Specification
Oil	1.0 ml/min	-	Number 2 diesel oil (regular or with pyridine)
Oxygen	Varying[2]	80	99.995%
Inert Gas (Argon)	Varying[3]	80	99.96%[5]
Air	Varying[4]	20	21-22% oxygen 79-78% nitrogen
Helium	825.0 ml/min	20	99.9%[6]

[1] Pressure measured on pressure regulator in psig.

	2	3	4
80% stoichiometric amount	4.75	16.85	21.60
100% stoichiometric amount	5.94	21.06	27.00
120% stoichiometric amount	7.13	25.27	32.40

[5] Likely impurities are nitrogen, oxygen, neon.

[6] Likely impurities are nitrogen, neon.

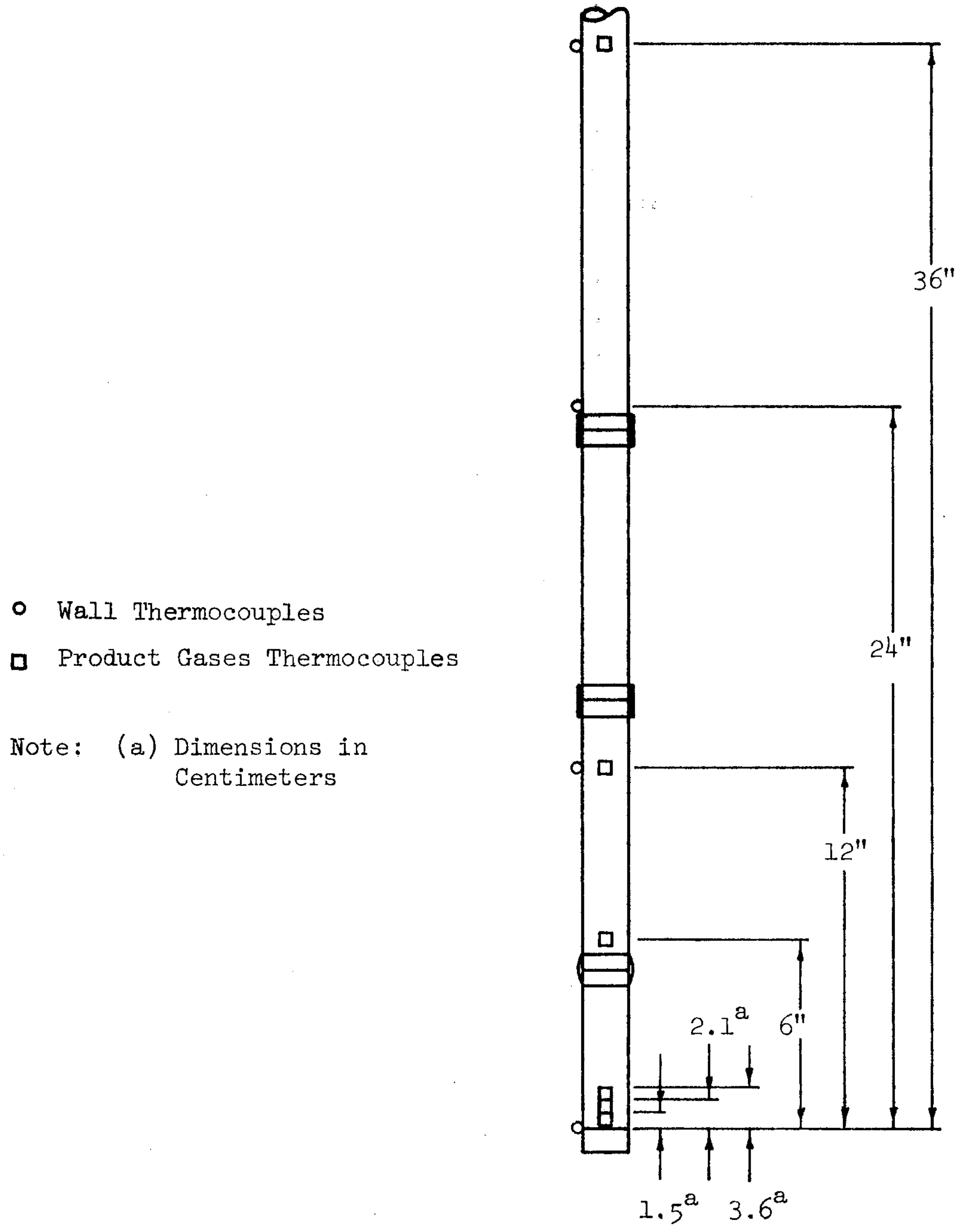


Figure 11. Overall Thermocouple Locations

CHAPTER V

GAS CHROMATOGRAPHIC ANALYSIS OF NO_x

Traditionally, wet chemistry techniques were used to analyze for NO and NO_2; Saltzman's well-known method was developed in 1954 (91). Since then, many other techniques have been used (5, 21, 25, 27, 29, 34, 43, 63, 93, 100, 111). Comer and Jensen described a spectrophotometric method for determining total NO_2 and N_2O_4 in the air (21). Faucett, McRight and Graham discussed the use of the modified Griess-Ilosay method for analyzing NO and NO_2 emitted from a nitric acid plant (34). Wilson and Kopczynski ran laboratory tests on analyzing NO with dichromate paper (111). Ellsworth discussed the efficiency of inexpensive glass culture tubes as disposable colorimetric cuvettes (29). DiMartini used a Nitrate-Specific-Ion Electrode in a flowing gas stream to measure NO and NO_2 (25).

A primary problem in analysis of NO_x is that the oxides of nitrogen do not separate easily, Thus, the methods listed above are all long and somewhat tedious. To reduce the time and effort involved, a gas chromatograph was used in this study. Separation of nitrogen oxides for gas chromatographic analysis has been effected various ways. DeGrazio used a 6 foot column of silica gel with a 4 inch molecular sieve column at 180°C to separate nitrous oxide and carbon dioxide in a gas-solid chromatographic study (24). Morrison and Corcoran analyzed for NO_2 by gas chromatograph using an electron-capture detector (73).

Healy and Urone used a flowing liquid colorimetric detector for determining NO_2 (56).

In the present study, NO_x analysis at near ambient conditions by gas chromatograph was desired. A first study of this type utilized a packed separation column and was carried out in 1957 by Szulczewski and Higuchi (97). Oxygen, nitrogen, nitric oxides, and carbon monoxide were successfully separated with a silica gel column at the temperature of dry ice/acetone. In 1958, Green and Pust used an unactivated Linde 5A molecular sieve column (49). Two milliliters of water were pipetted onto the interior end of the absorbent. NO_2 introduced to the column was rapidly converted to NO by the water absorbed on the column. The NO was then analyzed. Also in 1958, Smith and co-workers studied the chromatographic analysis of gas mixtures containing nitrogen, nitrous oxide, nitric oxide, carbon monoxide, and carbon dioxide (96). A column using iodine pentoxide between two layers of silica gel made possible the separation and determination of the gases in 10 minutes.

Sakaida, Rinker, Cuffel, and Corcoran used a silica gel column to separate NO from other nitrogen oxides and a dual-thermistor thermal conductivity cell as a sensing unit (90). The silica gel was pretreated at 150°C to 200°C for 20 hours with dry helium treated with NO and NO_2 so that active sites could adsorb these gases. The column had to be regenerated frequently to replace NO and NO_2 lost from active sites. Column temperature varied from 70° to 90°C, and retention time for NO was 190 seconds. Frossard, Rinker and Corcoran repeated this study for temperatures of 75° and 150°C (43). Retention time for the NO component increased at 75°C from 190 to 258 seconds but was reduced at 150°C to 126 seconds.

Trowell successfully separated the oxides of nitrogen using an elaborate three column arrangement (104). The first column was packed with 0.5% carbowax 1500 on silanized glass beads and treated with 1.0 milliliter of NO_2. Column 2 was packed with 40% dimethyl sulfoxide Gas Chrom RZ and prepared using acetone as a solvent; column 3 was packed with 13X molecular sieves, and activated for 5 minutes at 250°C with rapid helium purge. Column 1 temperature was -76°C while the other two were maintained at 25°C

A Micro Tek ultrasonic detector gas chromatograph suited for trace gas analysis was used for the current study. Noble, Abel, and Cook published one of the first articles covering the theory and instrumentation for a detector based on the measurement of the velocity of ultrasound (76). Later articles have also discussed the ultrasonic detector and gas chromatograph (32, 50, 62, 82, 102). This type of detector measures sound waves passing through a reference gas, normally grade 6 (99.9999%) helium, and compares this signal to that of a sound wave passed through a sample gas. The difference in phase between the two signals produces an EMF voltage which is sent to the receiving body, normally the recorder. One of the most useful features in the detector instrumentation is that even if the phase angle is greater than 360°, the signal is sent as one signal, thus eliminating fold-over. Kate thoroughly discusses the theory and instrumentation for the ultrasonic detector and gas chormatograph in his dissertation, Oklahoma State University (62). Interested parties should refer to this publication for detailed information.

Dietz used treatment molecular sieves to determine NO (26). Dietz's article is the basis for the technique used in this study.

His separation column consisted of a six foot stainless steel (¼ inch o.d.) tubing containing Linde 5A molecular sieves; this packed tubing was then coiled for easy fit into the gas chromatograph oven. Pretreatment for the column as specified by Dietz was as follows:

1. The molecular sieve was activated for 20 hours at 300°C under a vacuum to remove water vapor.
2. A low flow (undefined amount) of helium was introduced at 300° to minimize the possibility of oxygen adsorption (no time limit was given; ½ hour was assumed sufficient).
3. A low flow of NO (again, no amount was given) replaced the helium for 1 hour to saturate the column with NO.
4. The temperature was lowered to 20°C while maintaining the NO flow.
5. Following NO saturation of the sieve at 20°C for about ½ hour, the column was flushed with helium to remove excess NO, again taking care to exclude oxygen to prevent the premature formation of NO_2.
6. After flushing with helium for about ½ hour, oxygen was introduced to convert the remaining more tightly bound NO into permanent NO_2. Flow was maintained for about ½ hour at 25°C (no indication was given for temperature change).
7. The temperature was then raised to 100°C while maintaining oxygen flow for ½ hour to ensure complete conversion to NO_2.

After this, the column was installed into the oven and the gas chromatograph was ready for operation.

Dietz specified a carrier gas of ultra-pure helium to be fed at a rate of 25 cc/minute under a delivery pressure of 40 psig. Initial column temperature of 60°C was maintained for 4 minutes after which the temperature was increased to 250°C at a constant rate of 30°C per minute. The final temperature was held for 8 minutes to ensure the elution of carbon dioxide, the last component, prior to cooling to initial temperature.

Actual conditions for the present study differed from those described above in that if gases left the oven at 250°C, they could not cool down to 125°C (the temperature of the detector) before entering the detector. This temperature difference resulted in baseline drift, especially at low attenuations. Also, the temperature programming unit of the chromatograph oven did not have a functional upper temperature limit. For these reasons, the oven was maintained at 75°C. All gas chromatograph conditions for this study are presented in Table XIII. Some of the conditions were due entirely to certain idiosyncrasies of the gas chromatograph used.

The gas chromatograph was calibrated using purchased gas mixtures of 207, 532 and 1023 ppm nitric oxide in nitrogen gas. To ensure that the same amount of gas was introduced into the gas chromatograph on each analysis, a constant-back-pressure apparatus utilized by Kate (62) in his research at Oklahoma State University was installed on the sample loop. The constant conditions on the sample lines minimized the variation in sample size.

Table XIV contains representative data for the gas chromatograph calibration. The data were obtained from chromatograms; a typical calibration chromatogram is exhibited in Figure 12-A. Peak areas were computed by multiplying the height by the width at half-height, as shown in Figure 12-B. The NO peak area was then divided by the

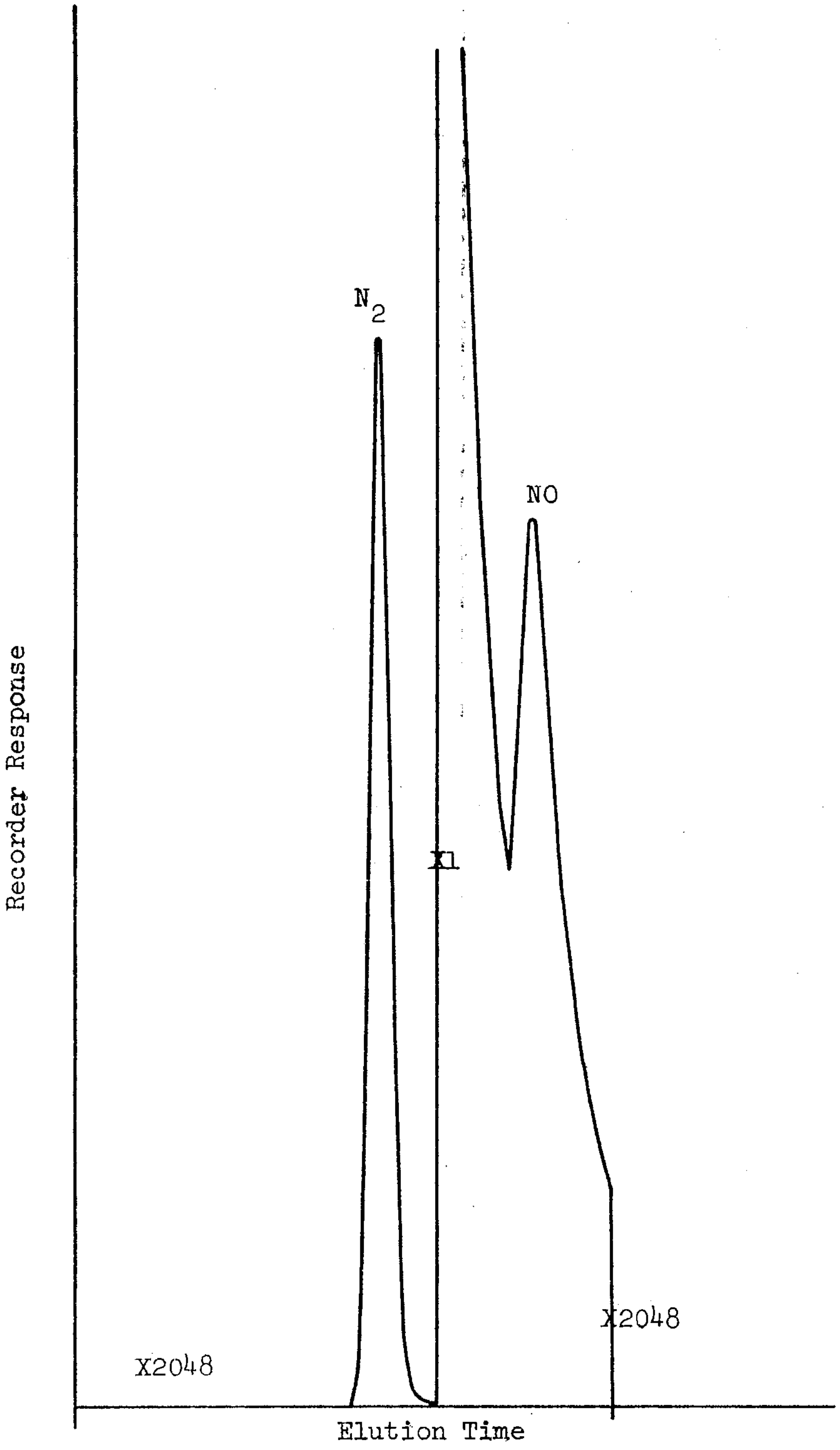
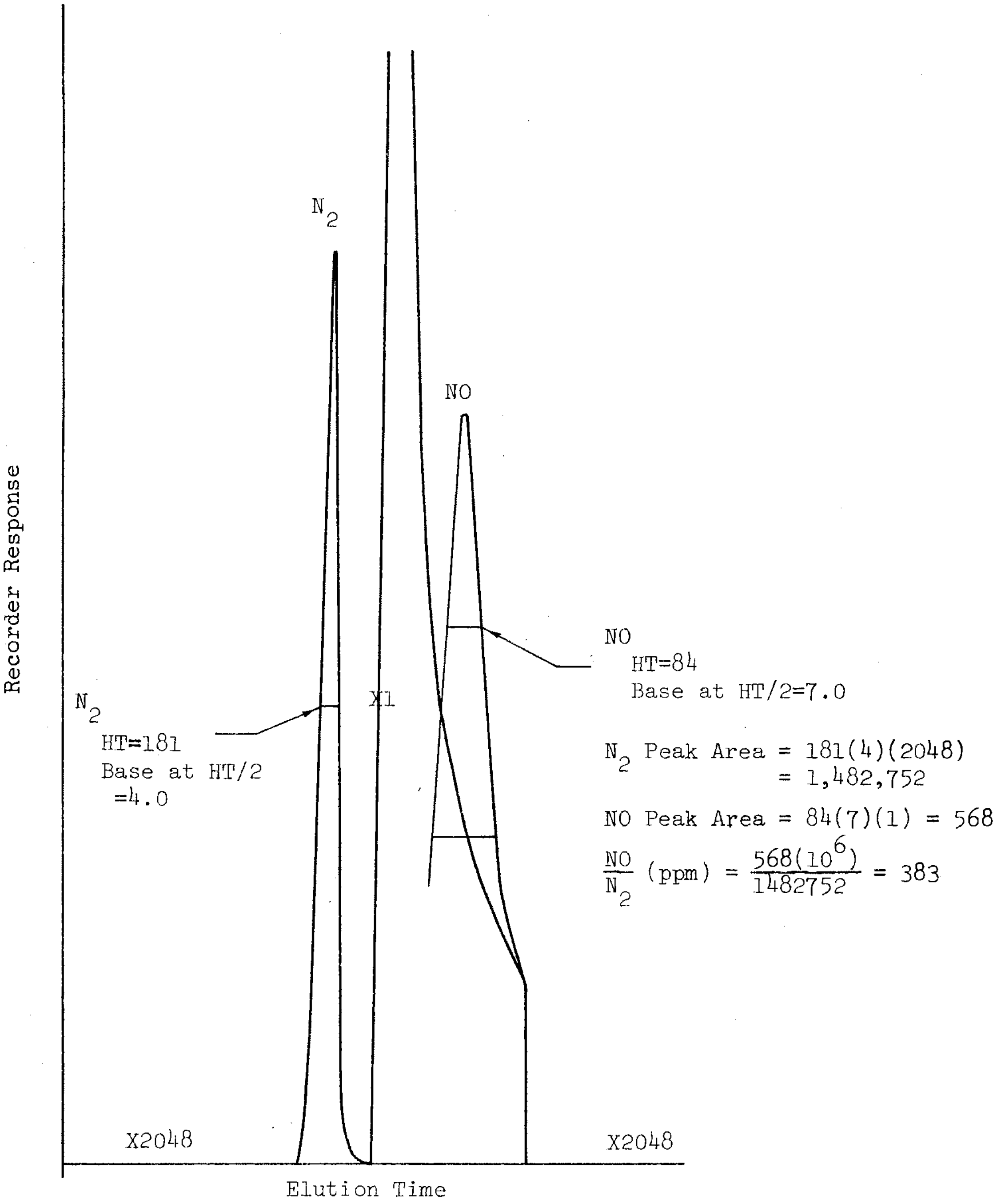


Figure 12A. Calibration Chromatogram



N_2 Peak Area = 181(4)(2048)
= 1,482,752

NO Peak Area = 84(7)(1) = 568

$$\frac{NO}{N_2}\ (\text{ppm}) = \frac{568(10^6)}{1482752} = 383$$

Figure 12-B. Computation of Calibration Chromatograph

nitrogen peak area to give ppm of NO. According to these calculations, only about one third of the NO introduced to the chromatograph was accounted for. The data taken over a day were averaged. The average are plotted in Figure 13 and show the "calibration factor" for the gas chromatograph.

TABLE XIII

GAS CHROMATOGRAPH CONDITIONS

Helium (Grade 6) Flow	25 cc/minute
Head Pressure	40 psig
Back Pressure	25 psig
Flow Rotameter Settings[1]	
(i) Channel A	5.1
(ii) Channel B	4.3
Column Temperature	75°C
Temperature Programmer	Isothermal Mode
Channel Selector[2]	"A" Mode
Zero Phase Angle Setting	18°

[1] Calibration curves are presented in Appendix A, pages 191-210.

[2] Sample fed only through "A" detector.

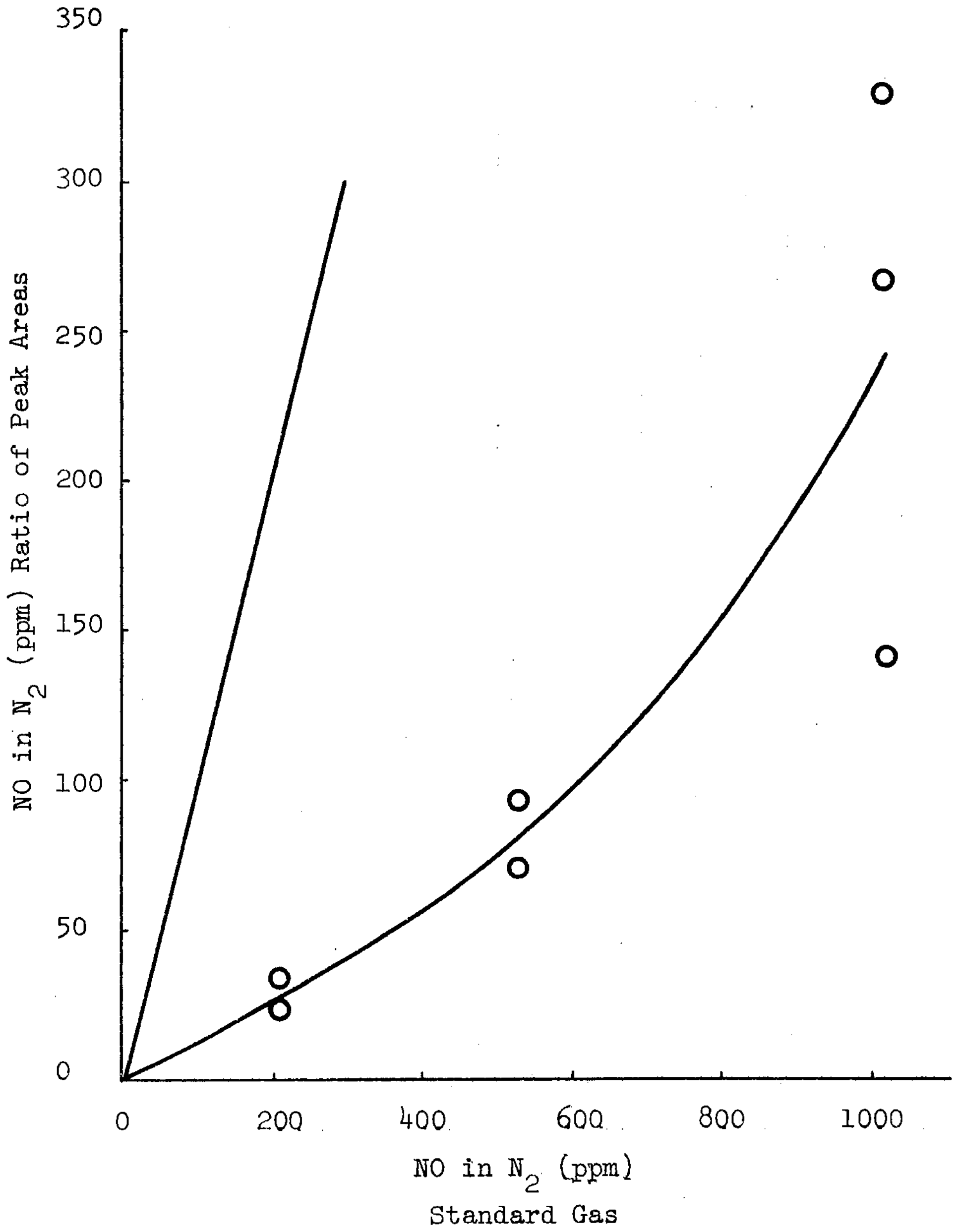


Figure 13. Chromatographic Calibration (Ratio of Peak Areas, NO/N_2 vs. NO/N_2(ppm))

TABLE XIV

CALIBRATION DATA

Standard Gas Concentration (ppm NO in N_2)	Sample Number	N_2 Peak Area x 10^6	NO Peak Area	ppm NO in N_2	Average
1023	1	1.2616	140.2	111.2	
	2	1.2816	185.5	144.7	
	3	1.3386	214.5	160.2	
	4	1.3160	206.2	156.7	
	5	1.4008	348.0	248.4	
	6	1.2902	396.8	307.5	
	7	1.2427	372.0	299.3	
	8	1.3427	306.0	327.9	
	9	1.2945	390.0	301.3	
	10	1.30744	381.0	291.4	
	11	1.2847	390.0	303.6	
	12	1.2931	532.0	411.4	
	13	1.2616	420.9	333.6	
	14	1.2931	378.0	292.3	
	15	1.3074	375.0	286.8	
					264.0
1023	1	1.3099	-	Not included	
	2	1.3517	91.0	67.3	
	3	1.3107	135.0	103.0	
	4	1.3312	187.5	140.8	
	5	1.3066	199.5	152.7	
	6	1.2939	186.0	143.7	
	7	1.3189	251.2	190.5	
	8	1.2861	238.0	185.0	
					140.0
1023	1	1.4828	481.4	324.6	
	2	1.4991	553.0	368.9	
	3	1.5366	471.0	306.5	
	4	1.5282	456.0	298.4	
	5	1.5240	518.0	339.9	
					328.0
532	1	1.3498	24.0	17.8	
	2	1.3853	77.0	55.6	
	3	1.3738	112.0	81.5	
	4	1.4295	81.0	56.7	
	5	1.4236	72.0	50.6	
	6	1.4107	126.0	89.3	
	7	1.4150	91.0	64.3	
	8	1.4023	140.0	99.8	
	9	1.3926	135.0	96.9	

TABLE XIV (Continued)

Standard Gas Concentration (ppm NO in N_2)	Sample Number	N_2 Peak Area x 10^6	NO Peak Area	ppm NO in N_2	Average
	10	1.4275	112.5	78.8	
	11	1.4008	112.0	80.0	
					70.0
532	1	1.5913	133.0	83.6	
	2	1.5618	130.0	83.2	
	3	1.5827	147.0	92.9	
	4	1.6204	176.0	108.6	
	5	1.5655	147.0	93.9	
					92.0
207	1	1.4090	28.0	19.9	
	2	1.4172	30.0	21.2	
	3	1.4008	35.0	25.0	
	4	1.4008	30.0	21.4	
	5	1.4008	30.0	21.4	
	6	1.4358	30.0	20.9	
	7	1.3885	28.0	20.2	
	8	1.4008	42.0	30.0	
	9	1.3926	24.5	17.6	
					22.0
207	1	1.5114	66.0	43.7	
	2	1.5483	35.0	22.6	
	3	1.5030	48.0	31.9	
	4	1.5114	56.0	37.0	
	5	1.4909	42.0	28.2	
					33.0

As evident in the data, two-thirds of the NO was adsorbed somewhere in the chromatograph, or the purchased, standard calibration gas mixtures contained different ratios of NO to N_2 than labeled. Unfortunately, the latter explanation came to light only recently and has not been explored. This theory arose from experimental work done by my present employer, Mississippi Chemical Corporation. Some standard NO gas was purchased for a gas chromatograph study. Laboratory personnel could not obtain the labeled concentration by gas chromatographic analysis. When wet analysis gave results comparable to those from the gas chromatograph, the standard gas was returned to the vendor. Future experimenters are advised to explore this avenue.

Complete results of the gas chromatograph analysis of the combustion products are presented in Table XXV, pages 132-138. These results were obtained from chromatograms similar to the sample shown in Figure 14-A. Computation of peak areas followed the procedure described above and are shown for this sample in Figure 14-B. NO peak area was then divided by the nitrogen peak area; this number was multiplied by a proportionality constant to change the ratio of peak areas to ppm based on total gas flow, as shown in Appendix C, page 223. Constants are summarized in Table XV.

The NO_x value (ppm) was placed on the ordinate axis of Figure 15 and projected horizontally until the curve was intersected. The intersection was projected onto the abscissa. This value is the amount of NO_x present in the combustion product gases. Figure 15 contains data not presented in Table XIV; this information can be found in Laboratory Notebooks (Ryan Moats, NO_x) filed with the School of Chemical Engineering, Oklahoma State University. Table XVI exhibits the procedure for

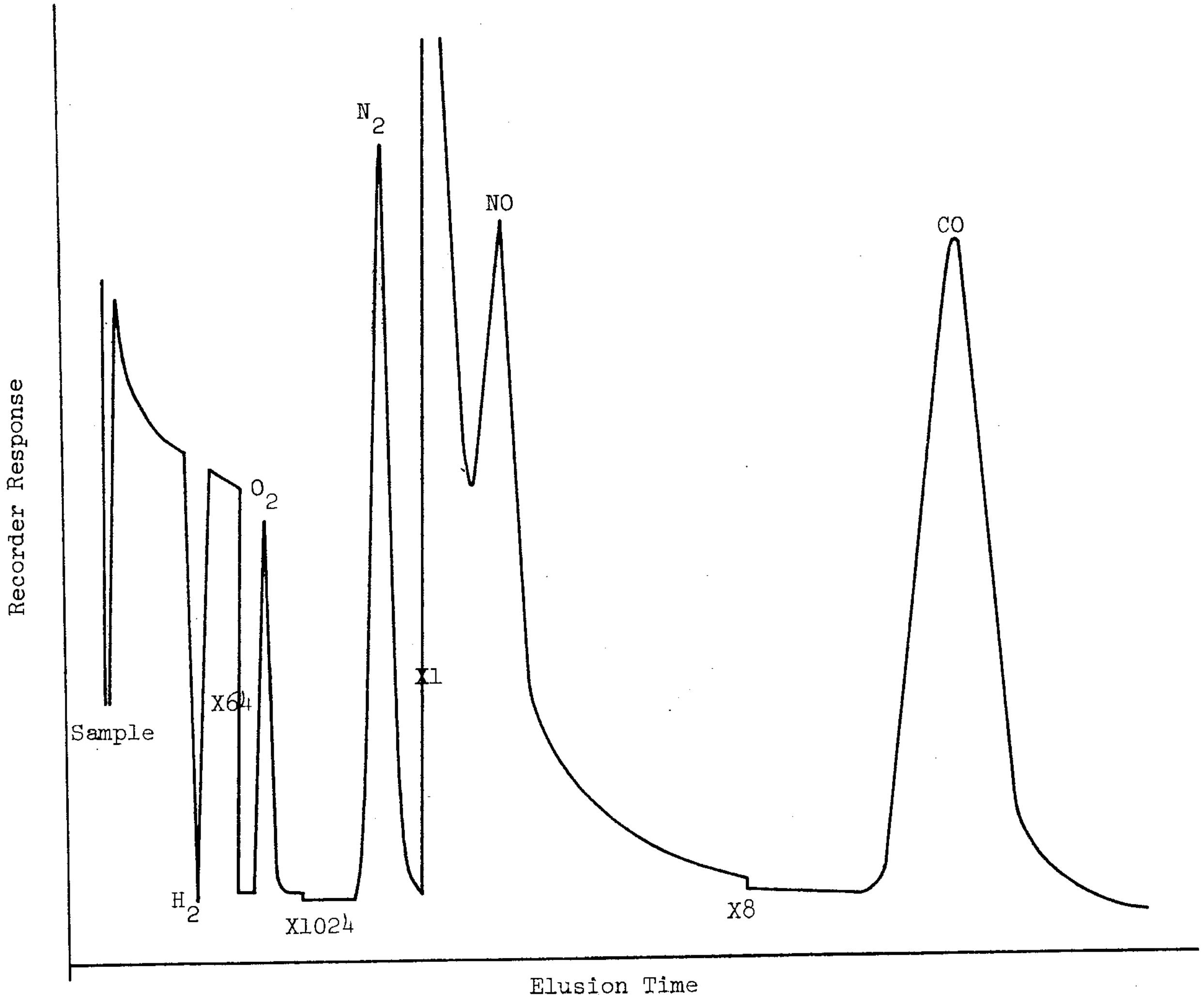
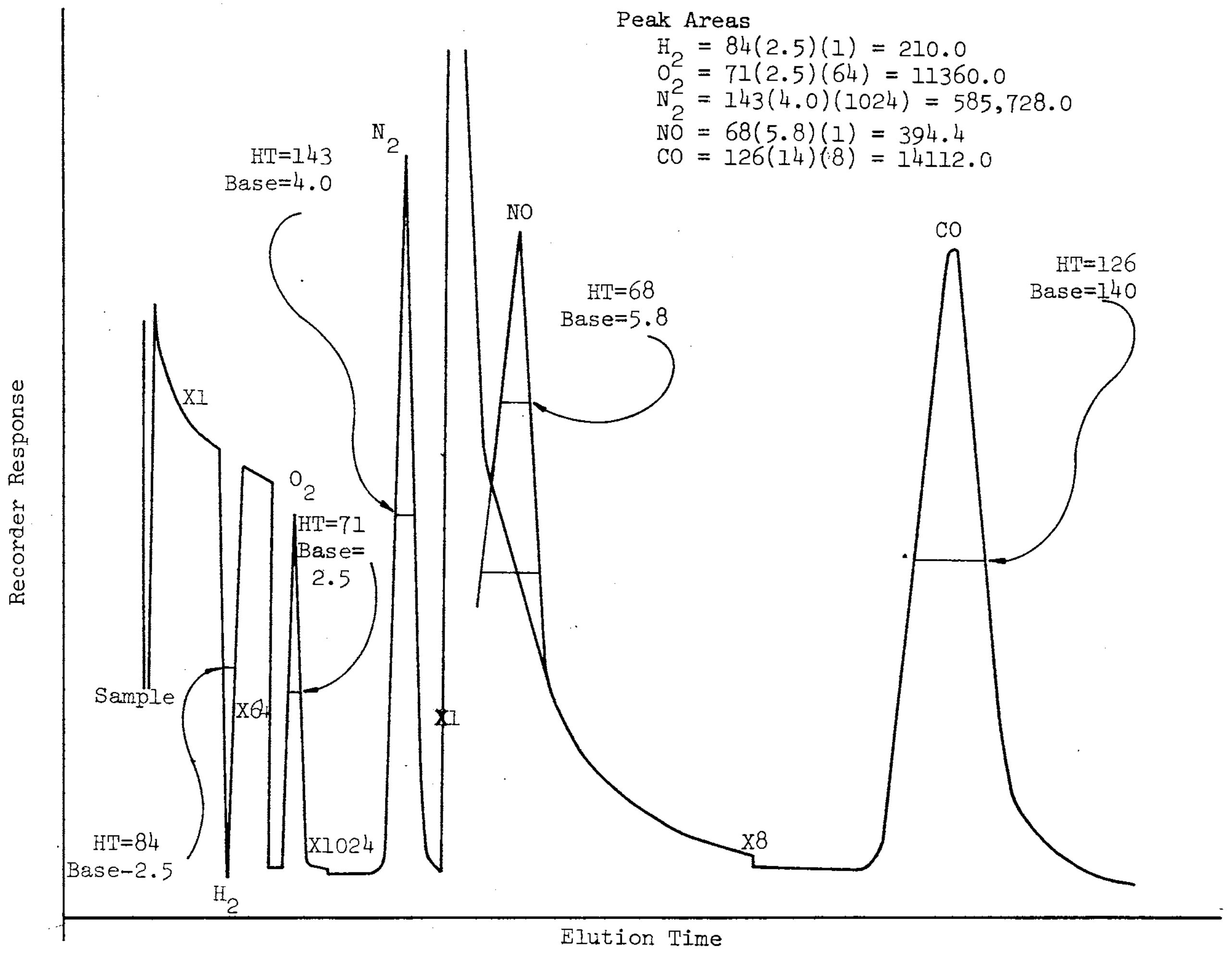


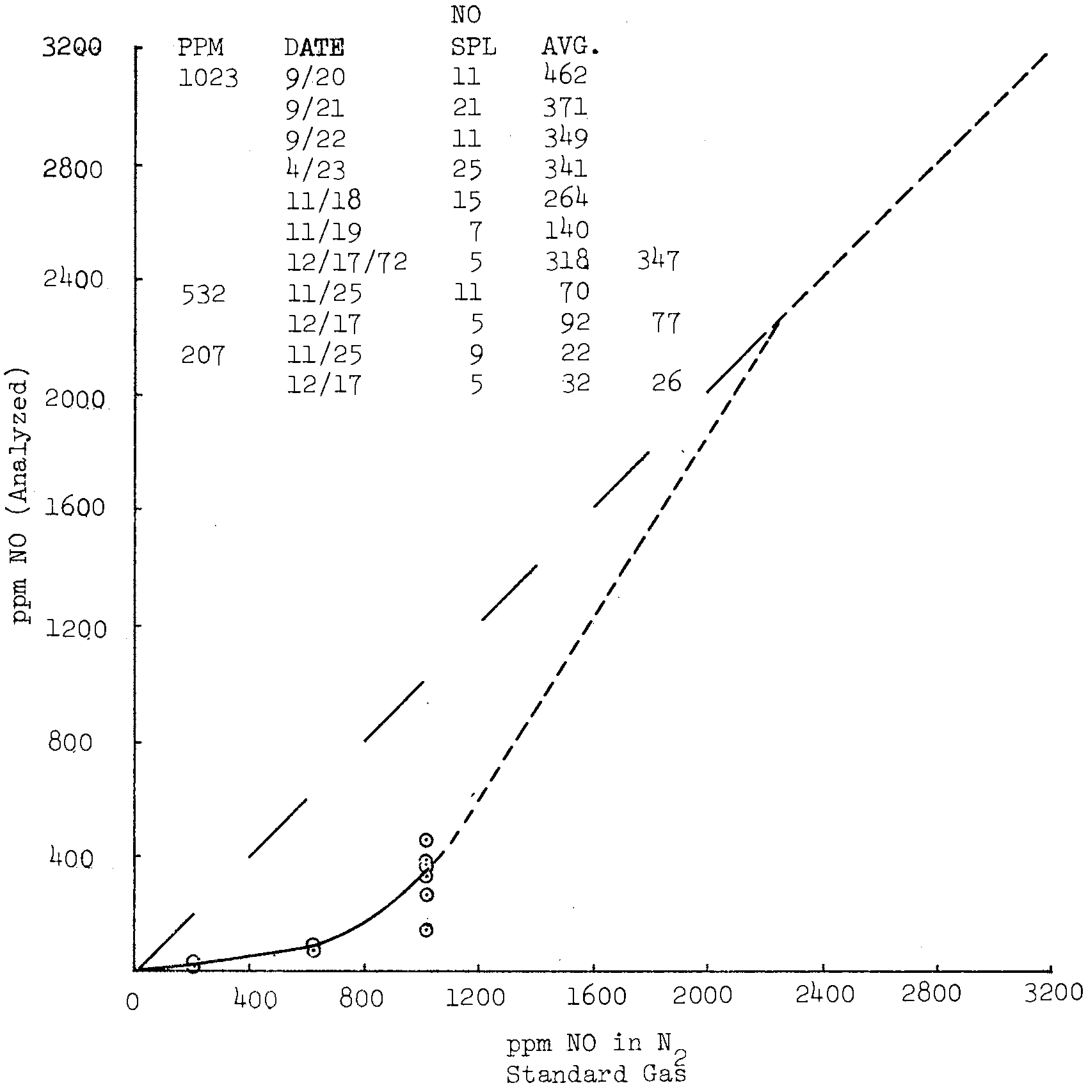
Figure 14-A. Typical Chromatogram of Analysis of Combustion Products



Peak Areas

H_2 = 84(2.5)(1) = 210.0
O_2 = 71(2.5)(64) = 11360.0
N_2 = 143(4.0)(1024) = 585,728.0
NO = 68(5.8)(1) = 394.4
CO = 126(14)(8) = 14112.0

Figure 14-B. Computation of Peak Areas



PPM	DATE	NO SPL	AVG.	
1023	9/20	11	462	
	9/21	21	371	
	9/22	11	349	
	4/23	25	341	
	11/18	15	264	
	11/19	7	140	
	12/17/72	5	318	347
532	11/25	11	70	
	12/17	5	92	77
207	11/25	9	22	
	12/17	5	32	26

Figure 15. Extended Calibration Curve

converting the chromatograms into useful results. These results will be discussed in the following chapters.

TABLE XV

PROPORTIONALITY CONSTANTS FOR PPM

Stiochiometric Oxygen	Air System	Argon-Oxygen
80	0.697	0.697
100	0.742	0.742
120	0.750	0.785

TABLE XVI

COMPUTATION PROCEDURE

1. Obtain measurements from peak height and width at half height. From Figure 14-B.

	Height	Base	Attenuation
H_2	84	2.5	1
O_2	71	2.5	64
N_2	143	4.0	1024
NO	68	5.8	1
CO	126	14.0	8

TABLE XVI (Continued)

---

2. Calculate peak areas (A = ht x base x attenuation)

H_2 = 84 (2.5) (1) = 210.0

O_2 = 71 (2.5) (64) = 11,360.0

N_2 = 143 (4.0) (1024) = 585,728.0

NO = 68 (5.8) (1) = 394.4

CO = 126 (14.0) (8) = 14,112.0

3. Calculate ratio of peak area to nitrogen peak area

H_2/N_2 = 210/585,728 = 358 x 10^{-6}

O_2/N_2 = 11360/585728 = 19,402 x 10^{-6}

NO/N_2 = 394.4/585728 = 673 x 10^{-6}

CO/N_2 = 14112/585728 = 24,089 x 10^{-6}

$\therefore$ NO/N_2 (ppm) = 673

4. Change NO/N_2 ratio to ppm NO_x. Since these data were from a run with 80% oxygen, proportionality constant = 0.697.

NO (ppm) = 673 (0.697) = 469

5. Adjust this number for loss in gc. using Figure 15.

NO (ppm) from graph = 1120

Therefore, the gas sample indicates that 1120 ppm NO_x is present in the combustion product gases leaving the combustor.

CHAPTER VI

RESULTS

Data

The research in this study covered the formation of the oxides of nitrogen during combustion of fuel oil. Three sets of variables were investigated:

(1) the percent excess oxygen

(2) the percent nitrogen in fuel oil

(3) nitrogen or argon as inert gas

Three levels of excess oxygen (80, 100, and 120% stoichiometric amount) and three levels of fuel nitrogen (0.0, 1.0, and 5.0% nitrogen) were used. Exact experimental run conditions are listed in Table XVII. In the following material, temperature data are presented first, and the concentration data are given in the next section.

Table XVIII contains temperature data (both raw and corrected values) taken during the three initial checkout runs (Runs 1, 2 and 3); the corrected temperature data are not presented in graphical form. Table XVIII is included only to show how the research evolved. The combustor was not closed during these first three runs and the combustion process utilized the oxygen present in the air.

Table XIX contains the temperature data for Runs 4 and 5. These two runs were initial checkout runs on a closed system. Based on

TABLE XVII

RUN CONDITIONS

Run Number	Combustible Gas	Inert Gas	% Oxygen	Wt % Nitrogen in Fuel
1	Air	-	ND[a]	0.01[b]
2	Air	-	ND	0.01
3	Air	-	ND	0.01
4	Air	-	ND	0.01
5	Air	-	70	0.01
6	Air	-	80	0.01
7	Air	-	80	0.01
8	Air	-	85	0.01
9A/B[d]	Air	-	71/86	0.01
10	Air	-	74	0.01
11	Air	-	100	0.01
12	Air	-	120	1.0[c]
13	Air	-	120	5.0[c]
14	Air	-	100	5.0
15	Air	-	100	5.0
16	Air	-	80	5.0
17	Air	-	120	0.01
18	Air	-	80	0.01
19	Air	-	80	1.0
20	Air	-	100	1.0
21	Air	-	120	1.0
22	Oxygen	Argon	80	0.01
23	Oxygen	Argon	100	0.01
24	Oxygen	Argon	120	0.01
25	Oxygen	Argon	120	0.01
26	Oxygen	Argon	80	1.0
27	Oxygen	Argon	120	1.0
28	Oxygen	Argon	100	1.0
29	Oxygen	Argon	100	1.0
30	Oxygen	Argon	80	5.0
31	Oxygen	Argon	80	5.0
32	Oxygen	Argon	100	5.0
33	Oxygen	Argon	120	5.0
34	Oxygen	Argon	80	0.01
35	Oxygen	Argon	100	0.01
36	Oxygen	Argon	120	0.01
37	Air	-	100	0.01
38	Air	-	80	0.01
39	Air	-	100	5.0
40	Air	-	120	5.0

a - ND means not determined
b - Regular No. 2 diesel oil
c - Doctored No. 2 diesel oil
d - Run continued over 2 days

TABLE XVIII

INITIAL CHECKOUT RUNS

		Raw Temperature Data (°F)					Corrected Temperature Data (°F)				
Run	Time[a]	1[b]	2	3	4	5	1[b]	2	3	4	5
1	0	0	0	0	0		0	0	0	0	
1	20	0	415	505	0		0	571	701	0	
1	25	0	434	512	0		0	599	711	0	
1	30	0	440	506	0		0	607	703	0	
1	35	0	473	535	0		0	655	745	0	
1	40	0	482	535	0		0	668	745	0	
1	45	0	478	546	0		0	662	761	0	
2	0	0	0	0	0		0	0	0	0	
2	5	330	372	484	500		441	509	671	682	
2	10	379	428	505	500		510	590	701	682	
2	15	393	446	537	519		530	616	748	709	
2	20	419	462	542	505		567	639	755	689	
2	25	427	471	561	517		578	652	782	706	
2	30	436	482	558	508		591	668	778	693	
2	35	446	489	565	492		605	678	788	671	
2	40	450	508	591	524		611	706	826	716	
2	45	560	519	583	548		625	722	814	750	
2	50	458	517	589	552		622	719	823	756	
2	55	462	512	589	528		628	711	823	722	
2	60	450	520	591	556		611	723	826	761	
3	0	0	0	0	0	0	0	0	0	0	0
3	5	0	358	528	654	759	0	480	735	917	1069
3	10	0	373	532	688	734	0	502	740	966	1033
3	20	394	402	579	720	771	531	548	808	1013	1086
3	25	465	428	593	723	785	632	580	829	1017	1107
3	30	507	436	601	739	784	692	591	840	1040	1105

a - Minutes
b - Thermocouple number (see Figure 11)
1 - wall
2 - 36 inches
3 - 24 inches
4 - 12 inches
5 - 6 inches

TABLE XIX

CHECKOUT RUNS 4 AND 5

		Raw Temperature Data (^{o}F)					Corrected Temperature Data (^{o}F)				
Run	Time ^{a}	1^{b}	2	3	4	5	1^{b}	2	3	4	5
4	0	72	68	63	70	50	74	69	62	72	43
4	10	242	320	473	677	695	316	426	655	950	976
4	15	280	249	506	717	783	370	468	703	1008	1104
4	20	384	375	538	729	729	517	504	749	1026	1026
4	25	417	412	574	783	830	564	557	801	1104	1172
4	30	468	424	598	770	884	636	574	836	1085	1250
4	35	517	446	617	810	891	706	605	863	1143	1260
4	45	560	459	638	812	821	767	624	894	1146	1159
4	55	590	475	646	834	874	810	646	905	1178	1235
4	60	612	475	651	820	889	841	646	913	1157	1257
4	70	616	438	593	788	971	847	594	829	1111	1376
4	75	618	438	591	784	982	849	594	826	1105	1392
4	80	622	435	592	798	1036	855	590	827	1125	1470
4	85	626	437	591	784	999	861	592	826	1105	1416
4	90	626	440	599	815	1038	861	597	837	1150	1473
5	0	0	0	0	0	0	0	0	0	0	0
5	30	378	400	516	784	1124	509	540	717	1033	1597
5	35	386	407	546	786	1281	520	550	761	1108	1824
5	40	458	420	464	785	1297	622	568	642	1107	1848
5	45	478	430	570	789	1362	644	583	795	1112	1942
5	50	486	432	574	794	1393	662	585	801	1120	1987

a - Minutes
b - Thermocouple number (see Figure 11)
  1 - wall
  2 - 36 inches
  3 - 24 inches
  4 - 12 inches
  5 - 6 inches

these runs, various changes were made:

(1) oil feed rates were lowered because at high rates, the gas system was unable to deliver a stoichiometric amount of oxygen

(2) a vaporization system was added to the burner-jet assembly since atomization of oil by the assembly alone was incomplete

(3) dead space in the combustor was blocked off.

Table XX exhibits the temperatures from Run 6. The corrected temperature values are plotted in Figure 16. The graph shows that there was at least a 1400°F temperature drop in the combustion product gases in the first six (6) inches of the combustor (measured from the burner top). Additional thermocouples were required in the region. Several sampling procedures were evaluated; none seemed sufficient.

Data from Run 7 are contained in Table XXI. The data were taken over 285 minutes on a closed system. Figure 17 shows the profiles for the four wall temperatures located at flame height, and 12, 24 and 36 inches from the flame. Note the similarity of the four curves. Figure 18 contains the plots of the five temperatures of the product gases. These temperatures were taken at flame height, and 12, 24, 36 and 48 inches above the flame. First, note that there was an appropriate 2000°F temperature drop in the first twelve (12) inches down stream of the flame; several other thermocouples were needed in this region. Secondly, note the flatness of the profiles; about 20 minutes were sufficient for the profiles to become steady. This would indicate that steady-state, temperature wise, was reached early in the run.

For the remaining experimental runs the temperature data are tabulated in Appendix D. Only the corresponding graphs are presented in the following text.

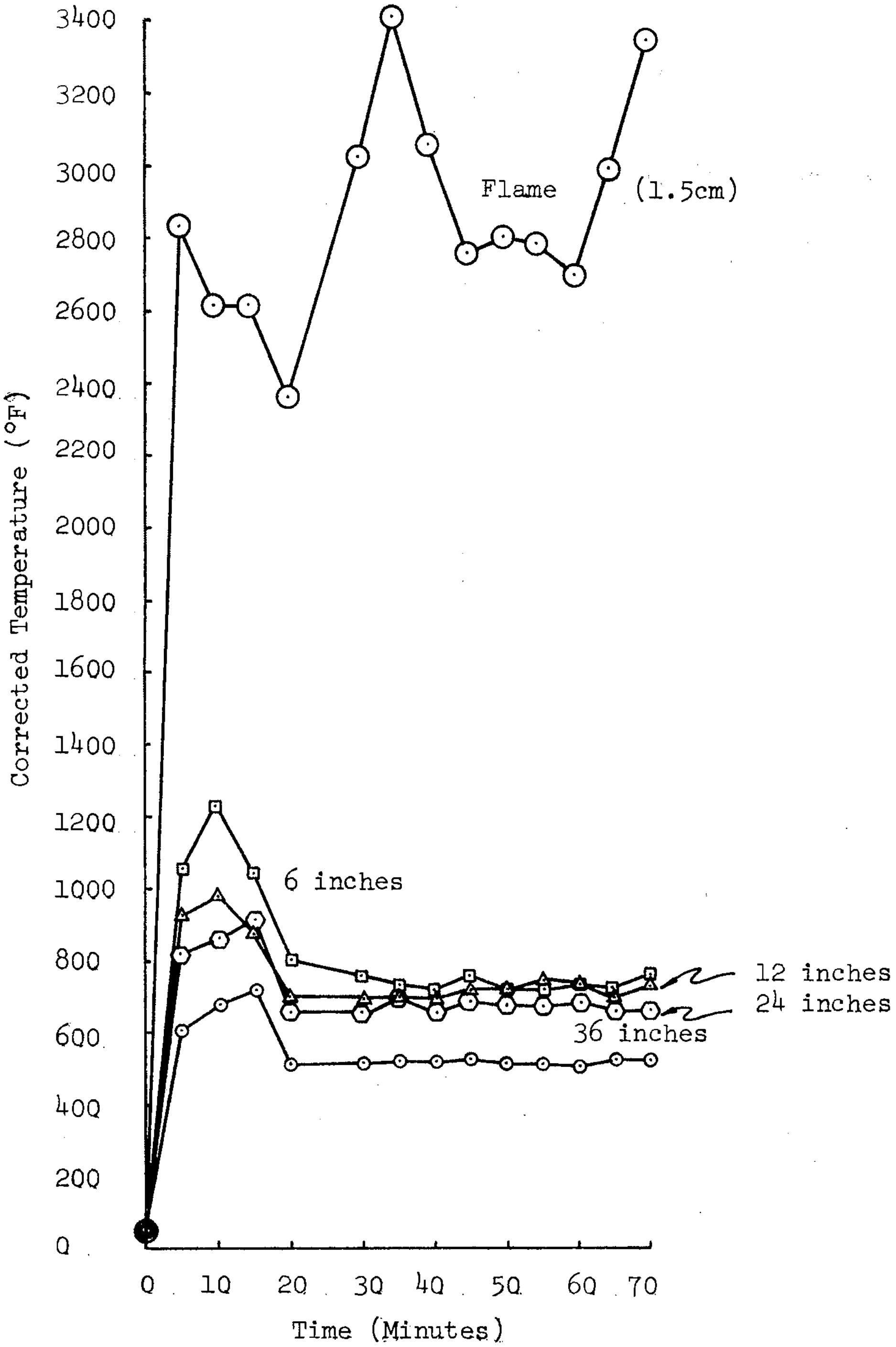


Figure 16. Run 6 - Temperature Profiles

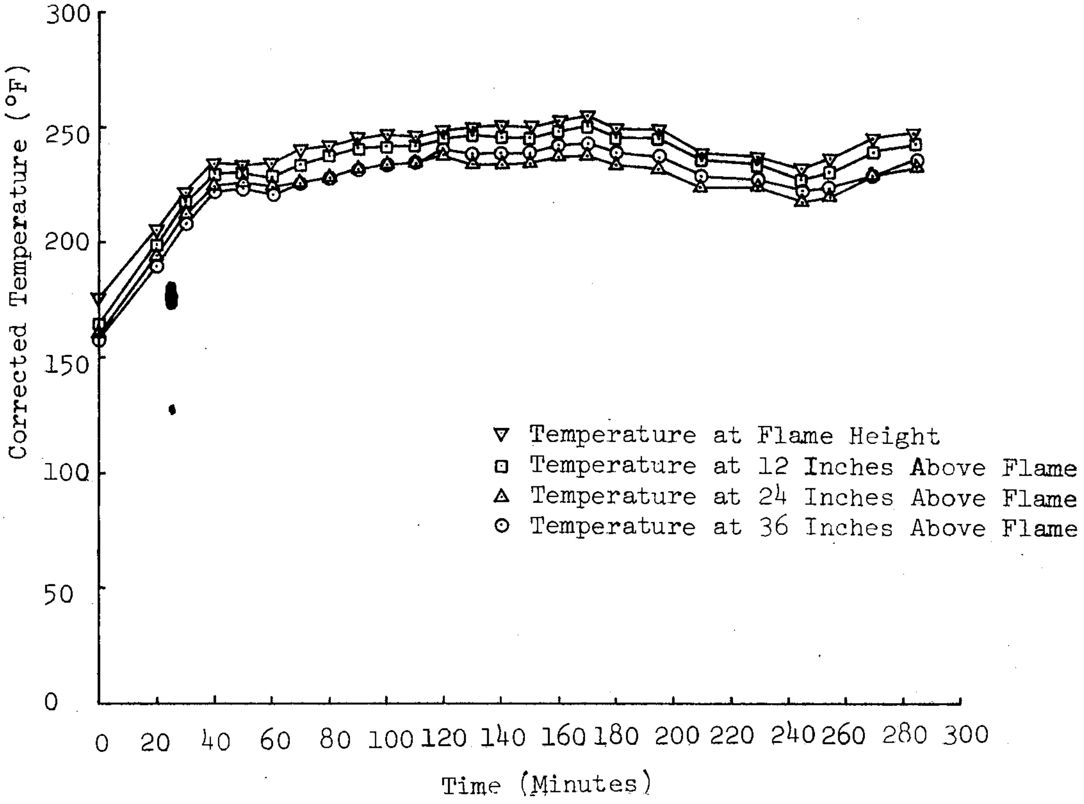


Figure 17. Run 7 - Wall Temperature Profiles

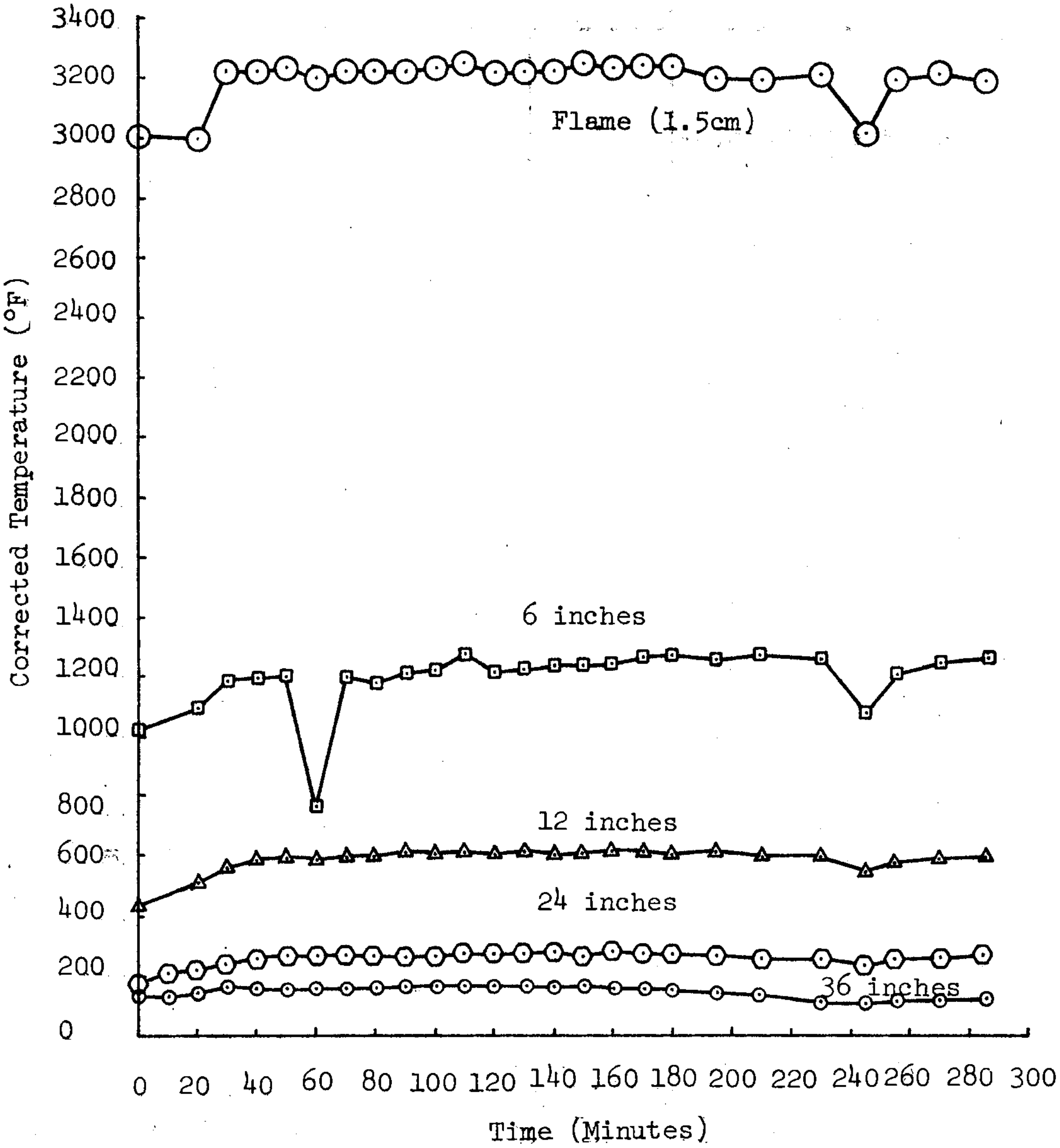


Figure 18. Run 7 - Temperature Profiles

TABLE XX

TEMPERATURE DATA, RUN 6

		Raw Temperature Data (°F)						
Run	Time	1[b]	2	3	4	5	6	7
6	0	63	74	65	63	57	55	74
6	5	180	440	578	675	747	1071	675
6	10	220	496	613	712	864	1821	508
6	15	258	521	641	622	740	1820	485
6	20	264	375	472	510	569	1649	486
6	30	267	377	472	504	537	2101	488
6	35	280	382	498	504	517	2369	490
6	40	285	376	472	506	511	2128	490
6	45	287	378	486	524	535	1918	490
6	50	284	374	480	421	511	1946	487
6	55	284	373	479	520	501	1938	484
6	60	279	370	483	533	515	1876	479
6	65	284	379	469	512	515	2078	490
6	70	284	383	468	528	534	2329	490
		Corrected Temperature Data (°F)						
6	0	63	74	65	63	57	55	74
6	5	228	597	807	930	1052	2823	675
6	10	284	676	858	983	1221	2606	508
6	15	338	712	898	869	1041	2605	485
6	20	347	504	654	696	794	2357	486
6	30	351	507	654	688	748	3011	488
6	35	370	514	691	688	719	3390	490
6	40	377	506	654	690	710	3050	490
6	45	380	509	674	716	745	2746	490
6	50	375	503	665	712	710	2787	487
6	55	375	502	664	710	696	2775	484
6	60	368	497	669	729	716	2686	479
6	65	375	510	649	699	716	2978	490
6	70	375	516	648	722	743	3241	490

a - Minutes
b - Thermocouple number (see Figure 11)
  1 - wall
  2 - c6 inches
  3 - 24 inches
  4 - 12 inches
  5 - 6 inches
  6 - 1.5cm (flame)
  7 - feed oil

TABLE XXI

TEMPERATURE DATA, RUN 7

		Raw Temperature Data (°F)										
Run	Time[a]	1[b]	2	3	4	5	6	7	8	9	10	11
7	0	157	163	160	175	163	113	130	320	721	2092	439
7	10	0	0	0	0	176	113	162	0	0	0	0
7	20	190	198	193	205	191	121	169	376	770	2095	442
7	30	208	216	210	221	204	130	184	411	834	2245	436
7	40	221	229	222	232	197	128	196	430	840	2255	441
7	50	223	231	224	234	203	129	200	436	847	2257	438
7	60	220	227	219	234	216	130	200	430	548	2240	445
7	70	225	233	226	240	214	131	203	435	846	2253	442
7	80	228	237	228	242	217	132	198	436	834	2253	447
7	90	231	240	231	244	213	132	195	447	852	2253	451
7	100	233	241	232	245	214	137	202	445	864	2261	452
7	110	234	241	233	244	214	136	206	449	901	2274	446
7	120	238	245	235	248	227	137	205	443	862	2249	450
7	130	238	246	234	250	224	135	209	452	864	2253	449
7	140	238	245	233	249	224	135	208	441	874	2253	447
7	150	238	245	235	248	222	135	205	449	874	2264	448
7	160	241	248	237	252	227	128	211	452	879	2262	456
7	170	242	250	237	253	240	128	206	450	893	2266	456
7	180	238	245	232	248	234	124	208	448	898	2263	459
7	195	237	245	232	247	223	121	202	445	888	2240	446
7	210	229	236	224	238	226	117	198	434	899	2240	423
7	230	226	233	223	236	240	100	196	436	888	2245	433
7	245	218	225	217	231	216	93	184	397	766	2112	456
7	255	223	230	219	235	215	98	193	426	856	2238	453
7	270	229	238	229	245	216	101	200	433	881	2245	454
7	285	234	242	232	246	227	102	202	438	892	2232	453
		Corrected Temperature Data (°F)										
7	0	157	163	160	175	204	133	159	426	1014	2998	595
7	10	0	0	0	0	222	133	205	0	0	0	0
7	20	190	198	193	205	243	144	215	506	1085	3003	600
7	30	208	216	210	221	262	157	237	556	1178	3220	591
7	40	221	229	222	232	252	154	254	583	1186	3234	598
7	50	223	231	224	234	260	155	260	591	1196	3237	594
7	60	220	227	219	234	279	157	260	583	764	3212	604
7	70	225	233	226	240	276	158	264	590	1195	3231	600
7	80	228	237	228	242	280	160	257	591	1178	3231	607
7	90	231	240	231	244	275	160	253	607	1204	3231	612
7	100	233	241	232	245	276	167	263	604	1221	3243	614

TABLE XXI (Continued)

Run	Time[a]	1[b]	2	3	4	5	6	7	8	9	10	11
7	110	234	241	233	244	276	165	269	610	1274	3262	605
7	120	238	245	235	248	294	167	267	601	1218	3225	611
7	130	238	246	234	250	290	164	273	614	1221	3231	610
7	140	238	245	233	249	290	164	271	598	1235	3231	607
7	150	238	245	235	248	287	164	267	610	1235	3247	608
7	160	241	248	237	252	294	154	276	614	1243	3244	619
7	170	242	250	237	253	313	154	269	611	1263	3250	619
7	180	238	245	232	248	304	148	271	608	1270	3246	624
7	195	237	245	232	247	289	144	263	604	1256	3212	605
7	210	229	236	224	238	293	138	257	588	1272	3212	573
7	230	226	233	223	236	313	114	254	591	1256	3220	587
7	245	218	225	217	231	279	104	237	536	1079	3027	619
7	255	223	230	219	235	277	111	250	577	1209	3210	615
7	270	229	238	229	245	279	116	260	587	1246	3220	617
7	285	234	242	232	246	294	117	263	594	1261	3201	615

a - Minutes

b - Thermocouple number (see Figure 11)

1 - wall, 36 inch level
2 - wall, 12 inch level
3 - wall, 24 inch level
4 - wall, flame level
5 -
6 - gas, 36 inch level
7 - gas, 24 inch level
8 - gas, 12 inch level
9 - gas, 6 inch level
10 - flame, 1.5 cm level
11 -

The purpose of experimental Run 8 was to evaluate the new thermocouples located at 2.1, 3.6 and 15.5 (6 inches) centimeters above the burner top (the flame tip was 1.5 centimeters above the burner top). The new thermocouples determined temperature profiles in the first six inches of the chamber. In Figure 19, the temperatures are plotted. Note that one thermocouple was defective and needed replacing. The flatness of each profile was again present to indicate steady state.

A procedure for collecting and storing samples of the product gases in sample bombs was also evaluated during this run. Several samples were collected in bombs and stored for later analysis. Analytical results are recorded in the author's laboratory notebook. The length of time required to analyze the samples made it impractical to utilize such a sampling system. Another sampling system was the only obvious answer, Run 9 was conducted to evaluate the use of syringe sampling.

Run 9A was aborted after three hours because the oil flow stopped. The vaporizor was completely carbonized closed and the packing had to be replaced. During the three hours of operation, two syringe samples were taken and analyzed; NO_x was not present in either sample. Run 9B was a 5 hour test with seven samples taken by syringe and 12 samples collected in bombs. Only one sample contained NO_x. At the end of this run, it was apparent that one experimenter could not collect samples in bombs, take temperature data, maintain control over the combustion, and analyze syringe samples. Secondly, the thermal stress imposed on the glass sample probes caused the probes to shatter whenever the bombs were disconnected. A continuous sampling system was thus deemed

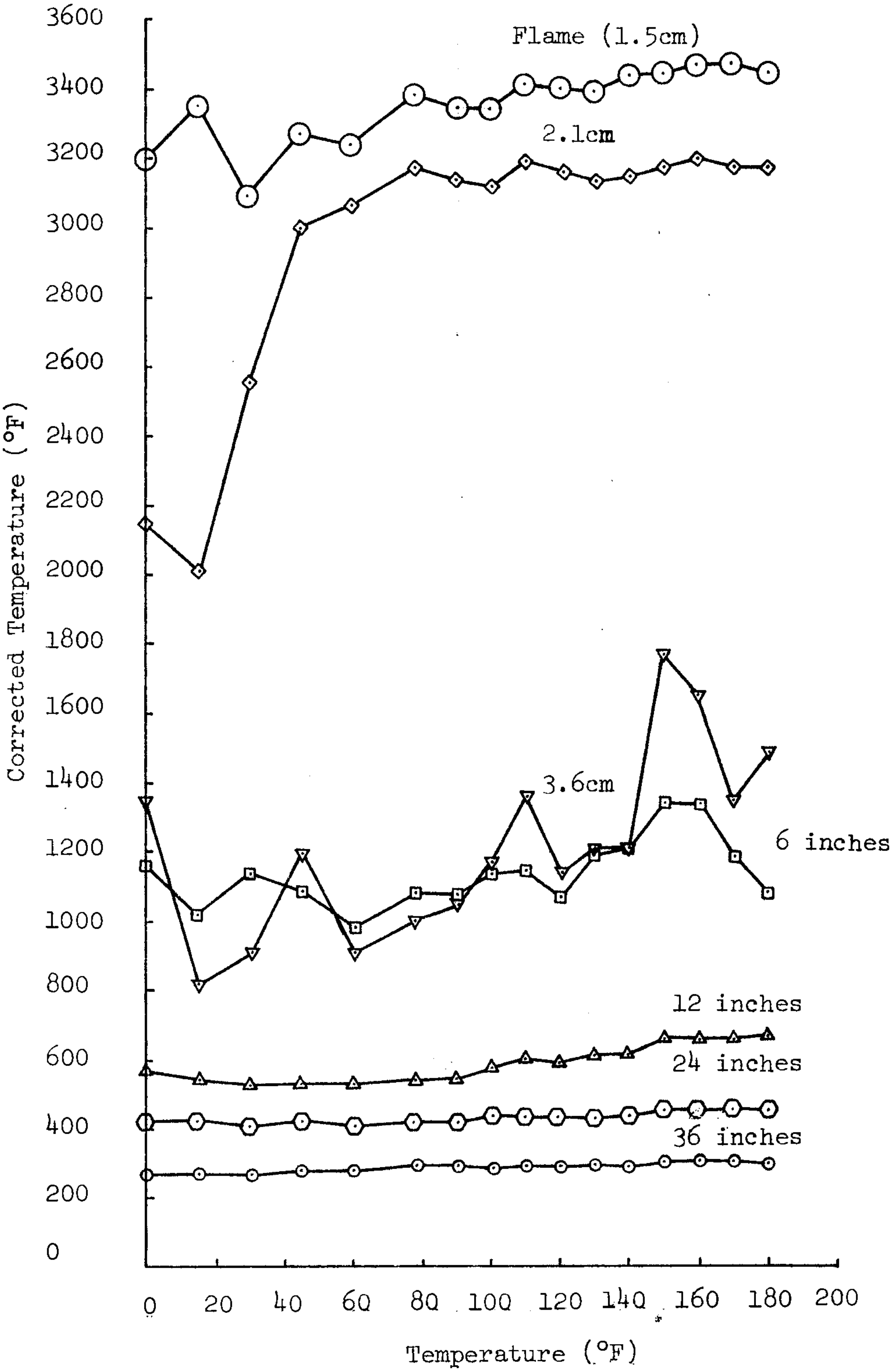


Figure 19. Run 8 - Temperature Profiles

the only practical method for sampling the combustor. Temperature profiles can be found in the author's laboratory notebook and are not presented here.

The purposes of Run 10 were twofold: to check out the continuous sampling procedure, and to set the base conditions for the research project. Samples were collected alternately at ports located 3.0 and 39.5 centimeters above the burner top. A gas stream was pulled from each port for 30 minutes prior to being introduced into the gas chromatograph. Only three samples seemed to contain NO_x. Figure 20 presents the temperature profiles of the product gases. Again, note the flatness of these curves, a definite sign of steady state.

The objective of Run 11 was to evaluate the continuous sampling under stoichiometric oxygen-fuel conditions. Temperature data are shown in Figure 21. Samples were again collected and analyzed every 30 minutes; sampling port locations remained the same. During the first 40 minutes, the sample analysis showed the absence of NO_x. An additional side stream of oxygen was added to assure complete combustion. The temperature profiles show the results of this change - a drop in temperatures. Still, there were no evidence of NO_x in the product gases. The run was terminated after three hours.

The temperature profiles are shown in Figure 22 for Run 12. The purpose of the run was to form NO_x by burning 1% nitrogen fuel oil in an excess oxygen atmosphere. All six samples analyzed contained NO_x. When the percent excess oxygen was determined, it was found that 153% stoichiometric oxygen had been supplied to the system instead of 120% excess. The significance of this run was the fact that NO_x had been formed.

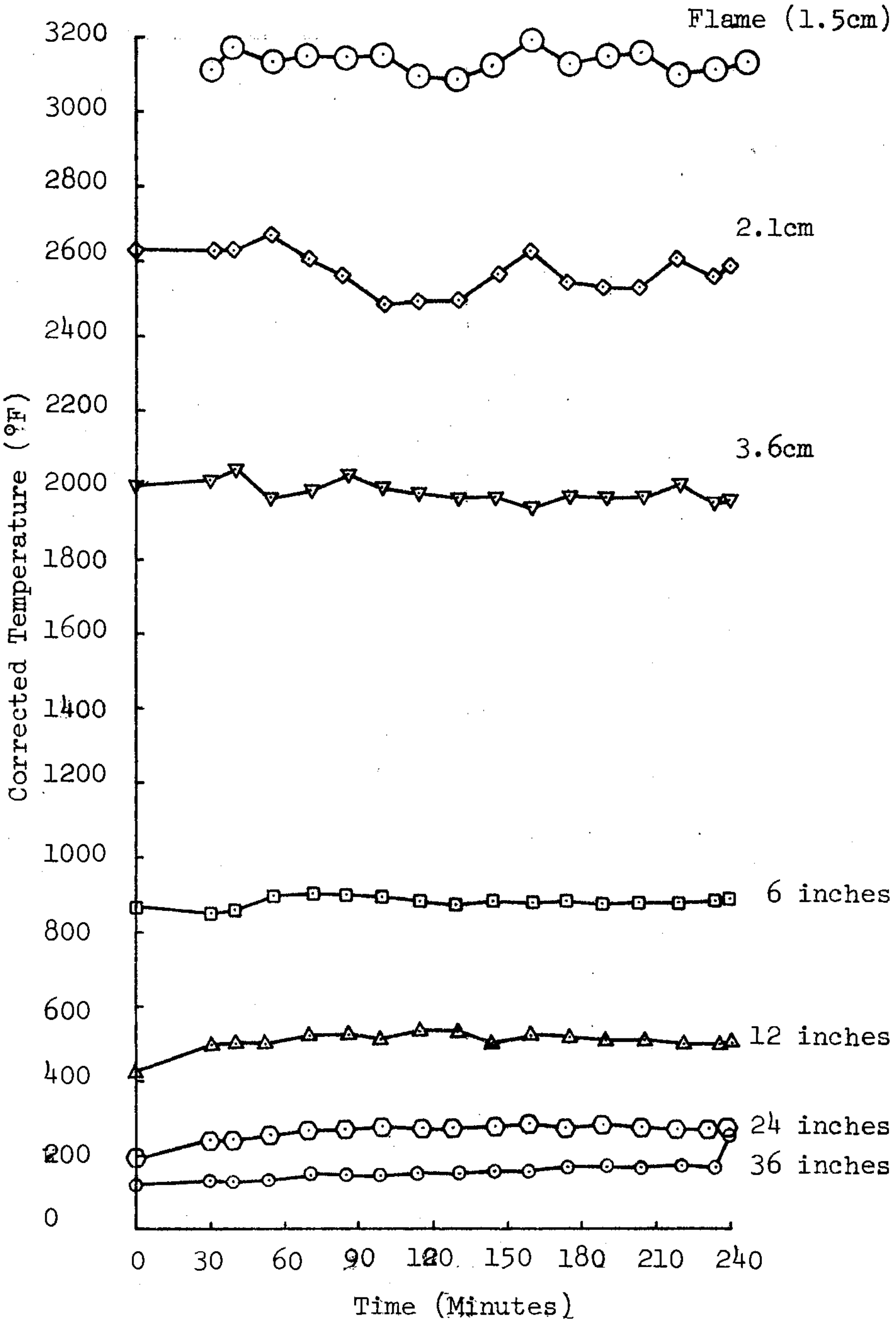


Figure 20. Run 10 - Temperature Profiles

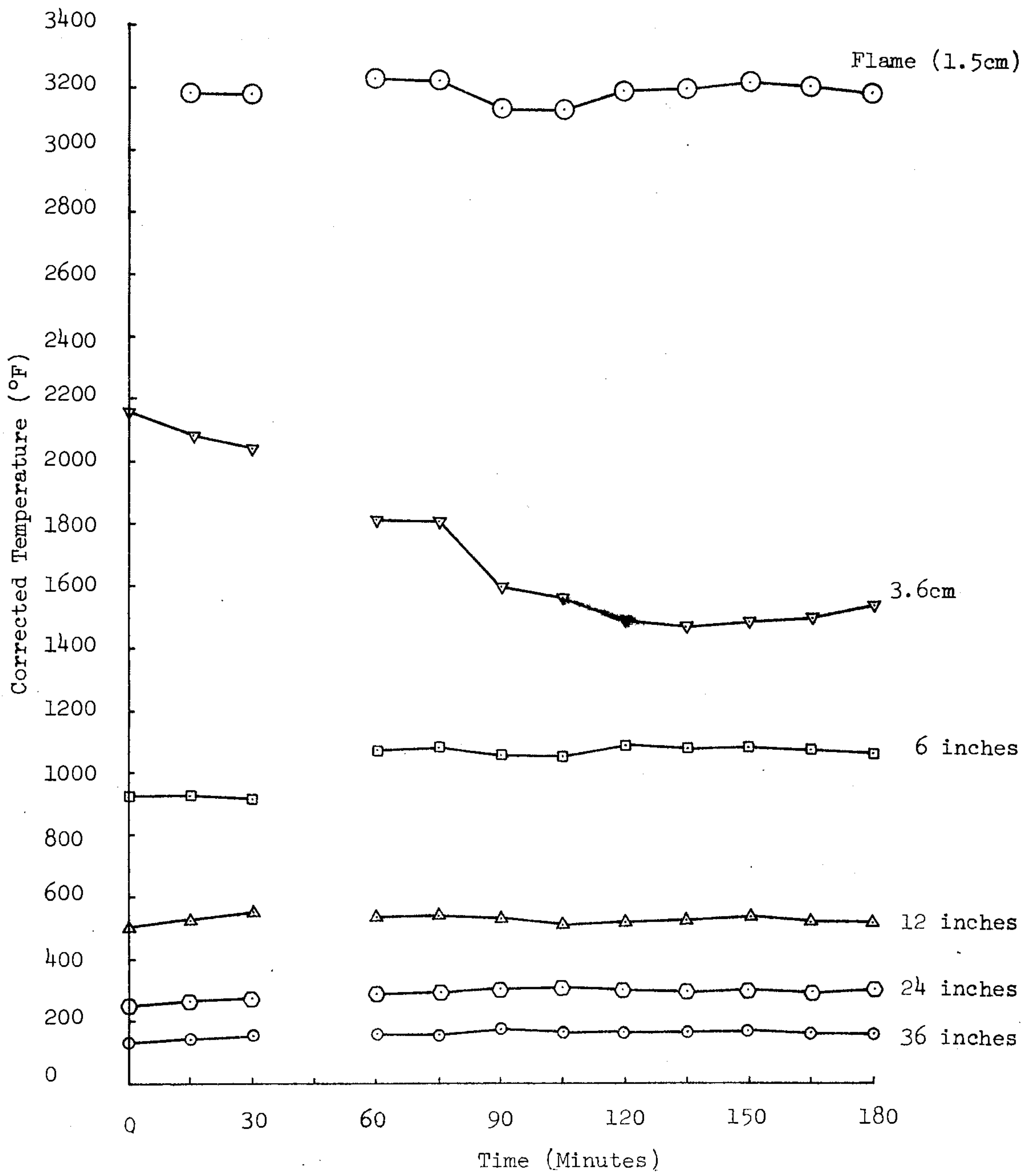


Figure 21. Run 11 - Temperature Profiles

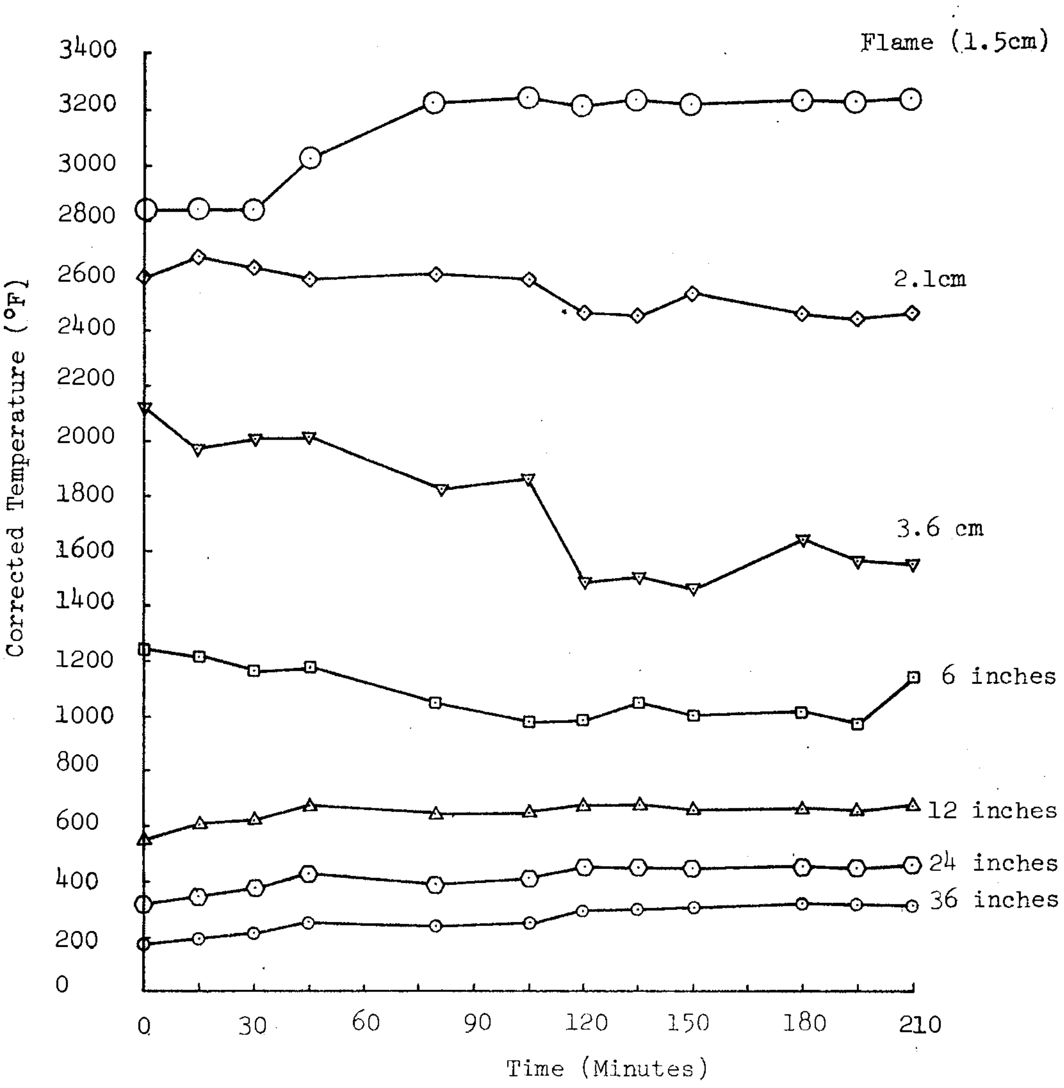


Figure 22. Run 12 - Temperature Profiles

Run 13 was to check out the system for a 10 hour period with 120% stoichiometric oxygen and 5% nitrogen fuel oil. Radial and axial temperatures were measured. Axial temperature data are plotted in Figure 23, and radial temperatures are presented in Figures 24-27. Radial profiles were taken at 1.5, 2.1, 3.6 and 15.5 centimeters above the burner top by measuring the temperatures across the combustor chamber at one half inch intervals. The NO_x data from Run 13 are presented along with the other NO_x data in Table XXV, page 132.

Following Run 13, each experimental run lasted for four hours, during which time one set of oxygen and fuel nitrogen conditions was evaluated for an inert gas, nitrogen or argon. A sample of the product gases was analyzed every 30 minutes. A presentation of the run conditions is shown in Table XXII for the air system and in Table XXIII for the argon/oxygen system.

TABLE XXII

AIR SYSTEM - RUN NUMBER(S) PER RUN CONDITIONS

Percent Excess Oxygen	Percent Fuel Oil Nitrogen		
	0	1	5
80	(38)	(19)	(16)
100	(18,37)	(20)	(14,15,39)
120	(17)	(21)	(13,40)

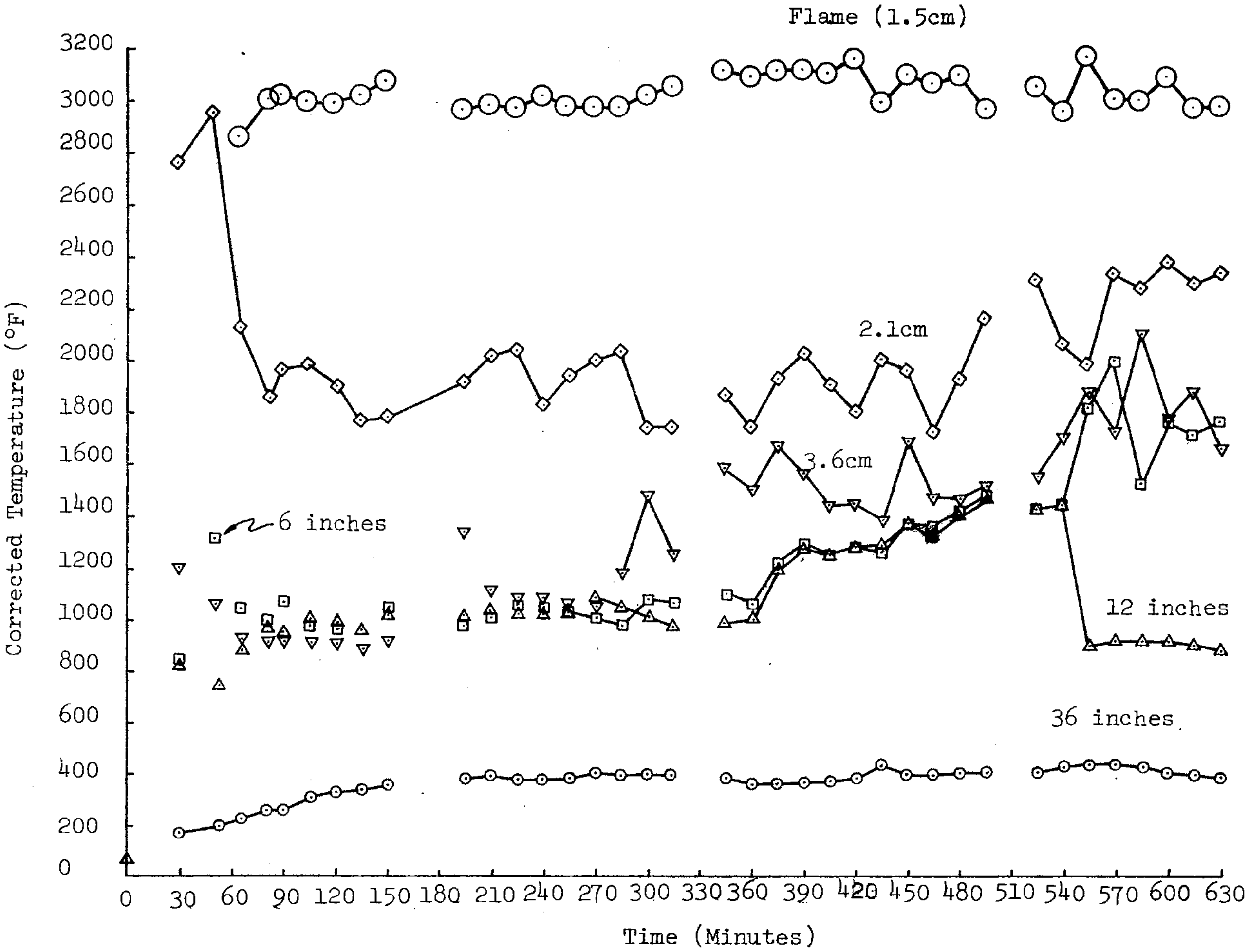


Figure 23. Run 13 - Correct Temperatures (°F) Vs Time (Minutes)

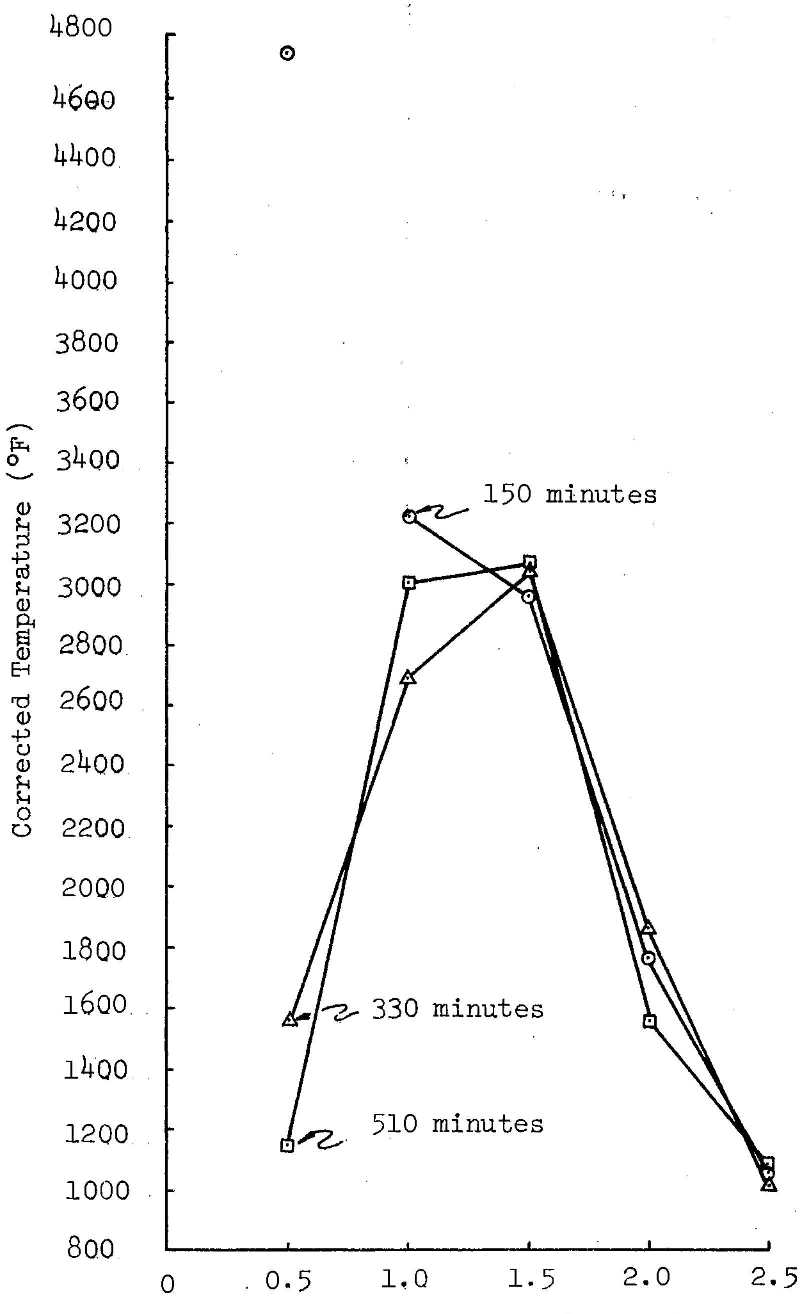
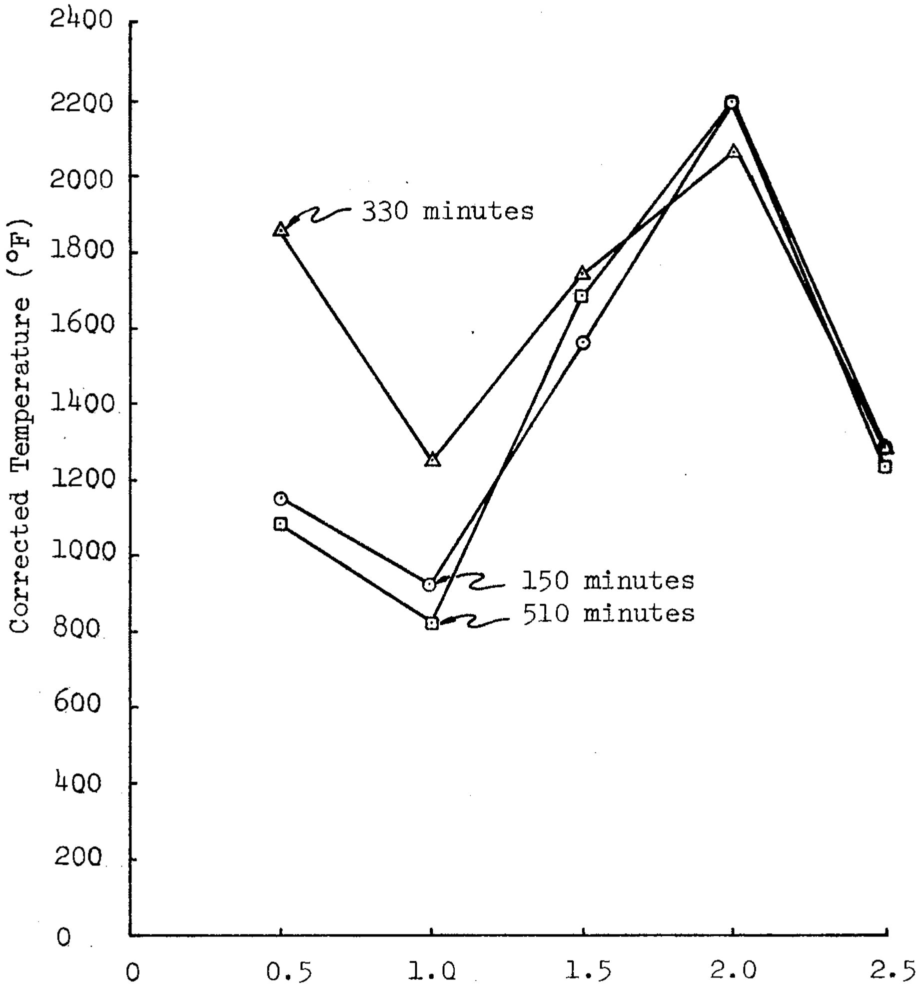


Figure 24. Run 13 - Radial Profile
(TC Located at X = 1.5cm)



Distance from Inlet (Inches)

Figure 25. Run 13 - Radial Profile (TC Located at 2.1cm)

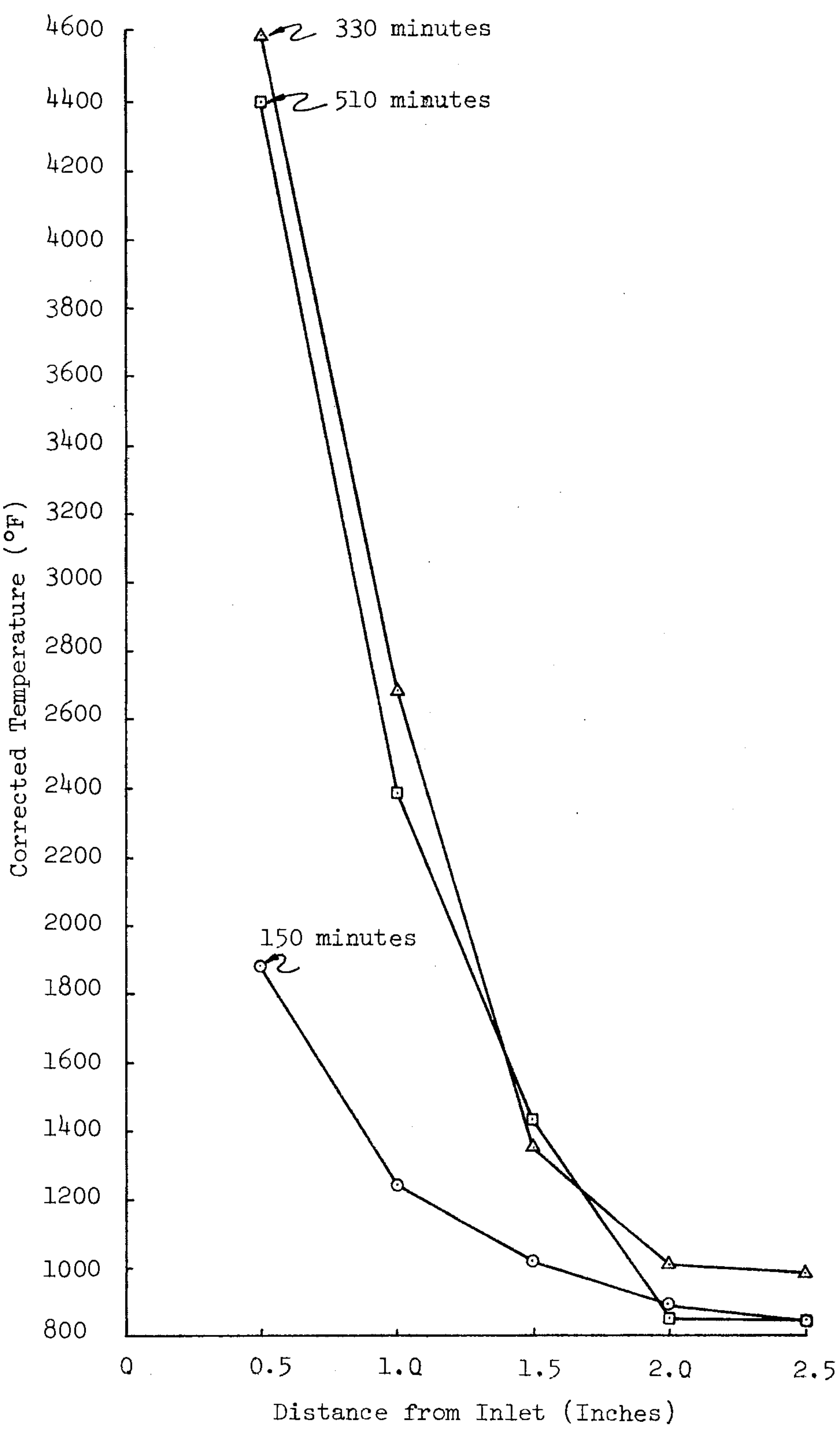


Figure 26. Run 13 - Radial Profile (TC Located at 3.6cm)

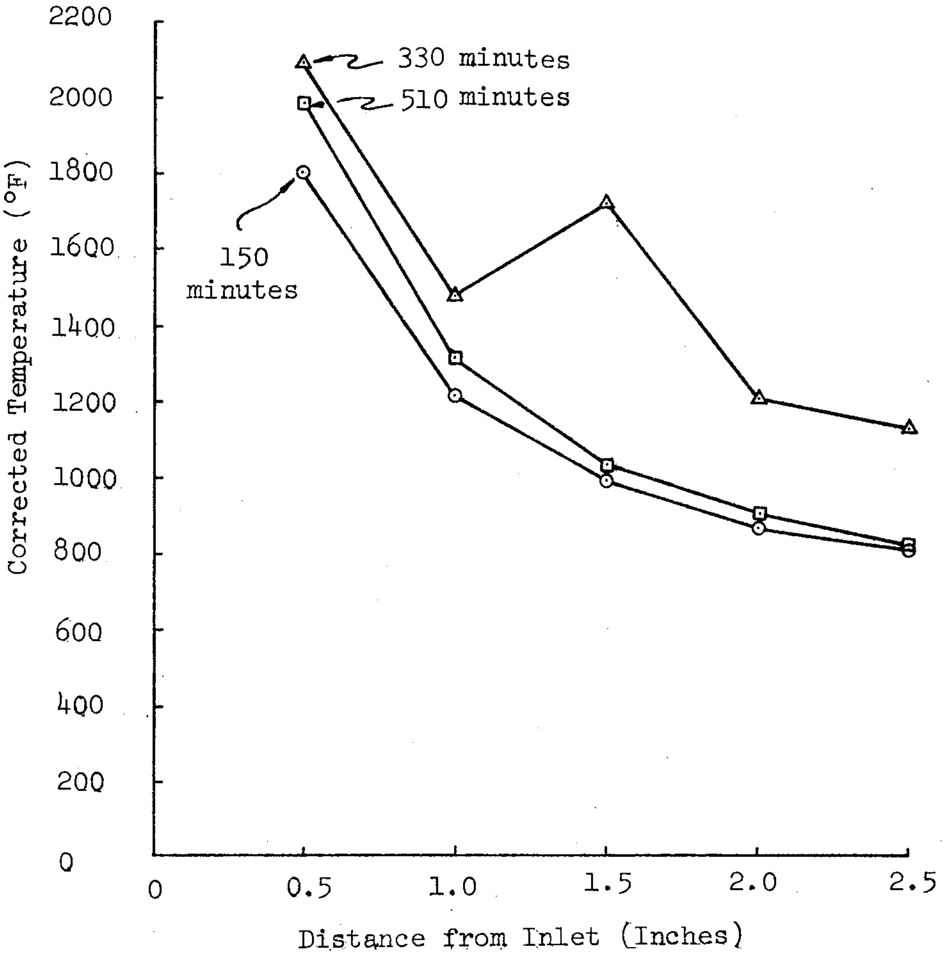


Figure 27. Run 13 - Radial Profile (TC Located at 15.5cm)

TABLE XXIII

ARGON/OXYGEN SYSTEM - RUN NUMBER(S) PER RUN CONDITIONS

Percent Excess Oxygen	Percent Fuel Oil Nitrogen		
	0	1	5
80	(22,34)	(26)	(30,31)
100	(23,35)	(28,29)	(32)
120	(24,25,36)	(27)	(33)

Temperature data for Runs 14 through 40 are graphed in Figures 28 - 51. Because some back-to-back runs had the same conditions, the graphical representation of the corrected temperatures are such as to give the impression of a long, extended run of up to 8 hours. Pairs of runs in this group are 24-25, 28-29, and 30-31.

Several sets of replicate runs were conducted; conditions are shown in Table XXIV.

Sample analyses for all runs are contained in Table XXV, p. 132. The results recorded are the peak areas of each component. Raw numbers are available in the author's laboratory notebooks. Table XXVI contains the corrected NO_x data; the values were determined by the procedure outlined in Table XVI, page 139. Figure 52 shows a typical graphic presentation of the NO_x data (in this case data are from Run 20). Such graphs proved almost useless in data analysis and are excluded from this report.

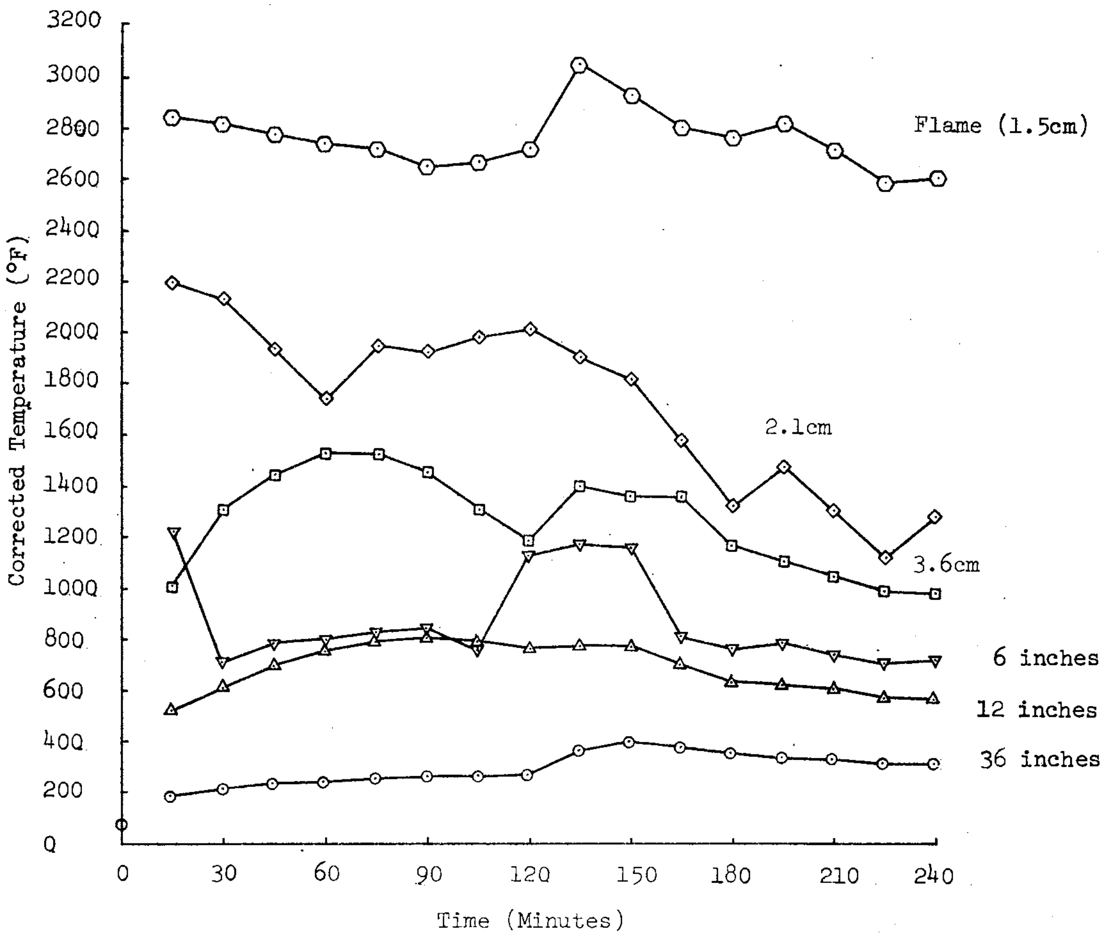


Figure 28. Run 14 - Temperature Profiles

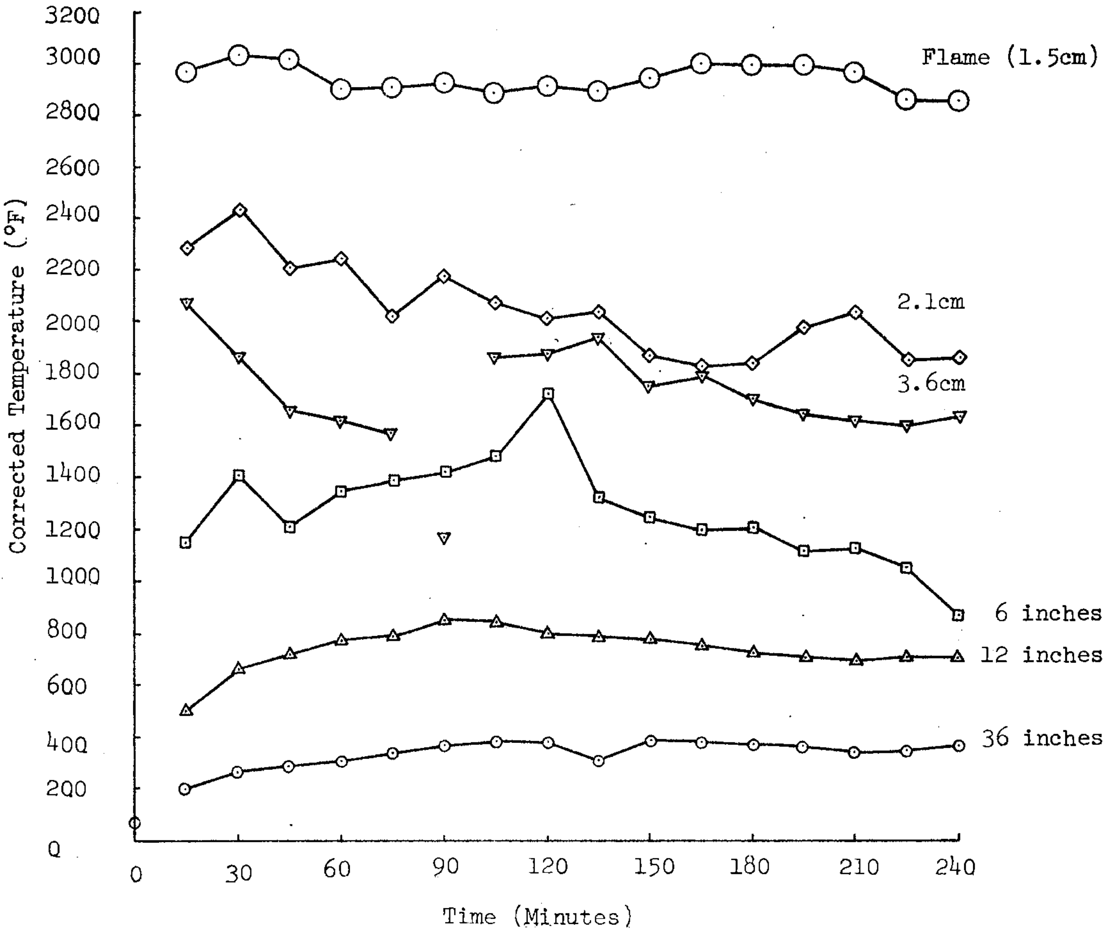


Figure 29. Run 15 - Temperature Profiles

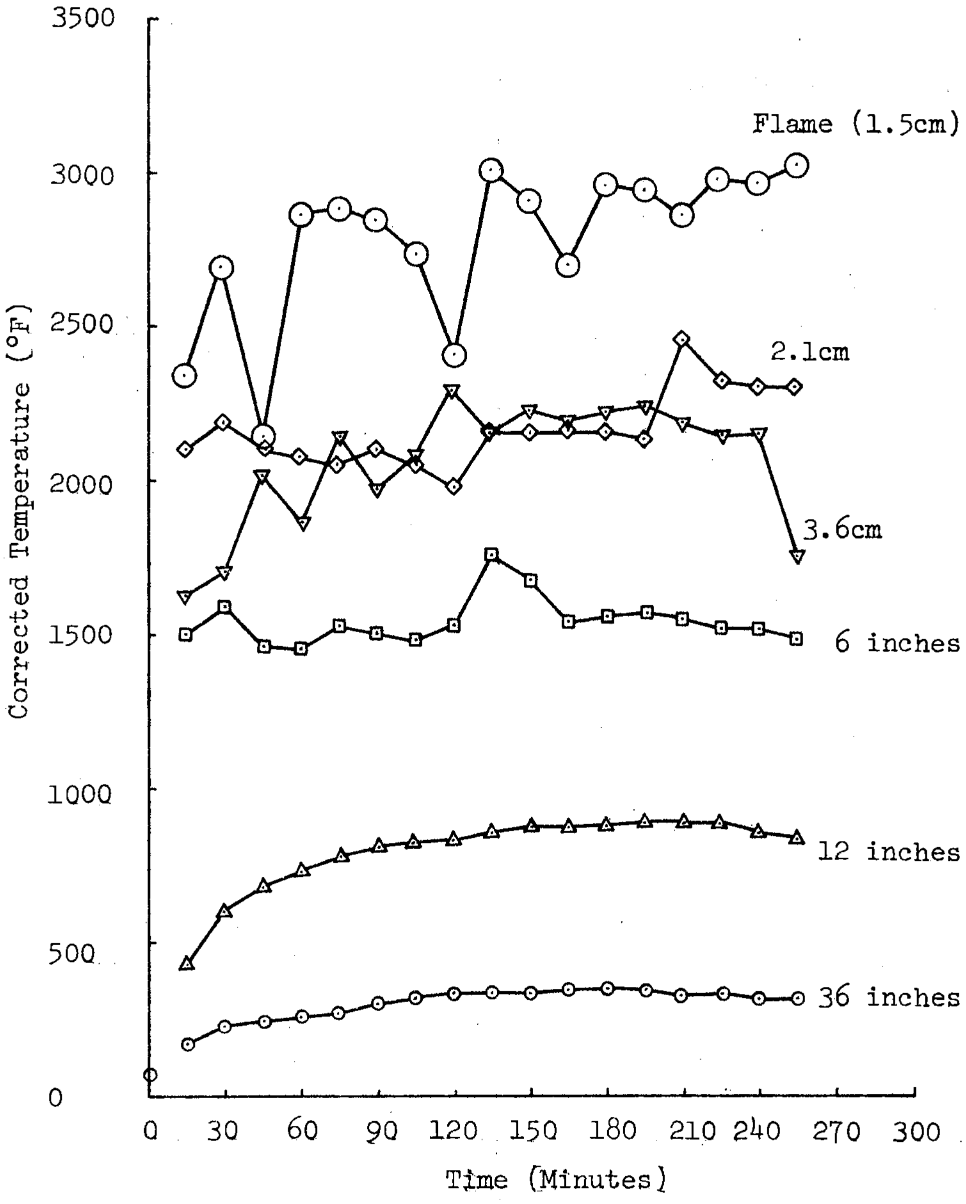


Figure 30. Run 16 - Temperature Profiles

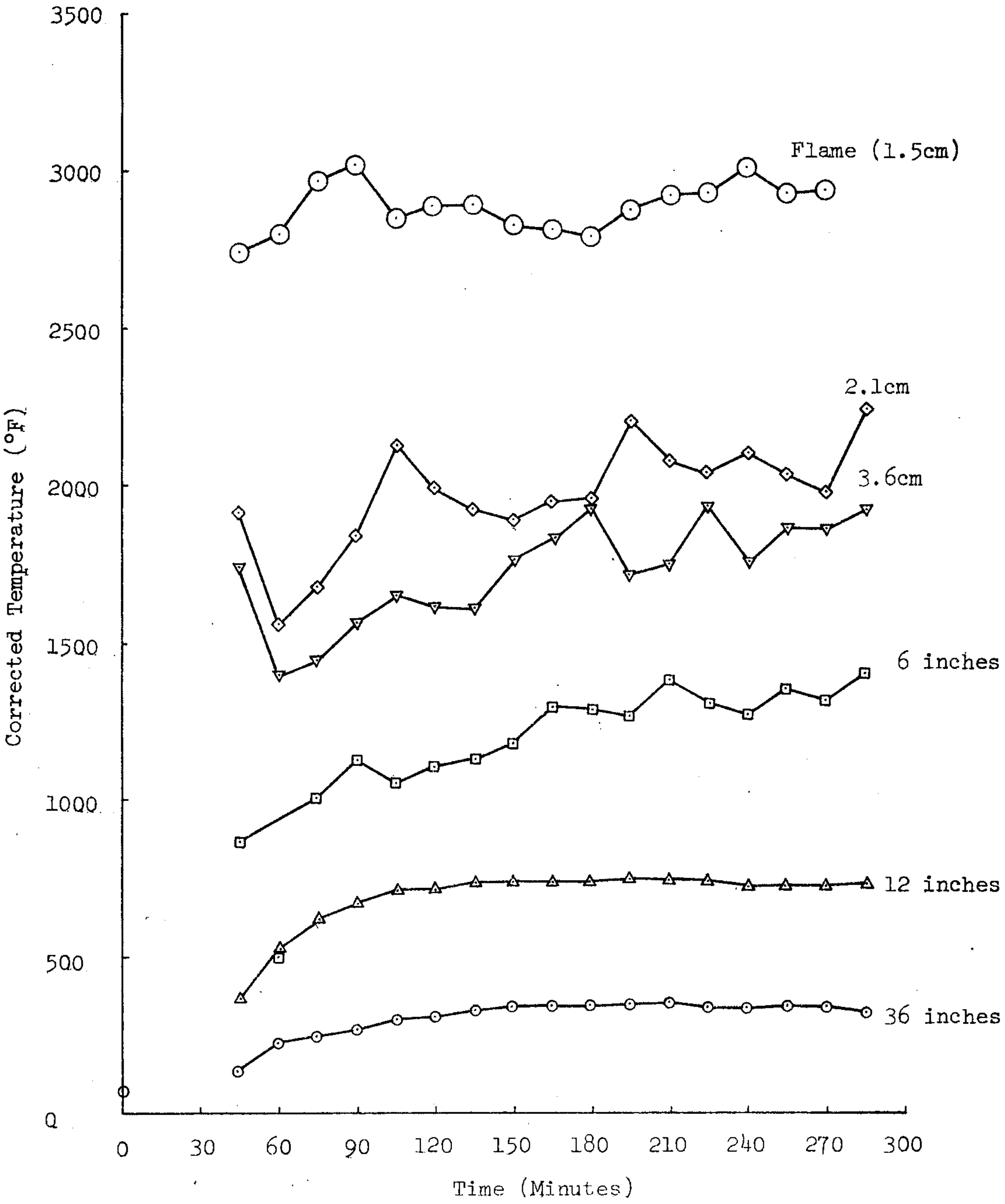


Figure 31. Run 17 - Temperature Profiles

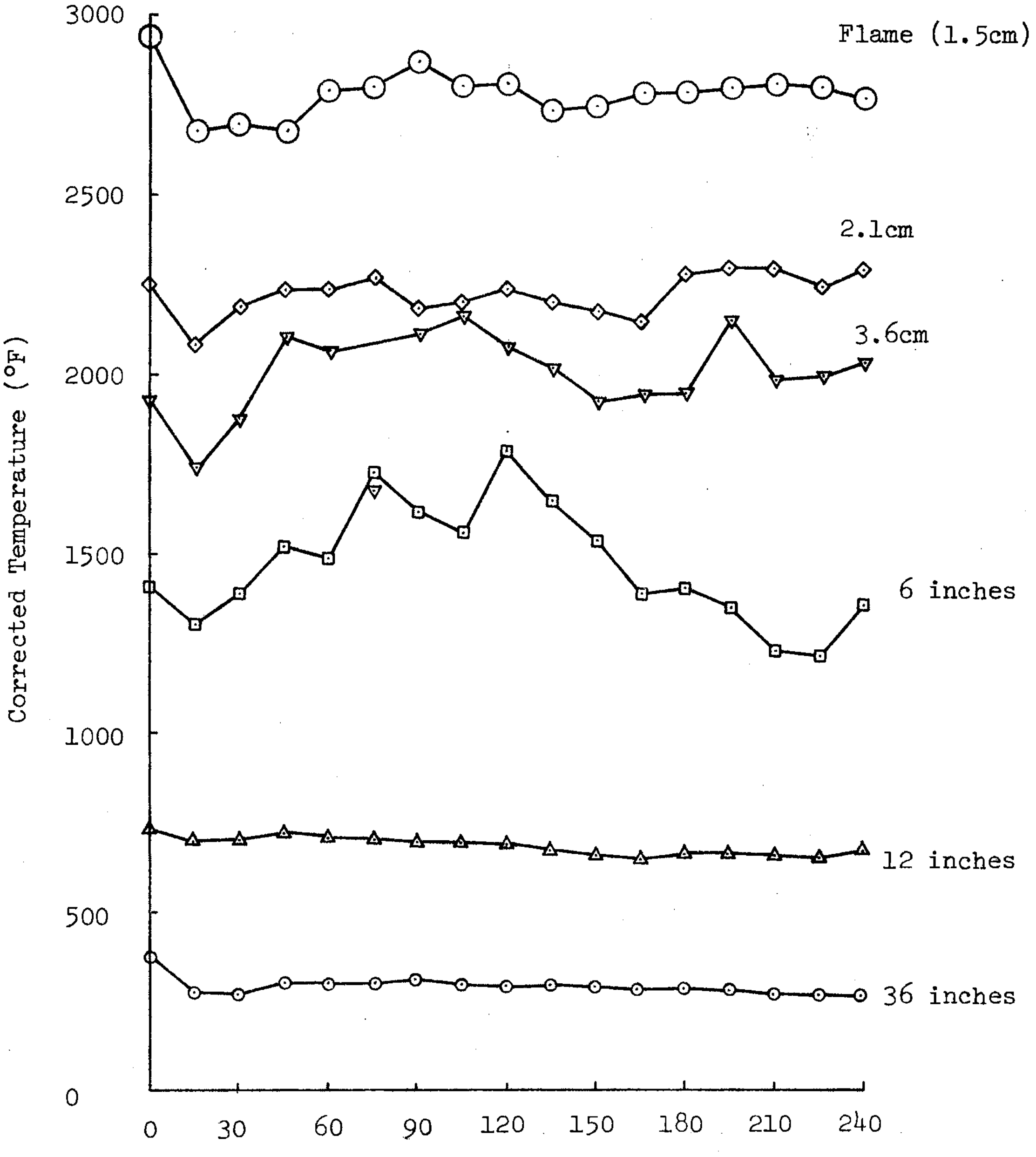


Figure 32. Run 18 - Temperature Profiles

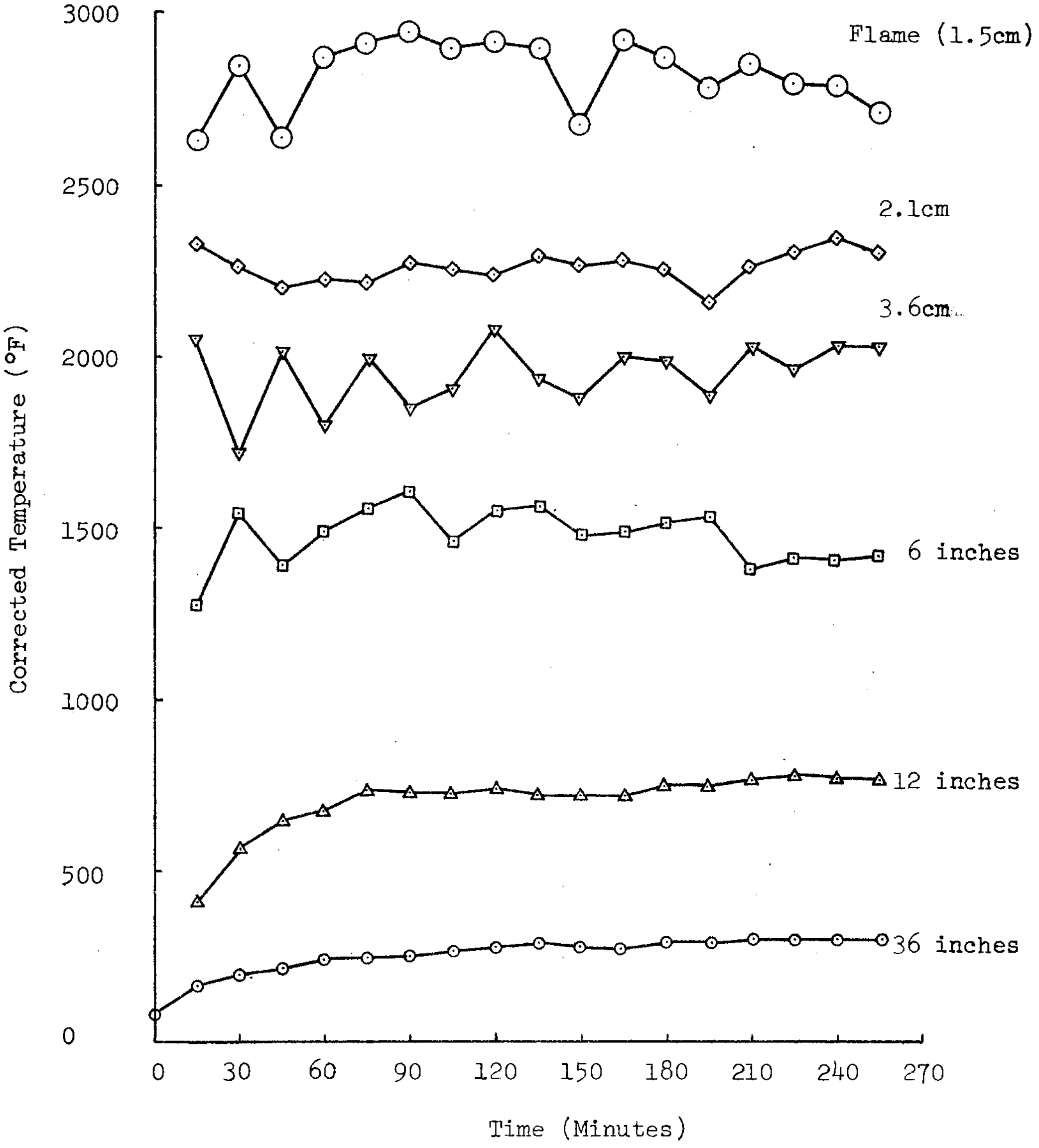


Figure 33. Run 19 - Temperature Profiles

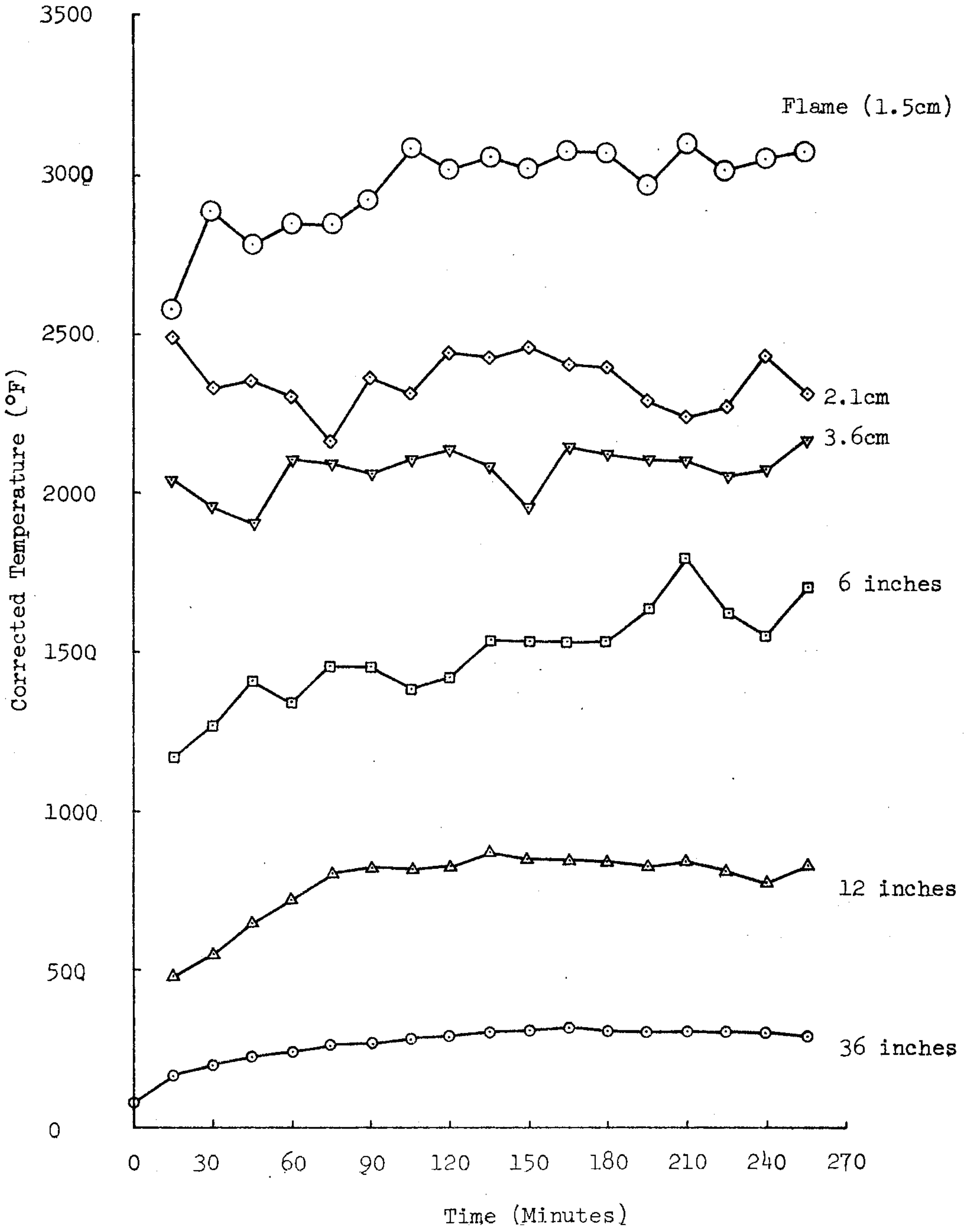


Figure 34. Run 20 - Temperature Profiles

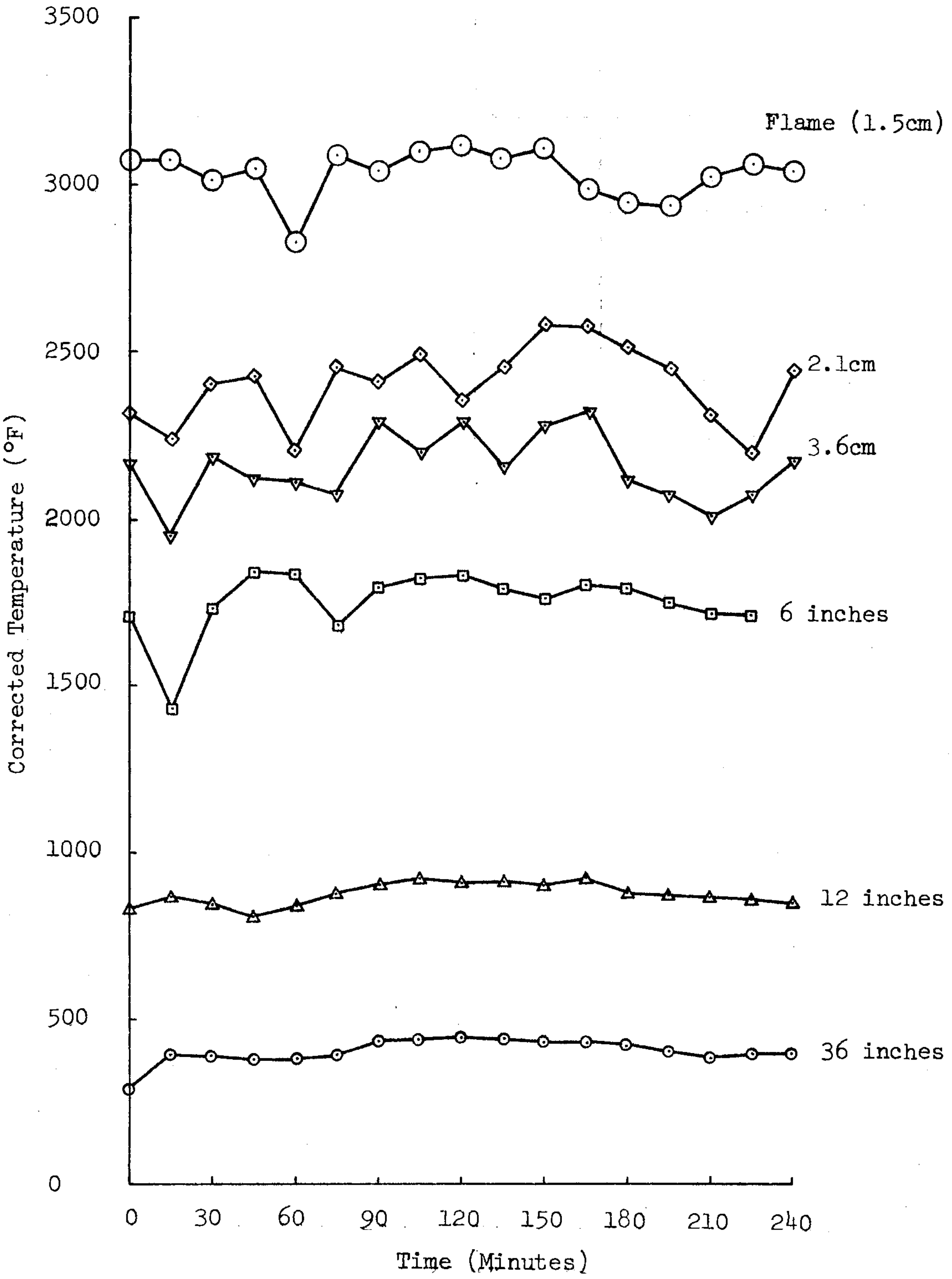


Figure 35. Run 21 - Temperature Profiles

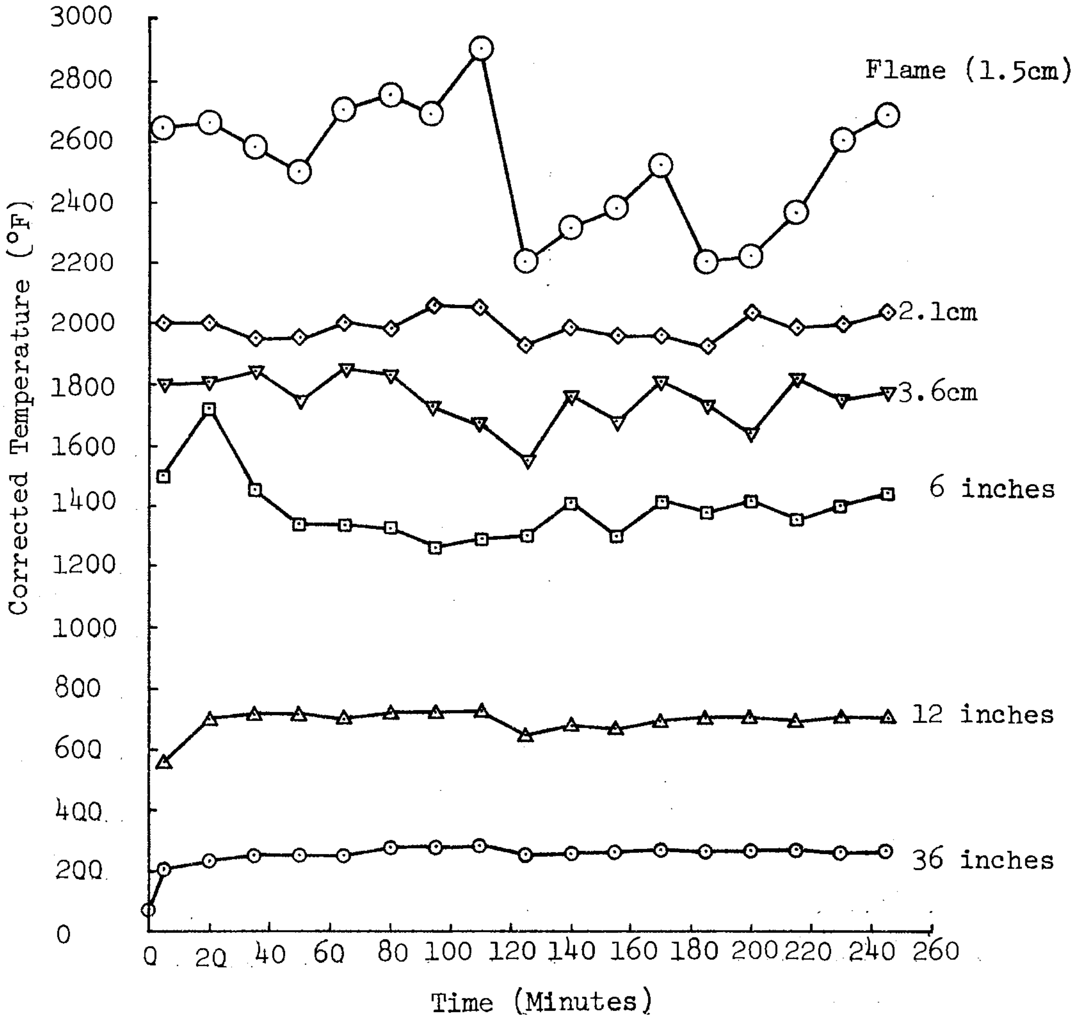


Figure 36. Run 22 - Temperature Profiles

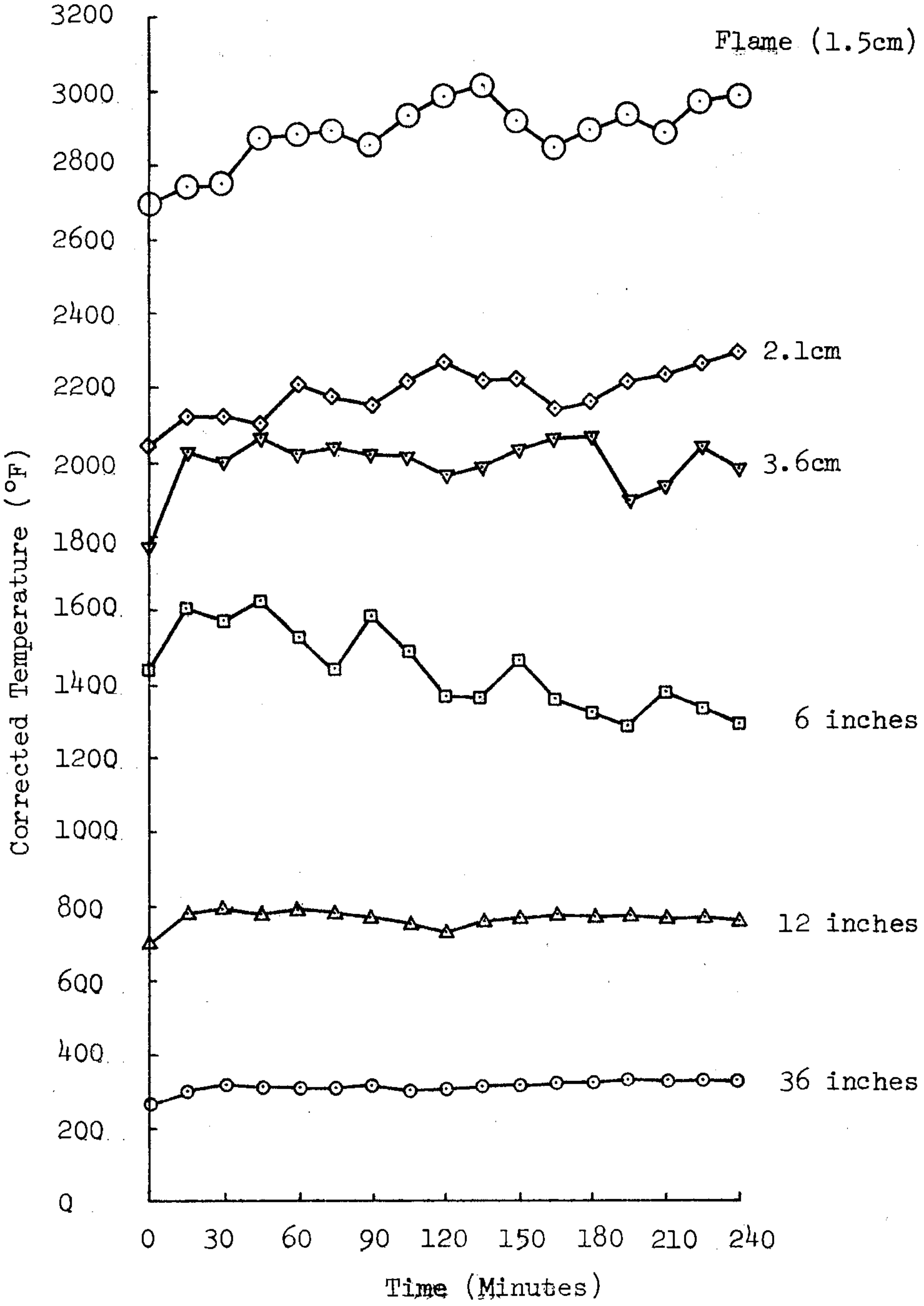


Figure 37. Run 23 - Temperature Profiles

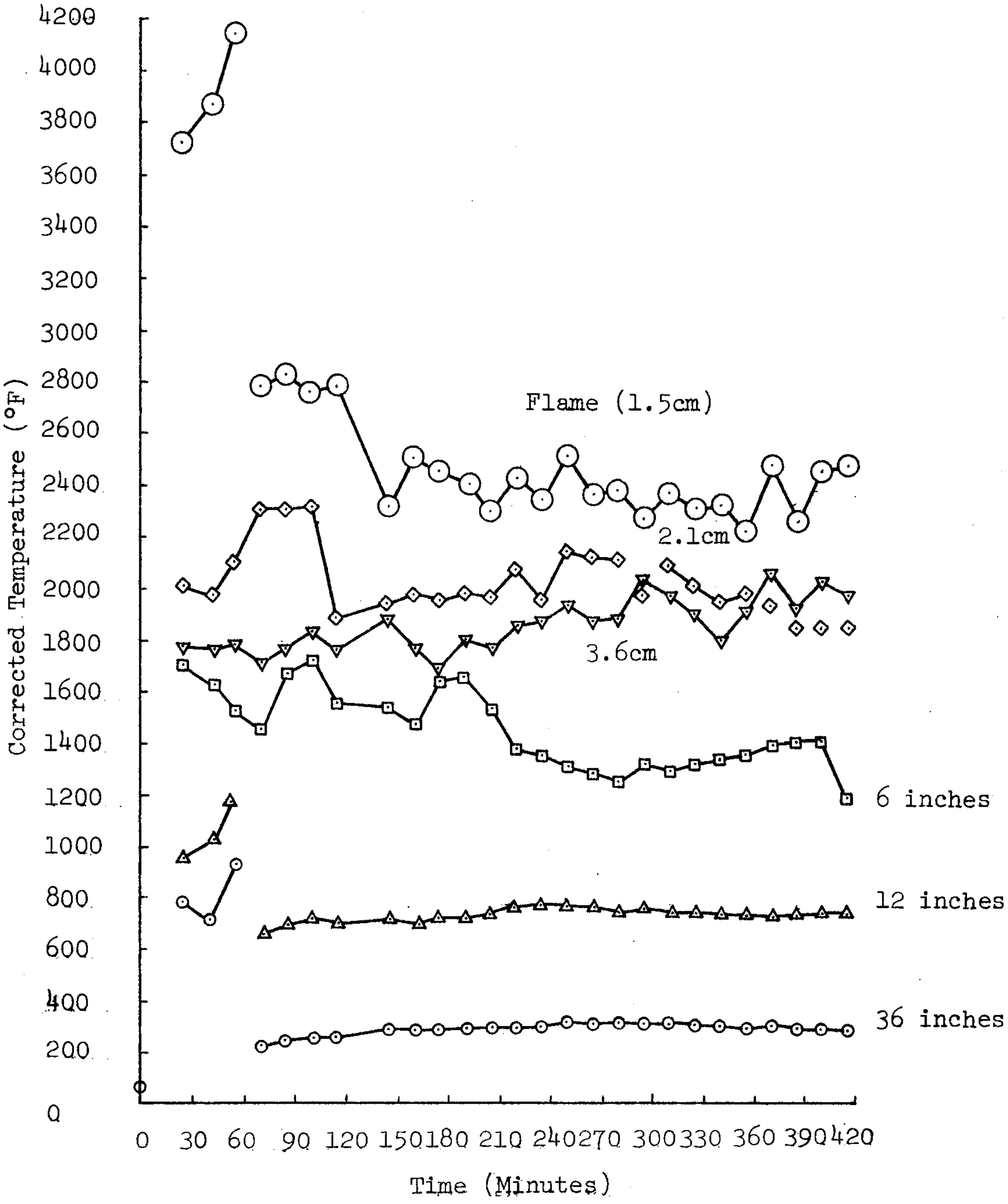


Figure 38. Runs 24-25 - Temperature Profiles

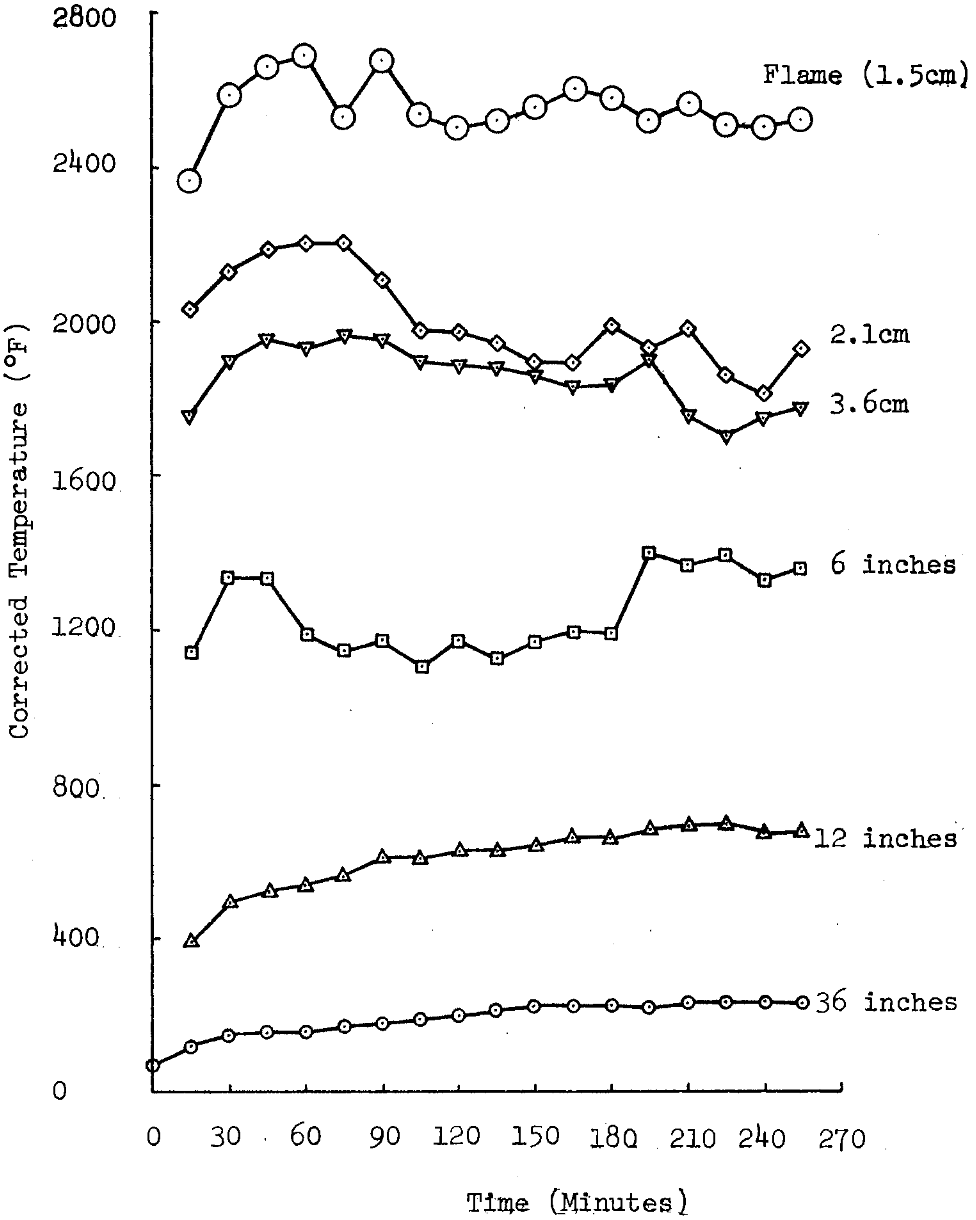


Figure 39. Run 26 - Temperature Profiles

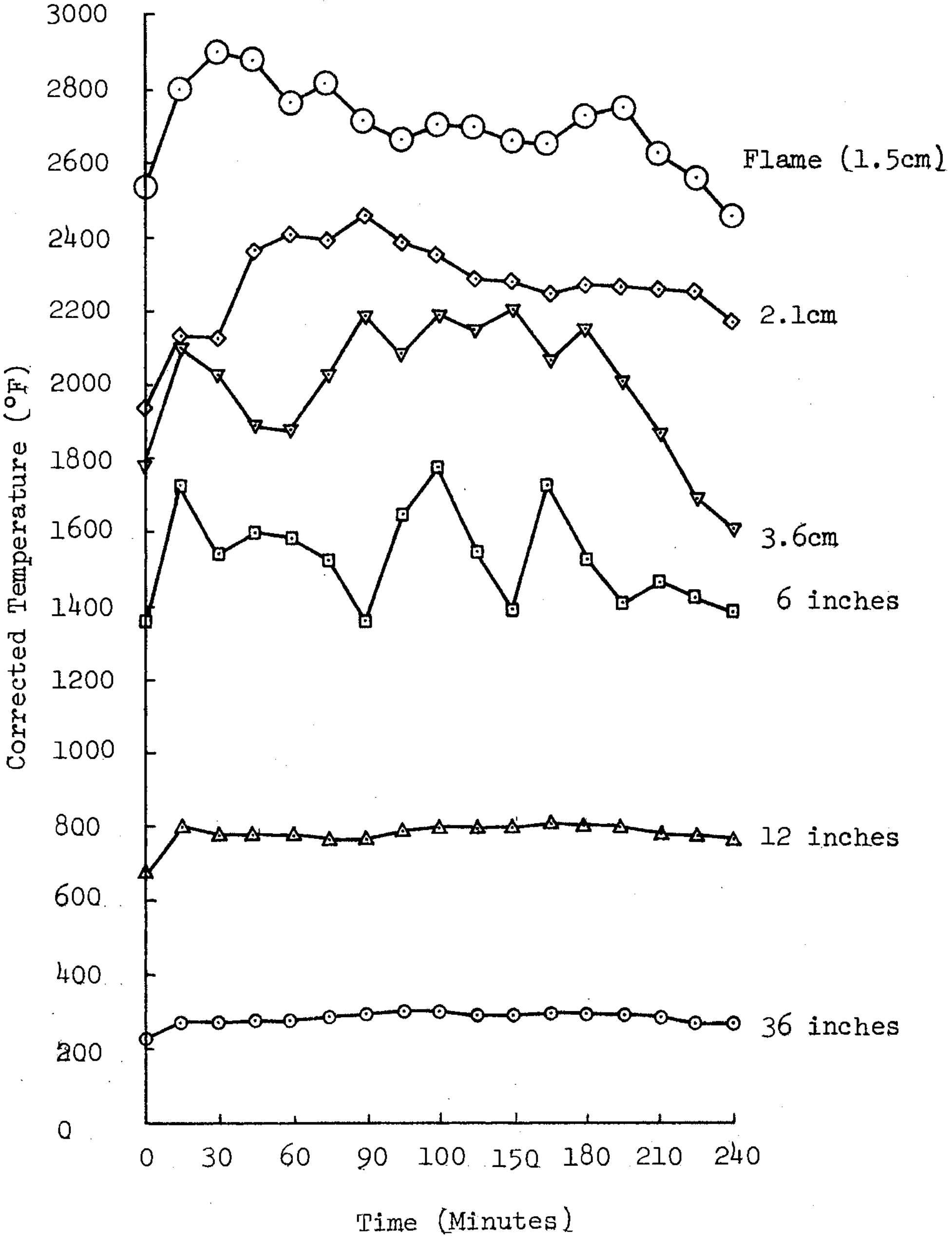


Figure 40. Run 27 - Temperature Profiles

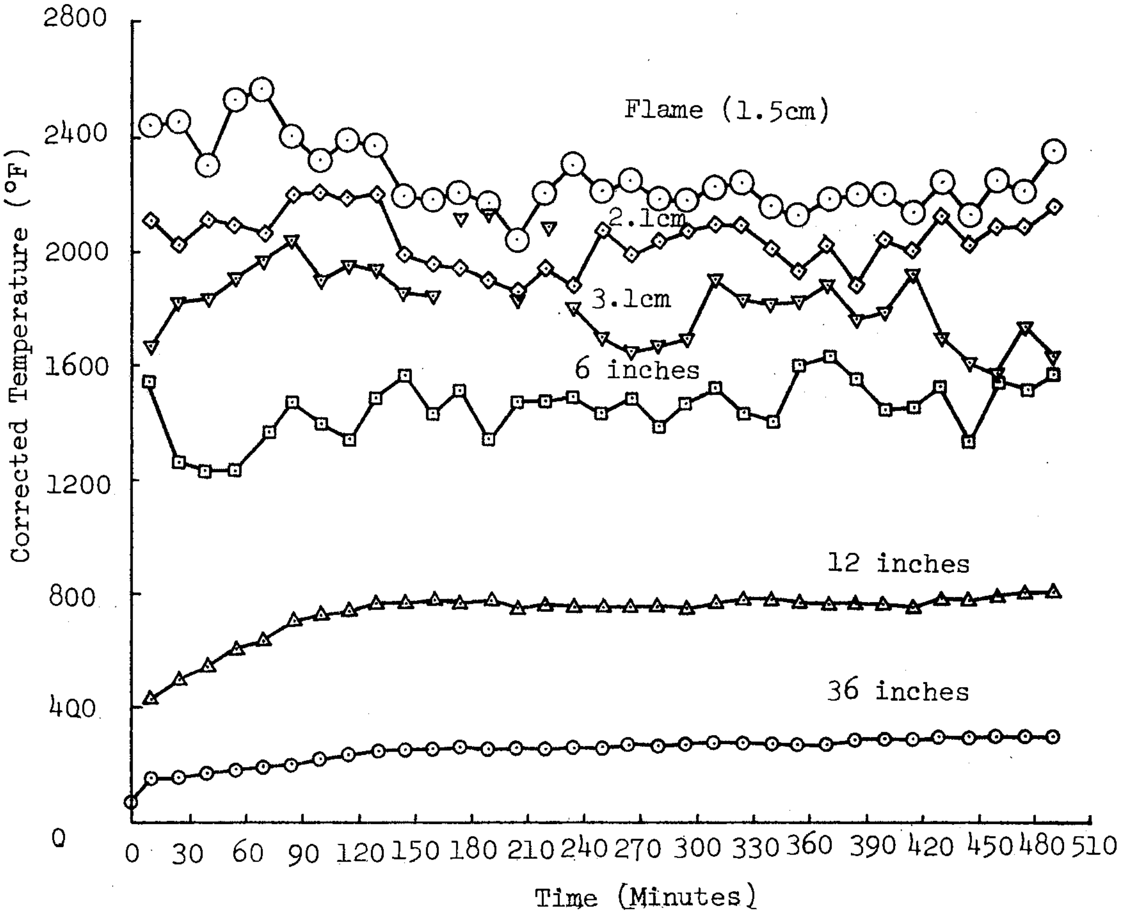


Figure 41. Runs 28-29 - Temperature Profiles

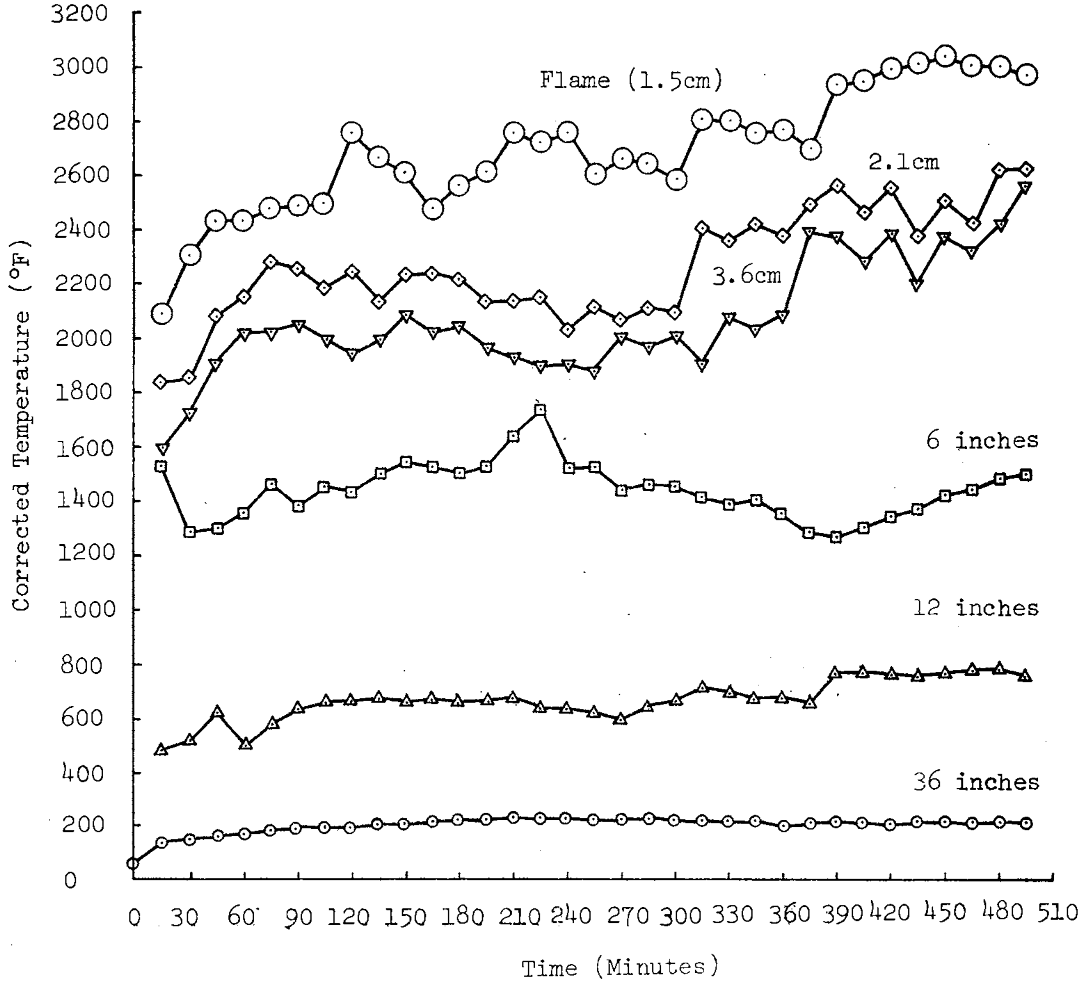


Figure 42. Runs 30-31 - Temperature Profiles

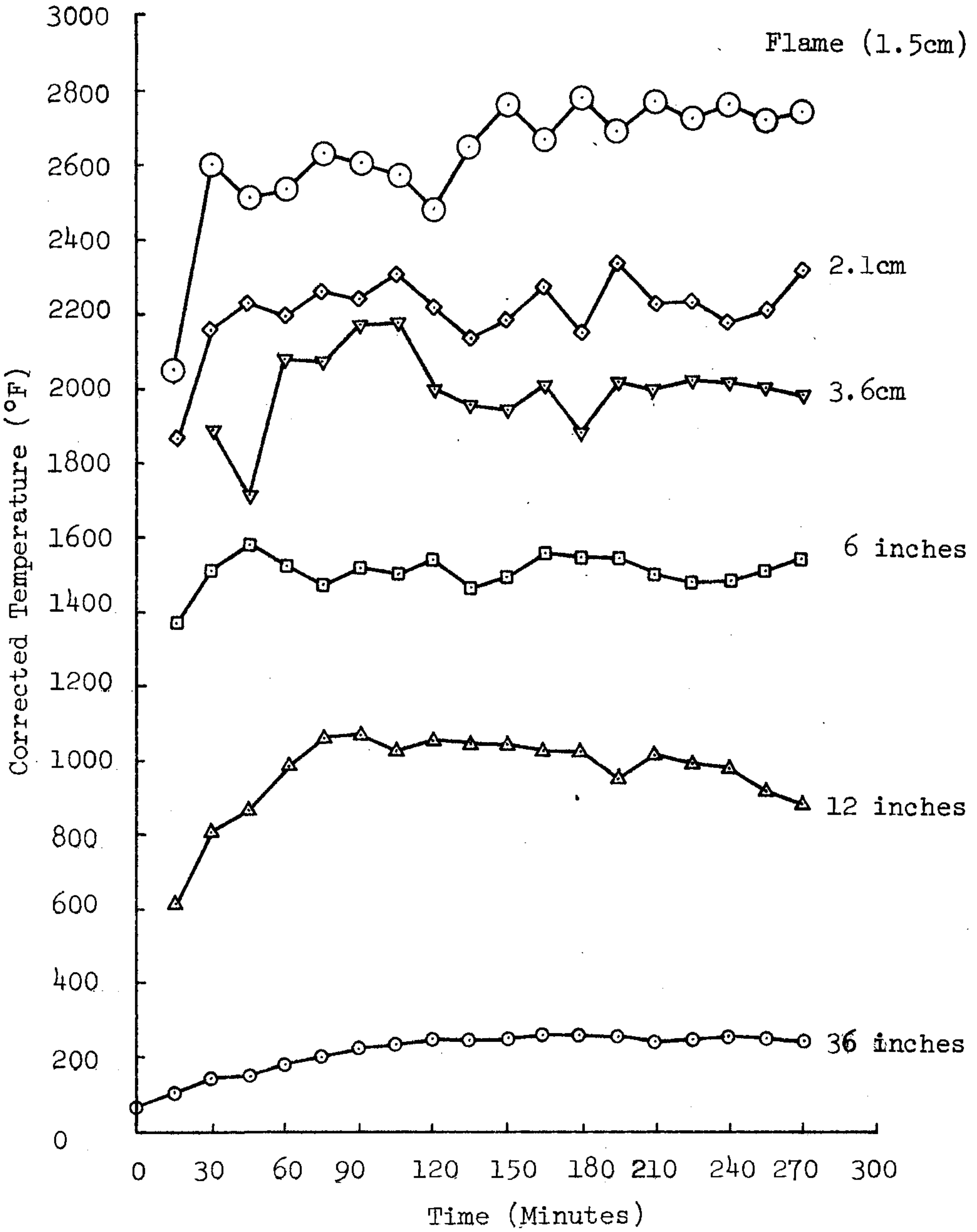


Figure 43. Run 32 - Temperature Profiles

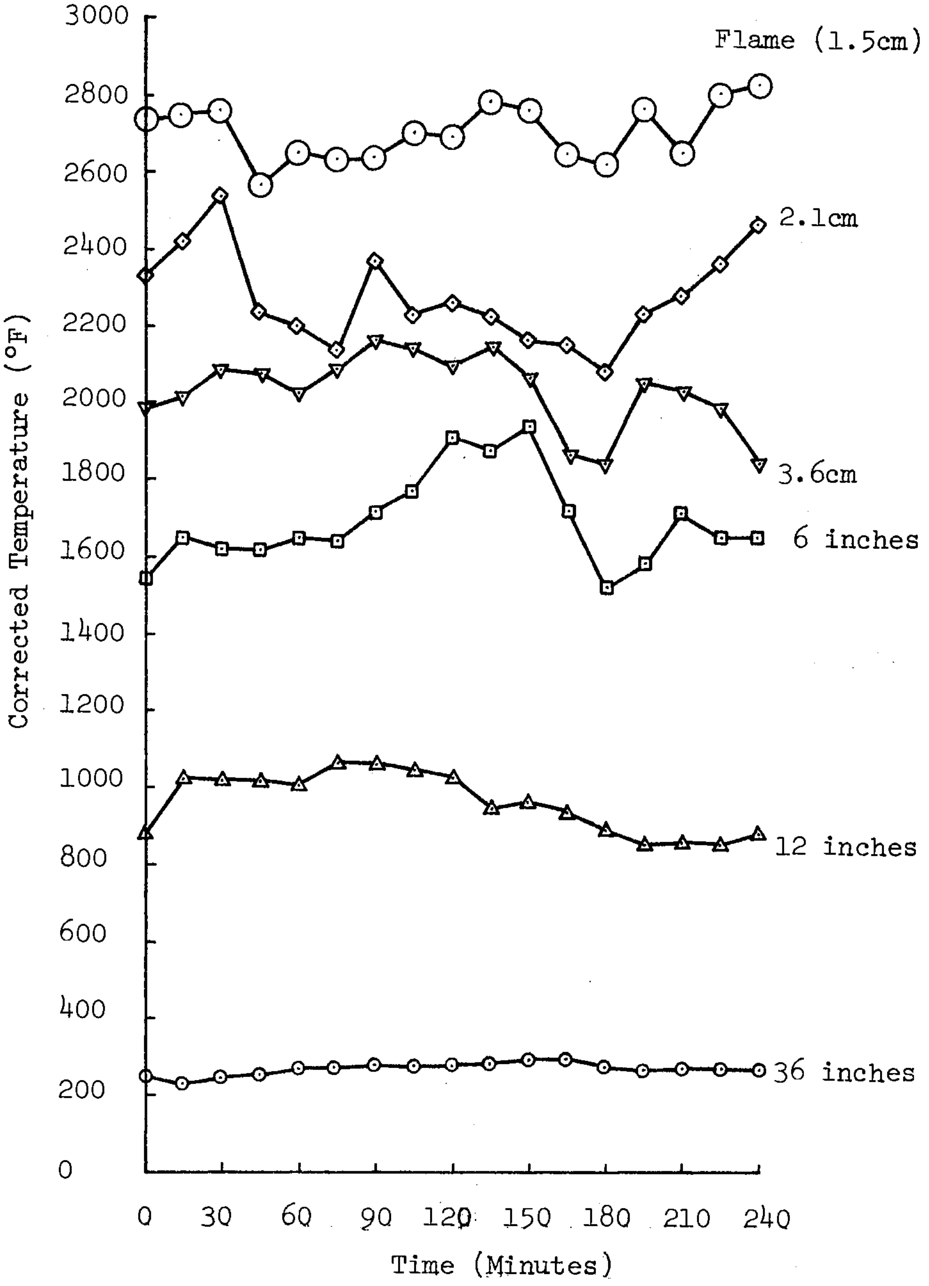


Figure 44. Run 33 - Temperature Profiles

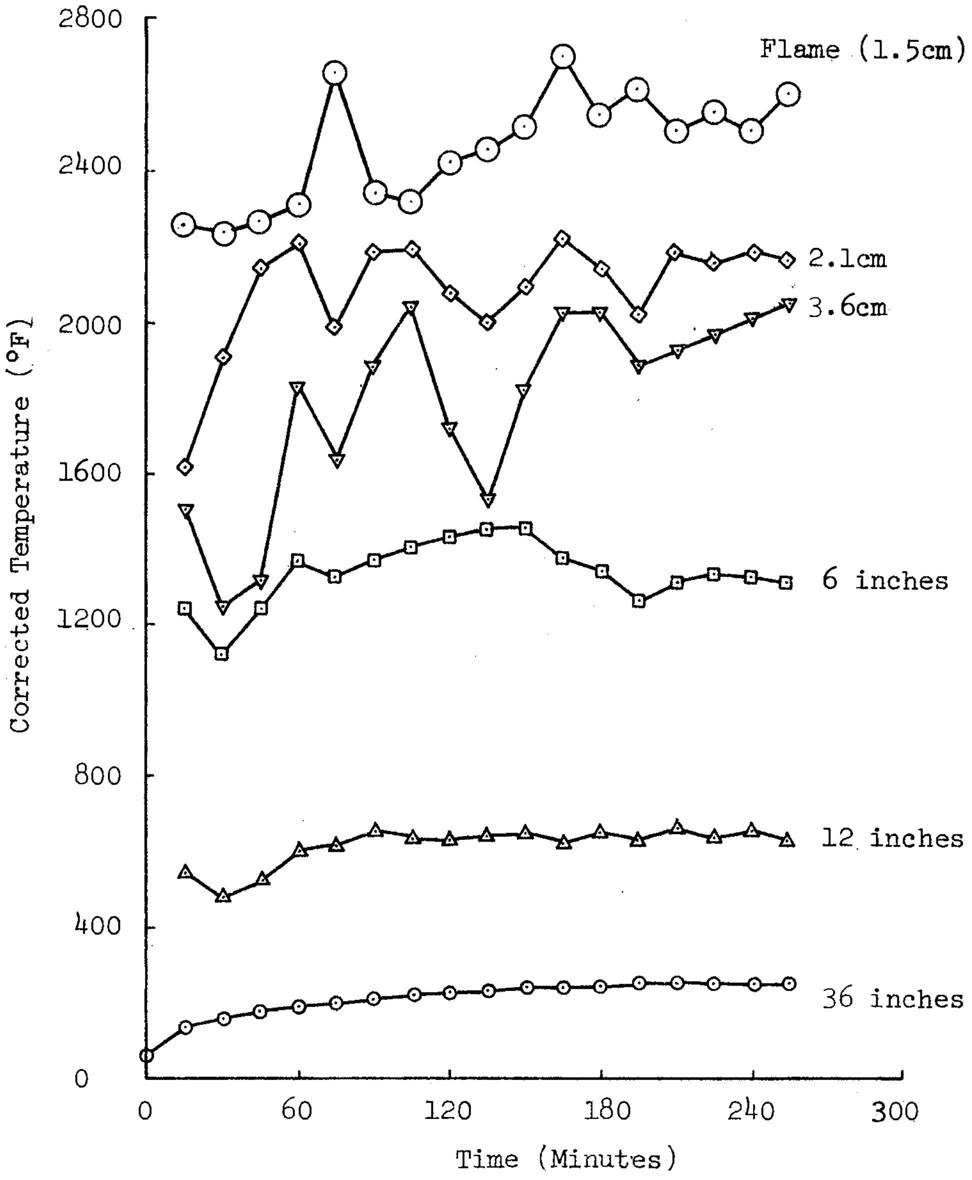


Figure 45. Run 34 - Temperature Profiles

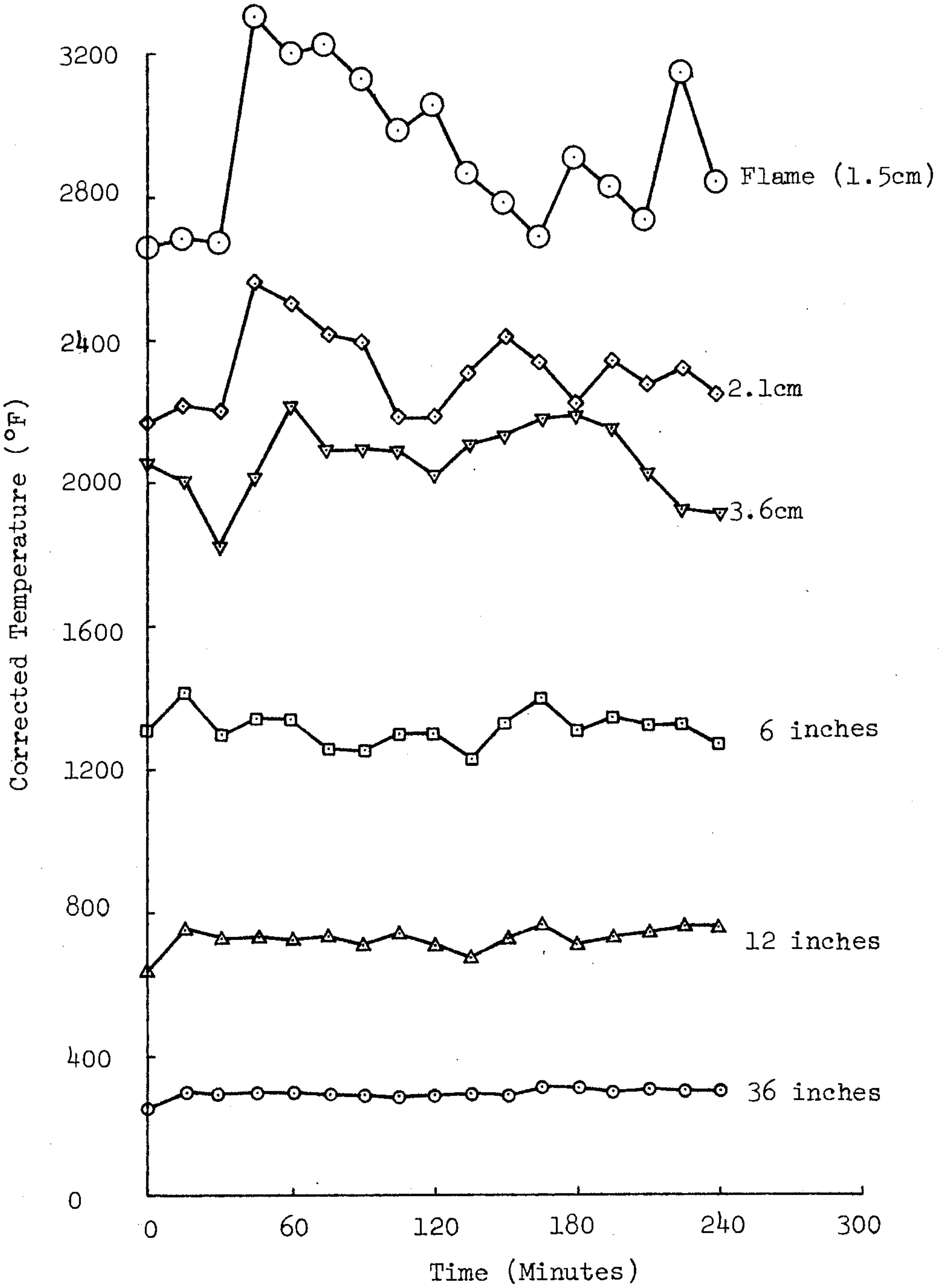


Figure 46. Run 35 - Temperature Profiles

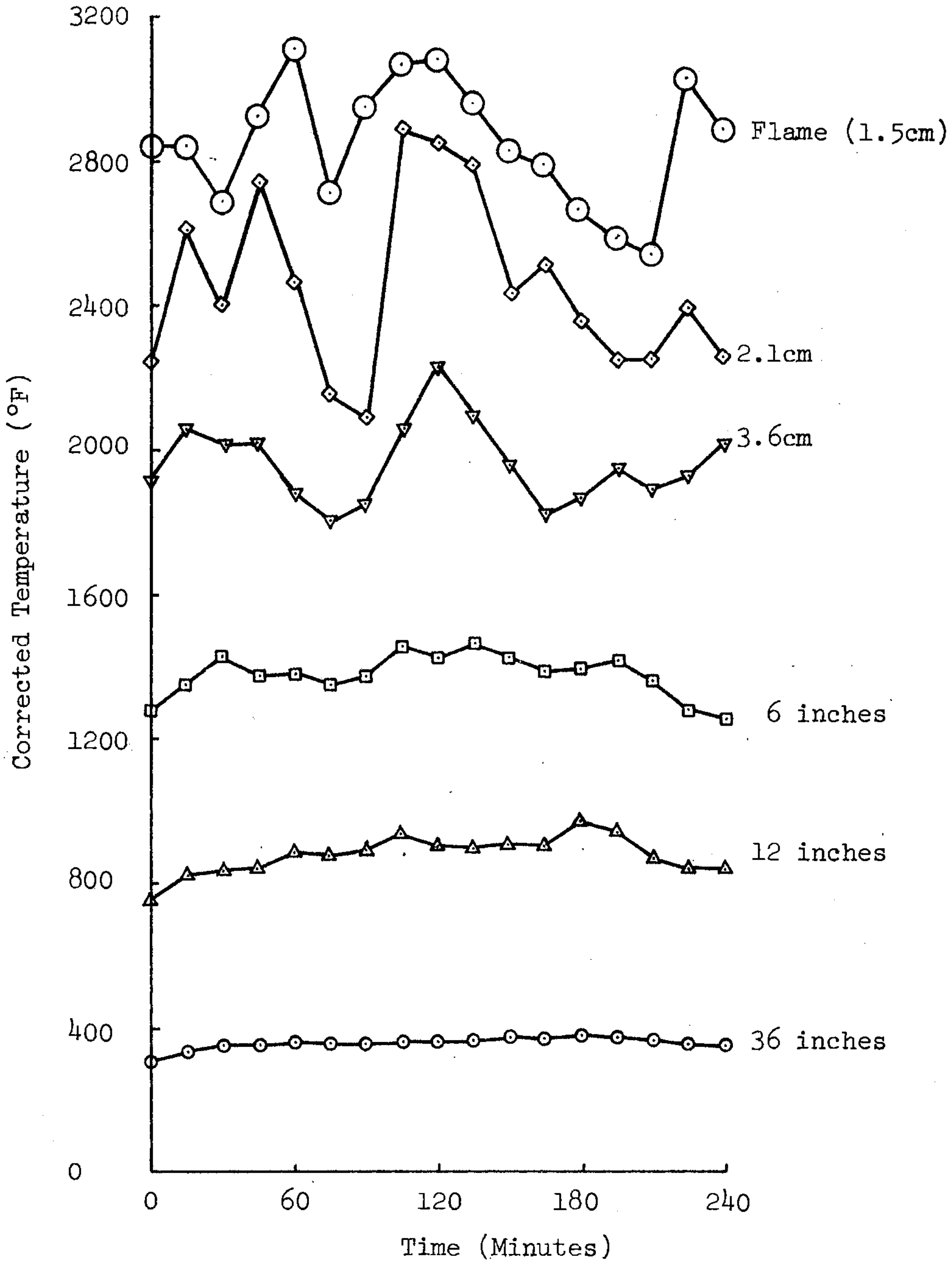


Figure 47. Run 36 - Temperature Profiles

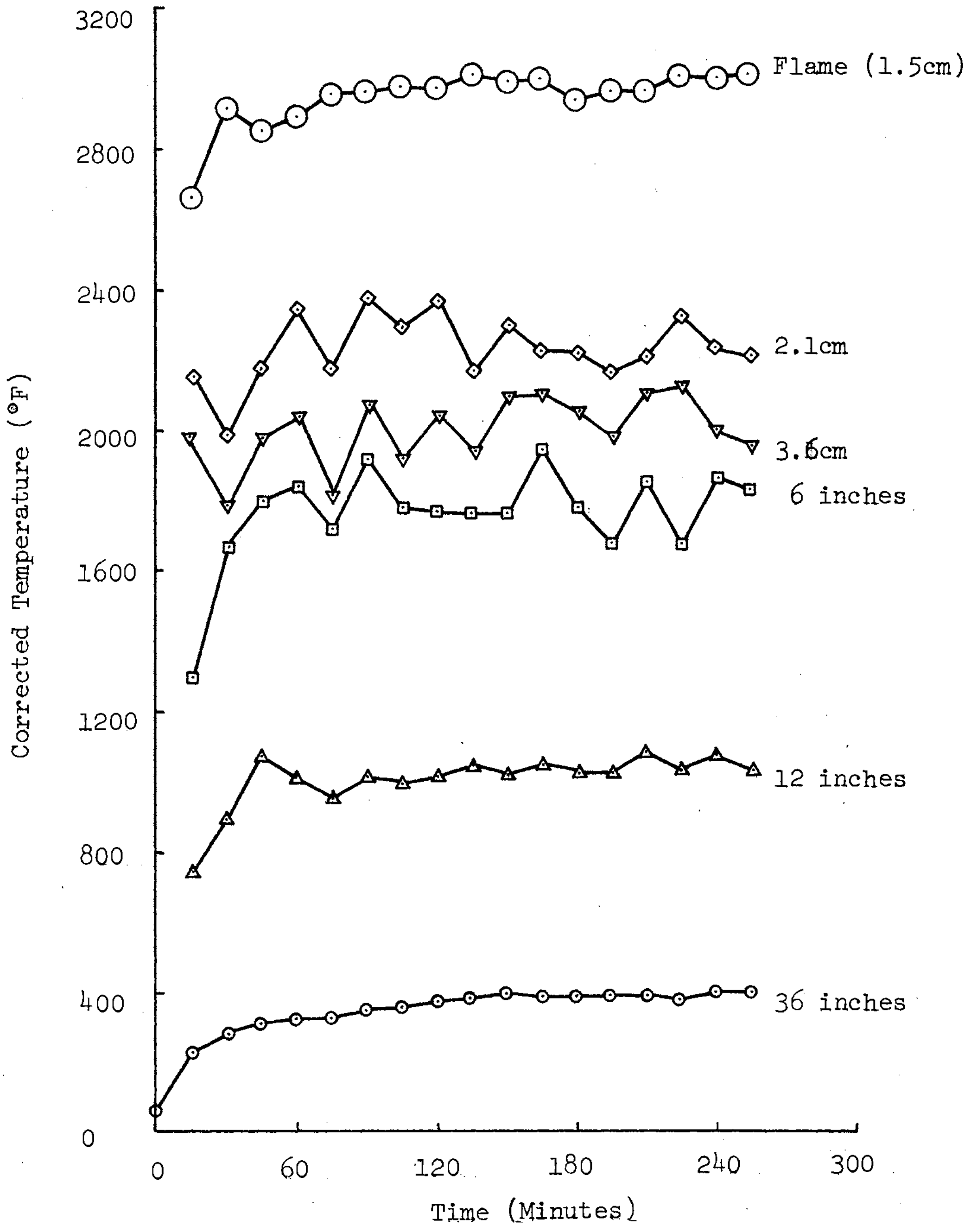


Figure 48. Run 37 - Temperature Profiles

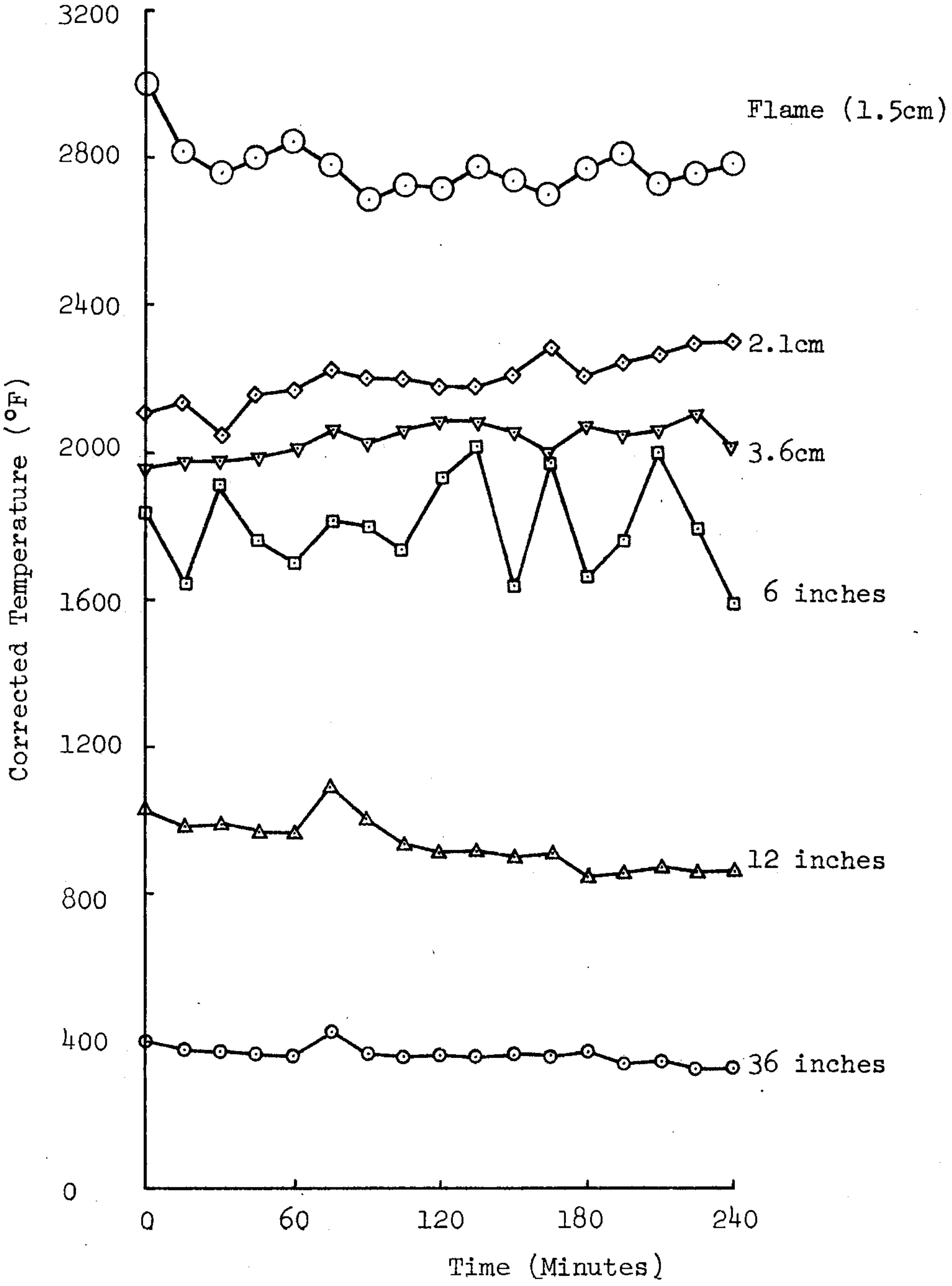


Figure 49. Run 38 - Temperature Profiles

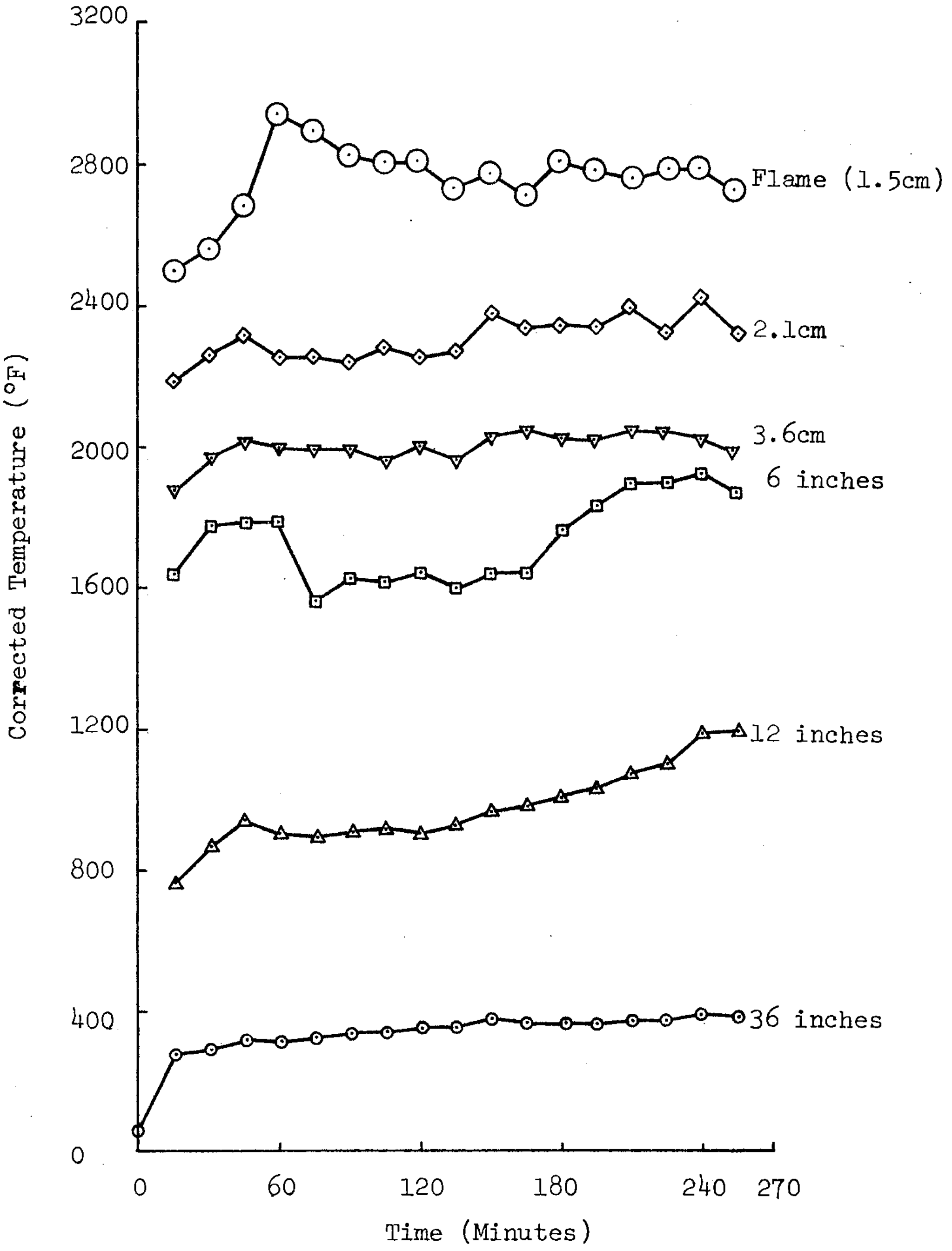


Figure 50. Run 39 - Temperature Profiles

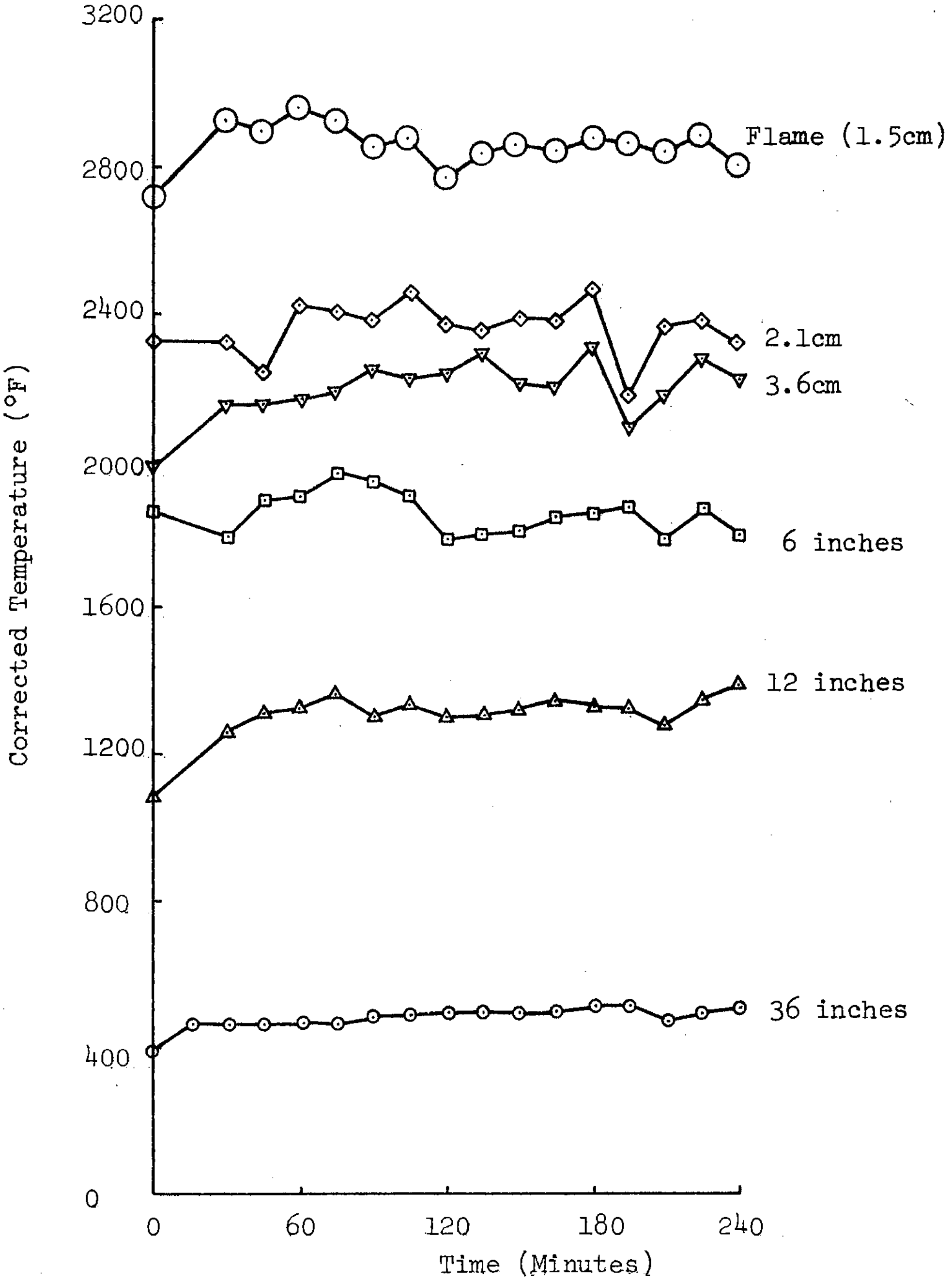


Figure 51. Run 40 - Temperature Profiles

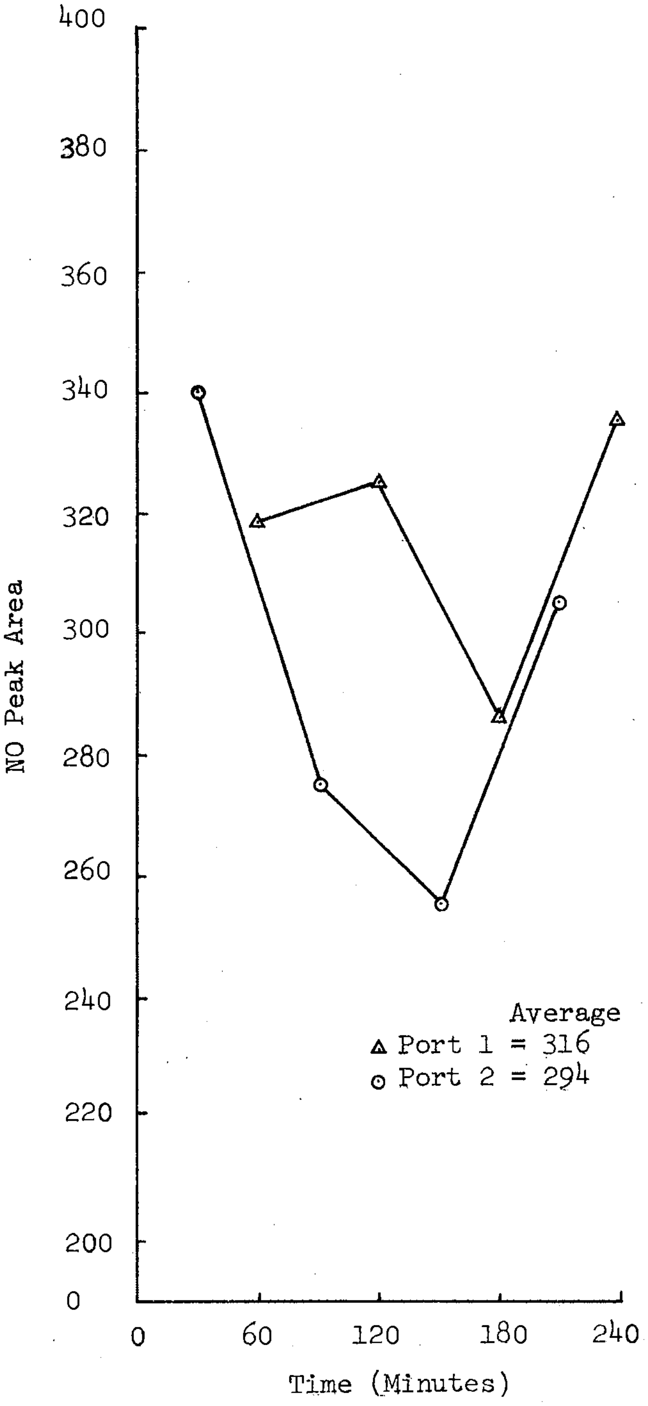


Figure 52. Run 20 - Concentration Profiles

TABLE XXIV

REPLICATE RUNS

Run Numbers	System	Conditions % Excess Oxygen	 % Fuel Nitrogen
18, 38	Air	80	0
14, 15, 39	Air	100	5
13, 40	Air	120	5
22, 34	Argon/Oxygen	80	0
30, 31	Argon/Oxygen	80	5
23, 35	Argon/Oxygen	100	0
28, 29	Argon/Oxygen	100	1
24, 25, 36	Argon/Oxygen	120	0

Analysis of Data

Temperature - A set of thermocouple readings was taken every fifteen minutes. Iron-constantan thermocouples manufactured by the researcher were used to measure the wall temperatures of the combustor. These were located within the chamber walls and read exact temperature. The temperatures of the combustion products were measured with sheathed chromel-alumel and tungsten-tungsten/26% rhenium thermocouples which extended approximately 4½ and 10½ inches into the combustor, respectively. Since there were conductive heat losses from the portion of

TABLE XXV

PRODUCT GAS ANALYSES (PEAK AREAS)

Run	Sample No.	Port	H_2	O_2/AR	N_2	NO_x	CO
13	1	1A-3/2[1]	12	84800	690176	72	5096
	2	2-3/2	10	4352	679936	56	3850
	3	1A-3/4	8	105600	679936	45	3600
	4	2-3/4	78	38861	671744	84	5088
	5	1A-0	-	151680	696934	55	2125
	6	1A-3/4	-	104832	675840	75	2796
	7	1A-3/2	-	*	670925	44	1464
	8	1B-0	-	*	675840	75	2076
	9	1B-3/4	-	*	684032	80	3762
	10	1B-3/2	-	141824	671744	60	3335
	11	2-3/4	-	*	618496	65	1794
	12	1B-3/2	-	182272	671744	90	2862
	13	1B-3/4	-	*	659456	72	943
	14	1B-0	-	11776	643072	78	528
	15	1A-0	-	113664	643072	54	3978
	16	1A-3/4	-	135782	686899	56	2142
	17	1A-3/2	-	153600	634880	65	1788
	18	2-0	18	*	591974	56	299
	19	2-0	-	76800	589824	45	388
	20	2-3/2	-	77824	608256	45	240
14	1	1	-	197837	663552	-	156
	2	2	-	105984	577536	30	348
	3	1	-	185344	663552	21	264
	4	2	-	56320	599040	10	242
	5	1	-	201062	645120	25	-
	6	2	-	132710	562278	-	1380
	7	1	-	**	671744	24	-
	8	2	-	115712	575488	-	-
15	1	2	-	42982	659456	-	1728
	2	1	260	18278	602112	18	33259
	3	2	17	46080	655360	25	3192
	4	1	212	6720	626688	35	35136
	5	2	-	75469	618496	**	990
	6	1	11	18432	651264	73	1440
	7	2	-	83059	667648	20	1553
	8	1	-	49152	655360	-	264

TABLE XXV (Continued)

Run	Sample No.	Port	H_2	O_2/AR	N_2	NO_x	CO
16	1	2	90	12902	634880	564	12740
	2	1	184	*	416154	732	13900
	3	2	287	9610	589824	855	23040
	4	1	104	122573	524288	414	9776
	5	2	118	80538	385024	259	7336
	6	1	116	60749	266240	240	5122
	7	2	116	51610	225280	231	4575
	8	1	136	56448	280576	370	7104
17	1	2	-	170394	642970	-	2448
	2	1	16	106982	655360	-	3841
	3	2	15	75264	651264	80	2952
	4	1	16	92160	643072	24	2388
	5	2	8	79565	641024	48	2538
	6	1	6	97792	612966	52	1116
	7	2	10	83866	643072	-	2030
	8	1	-	*	651264	44	529
18	1	1	-	93491	653312	-	437
	2	2	18	56986	614810	66	2760
	3	1	87	52736	638976	114	7440
	4	2	23	46771	638976	182	4416
	5	1	29	93005	641024	80	3264
	6	2	34	56960	634880	123	4152
	7	1	34	97715	630784	68	4264
	8	2	36	*	626688	280	5800
	9	1	8	169620	643072	60	1584
19	1	2	122	48640	249088	324	7056
	2	1	118	39245	184320	205	3910
	3	2	94	*	169267	152	3335
	4	1	93	29696	143770	185	3086
	5	2	104	25728	136397	250	4574
	6	1	94	25088	145920	297	4605
	7	2	108	24218	133786	324	4502
	8	1	106	25626	153600	369	5957
	9	1	120	28877	166912	438	6448

TABLE XXV (Continued)

Run	Sample No.	Port	H_2	O_2/AR	N_2	NO_x	CO
20	1	2	74	121712	60403	314	4464
	2	1	74	9139	98662	284	3900
	3	2	62	*	76800	252	3275
	4	1	63	9360	94208	312	4025
	5	2	66	6317	79872	243	3500
	6	1	59	7213	86016	248	4056
	7	2	56	6720	93414	293	7872
	8	1	58	7834	105677	297	1620
21	1	1	51	7728	107520	365	4875
	2	2	55	9856	113664	409	5356
	3	1	54	7987	115315	408	5350
	4	2	51	7654	121754	414	5555
	5	1	63	10701	175616	245	7271
	6	2	63	15488	253952	328	12240
	7	1	63	22246	278528	481	13104
	8	2	51	16614	408576	994	14592
22	1	2	-	161382	611942	-	120
	2	1	13	*	297523	-	696
	3	2	23	1256653	46144	160	4720
	4	1	16	1056768	28109	66	2990
	5	2	92	1083392	48307	412	1792
	6	1	68	647168	259840	165	3689
	7	2	135	974848	10880	879	10856
	8	1	139	1798963	6490	308	10824
23	1	1	206	1032192	9235	655	17181
	2	2	132	1032192	7987	894	10745
	3	1	170	958464	2736	561	15548
	4	2	131	950272	8269	913	10944
	5	1	176	980582	6926	429	13728
	6	2	132	946176	8128	799	10488
	7	1	311	1014989	1398	672	23814
	8	2	129	1040794	4368	905	12192
24 and 25	1	1	66	339763	118682	220	3776
	2	2	58	311296	104960	218	3600

TABLE XXV (Continued)

Run	Sample No.	Port	H_2	O_2/AR	N_2	NO_x	CO
24-25	3	2	74	350515	103245	270	4176
	4	1	73	419226	119808	290	4871
	5	2	74	288154	77056	248	3630
	6	1	73	478720	118784	341	5026
	7	2	73	*	118784	333	5357
	8	1	65	419021	114688	322	5179
	9	1	56	348365	97280	292	4416
	10	2	57	464486	109926	335	5232
	11	1	70	432230	120806	358	5472
	12	2	67	448307	123904	346	5612
	13	1	56	362701	97280	294	4536
26	1	2	-	184320	58368	120	1680
	2	1	29	110592	48640	88	1400
	3	2	32	122880	47104	80	1344
	4	1	27	96256	45568	70	2600
	5	2	27	106445	48768	88	1322
	6	1	25	96256	46336	105	1312
	7	2	23	95232	46592	99	1391
	8	1	20	121037	50643	119	1404
27	1	1	28	105370	52416	84	1456
	2	2	30	115405	50944	92	1388
	3	1	24	127181	54912	84	1482
	4	2	66	129024	56909	99	1755
	5	1	27	119347	54374	87	1452
	6	2	24	121856	65536	92	1512
	7	1	18	113664	61901	98	1416
	8	2	27	112640	63898	109	1332
28-29	1	2	24	119398	88320	78	1300
	2	1	22	128410	97792	96	1361
	3	2	27	120986	112845	108	1677
	4	1	21	177229	137626	108	1742
	5	2	26	206438	153754	126	1859
	6	1	29	202547	154624	118	1882
	7	2	22	*	159744	117	1714
	8	1	20	170957	145408	108	1714
	9	1	22	188160	160768	124	1898
	10	2	19	211661	154829	84	1742

TABLE XXV (Continued)

Run	Sample No.	Port	H_2	O_2/AR	N_2	NO_x	CO
28-29	11	1	24	215040	162816	120	1950
	12	2	24	227840	166400	130	1875
	13	1	25	187085	155648	120	1896
	14	2	23	207258	175104	91	1912
	15	1	21	224333	183296	126	1912
	16	2	26	*	177715	128	1825
30-31	1	2	22	170419	126208	99	1380
	2	1	14	178642	141312	134	1318
	3	2	19	188160	161792	115	1599
	4	1	20	201958	158208	104	1450
	5	2	25	209126	181760	88	1560
	6	1	18	200704	161280	78	1559
	7	2	15	210944	168896	105	1540
	8	1	7	182784	153254	99	1208
	9	1	16	206131	169984	99	1542
	10	2	32	*	218112	114	2280
	11	1	36	349184	318464	147	2391
	12	2	32	403200	311296	171	2600
	13	1	27	374477	325478	158	2418
	14	2	47	359322	329472	132	2816
	15	1	51	417280	304640	126	1748
	16	2	52	352256	309862	171	2576
32	1	2	69	326656	167731	154	2912
	2	1	77	403661	246400	208	3192
	3	2	82	403046	292864	195	3100
	4	1	79	432640	284160	180	3098
	5	2	70	414515	295526	190	3315
	6	1	76	410010	301568	190	3412
	7	2	66	425779	305459	216	3552
	8	1	65	443802	379597	216	3792
33	1	1	88	464077	284928	170	3792
	2	2	-	479846	293069	234	4114
	3	1	113	511078	311501	240	4330
	4	2	117	545587	308224	228	4787
	5	1	123	**	291533	256	5356
	6	2	156	499712	279552	276	5831
	7	1	132	647680	271565	300	6448
	8	2	138	655360	266240	318	6968

TABLE XXV (Continued)

Run	Sample No.	Port	H_2	O_2/AR	N_2	NO_x	CO
34	1	2	-	892109	6144	28	1476
	2	1	20	167936	12160	50	1344
	3	2	-	*	1280	-	168
	4	1	29	97843	544	66	2444
	5	2	21	97997	960	120	1512
	6	1	23	16896	*	66	780
	7	2	-	104448	1152	-	504
	8	1	27	84403	768	54	1248
35	1	1	32	31181	27584	46	1716
	2	2	12	40602	880	40	888
	3	1	11	14438	28330	60	495
	4	2	23	68813	832	75	1404
	5	1	60	80179	128	66	3516
	6	2	14	65024	853	30	460
	7	1	12	64512	888	42	495
	8	2	38	*	2816	115	2412
36	1	2	-	67584	737	24	352
	2	1	20	17280	28544	36	575
	3	2	18	89242	1050	38	748
	4	1	14	*	28570	36	564
	5	2	24	150016	2432	102	2297
	6	1	176	155136	2434	616	13248
	7	2	-	199014	2746	-	-
	8	1	62	141312	2176	255	-
37	1	2	7	*	117760	52	1920
	2	1	5	7392	115712	-	400
	3	2	-	*	114790	-	396
	4	1	129	**	119654	72	9792
	5	2	-	5510	80640	-	90
	6	1	-	17741	148480	6	154
	7	2	-	16800	140646	6	483
	8	1	84	1344	*	28	3419
38	1	1	182	172	130790	410	*
	2	2	-	*	78848	3	198
	3	2	6	6880	73728	66	756

TABLE XXV (Continued)

Run	Sample No.	Port	H_2	O_2/AR	N_2	NO_x	CO
38	4	1	-	4781	74752	6	492
	5	2	-	2870	66560	48	621
	6	1	-	10842	73728	21	154
	7	2	-	4083	65894	24	252
	8	1	-	8538	69632	10	90
39	1[2]	2	-	*	11264	-	-
	2	1	28	7322	38912	100	1740
	3	1	22	7594	36557	72	960
	4	2	19	288	28954	96	1292
	5	1	32	6266	37376	120	1572
	6	2	12	340	28160	90	1125
	7	1	36	4048	38400	121	2111
	8	2	12	451	27648	85	1044
40	1	1	40	*	37632	200	1952
	2	2	-	647	40960	46	540
	3	1	22	1869	88064	50	1307
	4	2	-	*	17664	30	380
	5	1	30	890	21760	142	1738
	6	2	26	92	*	90	1928
	7	1	39	15	21402	218	2756
	8	2	-	497	20454	40	529

[1] Port location - radial measurement

[2] Broken probe - sample contained only air

* attenuation too small

**attenuation too large

Note: Runs 13-21, 37-40 oxygen/argon should be all oxygen. Other runs, both oxygen and argon are present.

TABLE XXVI

RESULTS - DATA ANALYSIS

Run	NO_x - PPM				TEMPERATURES - °F					
	"As Is"		"Corrected"		Flame		2.1 cm		3.6 cm	
	X	O	X	O	X	O	X	O	X	O
13	493	74.5	-[1]	-[1]	3027	67.4	1987	185.1	1481	270.4
14	212	52.8	191	36.5	2754	111.4	1721	325.3	-[6]	-[6]
15	294	134.6	240	49.7	2937	56.8	2041	175.0	1704	197.3
16	1301	163.4	1267	129.7	2773	251.6	2158	114.0	2050	196.8
17	407	122.4	456	81.2	2884	74.7	1971	167.0	1724	154.1
18	662	172.2	683	174.9	2782	64.5	2226	58.8	1984	130.2
19	1586	302.6	1681	266.8	2806	90.4	2241	45.2	1940	94.1
20	2470	536.0	2294	130.6	2959	135.9	2357	75.4	2061	71.1
21	2077	486.1	1941	475.0	3032	72.6	2398	113.2	2151	100.3
22	755	278.0	749	141.8	2522	207.3	1989	39.7	1747	76.8
23	1152	83.1	1148	89.7	2884	87.4	2183	64.7	1993	72.1
24-25	1187	31.5	1195	26.7	2427	178.9	2008	135.9	1845	95.5
26	1184	73.9	1202	74.4	2555	73.9	1998	119.3	1850	79.5
27	1216	52.6	1219	60.4	2695	115.8	2263	124.1	1987	175.2
28	1119	48.5	1113	53.1	2298	144.3	2026	104.9	1900	128.4
29	1060	43.9	1065	29.0	2198	58.9	2040	65.8	1744	104.9

TABLE XXVI (Continued)

	NO$_x$ - PPM				TEMPERATURES - °F					
	"As Is"		"Corrected"		Flame		2.1 cm		3.6 cm	
Run	X	O	X	O	X	O	X	O	X	O
30	1036	55.2	1015	41.4	2532	173.8	2129	128.0	1938	124.2
31	978	55.3	957	47.0	2829	151.2	2365	190.6	2182	214.7
32	1025	15.8	1022	16.0	2626	165.7	2196	104.5	1996	104.2
33	1032	30.4	1041	22.1	2704	72.0	2274	121.6	2026	97.9
34	1221	762.4	1183	125.2	2460	147.6	2083	145.9	1785	250.1
35	1488	620.8	1205	131.3	2920	209.5	2305	111.8	2055	102.3
36	1546	726.2	1050[2]	67.4[2]	2861	151.6	2445	236.2	1957	107.7
37	671	356.4	588[3]	352.0[3]	2939	84.2	2213	100.2	1974	125.8
38	943	580.6	854[4]	278.8[4]	2774	72.0	2193	66.2	2028	43.2
39	2233	228.3	2260	235.6	2752	100.6	2300	59.7	1992	40.0
40	3174	2111.5	1492[5]	298.7[5]	2852	56.3	2361	56.6	2190	76.6

[1] Data unchanged
[2] 1,221,302.3
[3] 420,230.0
[4] 880,183.4
[5] 1,880,720.6
[6] Thermocouple bad

the thermocouples extending into the combustor, the measured temperatures were somewhat lower than the actual temperature.

A mathematical model of the heat transfer mechanism for the losses was developed as shown in Appendix C, page 224. This model was used to correct for the heat losses. A program for the IBM 360-65 computer was written and used to obtain the corrected temperatures. The temperatures in the tables of Appendix D represent the computed actual temperatures of the combustion product gases. These were shown in the preceding figures.

Mean temperatures and standard deviations of each run were computed for the flame temperature and the temperatures at 2.1 and 3.6 cm above the burner top utilizing a standard statistical program for the Wang 360 calculator. These values are shown in Table XXVI, and were useful in exploring the temperature profiles in the first 3.6 cm down stream of the burner tip. This topic will be discussed in the next chapter.

NO_x - A gas sample was taken every 30 minutes and analyzed for NO_x. Some samples did not contain NO_x for some reason (this will be discussed more fully later). The raw NO_x data as presented in Table XXV, except for zero values, were averaged over each run and presented in Table XXVI. Also included are standard deviations for each run.

The NO_x data in Table XXV were next examined and various values deleted. Since each run requires about 15 minutes to stabilize the temperature profiles, the NO_x value from the first gas sample taken from each port was discarded. Further, any extremely high or low value was omitted from consideration. As a rule of thumb, any value which seemed twice or half the average of the other values was labelled faulty. The corrected data were then averaged over each run and the respective standard deviations computed. The "corrected" means and standard deviations are also presented in Table XXVI.

Since the mean flame temperature of each run varied, any comparison of the NO_x data seemed to require adjusting the NO_x data to a base temperature. A base temperature of $3000^{\circ}F$ was arbitrarily selected. The kinetic expression for the formation of NO presented by Bartok, et al. (17) was solved (The integration and sample calculations are shown in Appendix C, page 224), and used to derive the following equation:

$$(NO_x)_{3000} = (NO_x)_T \, e^{5.7550 \, \frac{(1922.2 - T)}{T}},$$ where T is in $^{\circ}K$. This equation was then programmed on the Wang 360 calculator and the averaged NO_x values were adjusted to a $3000^{\circ}F$ temperature. Both sets of NO_x data ("as is," "corrected") from Table XXV were adjusted; new values are presented in Table XXVII.

The two sets of NO_x data from Table XXVII were then arranged in a 3 x 3 x 2 factorial complete-block design. The analysis of variance, and the computation of main effects and interactions were carried out according to the procedure outlined in Steel and Torrie: <u>Principles and Procedures of Statistics</u>, page 205. Complete statistical analyses are shown in Appendix C, page 224. The resulting effects will be discussed in the next chapter.

TABLE XXVII

NO_x DATA ADJUSTED TO 3000°F

Run	Data at Run Temperature	Data Corrected to 3000°F
13	471	-[1]
14	329	297
15	327	267
16	1949	1898
17	497	557
18	975	1006
19	2232	2366
20	2646	2458
21	1970	1841
22	1900	1885
23	1406	1402
24-25	3721	3746
26	2769	2811
27	2121	2126
28	4844	4818
29	6021	6049
30	2549	2498
31	1319	1291
32	2059	2053
33	1768	1784
34	3540	3430
35	1705	1381
36	1967	1336[2]
37	744	652[3]
38	1410	1277[4]
39	3482	3525
40	4105	1930[5]

---

[1] Data unchanged

[2] 1554

[3] 466

[4] 1316

[5] 2431

CHAPTER VII

DISCUSSION OF RESULTS

Several factors require discussion prior to undertaking the presentation and discussion of results. These factors include precision of data, operating conditions, and theoretical results.

Precision

Precision can be subdivided into six topics:

1. Variation in oil flows
2. Variation in gas flows
3. Variation in temperature readings
4. Variation in analytical technique
5. Variation in duplicate runs
6. Overall reproducibility.

Variations in oil flow were caused by the small quantity of oil fed into the combusting system. One milliliter of oil per minute was the designed flow rate. The oil pump fed this amount of oil in a pulsating fashion: pressure was increased to the point where oil could be introduced to the atomizer; when oil was introduced, pressure decreased; and pressure was increased again. This pulsating effect can be seen in the combustion. The overall oil flow rate was maintained at 1 cc/minute throughout each run. At times, flow adjustment was required to maintain the desired flow. Adjustment of the oil flow seemed to be necessary more often as the nitrogen content of the oil increased.

The gas flow was constant. Once the flowrate was set, the rate did not require adjusting during the remainder of the runs. However, the flows were checked every 10 to 15 minutes as an assurance that the gas flow remained constant.

Variation in the temperatures of the product gases was caused by the pulsating oil feed. The temperature of the flame (thermocouple located at 1.5 cm) and the temperature at 2.1 cm were read at the maximum of the pulsation. The pulsating effect was dampened-out as the distance above the flame increased. Pulse time variation in the wall temperatures were virtually non-existent; these readings were affected only by the changes of conditions within the laboratory and combustor. Several runs were initiated with the laboratory window and/or door closed. When both the window and door were opened, the air flow through the room caused the wall temperatures of the combustor to decrease. This drop in temperature will be discussed further during the presentation of the heat balance over the system.

Any deviation in analytical results should be related to a deviation in analytical technique. Once the analytical technique for continuous sampling was established, it was followed as precisely as possible. The thirty-minute purge of each sample port was maintained within ± 1 minute. The gas samples were introduced into the gas chromatograph in the same way; the sample size is not a function of the technique of operating the sample valve. However, small variations in temperature and pressure of the sample line did affect the size of the sample introduced to the gas chromatograph. (The peak size of the nitrogen and argon components did not remain constant.) To reduce the effect of sample size, a component was ratioed to the amount of nitrogen or argon present. This ratio was then related to the amount of nitrogen or argon present in the total gas stream to give the ppm of that component.

The combustor was closed tightly to assure that outside air effects were minimized. However, small air leaks were obvious in the data taken on the argon-oxygen system. The nitrogen peak areas were larger than those to be expected from the amount of nitrogen in the fuel oil. The effect of the air leaks on NO_x formation was not significant since more NO_x was formed with the argon system than with the air system even though the argon system had significantly less atmospheric nitrogen. Further, Bartok, et al. (14, 15, 16) presented Shaw and Thomas results which show that atmospheric nitrogen plays a negligible part in NO_x formation.

A list of replicate runs was presented in Table XXIV, page 131. A set of replicate runs covered the formation of NO_x under one given set of conditions. The following table, Table XXVIII, summarizes the results. However, since the replicate runs had different mean flame temperatures, see Table XXVI, page 139, the NO_x results were adjusted to the 3,000°F base temperature. Table XXIX summarizes these results. The differences in Table XXIX between replicate runs implies that the factors affecting the formation of NO_x are not all under control. In fact, the variations in base temperature results may indicate that: (1) temperature is only one of the major controlling factors and (2) the kinetic expression used to adjust the data does not explain the complete formation mechanism.

The overall reproducibility contains the same variation exhibited in the replicate run results. The statistical analysis based on a 3 x 3 x 2 fractorial complete-block design showed that the size of variations shown in Table XXII overweighed all other effects and interactions; the results are shown in Appendix C, page 223. This, in effect, says that the amount of data taken on replicate runs was not large enough to distinguish to effects of the variables of interest.

TABLE XXVIII

REPLICATE RUN RESULTS

Runs	System	% O_2	% N_2	NO_x	Difference
18, 38	Air	80	0	683, 854	+ 171
14, 15, 39	Air	100	5	191, 240, 2260	+ 2045[a]
13, 40	Air	120	5	493, 1492	+ 999
22, 34	Argon/Oxygen	80	0	749, 1183	+ 434
30, 31	Argon/Oxygen	80	5	1015, 957	- 58
22, 35	Argon/Oxygen	100	0	1148, 1205	+ 57
28, 29	Argon/Oxygen	100	1	1113, 1065	- 48
24, 25, 39	Argon/Oxygen	120	0	1195[b], 1050	- 145

[a] Change computed as 2260 - (191 + 240) / 2

[b] Did not distinguish between run 24 and 25

TABLE XXIX

REPLICATE RUN RESULTS

3000°F Base Temperature

Runs	System	% O_2	% N_2	NO_x	Difference
18, 38	Air	80	0	1006, 1277	+ 271
14, 15, 39	Air	100	5	297, 267, 3525	+ 3243
13, 40	Air	120	5	471, 1930	+ 1459
22, 34	Argon/Oxygen	80	0	1885, 3430	+ 1545
30, 31	Argon/Oxygen	80	5	2498, 1291	- 1207
23, 35	Argon/Oxygen	100	0	1402, 1381	- 21
28, 29	Argon/Oxygen	100	1	4818, 6049	+ 1231
24, 25, 39	Argon/Oxygen	120	0	3746, 1336	- 2410

Operating Conditions

Several factors will be discussed under this heading. They are oil properties, reactions in the vaporizer, steady-state operation, flame characteristics, combustion reactions, heat balance around the system, NO_x equilibrium concentration at operating conditions, a reference run, operation at various oxygen levels with and without nitrogen present, and docotred fuel oil.

Oil Properties

The No. 2 diesel oil used in this study came from the normal fuel oil used at Oklahoma State University. Samples of the oil were sent to Galbraith Laboratories, Inc. in Knoxville, Tennessee for complete analysis. Analytical results of these samples are presented in Table XXX. Using these analyses, the fuel oil has a C/H atom ratio of 7.23/12.78 which yields a formula for the oil of $C_{17}H_{30}$. The amount of nitrogen present in the fuel was 0.033% by wt. If all this nitrogen were converted to NO_x, less than 73 ppm of NO_x would be formed. Thus, any NO_x above 73 ppm would be formed from the nitrogen in the air.

Reactions in Vaporizer

The purpose of the vaporizer was to make the liquid fuel oil easier to feed into the system. Basically, the feed oil was boiled and the vapors were burned. An atmospheric boiling curve was determined for the oil and is presented in Figure 53. The vapor temperatures from Runs 6 - 12 when placed on this boiling curve indicate that the fuel

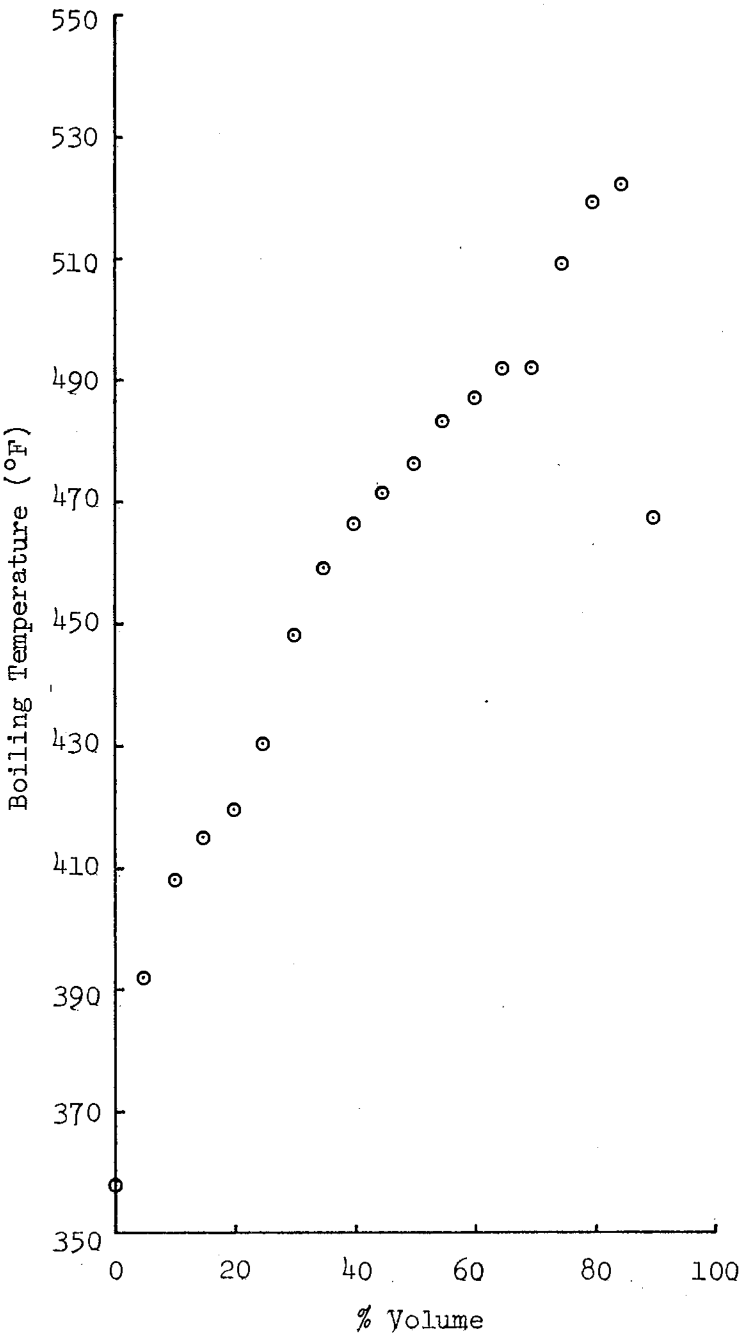


Figure 53. Atmospheric Boiling Data for NO 2 Diesel Oil

oil is boiling and not cracking. However, an inspection of the vaporizer revealed that the packings were carbonized, an indication that at least a small part of the fuel oil was being cracked. This was undesirable since the vapor feed composition would then be unknown. The temperature of the vaporizer was lowered so as to sustain boiling but not to crack the oil.

TABLE XXX

ANALYSIS OF FUEL OIL SAMPLES

Sample No.	% by Weight % C	% H	% N	% Ash	% S	% O
1 a	87.05	12.84	0.02	0.01	0.14	0.01
1 b	87.13	12.78	0.02	0.02	0.15	0.01
2	86.04	12.77	0.056	0.60	0.24	0.30
3	86.50	12.74	0.037	0.36	0.25	0.35
Average	86.68	12.78	0.033	0.24	0.20	0.17

Steady-State

Data taking was done during steady-state operation of the system, as evidenced by temperature profiles. These profiles became stable within the first 20 to 25 minutes of the run. The system was fairly sensitive to upsets and/or changes in conditions. An upset was immediately promulgated through the system. When two runs were made back-to-back, the conditions were changed at the end of the first run. By the time the first data were taken at 15 minutes into the run, the system was almost lined out as the temperature profiles were nearly flat.

Flame Characteristics

Flame characteristics are an indication of combustion efficiency. A stable-blue flame should be an example of complete combustion of fuel oil in air. During the runs, the flame color varied from blue-yellow to white-yellow to almost white. The blue-yellow flame occurred during the burning of oil in air while the almost white flame occurred when oil was burned in argon-oxygen. The white flame seemed to denote the presence of pure oxygen. Possibly the argon and oxygen were not completely mixed and the color of the flame was an indication of this.

Flame stability seemed independent of the percentage of excess air. However, it was obviously related to the percentage of nitrogen in the fuel oil. As the amount of nitrogen in the fuel oil increased, the stability of the flame decreased. Since the amount of pyridine (used to doctor the oil) was directly proportional to the percentage nitrogen in the fuel oil, the instability is attributed to the presence of pyridine in the fuel oil. The major decrease in stability occurred between 1% and 5% nitrogen in the fuel. Perhaps more uniform combustion would have taken place if 3% nitrogen fuel oil had been burned instead of 5%.

Combustion Reactions

Combustion reactions with normal, complete combustion are discussed by Fristrom (41); the end products are carbon dioxide and water vapor. Analytical results in the present study showed that both hydrogen and/or carbon monoxide were present in almost all samples, no matter what the run conditions were.

The peak labelled hydrogen on the chromatogram was a negative peak as shown on pages 77 and 78. Since helium was used as the carrier gas, the component with the negative peak must have a molecular weight lower than helium; i.e., it must have been hydrogen. This seems odd, since hydrogen and oxygen in the presence of a flame are very reactive. A possible explanation is that the sample contained a hydrocarbon radical when it was pulled into the sample lines. The cooling through the sample probe froze the NO_x reactions but did not prevent the radical from further breaking down to form hydrogen. The hydrogen was then present and showed up in the analysis. The hydrocarbon radical could have either completely decomposed to carbon and hydrogen (carbon deposited in sample lines) or adsorped onto the molecular sieve column packing. Either way, the sample analysis would not show anything except the presence of hydrogen. At the end of the 40 runs, the sample lines were checked and found to contain some small quantities of carbon or carbonaceous material.

Carbon dioxide forms in two steps; carbon reacts to form carbon monoxide, and then the carbon monoxide reacts to form carbon dioxide. The first sample port location could be such that the sample was taken before the second reaction occurred and that conditions within the sample lines were not conducive to further reaction. Another possibility is that there was insufficient mixing and the carbon monoxide and oxygen were not brought together and reacted. The presence of oxygen in the analyzed gas sample tends to support this theory.

Heat Balance

The adiabatic flame temperatures were computed; an example is shown in Appendix C, page 223. These computed temperatures were approximately 800 to 1600°F higher than the measured values. However, these first calculations did not include a stream of 825 cc/minute of helium which was introduced to the atomizer to carry the oil vapor to the burner. When the sensible heat of this stream was included in the computation, the adiabatic flame temperature fell into the range of the measured values. This second calculation is also presented in Appendix C, page 223. The adiabatic flame temperature for 80% excess oxygen combustion was 2825°R; similarly, for 100% and 120% excess oxygen the respective flame temperatures are 3159 and 2906°R, respectively.

A heat balance around the first 12 inches of the reactor was made for each set of operating conditions. Resutls are shown in Appendix C, page 223. Heat loss to the atmosphere was approximately equal to heat change in combustion gases.

Equilibrium NO_x

The equilibrium concentrations of NO_x at temperatures from 1400 to 4000°F were calculated using the equilibrium relationship presented by Zeldovich (114). This relationship is

$$\frac{NO}{\sqrt{N_2O_2}} = \frac{8}{\sqrt{3}} \quad e^{-\frac{21500}{RT}},$$

where T is temperature in °K and R is the gas constant. This equation was programmed for the Wang calculator. Results are graphed in Figure 54. Table XXXI shows both the average run NO_x and the equilibrium NO_x at the mean flame temperature. In all cases, the experimental NO_x values were lower than the equilibrium concentrations. This is to be expected since the residence time is short.

Reference Run

Run 13 was designated as the reference run. Run conditions were 120% excess oxygen, 5% fuel nitrogen, and a 10 hour operating period. The purpose of this run was to obtain operating information on the system's controls, axial and radial temperature and concentration profiles, and a basis for the remaining runs.

Operating information on the variations in oil and gas flows and the time required for controlling these systems were obtained. The expected operating life of a bottle of compressed air and the technique of switching empty and full bottles, the time required for taking temperature data (including maintenance of the various ice baths), and the time necessary for sampling and analyzing the product gases were also determined. Gas chromatograph maintenance routines and interpretation of the chromatograms with respect to the various components in the samples were established.

The axial temperature profiles were similar to those obtained in the checkout runs. No new information resulted. The radial profiles are described as follows. At the flame tip, a plateau temperature

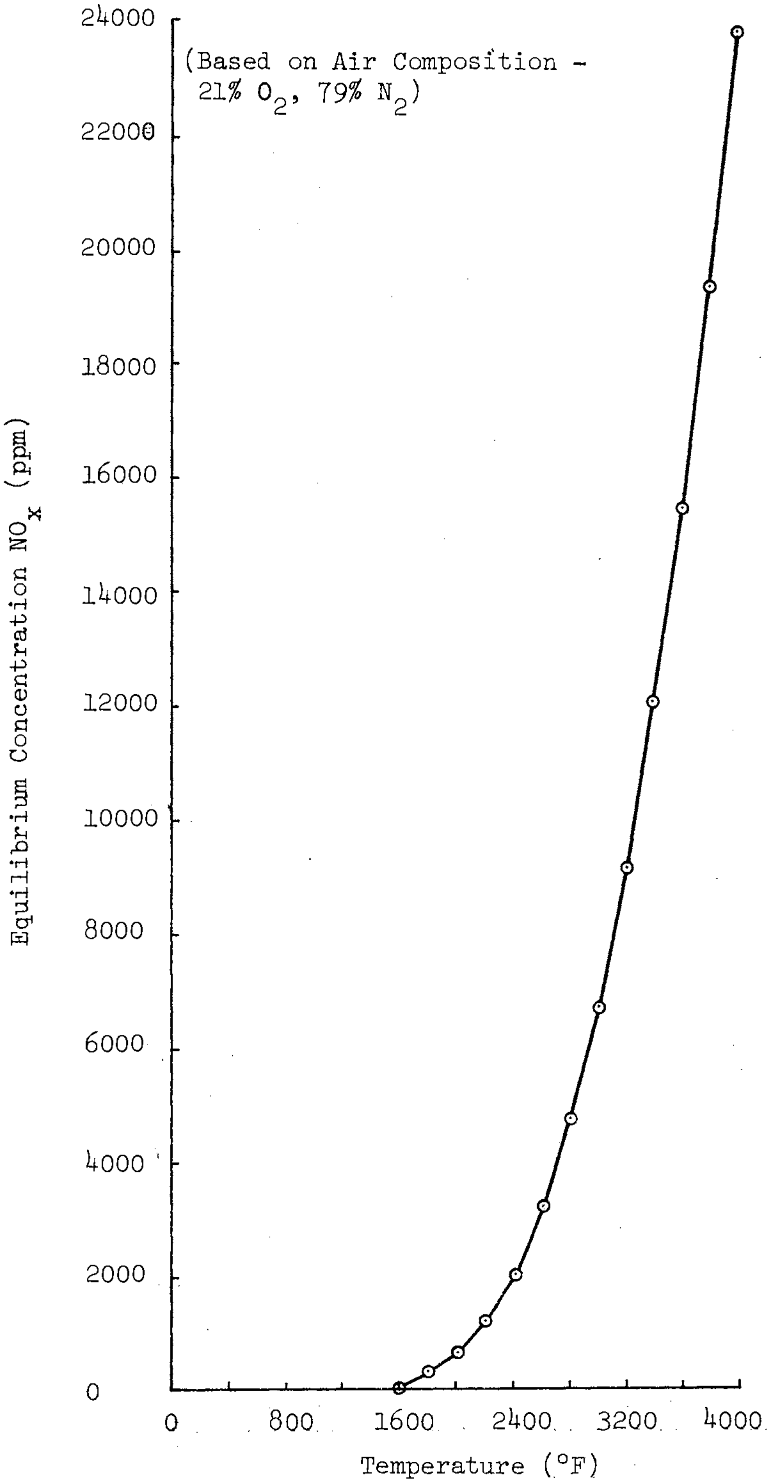


Figure 54. Equilibrium Concentration of NO_x Versus Temperature (°F)

TABLE XXXI

COMPARISON OF AVERAGED RUN NO_x CONCENTRATION AND EQUILIBRIUM NO_x CONCENTRATION

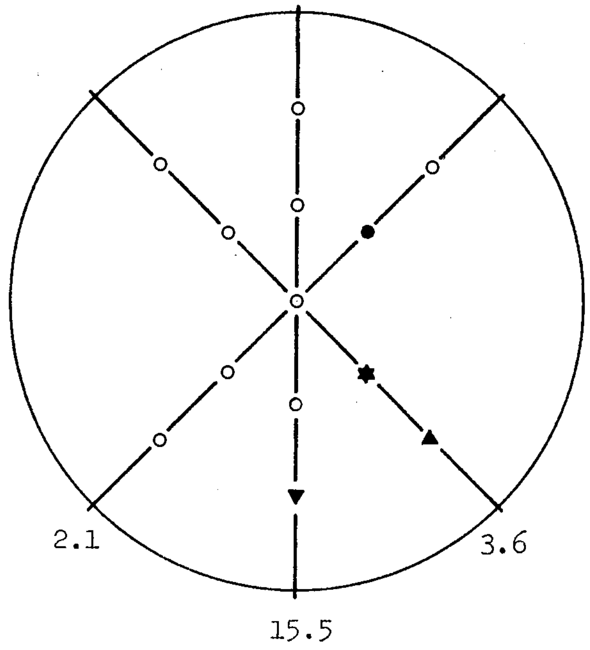
Run	Temperature °F	NO_x Average Run	NO_x Equilibrium
13	3,027	493	7,028
14	2,754	191	4,367
15	2,937	240	6,052
16	2,773	1,267	4,516
17	2,884	456	5,535
18	2,782	683	4,592
19	2,806	1,681	4,799
20	2,959	2,294	6,280
21	3,032	1,941	7,084
22	2,522	749	2,720
23	2,884	1,148	5,527
24-25	2,427	1,195	2,202
26	2,555	1,202	2,922
27	2,695	1,219	3,906
28	2,298	1,113	1,604
29	2,198	1,065	1,230
30	2,532	1,015	2,780
31	2,829	957	5,003
32	2,626	1,022	3,397
33	2,704	1,041	3,975
34	2,460	1,183	2,368
35	2,920	1,205	5,880
36	2,861	1,050	5,316
37	2,939	588	6,073
38	2,774	854	4,524
39	2,752	2,260	4,351
40	2,852	1,492	5,232

profile was present. At 0.6 centimeters above the flame, the profile tended to level out, while the profile at 2.1 centimeters showed a distinct parabolic form with higher temperature at one wall than at the other. Finally, at 14.0 centimeters, the profile tended to become flat again. The explanation for the differing profiles is that the profiles were taken from different base points. The locations above the flame were so close together that it was impossible to locate all the thermocouples directly in line with each other. Figure 55 shows the thermocouple locations and the corresponding maximum temperature locations.

The concentration profiles were taken over only half of the combustor chamber because the sample probes had stems only 3 inches long. Concentration data for the radial profiles are presented in Table XXXII and graphed in Figure 56. The implication from this plot is that there was no change in NO_x concentration in the samples taken at 1.5 and 2.5 centimeters above the flame. There was a change at 38.0 cnetimeters. Figure 57 shows the axial concentration profiles; the profiles near the wall and at the center of the combustor are the same. The profile at 3/4" into the chamber was somewhat different. The error associated with the NO_x data is large enough that all these readings are probably the same.

Run 13 provided the basis for all following runs in that operating data on the system were gathered. Also, the concentration profiles showed that the NO_x concentration remained fairly constant between the ports at 3.0 and 39.0 centimeters (1.5 and 38.0 centimeters above the flame). So a variation within axial location should not create a significant difference in NO_x concentration.

Duplicate runs have been discussed to some extent already. Complete discussion involves comparing the average flame temperatures,



○ Radial Locations
● Maximum Temperature at 2.1cm Above Flame
▼ Maximum Temperature at 15.5cm Above Flame
▲ Maximum Temperature at 3.6cm Above Flame
✱ Maximum Temperature at 1.5cm Above Flame

Figure 55 Radial Profile Locations and Maximum Temperature Locations

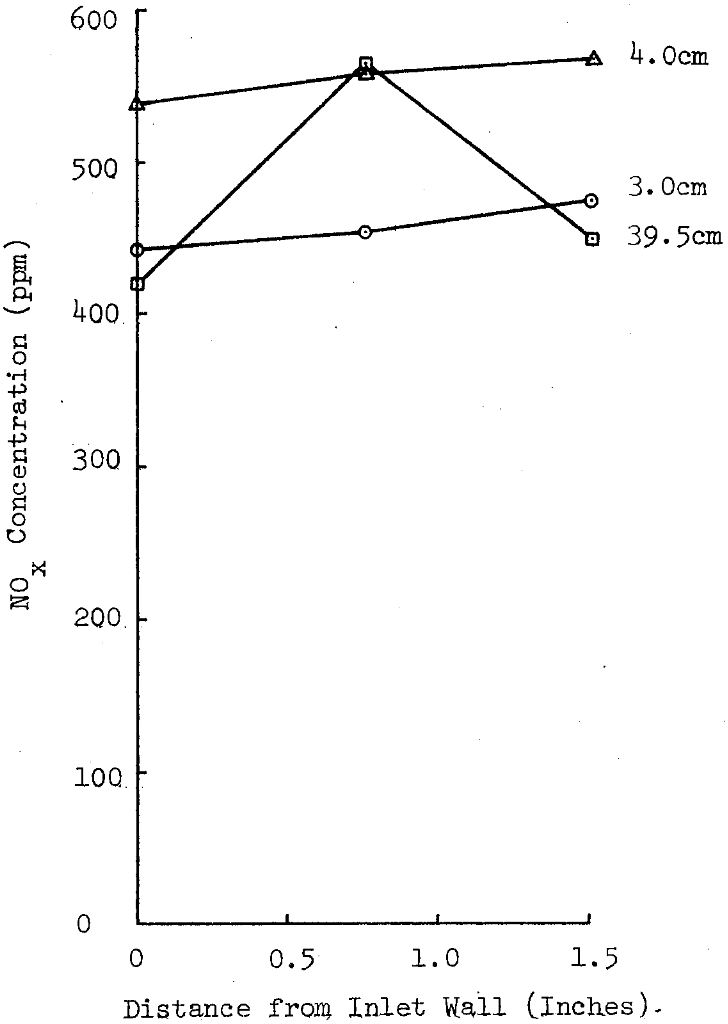


Figure 56. Radial Concentration NO_x Profile (ppm)

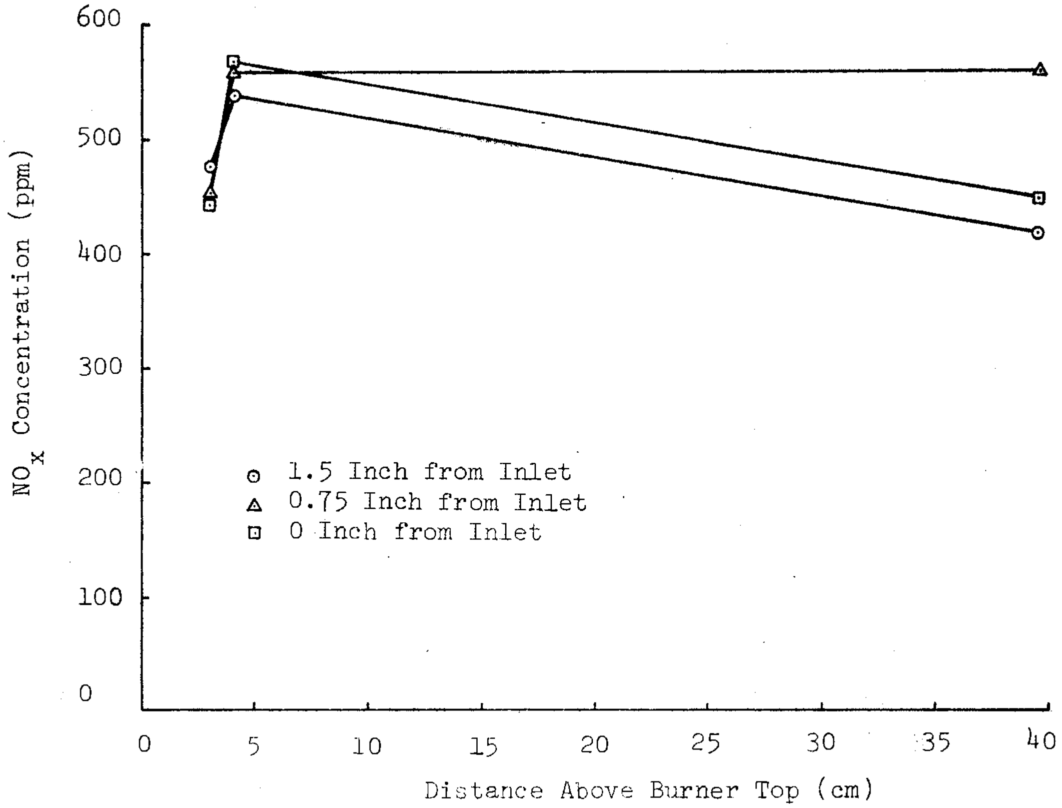


Figure 57. Axial NO$_x$ Concentration Profiles

TABLE XXXII

RADIAL PROFILE NO_x CONCENTRATION

Sample Port*	Location from Inlet (Inches)	NO_x-PPM	Average NO_x-PPM
3.0 cm	1.5	530	
	1.5	525	
	1.5	370	475
	0.75	370	
	0.75	550	
	0.75	440	453
	0	450	
	0	435	442
4.0 cm	1.5	460	
	1.5	615	538
	0.75	550	
	0.75	565	558
	0	550	
	0	585	568
39.5 cm	1.5	400	
	1.5	440	420
	0.75	595	
	0.75	530	562
	0	405	
	0	496	450

* Distance above burner top. Corresponding points above flame top are 1.5 cm, 2.5 cm and 38.0 cm.

the heat balances, average NO_x values, and temperature profile. A summary of this information, excluding temperature profiles is presented in Table XXXIII. The temperature profiles will be discussed later in this chapter. In the air system, the mean flame temperatures of the duplicate runs varied, on the average, 177°F (range: 157-185°F). In argon-oxygen system, the temperatures varied, on the average, 166°F (range: 62-334°F). A variation in the heat balance between duplicate runs was also present as would be expected. Variation in NO_x concentrations on duplicate runs was extremely large in the air system, 766 ppm on the average. In the argon-oxygen system, variation was smaller, 146 ppm (average). The main difference in the air system occurred with duplicate runs performed near the end of the research, Runs 37 and 39. However, these runs were conducted under the same conditions as the earlier runs. No noticeable deviation in run conditions was noted.

Operation at Various Oxygen Levels

The effects of the various levels of excess oxygen (with and without atmospheric nitrogen present) can be described by a simple comparison presented in Table XXXIV. The average information for each set of conditions is presented. The average flame temperature increases as the percent excess oxygen increases in both the air and argon-oxygen systems. There is a more pronounced increase in the air system. Within each system, average NO_x concentration varied no more than it does during a single run. Thus, NO_x seems to be independent of the percent excess oxygen in this study. There is a small difference between the air system and the argon-oxygen system. However, the effect seems to

TABLE XXXIII

COMPARISON OF DUPLICATE RUNS

Run	% Oxygen	% Nitrogen	Average Flame Temperature(°F)	Heat Balance (Btu/hour) Reactor Loss	Heat Balance (Btu/hour) Product Gases	NO_x (PPM)
18	100	0	2782	645	842	683
37	100	0	2939	745	855	588
14	100	5	2754	797	745	191
15	100	5	2937	848	817	240
39	100	5	2752	687	800	2260
13	120	5	3027	899	990	493
40	120	5	2852	713	1037	1492
22[a]	80	0	2522	565	652	749
34[a]	80	0	2460	462	800	1183
30[a]	80	5	2532	589	864	1015
31[a]	80	5	2859	655	1008	957
23[a]	100	0	2884	814	748	1148
35[a]	100	0	2920	843	964	1205
28[a]	100	1	2298	618	876	1113
29[a]	100	1	2198	550	977	1065
24-25[a]	120	0	2427	785	727	1195
36[a]	120	0	2861	912	917	1050

[a] argon/oxygen runs

decrease as the percent excess oxygen increases. Therefore, the effect cannot be caused by atmospheric nitrogen. Last, the heat balance follows closely the pattern of the average flame temperatures.

TABLE XXXIV

RESULTS AT VARIOUS EXCESS OXYGEN LEVELS

% Oxygen	Average Flame Temperature (^oF)	NO_x (PPM)[a]	Heat Balance(Btu/hr)	
			Reactor Loss	Product Gases
80	2786	1238	635	867
100	2904	1256	784	802
120	2952	1130	903	902
80[b]	2575	1051	574	833
100[b]	2592	1096	692	892
120[b]	2648	1128	846	942

[a] NO_x averaged over all levels of fuel nitrogen
[b] Argon-oxygen system

Changes in average flame temperature can be related to percent excess oxygen but there is some question whether a relationship between temperature and percent fuel nitrogen exists. As shown in Table XXXV, the average flame temperature increases with percent excess oxygen in both air and argon-oxygen systems. Table XXXV exhibits the average flame temperatures as a function of fuel nitrogen. In the air system, the average flame temperature increases between the 0 and 1 percent fuel nitrogen levels but decreases between the 1 and 5 percent nitrogen.

This relationship exists at each level of excess oxygen. A possible explanation is that at 5% fuel nitrogen, the amount of pyridine present in the fuel changed the heat of combustion enough to lower the flame temperature. Pyridine has a heat of combustion equal to 1.235×10^6 Btu/lb.-mole. The use of pyridine is discussed below.

TABLE XXXV

AVERAGE FLAME TEMPERATURES AT VARIOUS FUEL NITROGEN LEVELS

		Average Flame Temperature (°F)		
System	% Oxygen	Fuel Nitrogen: 0%	1%	5%
Air	80	2778	2806	2773
Air	100	2939	2959	2814
Air	120	2884	3032	2940
Argon-oxygen	80	2491	2555	2080
Argon-oxygen	100	2902	2248	2626
Argon-oxygen	120	2644	2695	2704

In the argon-oxygen system, two patterns were present. At 80 and 120 percent excess oxygen, the mean flame temperature increased with an increase in fuel nitrogen content. At 100% oxygen, the temperature decreased between 0 and 1 percent fuel nitrogen and then increased between 1 and 5 percent. Since there are three different patterns present under six sets of conditions, a definite relationship between mean flame temperature and percent fuel nitrogen does not exist.

Doctored Fuel Oil

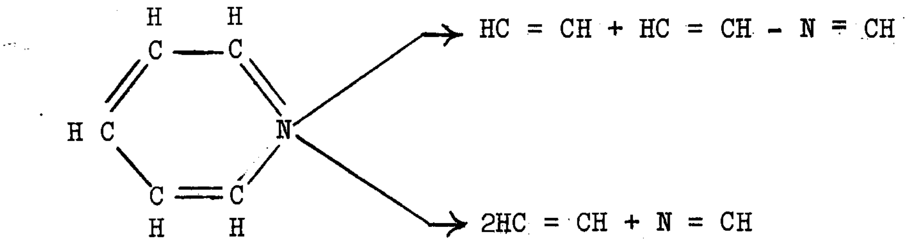
To vary the percent nitrogen in the fuel, pyridine was added to regular No. 2 diesel fuel oil. Pyridine, C_5H_5N, was selected because of its high nitrogen content (17.7%). The amounts of pyridine necessary to increase nitrogen content of the fuel from regular (0.033%) to 1 and 5 percent are calculated and presented in the author's laboratory notebook. The calculated amounts were:

1% fuel nitrogen - regular fuel oil, 94.4%; pyridine, 5.6%

5% fuel nitrogen - regular fuel oil, 71.8%; pyridine, 28.2%.

No noticeable change was found during the combustion of 1% nitrogen fuel oil. A definite change was present in flame characteristics when 5% nitrogen fuel was burned, however, The flame became very unstable and required extra attention if combustion was to be maintained.

Since the fuel oil was vaporized and fed as a vapor, the pyridine may possibly have been cracked during the vaporization process. The cracking of pyridine (as shown by the equations below) involves the rupture of the C-C bonds and then the breaking of the C-N bond.



The resulting products could have been vaporized and burnt in the combustor. However, the only supporting evidence for the occurrence of cracking was that the vaporizer carbonized up twice during the 40 runs, and one of these was during the initial runs when regular fuel oil was used. The single other time does not represent much evidence for concluding that pyridine was actually cracked.

One point worth noting for runs conducted with pyridine present in the fuel oil was that the fumes in the laboratory increased in relationship with the amount of pyridine used. The experimenter found it necessary not only to exhaust the product gases to the outside atmosphere but also to use a fan to increase the circulation through the laboratory.

Theoretical Results

Temperature, excess oxygen, nitrogen sources, and residence time are the major variables which are important in the formation of NO_x. Harris, et al. (55), Ermenc (31) and many other authors point out the temperature dependence on the formation of NO_x. As presented in Table V, page 11, the equilibrium concentration of NO_x varies with temperature; higher temperature gives rise to higher NO_x concentration. In fact, temperature is probably the controlling variable in forming NO_x.

Crynes and Maddox (22) point out the importance of excess oxygen in the formation of NO_x for propane-air combustion. At the same temperature, an increase in excess oxygen increases NO_x formation. Wasser, et al. (108) presented relationships for NO_x and excess oxygen for fuel oil combustion. Figure 58 shows this relationship. Note that the curve is a cubic function rather than a quadratic. Bartok, et al. (16), when presenting Shaw and Thomas' work, added evidence that excess

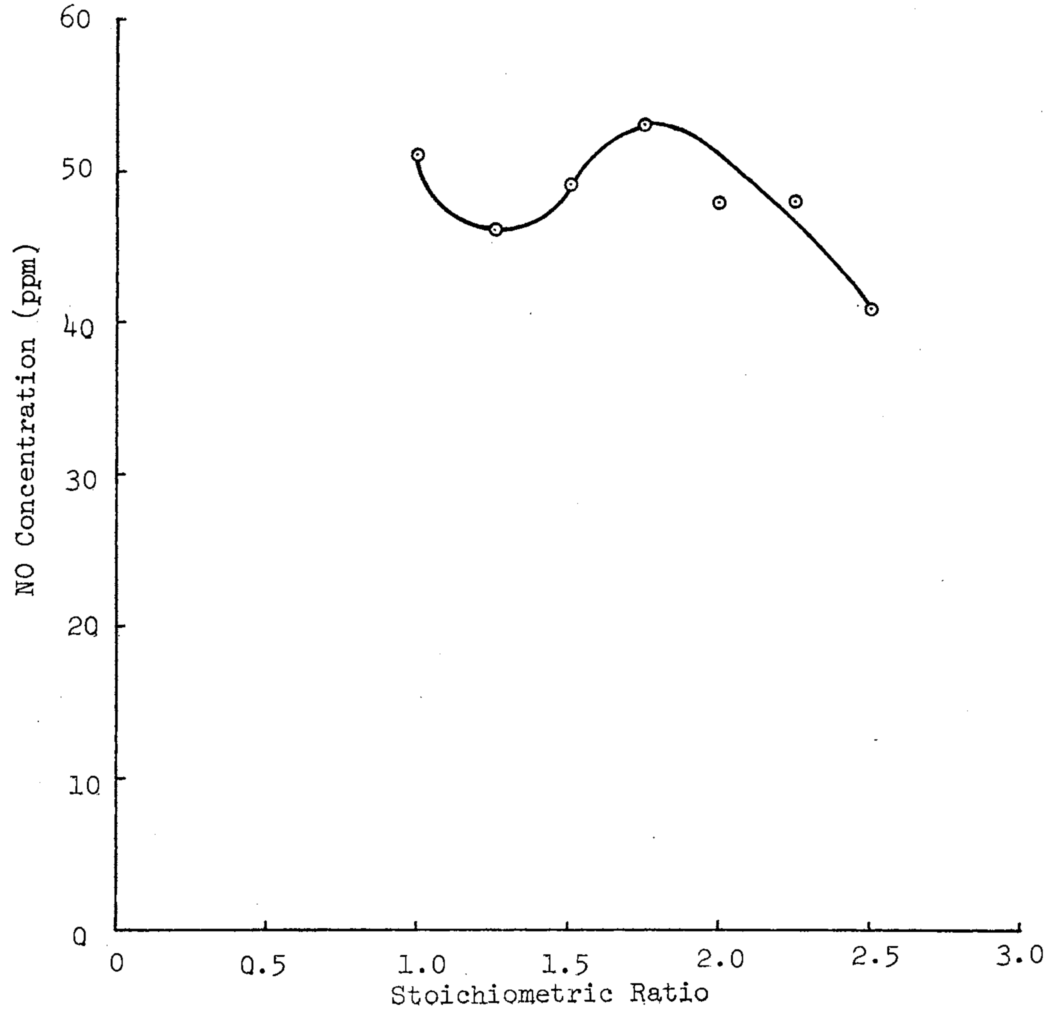


Figure 58. NO Concentration vs. Stoichiometric Ratio in Fuel Oil Combustion (108).

oxygen affects NO_x formation. The concensus of the information found in the literature is that excess oxygen enhances NO_x formation when gaseous fuel is burned.

Both atmospheric nitrogen and fuel nitrogen contribute to the formation of NO_x. Bartok, et al. (15) concluded that the role of fuel nitrogen appeared to be dominant at low temperatures but negligible at high temperatures, i.e. near equilibrium conditions. At high temperatures, fixation of nitrogen with oxygens forms NO in the combustion processes. The importance of fuel nitrogen was again noted by Bartok, et al. (16) as the works of J. T. Shaw and A. C. Thomas were stressed. Shaw and Thomas showed that fuel nitrogen enhances NO_x formation, with or without atmospheric nitrogen present.

Residence time is a major factor many authors overlook. Harris et al. (55) presents the information shown in Table VII, page 22. Here the time to reach equilibrium is shown. At 1340°F, 81.6 years are required to form one-half the equilibrium concentration from air; at 4040°F, this time has reduced to 0.0106 second. Thus, the residence time is also an important variable, especially at higher temperatures.

One last comment on these variables is that they are not independent of each other. For example, residence time and temperature interact in establishing the proper conditions for NO_x formation. Similar relationships exist among other variables.

Several kinetic expressions for the formation of NO_x can be found in the literature. The simplest form is an Arrhenius type equation as presented in (55).

$$\frac{d\,(NO)}{dt} = A\ (O_2)^{\frac{1}{2}}\ (N_2)\ \exp\ (\ -E\ /\ RT)$$

Where A is frequency factor (units of specific reaction rate),

E is energy of activation,

R is the gas constant, and

T is temperature.

Harris (55), Iya (59), and Bartok (15) all use the basic form of the Arrhenius equation. Harris and co-workers divided the reaction zone in two parts. In the primary flame zone, they used the following equation for NO_x formation.

$$\frac{d\ (NO)}{dt} = (O_2)^{\frac{1}{2}}\ (N_2)\ \exp\ (\ -\ 115/RT + 27,219)$$

In the secondary flame zone, which extends from 0 to 6 inches above the primary flame zone, the formation equation of NO_x was expressed as

$$\frac{d\ (NO)}{dt} = (O_2)^{\frac{1}{2}}\ (N_2)\ \exp\ (-110/RT + 24,088)$$

In all three of these equations, the formation of NO_x is a direct function of the partial pressure of oxygen and nitrogen molecules. More precisely, the change of the partial pressure of NO with respect to time is directly proportional to the partial pressure of nitrogen and the square root of the partial pressure of oxygen.

Iya (59) used an Arrhenius type equation for NO_x formation but in terms of concentrations:

$$\frac{d\ (NO)}{dt} = 2.72 \times 10^{14}\ \exp\ (-75.4/RT)\ (N_2)\ (O)$$

where (N_2) is the concentration of nitrogen molecules and

(O) is the concentration of oxygen atoms (approximately equal to the oxygen equilibrium concentration in the hot product gases/ The difference in Iya's equation is that the concentration of oxygen atoms is used instead of the concentration of oxygen molecules. If Zeldovich's relationship (114) between the oxygen atoms and molecules, $O = C_o \sqrt{O_2}$, is substituted in Iya's equation, the equation assumes the same form as Harris'. The remaining differences lie in the activation energy and the frequency factors.

Bartok, et al. (15) used an Arrhenius type equation to predict both the formation and decomposition of NO_x. The combined equation for the net rate of NO_x formation is

$$\frac{d\,(NO)}{dt} = 9 \times 10^{14} \exp(-135{,}000/RT)\,(N_2)\,(O_2)^{\frac{1}{2}} - 4.1 \times 10^{13}$$
$$\exp(-\,91{,}000/RT)\ (NO)^2\,(O_2)^{-\frac{1}{2}}$$

This equation is based upon the following chain mechanism,

$$O_2 + M \longrightarrow 2O + M$$
$$O + N_2 \longrightarrow NO + N$$
$$N + O_2 \longrightarrow NO + O$$

and assumes equilibrium between oxygen atoms and oxygen molecules. As shown in Appendix C, page 223, the integrated form of this equation is

$$(NO) = 14.79 \times 10^{-3}\,(N_2)^{\frac{1}{2}}\,(O_2)^{\frac{1}{2}}$$

Thus, the concentration of NO_x is directly proportional to the square roots of the concentrations of nitrogen and oxygen.

Discussion of Results

The NO_x data presented in Table XXVII and the summary of the temperature data shown in Table XXVI comprise the results from this study.

NO_x

The NO_x data not corrected to 3,000°F are summarized in Table XXXVI, A similar summary of the data corrected to 3,000° is exhibited in Table XXXVII. Statistics presented in Appendix C, page 223, indicate that sum of the errors within the data is large enough to overshadow any significant effects and interactions.

Some of the indications within the NO_x data not corrected to 3,000°F are:

In the air system, NO_x formation does not seem to be related to the percent excess oxygen. However, NO_x seems to be related to the fuel nitrogen. In the argon-oxygen system, there is no indication that NO_x is a function of either percent excess oxygen or percent fuel nitrogen.

One interesting occurrence is that the amount of NO_x formed at 5% fuel nitrogen is less than that formed at 1%. The reason could be that pyridine affects NO_x formation in an adverse fashion. At 1% nitrogen level, the effect of pyridine is not strongly exhibited because the amount of pyridine present is small. At 5% nitrogen, 28.2% of the fuel burned is pyridine.

A comparison of the air system NO_x data with that from the argon-oxygen system will give an indication of the relationship between the formation of NO_x and atmospheric nitrogen. The data in Table XXXVI show that, out of nine sets of conditions, atmospheric nitrogen could have contributed to the formation of NO_x in five cases and did not in the other four. Thus, there can be no definite conclusions as to the effect of atmospheric nitrogen on NO_x formation.

Table XXXVII displays NO_x values adjusted to a flame temperature of 3,000°F. The purpose of adjusting the data was to eliminate the

TABLE XXXVI

SUMMARY OF NO_X DATA (NOT CORRECTED TO 3,000°F)

Percent Excess Oxygen		Percent Nitrogen in Fuel		
		0	1	5
80	Air	768	1681	1267
	Argon-oxygen	966	1202	986
100	Air	588	2294	888
	Argon-oxygen	1176	1089	1022
120	Air	456	1941	992
	Argon-oxygen	1123	1219	1041

TABLE XXXVII

SUMMARY OF NO_X DATA (CORRECTED TO 3,000°F)

Percent Excess Oxygen		Percent Nitrogen in Fuel		
		0	1	5
80	Air	1140	2366	1898
	Argon-oxygen	2607	2811	1773
100	Air	652	2458	1231
	Argon-oxygen	1391	5386	2053
120	Air	557	1841	1098
	Argon-oxygen	2173	2126	1784

effect of temperature on NO_x formation. This has been discussed earlier in this chapter. From Table XXXVII, the following effects can be noted.

Air System: The formation of NO_x increases with increase from 0 to 1% fuel nitrogen but decreases with an increase from 1 to 5 fuel nitrogen for all levels of excess oxygen. The NO_x formation seems to decrease as the level of excess oxygen increases.

Argon-oxygen System: For the most part, the formation of NO_x is affected by fuel nitrogen in the same manner as in the air system. The effects of excess oxygen upon NO_x formation are not clearly defined.

A comparison of the two sets of data should indicate the effect of atmospheric nitrogen. There is more NO_x formed in the argon-oxygen system than in the air system. Although most of the differences can be attributed to the temperature adjustment, atmospheric nitrogen centainly appears to have a negligible effect on NO_x formation under conditions studied here.

Temperature

The average temperature data on Table XXVI were used to plot axial temperature profiles over the first 4.0 centimeters of the combustor chamber. These profiles include the flame temperature plus the next two readings downstream of the flame. Figure 59 shows the profiles for the air system while Figure 60 for the argon-oxygen system.

The temperature profiles on the air system show the following facts: flame temperature is a function of percent excess oxygen. At 80% oxygen, average flame temperature is 2787°F; at 100%, the temperature is 2883°F; and temperature at 120% oxygen is 2949°F.

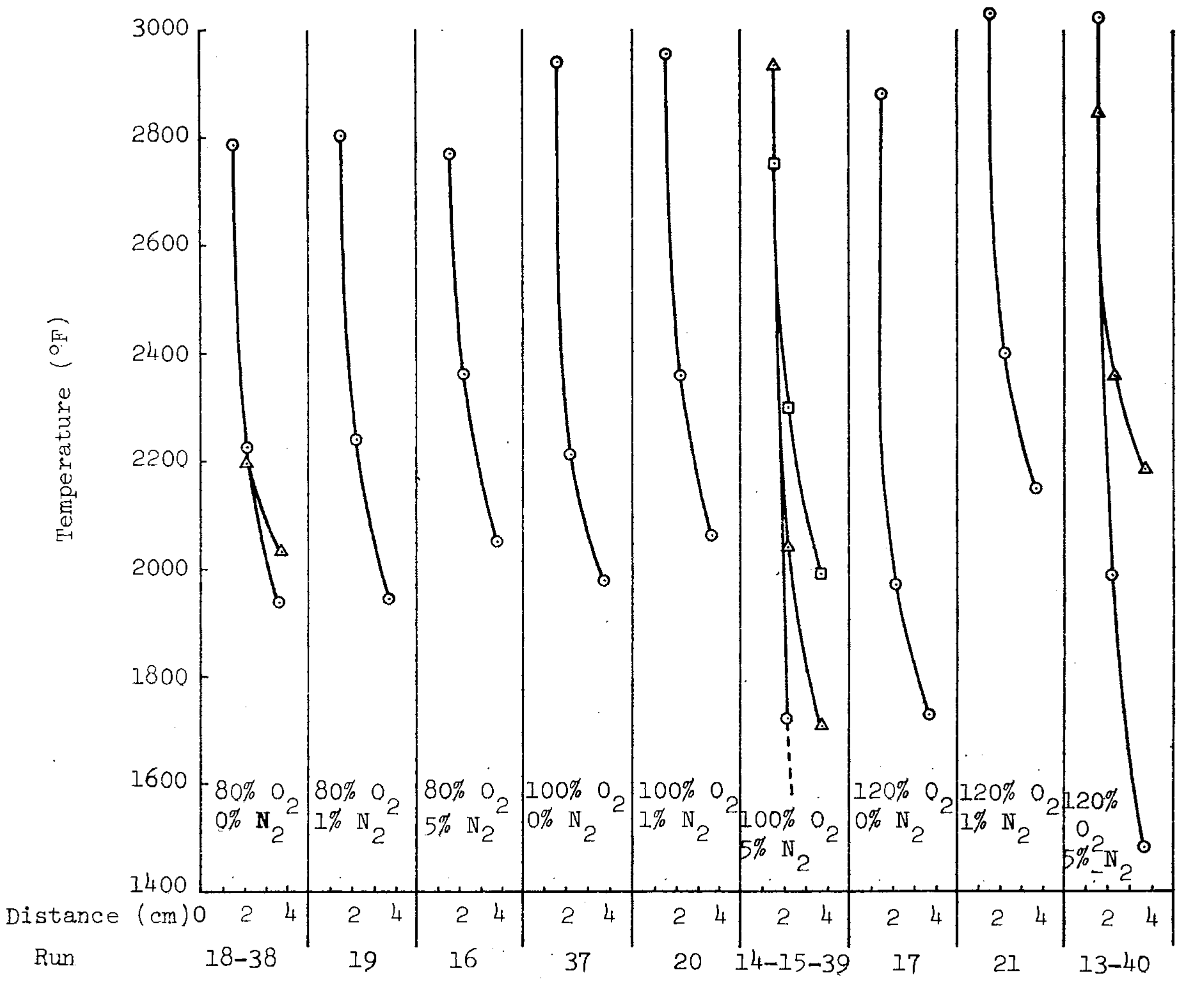


Figure 59. Temperature Profiles in First 4 Centimeters Above Burner Top (Air System)

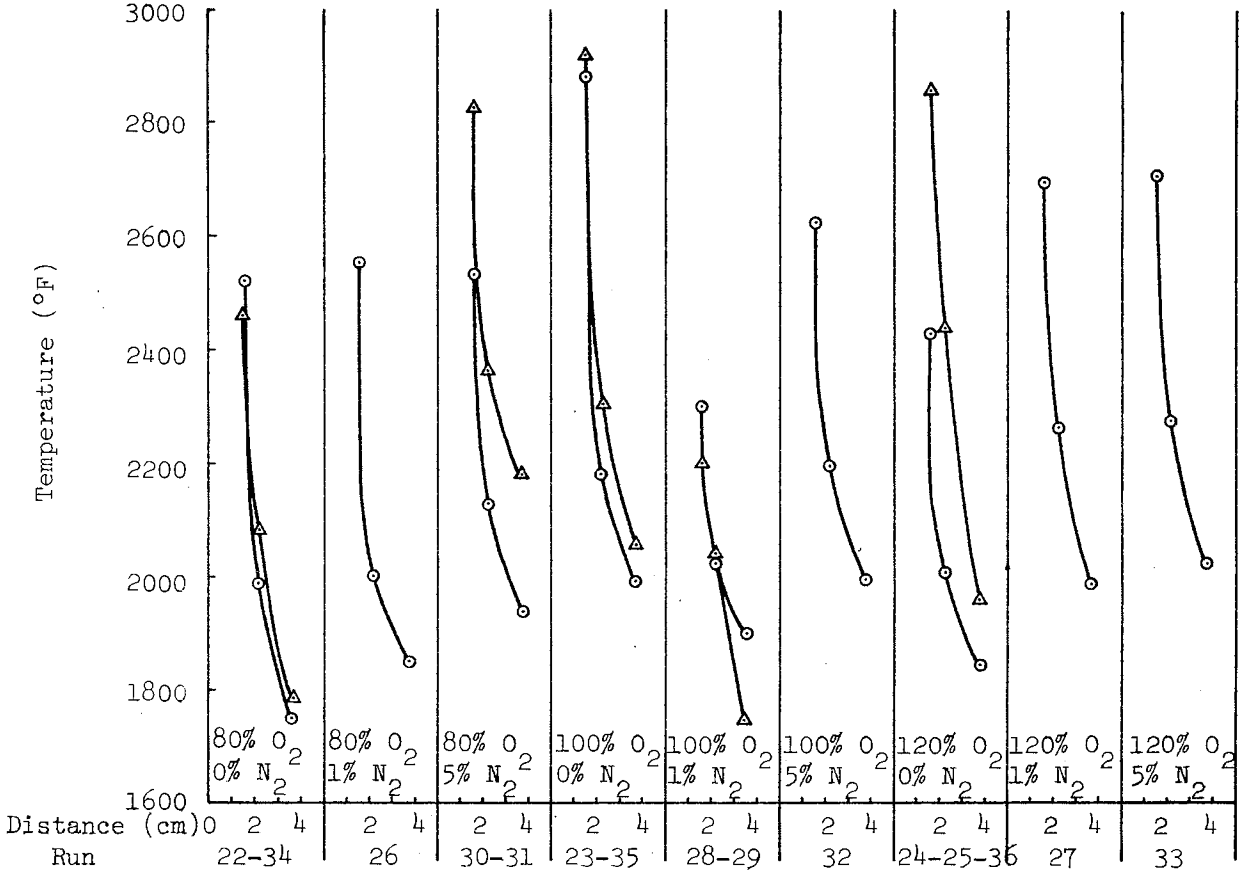


Figure 60. Temperature Profiles in First 4 Centimeters Above Burner Top (Argon-Oxygen System)

Within a set of duplicate runs, the higher temperature profile is an indication that more NO_x was formed. At 80% excess oxygen and 0% fuel nitrogen, the upper profile refers to 854 ppm NO_x while the lower profile is for 683 ppm NO_x. At 5% fuel nitrogen, there are two sets of duplicate runs, 100% and 120% excess oxygen. At 100%, there are three profiles. From high to low, the amount of NO_x formed is 2260, 191, and 240 ppm. For 120% oxygen, the two profiles are for 1492 and 493 ppm NO_x.

The temperature profile on the argon-oxygen system contains some of the same indications that the air system did. Flame temperature is a function of the percent excess oxygen. However, there was not such a clear indication that the temperature and NO_x were related.

Comparison to Published Results

Figures 61 and 62 are plots of the relationship between NO_x formation and fuel nitrogen for each level of excess oxygen. There is no published data on the formation of NO_x at various levels of nitrogen in the fuel oil. However, gaseous fuel at various nitrogen levels have been tested as per Bartok (14, 15, 16). Results showed that NO_x formation is directly related to amount of fuel nitrogen. Further, atmospheric nitrogen did not contribute to the formation of NO_x. These results were reproduced in this study.

In Wasser's study (108) with fuel oil combustion, excess oxygen levels were related to NO_x formation. A cubic relationship was found which has been discussed earlier in this chapter. The NO_x formed by combustion of regular fuel oil over 80 to 120% excess oxygen follows this same cubic trend.

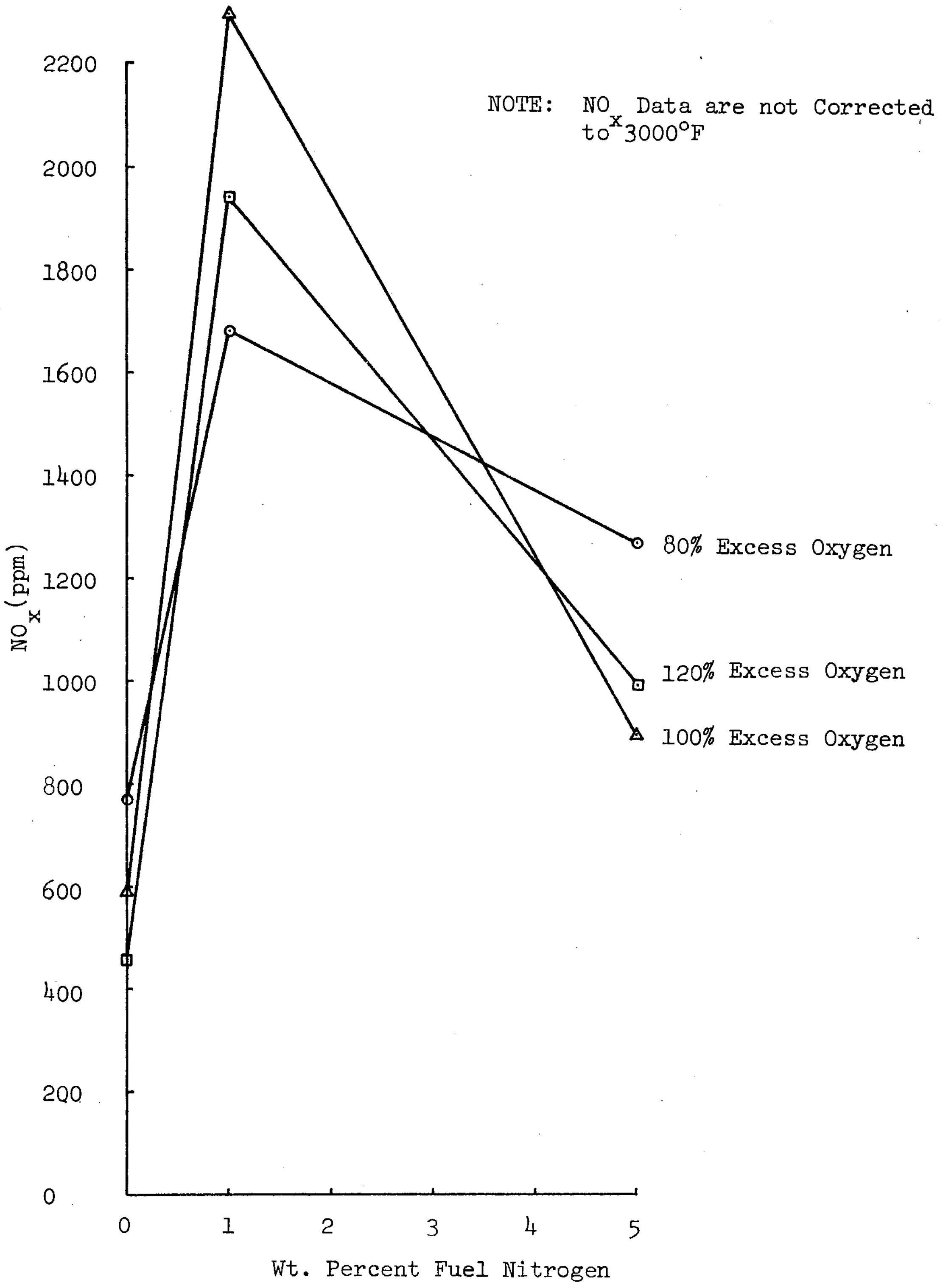


Figure 61. NO_x as a Function of Fuel Nitrogen at Various Levels of Excess Oxygen (Air)

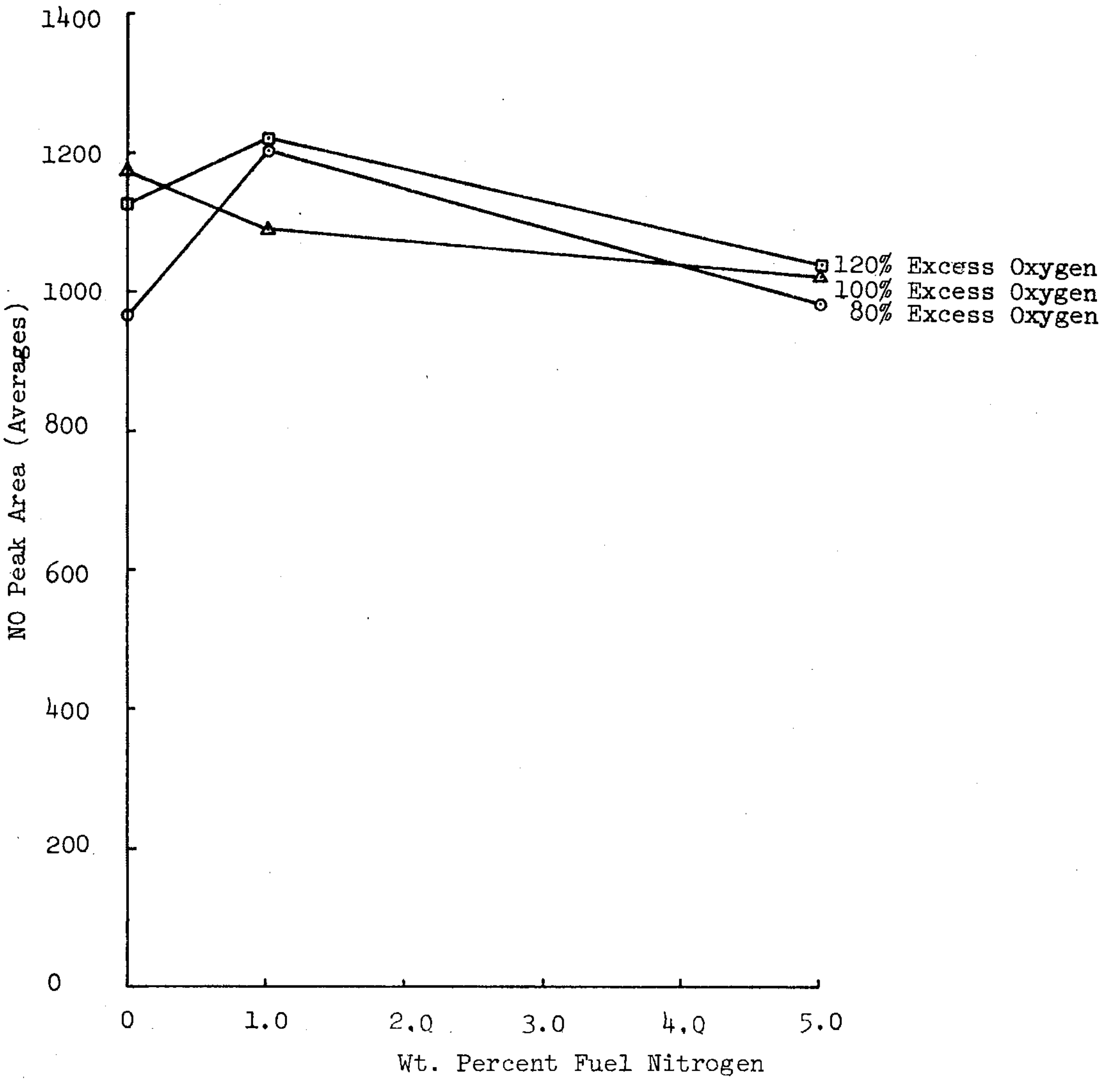


Figure 62. NO_x as a Function of Fuel Nitrogen at Various Levels of Excess Oxygen (Argon-Oxygen)

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

NO_x formed during the combustion of fuel oil depends upon the flame temperature and the percent fuel nitrogen. Since temperature is a function of percent excess oxygen, NO_x will also depend upon excess oxygen. Atmospheric nitrogen does not play a dominant role in forming NO_x. The results possess sufficient experimental variance that statistics applied to the NO_x data could not indicate any significant differences between variables. This study should help establish guidelines for further studies into the formation of NO_x from fuel oil combustion.

Recommendations

Recommendations listed below should be considered in future studies on NO_x formation from fuel oil combustion.

(1) Each set of conditions should be duplicated at least once. Also, to reduce the sum of the squares of the errors, one set of conditions should be run several times to determine the reproducibility of NO_x data.

(2) When pyridine is used to enrich the nitrogen content of fuel oil, the amount should not exceed 3% nitrogen. 5% fuel nitrogen

requires a fuel of about 1/3, by volume, pyridine. Not only is this mixture very difficult to handle but the toxic fumes are overwhelming, see Physical Effects in Appendix B, page 211. Several problems were encountered in maintaining a constant flowrate when 5% nitrogen fuel oil was fed. Finally, 5% nitrogen fuel oil results in unstable, unclean combustion.

(3) The problem with fumes in the laboratory suggests that the combustor should be in an open air research space.

The following recommendations apply specifically to the research facility at Oklahoma State University.

(1) The temperature programmer for the gas chromatograph oven should be repaired. Analytical procedures could benefit from temperature programming to elude the carbon dioxide component of the combustion products. This inforamtion would assist one in computing a material balance over the combustor.

A chemiluminescence NO_x monitor installed in the combustor chamber downstream of the flame would provide for continued NO_x analysis. Such an instrument will eliminate the problems associated with sampling and gas chromatograph analysis.

(2) Additional equipment might be purchased to allow

a. An immediate digital thermocouple readout. Such an instrument would reduce the time required for taking temperature data.

b. A uniform oil feed system that eliminates pulsing. This would do much to stabilize the flame.

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APPENDIX A

APPENDIX A

1. Discussion of Calibration Methods
2. Calibration Curves
    a. Air/Argon Gas System -- Rotameter Model 75
    b. Enlarged portion of (b)
    c. Helium/Argon Gas System -- Rotameter Model 75
    d. Oxygen Gas System -- Rotameter Model 73
    e. Oxygen Gas System at 90 psig
    f. Air System -- Rotameter Model 72
    g. Oil Feed System -- Rotameter R-2-15-AA
    h. Flow Calibration of Gas Chromatograph
    i. Rotameter Settings Versus Helium Flow Through Gas Chromatograph at Column Temperature of 75°C
    j. Tungsten-Tungsten/26% Rhenium Thermocouples
    k. Iron-Constantan Thermocouples
    l. Chromel-Alumel Thermocouples
3. Temperature-Millivolt Table for Tungsten-Tungsten/26% Rhenium Thermocouples

A-1 DISCUSSION OF CALIBRATION METHODS

Calibration of equipment can be separated into three distinct parts: calibration of rotameters, calibration of gas chromatograph flow meters, and calibration of thermocouples.

Rotameters

Flow through rotameters was measured with a standard laboratory setup as described in Figure 63. In Part A of Figure 63, a bottle of compressed gas was attached to the gas lines at the normal location for the feed. The flow control valve of the gas system was used to regulate gas flow through the rotameter and the entire feed system. Finally, a wet-test meter was attached to the outlet of the rotameter.

Gas flow through this setup was allowed to continue until the wet-test meter was saturated with that gas. After this, various rotameter settings and related gas flow data were obtained at atmospheric pressure and 75°F. The correction of the wet-test meter for vapor pressure of water was calculated by the following equation:

$$\text{corrected flow:}\quad \text{flow} \times \frac{Tm}{Tg} \times \frac{Pg - VPg}{P_B - VP_w - vac}$$

where flow is the volume of gas per unit of time

T_m is the temperature of the meter

T_g is the temperature of the gas

T_m/T_g is approximately 1

P_g is the pressure of the gas

P_B is barometric pressure

VP_g is vapor pressure of water at gas conditions

VP_w is vapor pressure of water at meter conditions

Vac is the pressure on the meter (3 inches of water = 5.6 mm).

$$\text{So corrected flow} = \text{flow}\ (1)\ \frac{(\ 760-22.4\ )}{760-22.4-5.60}$$

$$= \text{flow}\ \frac{(\ 737.6)}{732} = \text{flow}\ (1.008)$$

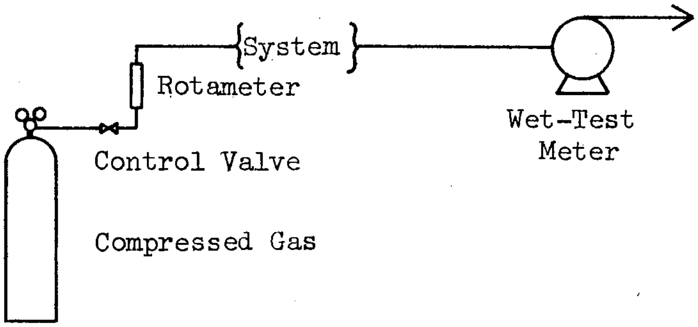
For all purposes, the vapor pressure of water can be neglected.

As shown in Part B of Figure 63, the oil feed system was operated normally. A graduated cylinder was filled to a specific volume and the related time required for filling was recorded. Various flow rates were measured to calibrate the oil rotameter. All calibration curves were then drawn, see Figures 64-70.

Gas Chromatograph Flowmeters

Calibration for the gas chromatograph flow meters was rather simple. The carrier gas for the gas chromatograph was used; a bubble meter attached to the outlet from the gas chromatograph was the only modification. Various flow settings and time required for a bubble to travel the length of the tube were obtained and the data plotted in Figures 71-72. Calibration was performed at gas chromatograph operating conditions, oven temperature-75°C, head pressure-40 psig and back pressure-20 psig.

Part A (Gas)



Part B (Oil)

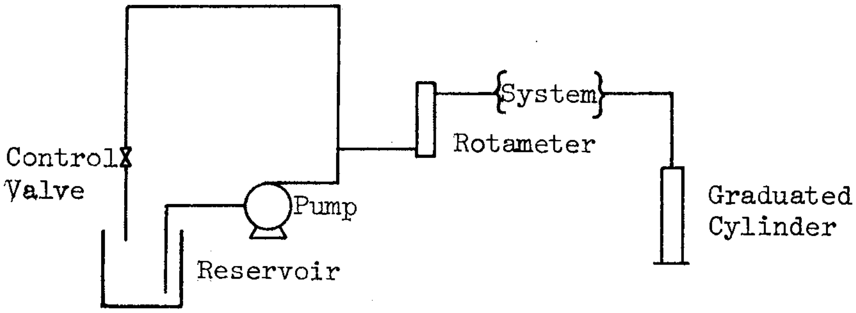


Figure 63. Schematic of Rotameter Calibration Setup

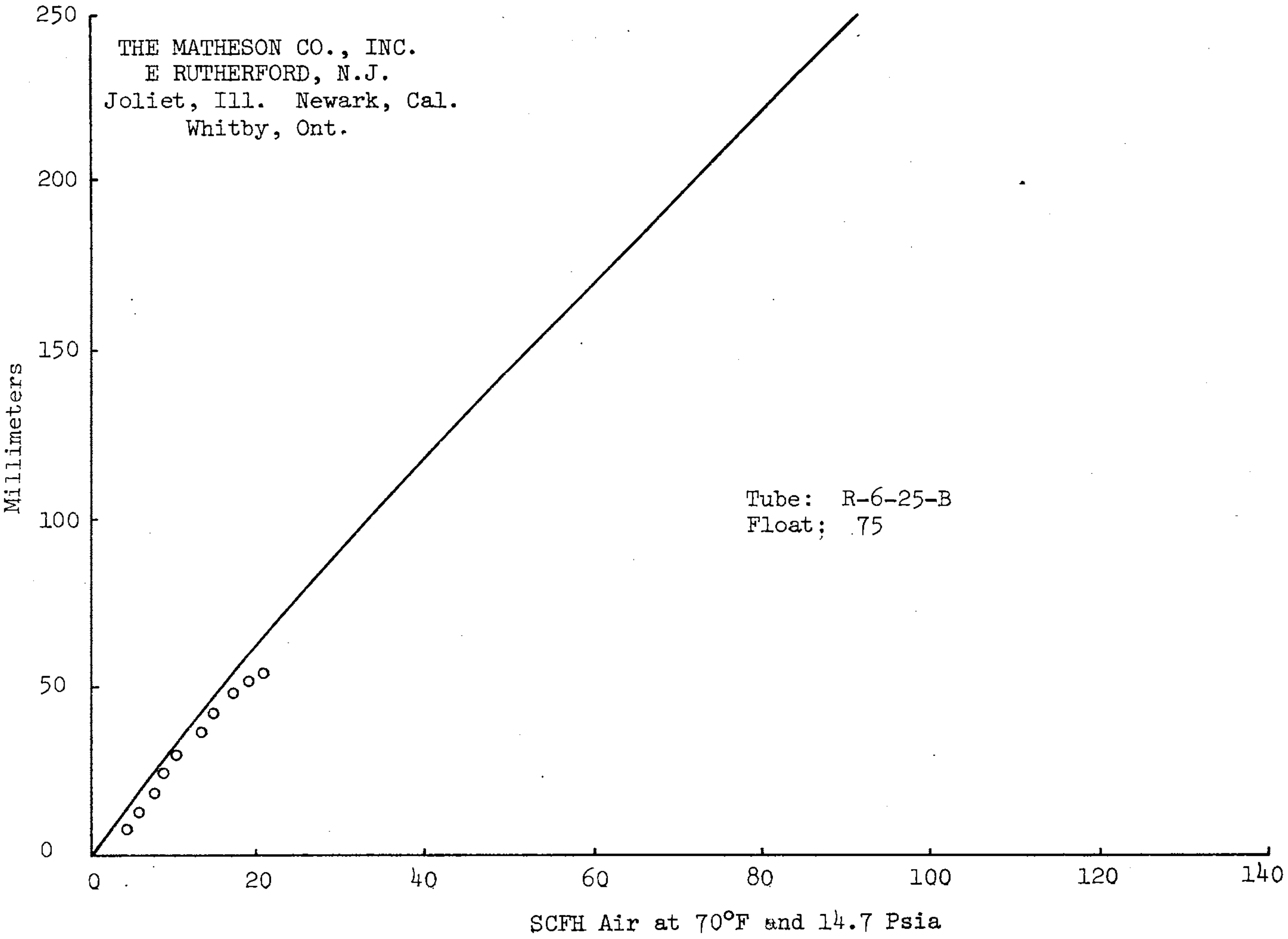


Figure 64. Calibration Curve for Model No. 75 Rotameter

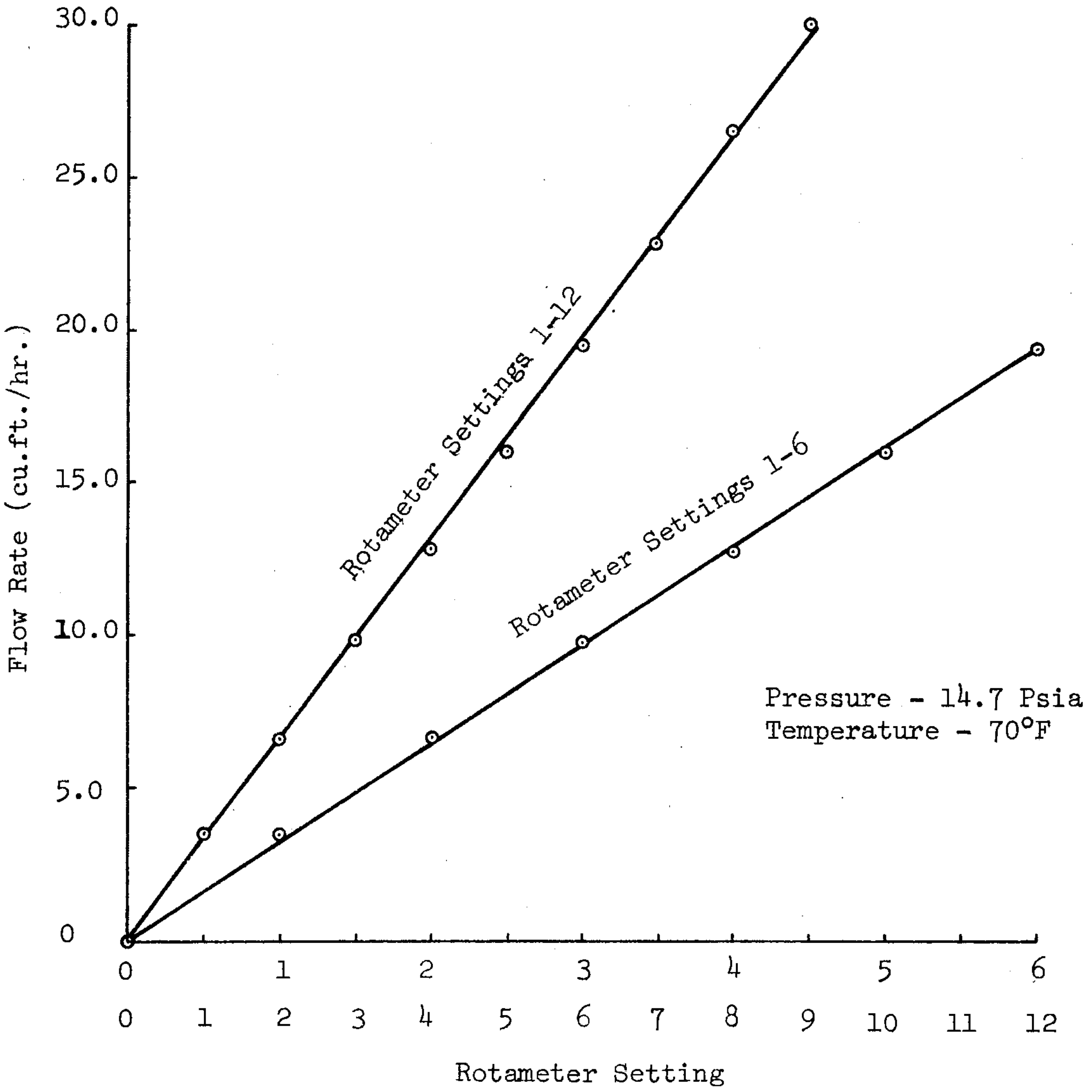


Figure 65. Calibration Curve for Model 75 Tube

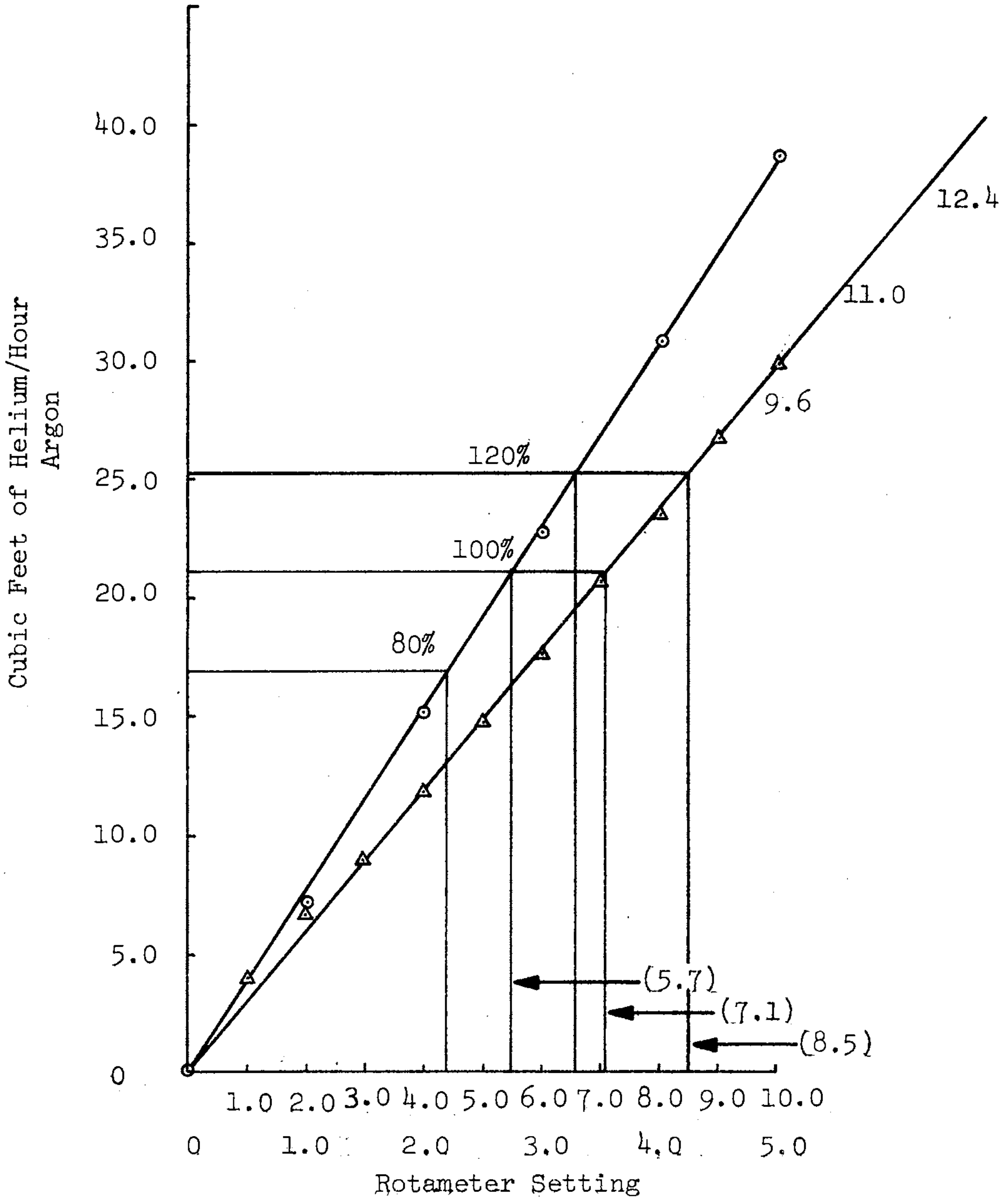


Figure 66. Calibration of Rotameter Tube #75 with Helium and Argon

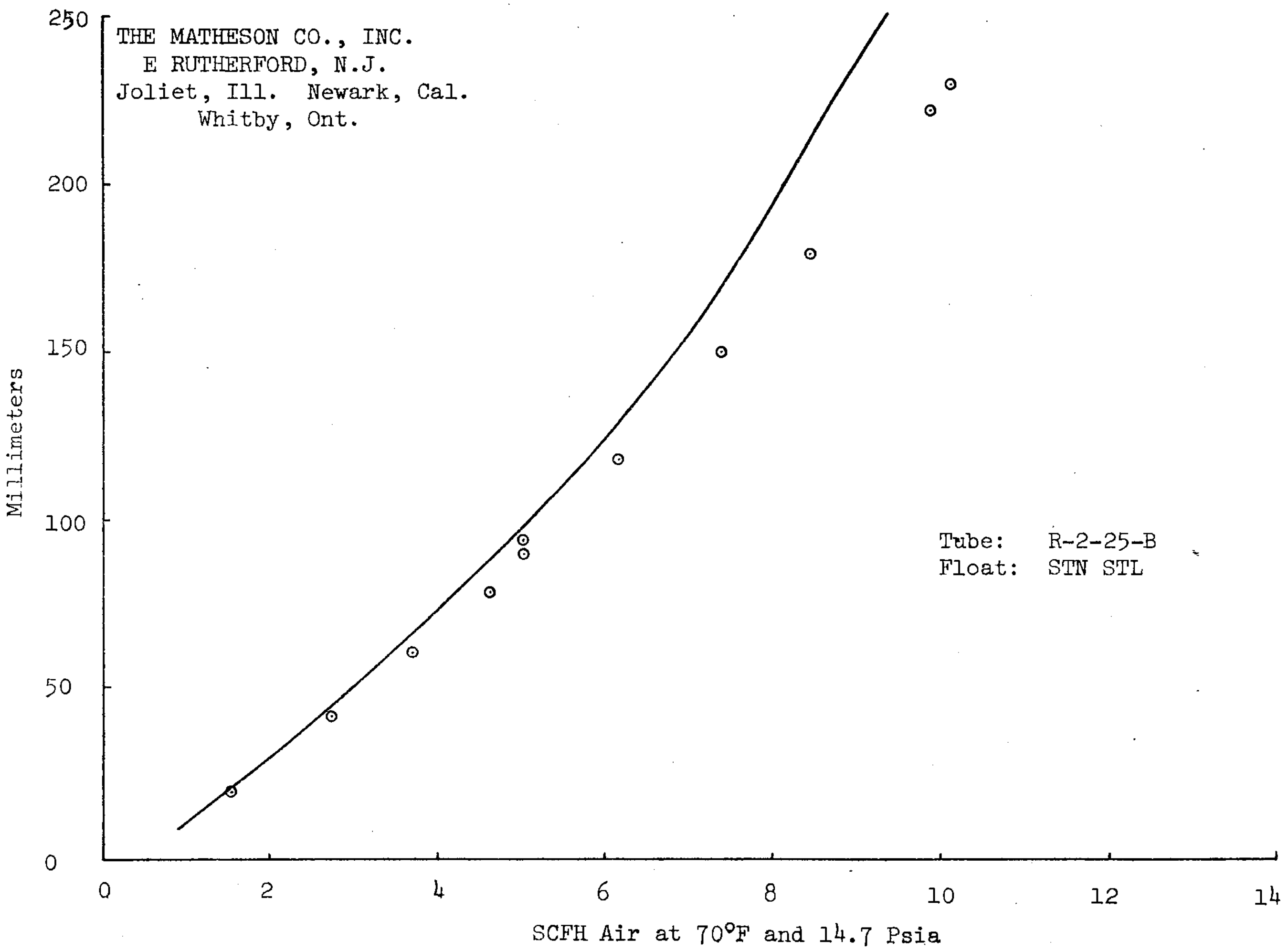


Figure 67. Calibration Curve for Model No. 73 Rotameter

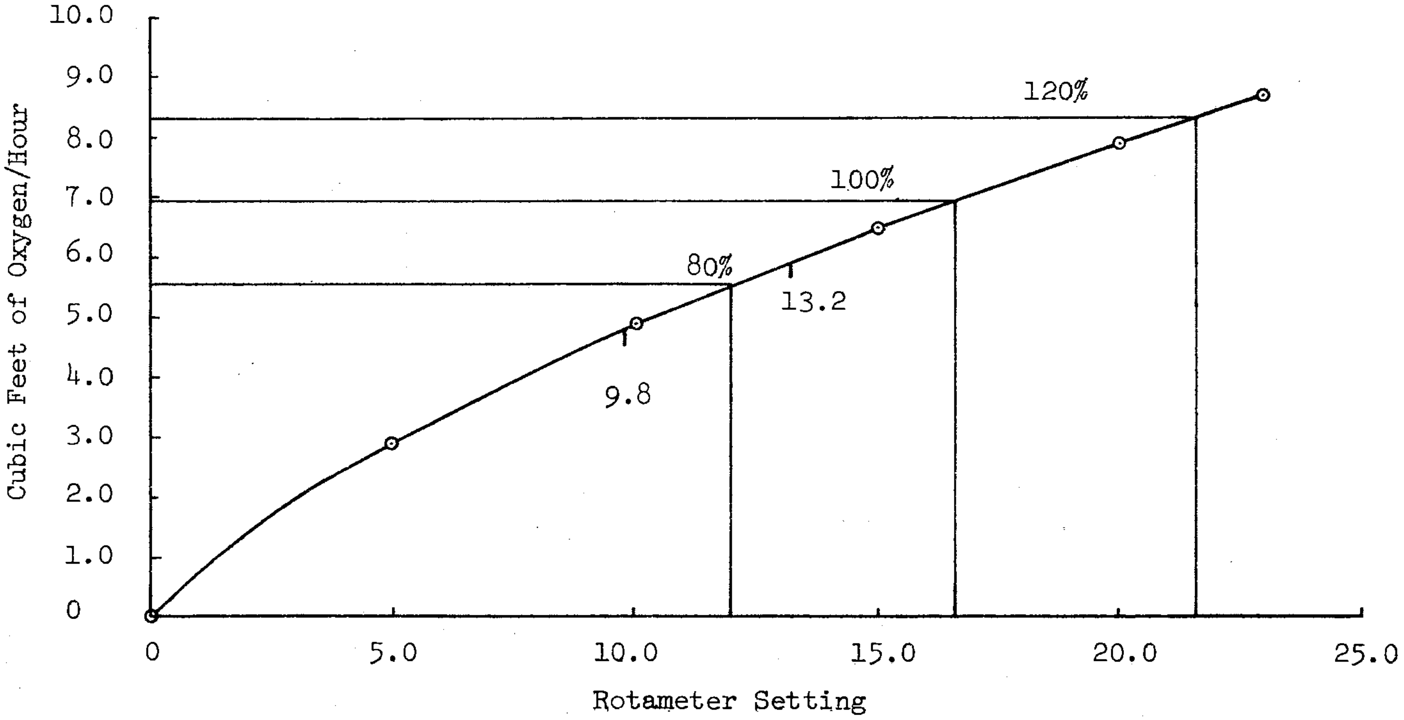


Figure 68. Calibration of Rotameter Tube #73 with Oxygen at 90 Psia

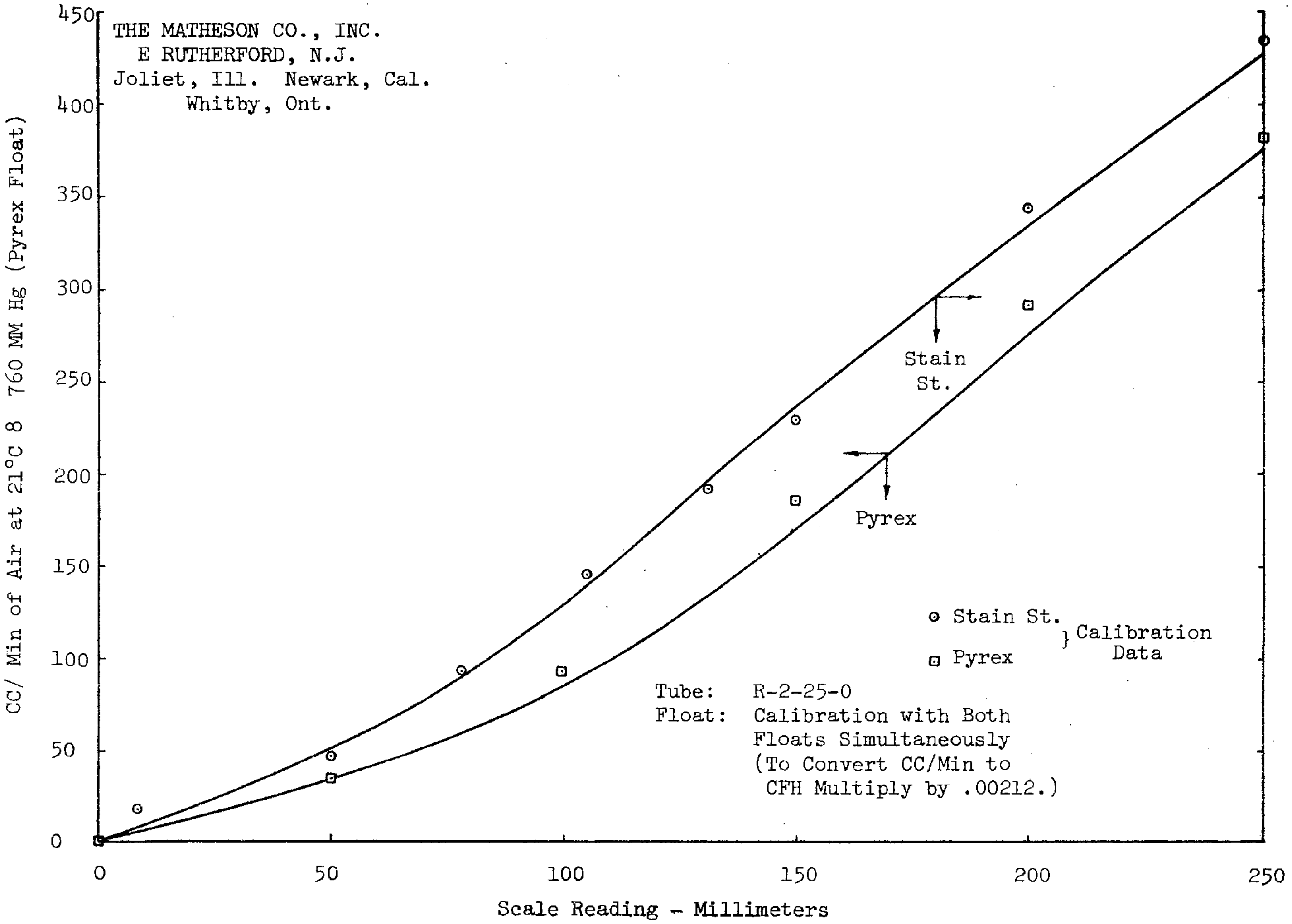


Figure 69. Calibration Curve for Model No. 72 Rotameter

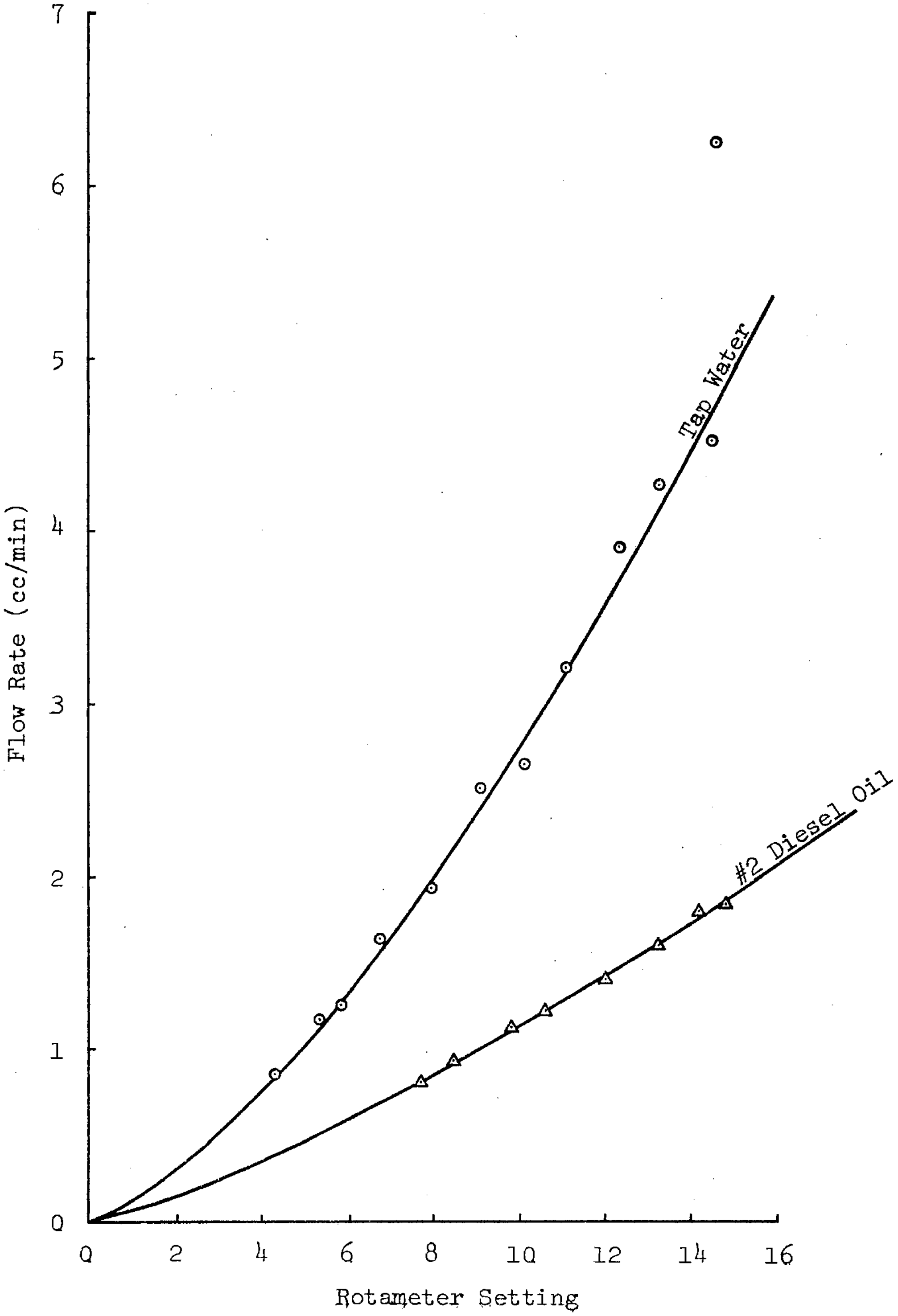


Figure 70. Calibration of Rotameter R-2-15-AA [for Oil Feed Metering]

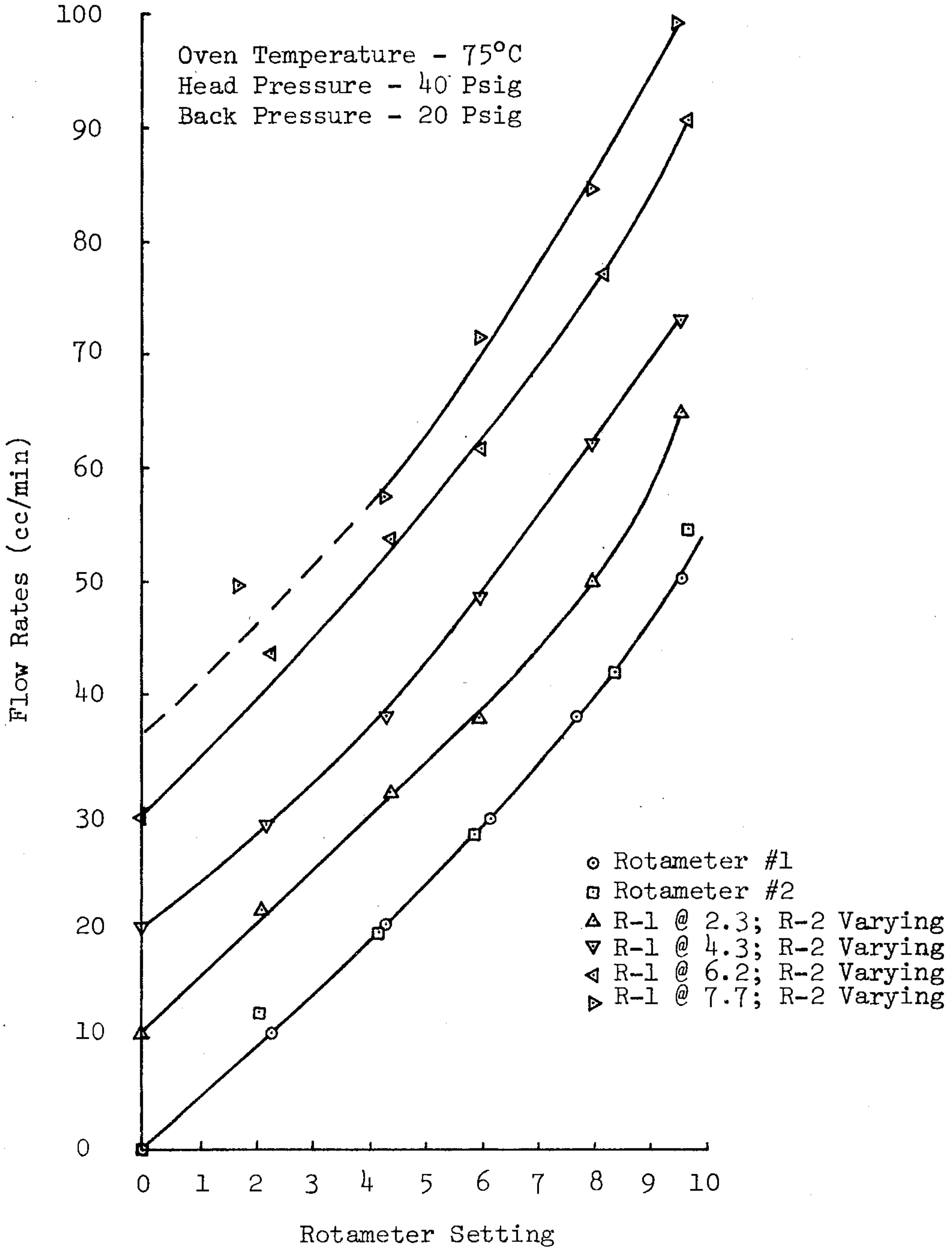
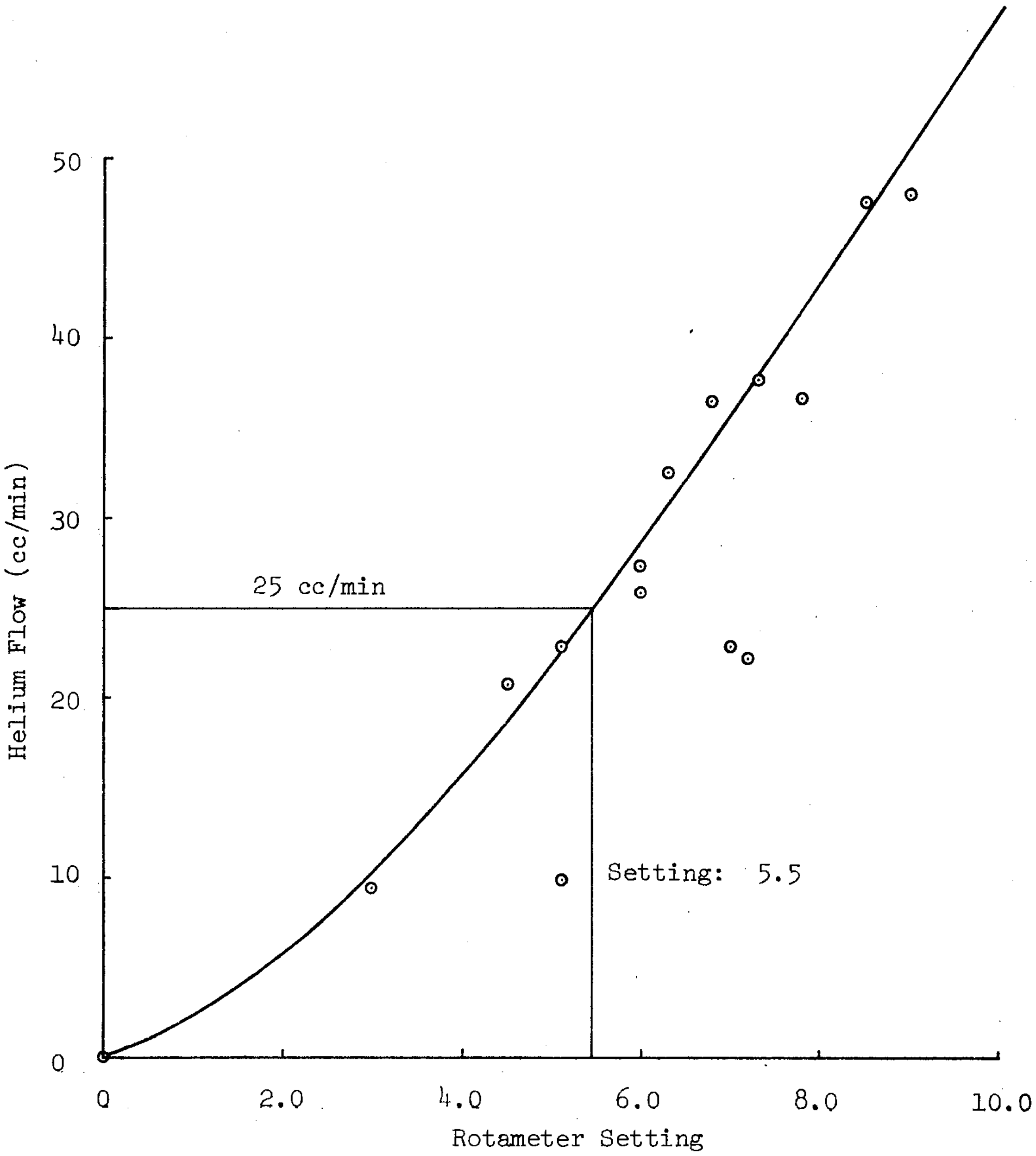


Figure 71. Flow Calibration for G-C



NOTE: Path A - Path Thru Column
Path B - Set at Zero

Figure 72. Plot of Rotameter Settings vs. Helium Flow Through G-C at Column Temperature of 75°C

Thermocouples

Although two different setups were used to calibrate the various thermocouples, the procedure as outlined in ASTM-E207-66 was followed (8). The tungsten-tungsten/26% rhenium thermocouples were calibrated against a reference platinum-platinum/10% Rhodium thermocouple. The reference thermocouple was standarized on 7-1-63 by Leeds and Northrup Company, Test No. 175190-K-35 at gold point (1063°C), at silver point (9608°C), at antimony point (630.5°C) and at zinc point (419.5°C). The reference thermocouple has a ± 0.75°C error in the range 0-1100°C and a ± 3°C at 1400°C. Figure 73 shows the calibration of this data; all data are within ± 1% of the values shown in Table XXXVIII. This data range is the normal expected range for these thermocouples (8).

Iron-constantan and chromel-alumel thermocouples were calibrated against the tungsten-tungsten/26% rhenium thermocouples. Both calibrations show that the thermocouples followed standard temperature-millivolt tables. The calibration curves are shown in Figures 74-75.

Thermocouple Switching System

A check of the potential drop across the thermocouple switching system showed that the drop was negligible when compared to the overall implied voltage.

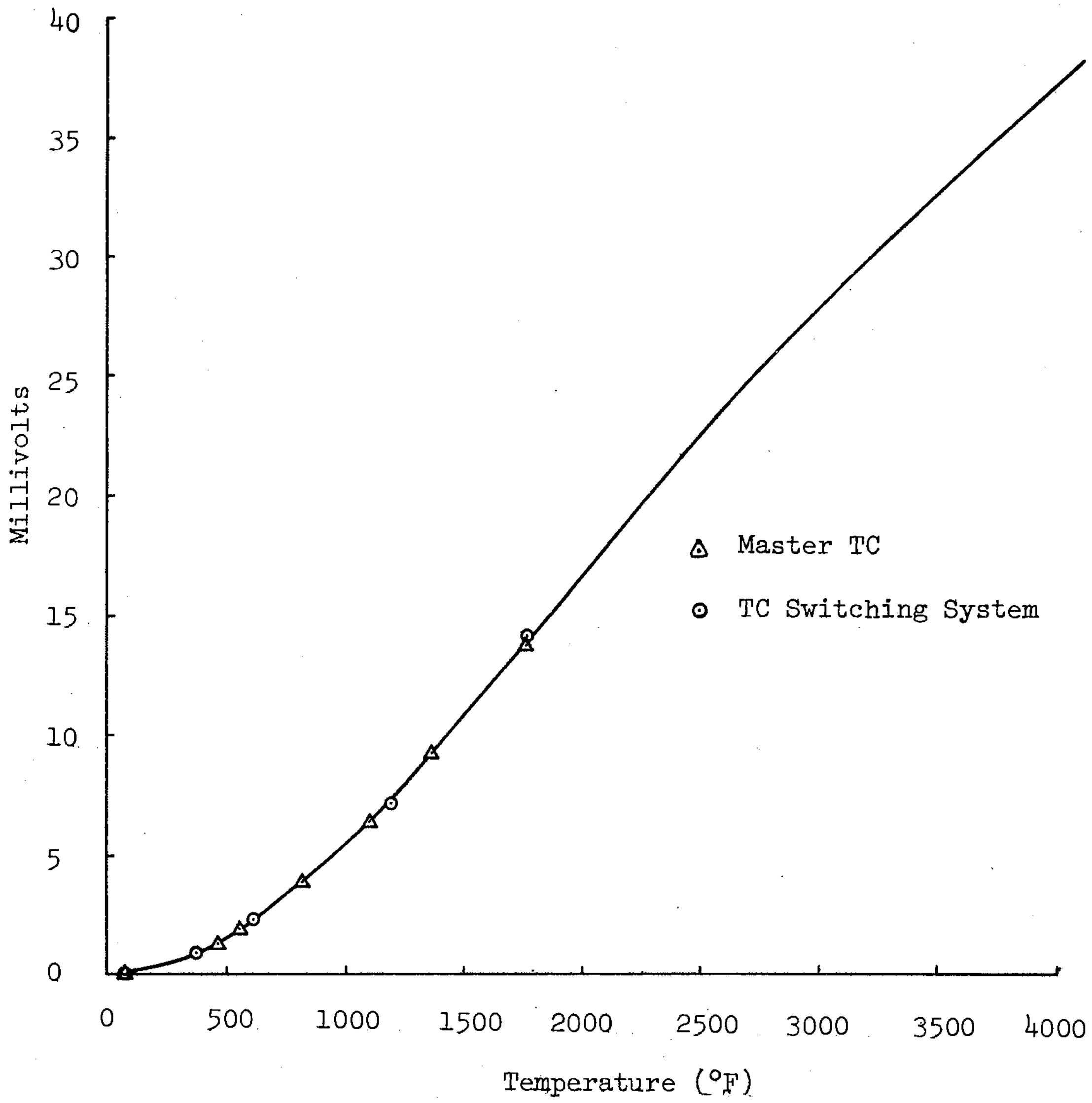


Figure 73. Temperature vs. Millivolts-Tungsten-Tungsten/26%Rhenium Thermocouple Calibration Curve (Conax Corporation)

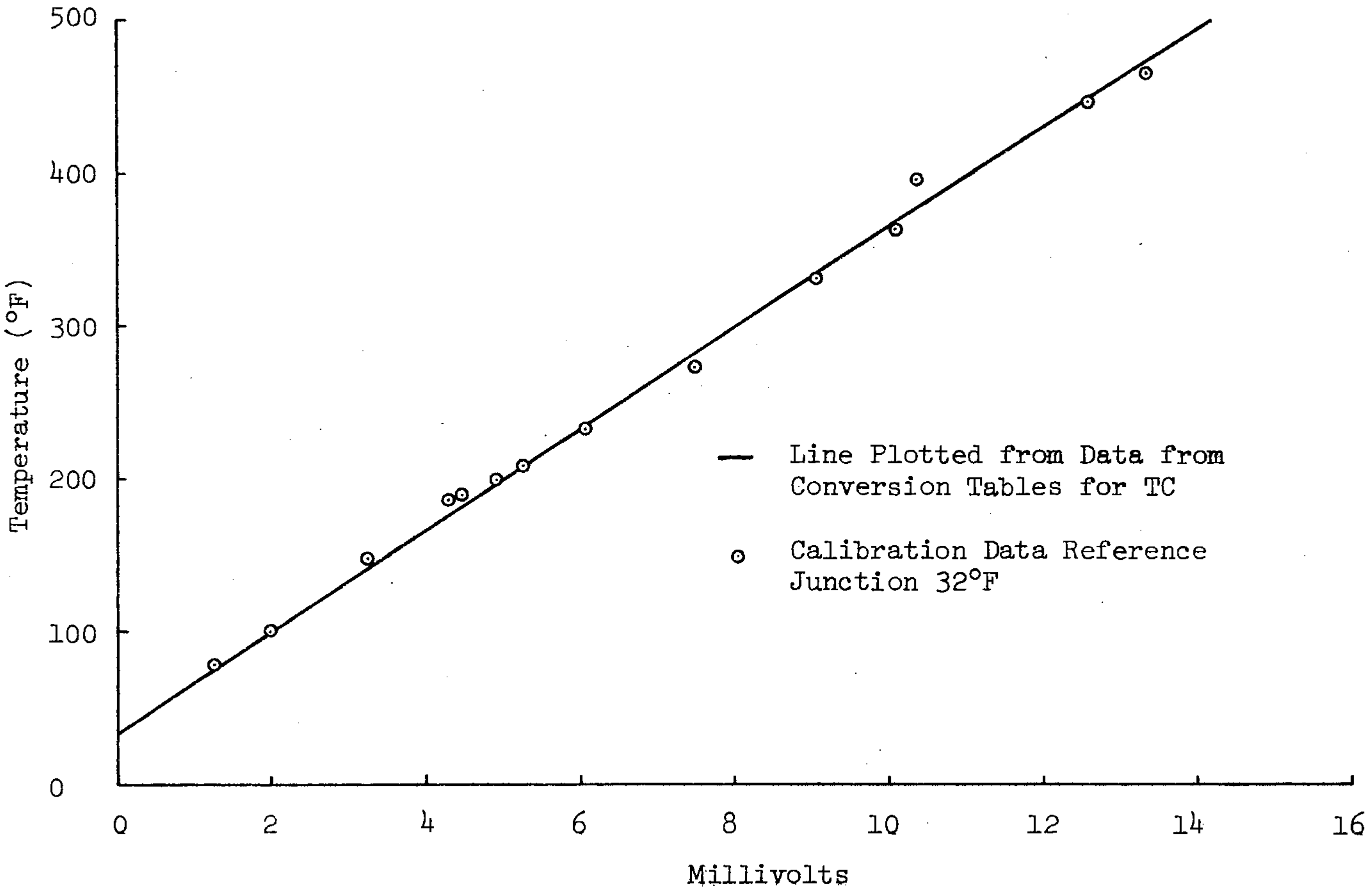


Figure 74. Plot for Checking Calibration of Manufactured Iron-Constantan TC

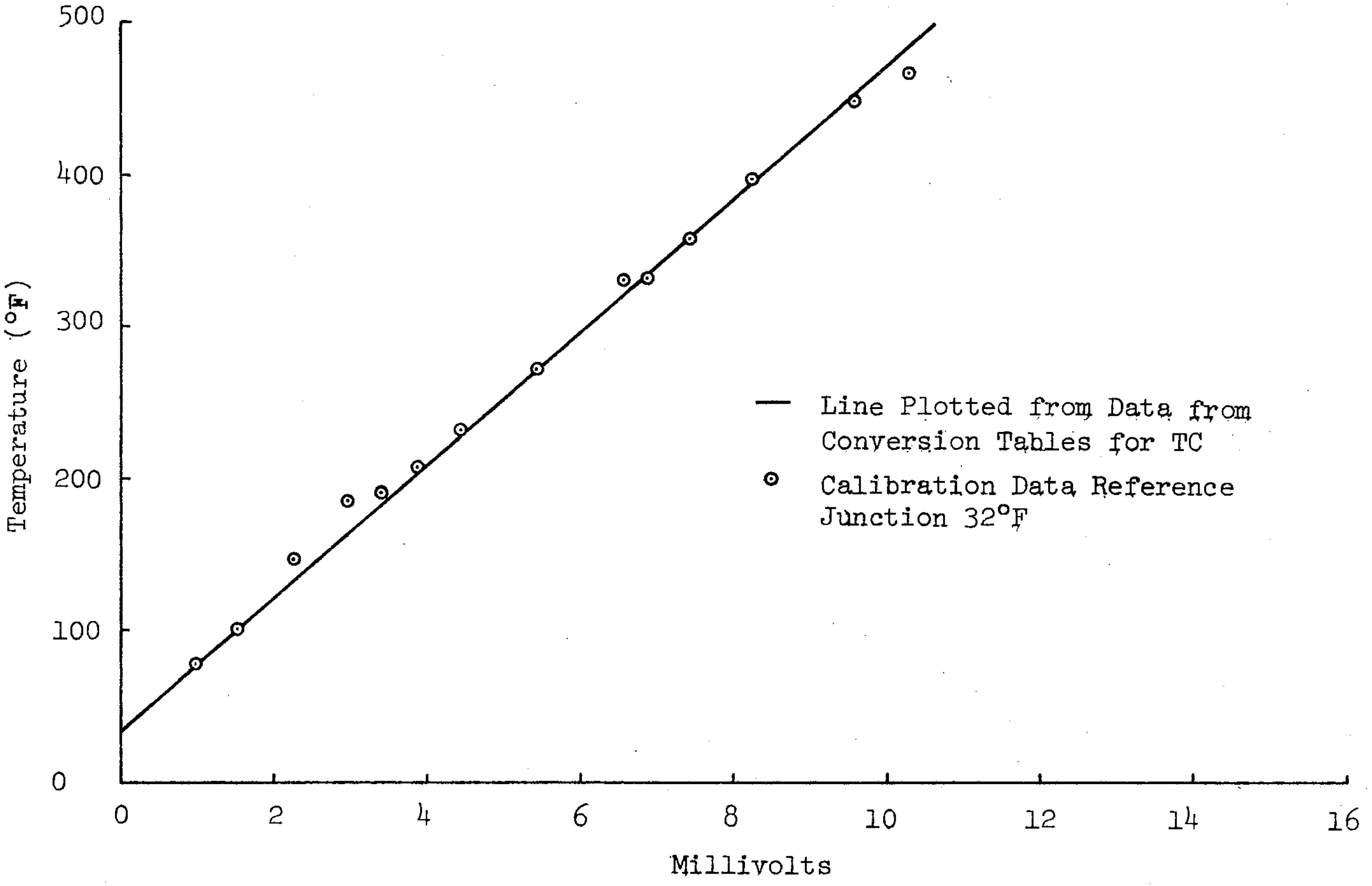


Figure 75. Plot for Checking Calibration of Chromel-Alumel TC's

TABLE XXXVIII

TEMPERATURE MILLIVOLT TABLE

Conax Corporation
2300 Walden Avenue
Buffalo, New York 14225
INDUSTRIAL PRODUCTS DIVISION

TUNGSTEN - TUNGSTEN/26% RHENIUM
Reference Junction 32° F

Degrees	0°	100°	200°	300°	400°	500°	600°	700°	800°	900°	1000°	Degrees
0	--	.103	.320	.673	1.064	1.573	2.212	2.927	3.716	4.565	5.470	0
20	--	.136	.384	.750	1.148	1.692	2.350	3.079	3.881	4.741	5.660	20
40	.012	.173	.452	.828	1.246	1.816	2.492	3.235	4.049	4.919	5.851	40
60	.042	.215	.522	.906	1.349	1.944	2.635	3.393	4.219	5.100	6.043	60
80	.072	.264	.597	.985	1.458	2.076	2.779	3.553	4.391	5.283	6.236	80
100	.103	.320	.673	1.064	1.573	2.212	2.927	3.716	4.565	5.470	6.430	100

Degrees	1100°	1200°	1300°	1400°	1500°	1600°	1700°	1800°	1900°	2000°		Degrees
0	6.430	7.436	8.481	9.576	10.702	11.837	12.984	14.149	15.339	16.549	-	0
20	6.626	7.641	8.696	9.800	10.928	12.065	13.215	14.385	15.580	16.791	-	20
40	6.826	7.848	8.913	10.025	11.155	12.294	13.447	14.622	15.822	17.033	-	40
60	7.028	8.057	9.132	10.250	11.382	12.523	13.680	14.860	16.064	17.274	-	60
80	7.232	8.268	9.353	10.476	11.609	12.753	13.914	15.099	16.307	17.515	-	80
100	7.436	8.481	9.576	10.702	11.837	12.984	14.149	15.339	16.549	17.755	-	100

Degrees	2100°	2200°	2300°	2400°	2500°	2600°	2700°	2800°	2900°	3000°		Degrees
0	17.755	18.940	20.113	21.280	22.424	23.529	24.587	25.616	26.636	27.646	-	0
20	17.994	19.175	20.347	21.512	22.649	23.744	24.794	25.821	26.839	27.847	-	20
40	18.232	19.410	20.581	21.742	22.872	23.957	25.000	26.026	27.041	28.048	-	40
60	18.469	19.645	20.814	21.970	23.093	24.169	25.206	26.230	27.243	28.249	-	60

TABLE XXXVIII (Continued)

Degrees	2100°	2200°	2300°	2400°	2500°	2600°	2700°	2800°	2900°	3000°		Degrees
80	18.705	19.879	21.047	22.198	23.312	24.379	25.411	26.433	27.445	28.449	-	80
100	18.940	20.113	21.280	22.424	23.529	24.587	25.616	26.636	27.646	28.649	-	100

Degrees	3100°	3200°	3300°	3400°	3500°	3600°	3700°	3800°	3900°	4000°	4100°	Degrees
0	28.649	29.640	30.627	31.606	32.575	33.531	34.477	35.412	36.338	37.209	37.926	0
20	28.848	29.838	30.824	31.801	32.767	33.721	34.665	35.598	36.520	37.369	38.040	20
40	29.047	30.036	31.020	31.995	32.959	33.911	34.852	35.784	36.699	37.523	38.151	40
60	29.245	30.233	31.216	32.189	33.150	34.100	35.039	35.969	36.874	37.669	38.260	60
80	29.443	30.430	31.411	32.382	33.341	34.289	35.226	36.154	37.044	37.804	38.368	80
100	29.640	30.627	31.606	32.575	33.531	34.477	35.412	36.338	37.209	37.926	38.474	100

APPENDIX B

APPENDIX B

- B-1. Operating Instructions
  - a. Startup
  - b. Normal Operation
  - c. Shutdown
- B-2. Safety and Toxic Properties
  - a. Laboratory Safety
    - 1. Experimental Operation
    - 2. Emergency Shutdown
    - 3. Combustible Materials
    - 4. Poisonous Gases
  - b. Toxic Properties
    - 1. NO_x
    - 2. Pyridine

B-1 OPERATING INSTRUCTIONS

Startup Procedure - Normally 5-7 minutes in length.

1. Start up gas chromatograph; record settings.
2. With chamber opened, fill all ice baths and take initial thermocouple readings (time is zero).
3. Set pressure at 20 psig for helium purge gas to atomizer.
4. Set all powerstats at 100.
5. Turn on combustible gas flow at 80% stoichiometric.
6. Turn on ignitor, assuring the thermoswitch is closed (igniting spark should be on).
7. Turn on oil pump to full flow to flush oil system.
8. As oil reaches atomizer-vaporizer and vaporizes, smoke can be detected flowing from the combustor.
9. As fuel vapors reach the spark, flame is introduced in the chamber; reduce oil to 8.9 setting.
10. As soon as the flame seems stable, close the chamber.
11. Slowly adjust flow to run conditions and prepare to take reading every 15 minutes.
12. Introduce sample probes and turn on vacuum pump (first sample should be collected at port two).

Normal Operating Instructions

1. Items to check:
    - a. ice in thermocouple reference baths.
    - b. oil and gas flows.
    - c. sampling
    - d. thermoswitch
    - e. chart paper - gas chromatograph recorder

2. Take temperature readings every 15 minutes.
3. Sample a port every 30 minutes.

Shutdown

1. Turn off oil.
2. Open chamber.
3. Shut off combustible gas after flame is out.
4. Shut off thermoswitch.
5. Shut off powerstat.
6. Pour out ice baths.
7. After last sample eludes from the gas chromatograph, shut off helium to atomizer.
8. Place gas chromatograph on standby.

B-2 SAFETY AND TOXIC PROPERTIES

Laboratory Safety

Laboartory safety is very important in this research due to the presence of the combustion of fuel and the resulting products gases. The Safety Instructions for this research are presented on the next page and are posted inside the laboratory door. Also included are emergency shutdown procedures for the combustor. Basic items included here are locations of combustible gases, all "on-off" switches, and the fire extinguisher. Warnings were stated for electrical potential of the ignitor system, pressure operating limits for various gases, and power stat settings. A thermoswitch was included in the combustor to ignite vapors in the combustor automatically if the flame ever goes out.

SAFETY INSTRUCTIONS

EXPERIMENTAL OPERATION:

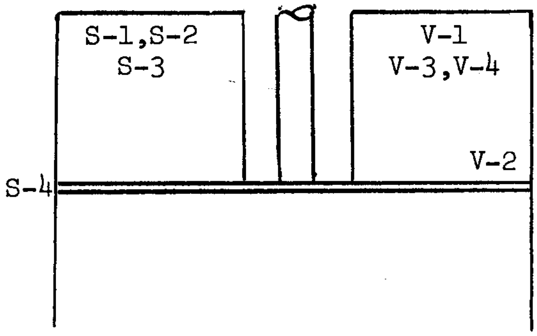
Concerns combustion of fuel oil using either air or oxygen mixture. The flame is enclosed in a combustion chamber and should be exposed only to gases metered into the system.

Ignitor system consists of a spark gap between the poles of a 10,000 volt transformer. Caution must be exercised when actuating and using the ignitor system. A safety thermoswitch has been installed into the ignitor system to re-establish the flame if it should blow out during testing. This switch is set to activate the ignitor if the temperature drops 5° F.

There are two "on-off" electrical switches used to actuate the ignitor system; they are located in the upper left hand corner of the left control panel, see drawing below. Switch # 1 actuates the power to the ignitor system. Switch #2 actuates the thermoswitch. NOTE: The flame may be ignited through use of the push button switch (switch #3) without the thermoswitch being actuated.

The vaporizer and the preheating system require various amounts of voltage and thus are connected to rheostats. Voltage settings should never go above 100.

Gas flow from the mixing chamber should be such that flame lift-off does not occur. Suggested starting conditions to avoid this are oil rotameter set at 7.6 to 7.8, air rotameter set at 5.3 or 5.4, and argon rotameter at 9.0.

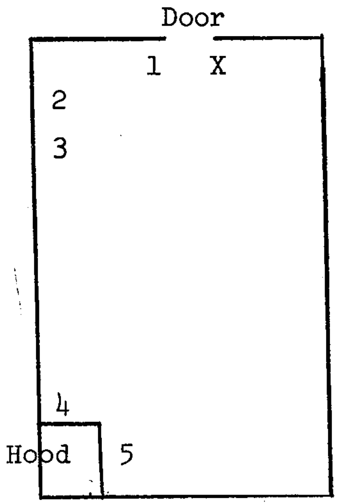


EMERGENCY SHUTDOWN:

1. Turn off pump switch - located on left side of table (switch #4 on above drawing).
2. Turn off argon flow to atomizer (valve #1).
3. Turn off air or oxygen flow (valve #2 or #3). LEAVE INERT GAS FLOWING THROUGH THE COMBUSTION CHAMBER. (DO NOT TURN OFF VALVE #4).
4. Turn off ignitor switch #1.

COMBUSTIBLE MATERIALS:

1. Cylinder of compressed oxygen (pure) - located right inside the door opposite the fire extinguisher.
2. Cylinder of compressed air - located behind the experimental equipment next to the telephone.
3. Gallon glass jar of No. 2 diesel oil - located behind the equipment.
4. Storage area for compressed gases (both oxygen and air) - located next to the exhaust hood.
5. Five gallon container of No. 2 diesel oil - located in front of the hood.



X - Fire Extinguisher

POISONOUS GASES:

Two cylinders of NO are stored in the exhaust hood. Be SURE exhaust fan is left on.

The concentration of NO, NO_2 and SO_2 produced during experimentation are not sufficient to be poisonous.

TOXIC PROPERTIES OF NO_x (92)

Hazard Analysis

Toxic Hazard Rating:[a]

Acute local: Irritant 3; Ingestion 3; Inhalation 3.

Acute systemic: Ingestion 3; Inhalation 3.

Chronic local: U

Chronic systemic: Ingestion 3; Inhalation 2.

Toxicology: Exposure to nitrogen oxides may occur whenever nitric acid acts upon organic materials, such as wood, sawdust and refuse; it occurs when nitric acid is heated, and when organic nitro compounds are burned, as for example, celluloid, nitrocellulose (guncotton) and dynamite. The action of nitric acid upon metals as in metal etching and pickling, also liberates the fumes. In high-temperature welding, as with the oxyacetylene or electric torch, the nitrogen and oxygen of the air unite to form oxides of nitrogen. Exposure may also occur in many manufacturing processes when nitric acid is made or used.

The oxides of nitrogen are somewhat soluble in water, reacting with it in the presence of oxygen to form nitric and nitrous acids. This action takes place deep in the respiratory system. The acids formed cause congestion of the throat and bronchi, and edema of the lungs. They are neutralized by the alkalis present in the tissues, with the formation of nitrates and nitrites. The latter may cause some arterial dilation, fall in blood pressure, headache and dizziness, and there may be some formation of methemoglobin. However, the nitrite effect is of secondary importance.

Because of their relatively low solubility in water, the nitrogen oxides are only slightly irritant to the mucous membranes of the upper respiratory tract. Their warning power is therefore low, and dangerous amounts of the fumes may be breathed before the workman notices any real discomfort. Higher concentrations (60 to 150 ppm) cause immediate irritation of the nose and throat, with coughing and burning in the throat and chest. These symptoms often clear up on breathing fresh air, and the workman may feel well for several hours. Some 6 to 24 hours after exposure, he develops a sensation of tightness and burning in the chest, shortness of breath, sleeplessness and restlessness. Dyspnea and air hunger may increase rapidly, with development of cyanosis and loss of consciousness, followed by death. In cases which recover from the pulmonary edema, there is usually no permanent disability but pneumonia may develop later. Concentrations of 200 to 700 ppm may be fatal after even very short exposures.

Continued exposure to low concentrations of the fumes, insufficient to cause pulmonary edema, is said to result in chronic irritation of the respiratory tract, with cough, headache, loss of weight, loss of appetite, dyspepsia, corrosion of the teeth and gradual loss of strength.

Exposures to nitrous fumes is always potentially serious, and persons so exposed should be kept under close observation for at least 48 hours.

Disaster Hazard: Dangerous; when heated they evolve highly toxic fumes; they will react with water or steam to produce heat and corrosive liquids; they can react vigorously with reducing materials.

TOXIC HAZARD RATING CODE

1 - Slight: Causes readily reversible changes which disappear after end of exposure.

2 - Moderate: May involve both irreversible and reversible changes; not severe enough to cause death or permanent injury.

3 - High: May cause death or permanent injury after very short exposure to small quantities.

U - Unknown: No information on humans considered valid by authors.

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[a] Terms defined on page 222.

TOXIC PROPERTIES OF PYRIDINE (92)

General Information

Description: Colorless liquid; sharp, penetrating, empyreumatic odor; burning.

Formula: NCHCHCHCHCH

Constants: Molecular weight: 79.10, boiling point: 115.3°C, lower explosive limit: 1.8%, upper explosive limit: 12.4%, freezing point: -42°C, flash point: 68°F (closed cup), density: 0.982, autoignition temperature: 900°F, vapor pressure: 10 mm at 13.2°C, vapor density: 2.73.

Hazard Analysis

Toxic Hazard Rating:[a]

Acute local: Irritant 1; Ingestion 2; Inhalation 1

Acute systemic: Ingestion 2; Inhalation 1

Chronic local: U

Chronic systemic: Ingestion 2; Inhalation 2

Toxicology: Is mildly irritating to skin and can cause central nervous system depression. Kidney and liver damage has been reported in experimental animals.

Threshold limit value: American Conference of Governmental and Industrial Hygienists (accepted): 5 parts per million in air; 15 milligrams per cubic meter of air.

Fire Hazard: Dangerous, when exposed to heat or flame.

Spontaneous Heating: No

Explosion Hazard: Severe, in the form of vapor, when exposed to flame or spark.

Disaster Hazard: Dangerous; when heated to decomposition, it emits highly toxic fumes of cyanides; can react vigorously with oxidizing materials.

TOXIC HAZARD RATING CODE

1 - Slight: Cause readily reversible changes which disappear after end of exposure.

2 - Moderate: May involve both irreversible and reversible changes; not severe enoguh to cause death or permanent injury.

3 - Unknown: No information on humans considered valid by authors.

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[a] Definitions:

Acute - means "of short duration."
Chronic - means "of long duration."
Local - refers to the site of the action of an agent and means that the action takes place at the point or area of contact.
Systemic - refers to a site of action other than the point of contact and presupposes that absorption has taken place.

APPENDIX C

APPENDIX C

CALCULATIONS AND DERIVATIONS

1. Ratio of N_2 to Total Gas
2. Heat Loss from Thermocouples
3. Formation of NO_x
4. Statistics - NO_x at Run Temperature
5. Adiabatic Flame Temperature
6. Heat Balance

C-1 RATIO OF N_2 TO TOTAL GAS

Calculation of the ratio of N_2 to total gas flow through combustor.

$$2C_{17}H_{30} + 49O_2 + \frac{79}{21}(49)\ N_2 \longrightarrow 34\ CO_2 + 30H_2O + \frac{79}{21}(49)\ N_2$$

$$\text{total moles of gas out:}\quad 34 + 30 + \frac{79}{21}(49) = 248\ 1/3$$

$$N_2/\text{Total gas:}\quad 184\ 1/3\ /\ 248\ 1/3 = 0.742$$

Since the volume of NO_x and NO_2 was measured at 75°C and 1 atm, ratio NO_x/N_2 is at 75°C and 1 atm.

Assume that Charles' Law holds $\frac{N_1}{V_2} = \frac{T_1}{T_2}$

$$\frac{\left[\text{Vol } NO_x\right]_1}{\left[\text{Vol } NO_x\right]_2} = \frac{348}{298}\ ; \frac{\left[\text{Vol } N_2\right]_1}{\left[\text{Vol } N_2\right]_2} = \frac{348}{298}$$

$$\frac{\left[\text{Vol } NO_x\right]_1}{\left[\text{Vol } N_2\right]_2} = \frac{\frac{348}{298}\left[\text{Vol } NO_x\right]_2}{\frac{348}{298}\left[\text{Vol } N_2\right]_2}\ ,$$

therefore, ratio of NO_x/N_2 measured at 75° will be same at 25°C.

	T_c (°K)	P_c (atm)	T_r (25°C)	T_r (75°C)	P_r	$Z_{25°C} = Z_{75°C}$
N_2	126	33.5	2.36	2.76	~0.03	~1.00
NO_x	179	65.0	1.66	1.94	~0.015	~1.00

$Pv = ZnRT \equiv$ ideal gas low since $Z \sim 1$.

The volume ratio will equal the mole ratio.

At 100% oxygen: $\left(\frac{NO_x}{N_2}\right)$ (0.742) N_2/total gas = $\frac{NO_x}{\text{total gas}}$ = ppm NO_x

$$\therefore \frac{NO_x}{N_2} * 0.742 = \text{ppm } NO_x$$

At 80% oxygen: $2C_{17}H_{30} + 0.8\,(49)\,O_2 + \frac{79}{21}\,(.8)\,(49)\,N_2 \longrightarrow$

$\frac{79}{21}\,(.8)\,(49)\,N_2 + 30H_2O + 18.4CO + 15.6\,CO_2$

Total moles gas out: 147.5 + 30 + 18.4 + 15.6 = 211.5

N_2/total gas: 147.5/211.5 = 0.697

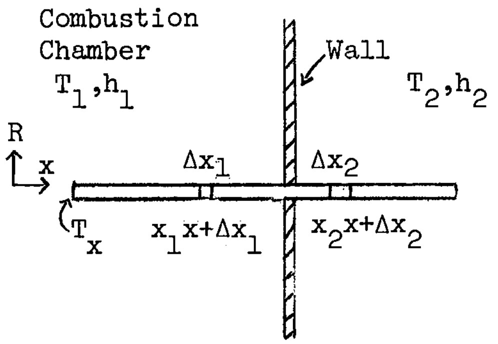
At 120% oxygen: $2C_{17}H_{30} + 1.2\,(49)\,O_2 + \frac{79}{21}\,(1.2)\,(49)\,N_2 \longrightarrow$

$34CO_2 + 30H_2O + \frac{79}{21}\,(1.2)\,(49)\,N_2 + .2\,(49)\,O_2$

Total moles gas out: 34 + 30 + 9.8 + 221.2 = 295

N_2/total gas: 221.2/295 = 0.750

C-2 HEAT LOSS FROM THERMOCOUPLES



Assumption:
1 Steady state
2 Zero wall thickness
3 Constant properties
4 No radial heat transfer

Inside Combustion Chember (Region 1)

Input at x_1: $q_x|_{x_1} = -k \frac{\partial T}{\partial x} \pi R^2$

Input over Δx_1: $-h_1 \, (T-T_1) \, \Delta x_1 \, 2\pi R$

Output at $x_1 + \Delta x_1$: $q_x|_{x_1+\Delta x_1} = -K \frac{\partial T}{\partial x} \pi R^2 - \frac{\partial}{\partial x} (K \frac{\partial T}{\partial x} \pi R^2) \, \Delta x$

Generation and accumulation = zero

Balance: Input = Output + Generation = Accumulation

$$K \frac{\partial^2 T}{\partial x^2} \pi R^2 \Delta x_1 - 2\pi R h_1 (T-T_1) \Delta x_1 = 0$$

Let $\Theta = T-T$, then $d\Theta = dt$

Let $A^2 = 2h_1/KR$

$$\frac{\partial^2 \Theta}{\partial x^2} - A^2 \, \Theta = 0 \qquad (1)$$

Similarly for outside the chamger (Region 2)

$$K \frac{\partial^2 T}{\partial x^2} \pi R^2 \Delta X_2 - 2\pi R h_2 \ (T-T_2)\Delta x_2 = 0$$

Let $\phi = (T-T_2)$, then $d\phi = dT$

Let $B^2 = 2h_2/RK$

$$\frac{\partial^2 \phi}{\partial x^2} - B^2 \ \phi = 0 \qquad (2)$$

Boundary conditions for Equations (1) and (2) are:

1. at $X = 0$, $-K \frac{\partial \theta}{\partial x} A = h_1 \ \theta A$
2. at $X = L$ (length of thermocouple), $\phi = 0$ and/or $\frac{\partial \phi}{\partial x} = 0$
3. At $x = Lw$ (at the wall), $\theta + T_1 = \theta + T_2$ and $\frac{\partial \theta}{\partial x} = \frac{\partial \phi}{\partial x}$

Solving equations (1) and (2)

$$\theta = C_1 e^{AX} + e_2 C^{-AX} \qquad (3)$$

$$\phi = C_3 e^{BX} + C_4 e^{-BX} \qquad (4)$$

Now, using BC #1 on Equation (3)

$$\frac{\partial \theta}{\partial x} = AC_1 e^{AX} - C_2 A e^{-AX}, \ -K \frac{\partial \theta}{\partial x} \Big| _{x=0} A = h_1 \ \theta A$$

$$-K \left[AC_1 e^{AX} - C_2 A e^{-AX}\right] \Big|_{x=0} = h_1 \left[C_1 e^{AX} + C_2 e^{-AX}\right] \Big|_{x=0}$$

$$-KA \ (C_1 - C_2) = h_1 (C_1 + C_2)$$

Let $\eta = h_1/KA$ (5)

$$C_2 - C_1 = \eta (C_1 + C_2)$$

$$C_2 = C_1 \ (\frac{1+\eta}{1-\eta})$$

Let $\delta = \frac{(1+\eta)}{(1-\eta)}$ (6)

therefore $C_2 = \delta C_1$ (7)

Using BC # 2 on Equation (4)

$0 = C_3e^{BL} + C_4e^{-BL}$, therefore

$$C_3 = -C_4e^{-2BL}$$

or $0 = BC_3e^{BL} - BC_4e^{-BL}$, therefore

$$C_3 = C_4e^{-2BL}$$

Using the positive sign

Thus $C_3 = C_4e^{-2BL}$ (8)

Let $\beta = e^{-2BL}$ (9)

Lastly, use BC #3 on Equations (3) and (4)

$$C_1 e^{ALw} + C_2e^{-ALw} + T_1 = C_3e^{BLw} + C_4e^{-BLw} + T_2 \quad (10)$$

and $A(C_1e^{ALw} - C_2e^{-ALw}) = B(C_3e^{BLw} - C_4e^{-BLw}$ (11)

Combining Equations (7), (9), (10) and (11) yields

$$C_1 \left[e^{ALw} + \delta e^{-ALw}\right] + T_1 = C_4 \left[\beta e^{BLw} - e^{-BLw}\right] + T_2$$

$$AC_1 \left[e^{ALw} - \delta e^{-ALw}\right] = BC_4 \left[\delta e^{BLw} - e^{-BLw}\right]$$

Let $\alpha_1 = e^{ALw} + \delta e^{-ALw}$ (12)

$$\alpha_2 = e^{ALw} + \delta e^{-ALw} \quad (13)$$

$$\gamma_1 = \beta e^{BLw} + e^{-BLw} \tag{14}$$

$$\gamma_2 = \beta e^{BLw} + e^{-BLw} \tag{15}$$

Thus $C_1 \alpha_1 + T_1 = C_4 \gamma_1 + T_2$ (16)

$$AC_1\alpha_2 = BC_4 \gamma_2 \tag{17}$$

Solving (16) and (17) for C_1

$$C_1 \alpha_1 + (T_1 - T_2) = C_4 \gamma_1$$

$$AC_1 \alpha_2/B\gamma_2 = C_4$$

so $C_1 \alpha_1 + (T_1 - T_2) = \gamma_1 AC_1\alpha_2/B\gamma_2$

$$C_1 (\alpha_1 - \gamma_1 A\alpha_2/B\gamma_2) = (T_2 - T_1)$$

$$C_1 = \frac{(T_2 - T_1)}{(\alpha_1 - \gamma_1 A\alpha_2/B\gamma_2)} \tag{18}$$

Actually, the solution is finished since T_x is measured and T_1 is unknown. Using Equations (3), (7), and (18) to solve for T_1

$$\theta = C_1 e^{AX} + C_2 e^{-AX}$$

$$\theta = C_1 \left[e^{AX} + \delta e^{-AX}\right]$$

$$\theta = \left[e^{AX} + \delta e^{-AX}\right] \left[\frac{T_2 - T_1}{\alpha_1 - \gamma_1 A\alpha_2/B\gamma_2}\right]$$

Now at $x = 0$, $T = T_x$ and T_1 is unknown (recall $\theta = T - T_1$)

$$T_x - T_1 = [1 + \delta] \left[\frac{T_2 - T_1}{\alpha_1 - \gamma_1 A\alpha_2/B\gamma_2}\right]$$

$$\text{Let } \Gamma = \frac{L + \delta}{\alpha_1 - \gamma_1 A\alpha_2/B\gamma_2} \tag{19}$$

$$\text{so } T_x - T_1 = \Gamma\ (T_2 - T_1)$$

$$T_1(1 - \Gamma) = Tx - \Gamma T_2$$

$$T_1 = \frac{T_x - \Gamma T_2}{1 - \Gamma} \tag{20}$$

Equation 20 was used on the IBM 360 computer to calculate heat losses. Interim Equations (5), (6), (8), (12), (13), (14), (15) and (19) are used in the computer programs; these have been labelled in the following manner:

(1)	Lines 1 - 20:	Definition of variables; Print Headings; Input of Data
(2)	Lines 21 - 48:	Calculations using Equations 5, 6, 8, 12, 13, 14 and 19
(3)	Lines 46 - 62:	Output of data and results, Exit from computer

Results are presented in Tables XXXX-LXXIV.

SAMPLE PROGRAM FOR IBM 360 MODEL 365

PROGRAM TO CORRECT TEMPERATURES FOR HEAT LOSS FROM TO N IS
NUMBER OF DATA POINTS, AND NN IS NUMBER OF TEMPERATURES.
GOOD FOR ONLY RUNS 1 - 2.

```
      DIMENSION TEMP(50,20), ORTEMP(50,20), 0(50,20), TIME(50),
     RUN(50,) N(5,10,20), DD(20), 01(50)

      INTEGER TEMP
      INTEGER TIME
      INTEGER RUN
      REAL 1
      DO 7000 II=1,2
 1000 READ(5,1) N,NN
    1 FORMAT (212)
      WRITE (6,10)
   10 FORMAT (1H1,20X,'RAW TEMPERATURE DATA')
      WRITE (6,11)
   11 FORMAT(1H0,2X,'RUN',1X,'TIME',3X,'1',4X,'2',4X,'3',4X,'4',
      4X,'5')
      DO 100 I=1,N
      READ(5,2)RUN(I),01(I),TIME(I),(TEMP(I,J),J=1,NN)
    2 FORMAT (14,A1,1215)
      IF(RUN(I).EQ.0) GO TO 2000
  100 CONTINUE
 2000 N=1-1
   50 T2=65.0
   55 CONTINUE
      A=SORT(12.*24./(42.*0.125))
      B=SORT(12.*08./(42.*0.125))
      DO 300 I=1,N
      DO 200 J=1,4
      M(I,J)=TEMP(I,J)
  200 CONTINUE
      DO 250 J=1,NN
      L=6.0
      IF(J.EQ.2) L=12.0
      IF(J.EQ.3) L=12.0
      IF(II.EQ.1) L=12.0
      C(I,J) = TEMP(I,J)
      XX=1.5/12.
      X=L/12.
      E=6.0/42.0/A Equation 5
      Y=(1.E)/(1.-E) Equation 6
      Z=EXP(-2.0*B*X) Equation 8
      R1=EXP(A*XX)+Y*EXP(-A*XX) Equation 12
```

```
      R2=EXP(A*XX)-Y*EXP(-A*XX) Equation 13
      S1=Z*BXP(B*XX) + EXP (-B*XX) Equation 14
      S2=Z*EXP(B*XX)=EXP(-B*XX) Equation 15
      D=(1.+Y)/(B1-A/B*F2/S2*S1) Equation 19
      ORTEMP(I,J)=(C(I,J)=T2*D)/(1.-D) Equation 20
      IF(C(I,J).EQ.0.0)ORTEMP(I,J)=0.0
      M(I,J)=ORTEMP(I,J)
      IF(T2.EQ.65.0) GO TO 250
      M(I,J)=TEMP(I,J)
  250 CONTINUE
      WRITE (6,4) RUN (I),01(I),TIME(I), (TEMP(J,J),J=1,NN)
    4 FORMAT (1H, I4,A1,1315)
  300 CONTINUE
      WRITE (6,12)
   12 FORMAT ( //,17X,'CORRECTED TEMPERATURE DATA')
      WRITE (6,11)
      DO 400 I=1,N
      WRITE (6,4) RUN (I), 01(I), TIME(I), (M(I,J),J=1,NN)
  400 CONTINUE
 7000 CONTINUE
      WRITE (6,7001)
 7001 (FORMAT (1H1)
      STOP
      END

 $ENTRY
```

C-3 FORMATION OF NO_x

(1) From Bartok, et al (15)

$$\frac{d(NO)}{dt} = 9\text{x}10^{14}e^{-135,000/RT}(N_2)(O_2)^{\frac{1}{2}} - 4.1\text{x}10^{13}e^{-91,000/RT}(NO)^2(O)^{-\frac{1}{2}}$$

where R/is 1.98 cal/gmol °K, T is temperature, °K.

I assume that (N_2) and (O_2) are constant;

$$\text{let } A = 9\text{x}10^{14}e^{-135,000/RT}(N_2)(O_2)^{\frac{1}{2}}$$

$$B = 4.1\text{x}10^{13}e^{-91,000/RT}(O_2)^{-\frac{1}{2}}$$

$$x = (NO)$$

$$\text{then } \frac{dx}{dt} = A - BX^2$$

Integrate x from 0 to NO during t = 0 to t

$$\int_0^{(NO)} \frac{dx}{A-BX^2} = \int_0^t dt$$

$$t = \frac{1}{2\sqrt{AB}}\left[\ell n \left| \frac{\sqrt{B} + \sqrt{B}\,x}{\sqrt{A} - \sqrt{B}\,x}\right.\right]_0^{(NO)}$$

$$2 = \sqrt{AB}\,t - \ell n \left| \frac{\sqrt{A} - \sqrt{B}\ (NO)}{\sqrt{A} - \sqrt{B}\ (NO)} \right| - \ell n \left| \frac{\sqrt{A} + 0}{\sqrt{A} - 0} \right|, \text{ therefore}$$

$$\frac{\sqrt{A} + \sqrt{B}\,(NO)}{\sqrt{A} + \sqrt{B}\,(NO)} = e^{2\sqrt{AB}\,t}$$

Since the left hand side contains absolute values, the solution may be either of two cases; ie, $\pm e^{2\sqrt{AB}\,t}$

Case 1	Case 2
$\frac{\sqrt{A} + \sqrt{B}\,(NO)}{\sqrt{A}\quad \sqrt{B}\,(NO)} = e^{2\sqrt{AB}\,t}$	$\frac{\sqrt{A} + \sqrt{B}\,(NO)}{\sqrt{A} - \sqrt{B}\,(NO)} = -e^{2\sqrt{AB}\,t}$
$\sqrt{A}+\sqrt{B}(NO)=\sqrt{A}e^{2\sqrt{AB}t}-\sqrt{B}e^{2\sqrt{AB}t}(NO)$	$\sqrt{A}+\sqrt{B}(NO)= -e^{2\sqrt{AB}t}\sqrt{A}+\sqrt{B}e^{2\sqrt{AB}t}(NO)$
$(NO)\sqrt{B}\,(1+e^{2\sqrt{AB}t})=\sqrt{A}\,(e^{2\sqrt{AB}t}-1)$	$(NO)\sqrt{B}\,(1-e^{2\sqrt{AB}t})= -\sqrt{A}(1+e^{2\sqrt{AB}t})$
$(NO) = \sqrt{\frac{A}{B}}\left\lvert\frac{e^{2\sqrt{AB}\,t}-1}{e^{2\sqrt{AB}\,t}+1}\right\rvert$	$(NO) = \sqrt{\frac{A}{B}}\left\lvert\frac{e^{2\sqrt{AB}\,t}+1}{e^{2\sqrt{AB}\,t}-1}\right\rvert$

From above, $A = 9x10^{14}e^{-135,000/RT}(N_2)(O_2)^{\frac{1}{2}}$

$$B = 4.1x10^{13}e^{-91,000/RT}(O_2)^{-\frac{1}{2}}$$

$$AB = 36.9x10^{27}e^{-226,000/RT}(N_2)$$

$$\frac{A}{B} = 22.0e^{-44,000/RT}(N_2)(O_2)$$

$$\sqrt{A/B} = 4.68e^{-22,000/RT}\sqrt{(N_2)(O_2)}$$

$$\sqrt{A/B} = 1.92.10^{14}e^{-113,000/RT}\sqrt{(N_2)}$$

Look at Case 1

$$(NO) = 4.68e^{-22,000/RT}\sqrt{(N_2)(O_2)}\left[\frac{e^{3.84tx10^{14}e^{-113,000/RT}\sqrt{N_2}}-1}{e^{3.84tx10^{14}e^{-113,000/RT}\sqrt{N_2}}+1}\right]$$

Let's explore the term in { }. Assume t = 1 second; $(N_2) = 0.78$, $\sqrt{(N_2)} = 0.88$; $T = 3000^{\circ}F$ or $1922^{\circ}K$; $R = 1.988$.

$$e^{3.84(1)x10^{14}e^{113,000/1.998(1922)}\ 0.88} = e^{48.78}$$

and

$e^{48.78}$ >>>> 1 or -1. ∴ the terms in { } = 1

so $(NO) = 4.68e^{-22,000/RT}\sqrt{(N_2)(O_2)}$

Similarly, Case 2 → $(NO) = 4.68\ e^{-22,000/RT}\sqrt{(N_2)(O_2)}$

(2) <u>Sample Calculations</u>

$T = 3000^\circ F$, $R = 1.988$.

% Excess O_2	% NO_2	% O_2	N_2O_2	N_2O_2	(NO)
80	78.17	20.77	0.1624	0.4029	5999
100	78.32	20.82	0.1631	0.4038	5972
120	78.44	20.85	0.1635	0.4044	5981

(3) NO_x to be adjusted to a base temperature of 3000°F to eliminate temperature as a variable in NO_x formation.

$$(NO)_T + 4.68\ 3^{-22,000/RT}\sqrt{(N_2)(O_2)}$$

$$(NO)_{3000^\circ F} = 4.68\ e^{-27,000/R(1922)}\sqrt{(N_2)(O_2)},\ \text{recall } 3000^\circ F{=}1922^\circ K$$

$$\frac{(NO)_T}{(NO)_{3000^\circ F}} = \frac{4.68\ e^{-22,000/RT}\sqrt{(N_2)(O_2)}}{4.68\ e^{-22,000/RT(1922)}\sqrt{(N_2)(O_2)}}$$

$$\frac{(NO)_T}{(NO)_{3000^\circ F}} = e^{-22,000/RT}e^{22,000/R(1922)}$$

$$\frac{(NO)_T}{(NO)_{3000^\circ F}} = 3^{\frac{-22,000}{R}\left(\frac{1}{T}-\frac{1}{1922}\right)}$$

$$\frac{(NO)_T}{(NO)_{3000^\circ F}} = e^{\frac{-22,000}{R}\left(\frac{1922-T}{1922T}\right)} \quad \text{where } R = 1.988$$

Therefore, $(NO)_{3000^\circ F} = (NO_T)\ e^{5.7570\left(\frac{1922-T}{T}\right)}$

(4) Sample Calculation

Run 19, NO_x = 1681ppm, T = 2806°F

$$(NO)_{3000^\circ F} = 1681e^{5.7570\left(\frac{1922-1814}{1814}\right)}$$

$$= 2366 \text{ ppm}$$

C-4 STATISTICS - NO_x AT RUN TEMPERATURE

	$\%N_2$		0	1	5	X_i
Percent Oxygen	80%	Air,	768	1681	1267	3716
		Ar/O_2	966	1202	986	3514
			1734	2883	2253	6870
	100%	Air,	588	2294	888	3770
		Ar/O_2	1176	1089	1022	3287
			1764	3383	1910	7057
	120%	Air,	456	1941	992	3389
		Ar/O_2	1123	1291	1041	3383
			1579	3160	2033	6772
		Σ Air,j	1812	5916	3147	10875
		$\Sigma\ Ar/O_{2,j}$	3265	3510	3049	9824
		$\Sigma x_{,j}$	5077	9426	6196	20699

$X_{..} = 20699$

$\sum_y(\chi_y^2)=27{,}171{,}387$

$r_1 = 2$

$t_1 = 18$

1. Correction term $C = \dfrac{(X_{..})^2}{r_1 t_1} = \dfrac{(20699)^2}{3(6)(2)} = 11{,}901{,}350$

2. Total SS $= \sum_y(\chi_y^2) - C = 27{,}171{,}387 - 11{,}901{,}350 = 15{,}270{,}037$

3. Block SS $= \sum_y(\chi_y^2)/t_1 - C = \dfrac{5077^2 + 9426^3 + 6196^2}{18} - 11{,}901{,}350$

   $= 3{,}400{,}741$

4. Treatment SS $= \sum_y(\chi_y^2)/r_1 - C = \dfrac{27{,}171{,}387}{(2)} - 11{,}901{,}350 = 1{,}684{,}344$

5. Error SS = total SS - Blorla SS - Treatment SS

$$= 15{,}270{,}037 + 3{,}400{,}741 - 1{,}684{,}344 = 16{,}986{,}434$$

$r = 2,\ a = 3,\ b = 3,\ c = 2$

6. $$SSC(\%O_2) = \sum_i (\%O_{2_i})^2/rbc - C = \frac{6870^2+7057^2+6772^2}{(2)(3)(2)} - 11{,}901{,}350 = 3494$$

7. $$SS(\%N_2) = \sum_j (\%N_2)^2/rac - C = \frac{5077^2+9426^2+6196^2}{2(3)(2)} - 11{,}901{,}350 = 849{,}968$$

8. $$SS(Air\text{-}Ar/O_2) = \sum_k (Ck)^2/rab - C = \frac{10875^2+9824^2}{2(3)(3)} - 11{,}901{,}350 = 30683$$

9. $$SS(\%O_2\%N_2) = \sum_y \frac{(\%O_2\%N_2)^2}{rc} - C - SS(\%O_2) - SS(\%N_2)$$

$$= \frac{1734^2+2883^2+\cdots+2033^2}{4} - 11{,}901{,}350 - 3494$$

$$- 849{,}968 = 7905$$

10. $$SS(\%O_2 air - Ar/O_2) = \frac{\sum_{ik} (a_i Ck)^2}{rb} - C - SS(\%O_2) - SS(Air\text{-}Ar/O_2)$$

$$= \frac{3716^2+3514^2+\cdots+3383^2}{6} = 11{,}901{,}350 - 3493 - 30683$$

$$= 415{,}162$$

11. $$SS(\%N_2 Air\text{-}Ar/O_2) = \frac{\sum_{ik} (k_j Ck)^2}{ra} - C - SS(\%N_2) - SS(Air\text{-}Ar/O_2)$$

$$= \frac{1812^2+5916^2+\cdots+3049^2}{6} - 11{,}901{,}350 - 849{,}968$$

$$- 30683 = 628{,}455$$

12. $$SS(\%O_2\%N_2 Air\text{-}Ar/O_2) = \frac{\sum_{yb} (a_i b_j C_k)^2}{r} - C - SS(\%O_2) - SS(\%N_2)$$

$$- SS(Air\text{-}Ar/O_2) - SS(\%O_2\%N_2) - SS(\%O_2 Air\text{-}Ar/O_2)$$

$$- SS(\%N_2 Air\text{-}Ar/O_2) = \frac{768^2+1681^2+\cdots+1041^2}{2} - 11{,}901{,}350$$

$$- 849{,}968 - 30683 - 47905 - 415{,}162 - 628{,}455 = -291{,}324$$

ANALYSIS OF VARIANCE

Source	Degree of Freedom	Sum of Squares	MSS	F	
Block	r-1 = 1	-3,400,741	-3,400,741	-3.40	6.04
%O_2(A)	a-1 = 2	3494	1747	0.002	
%N_2(B)	b-1 = 2	849,968	424984	0.425	**Significant at 95% confidence level.
Air-Ar/O_2	c-1 = 1	30683	30683	0.031	
AB	(a-1)(b-1)=4	47905	11976	0.012	
AC	(a-1)(c-1)=2	415,162	207581	0.008	
BC	(b-1)(c-1)=2	628,455	314,228	0.314	
ABC	(a-1)(b-1)(c-1)=4	-291324	-72831	-0.073	
Error	(r-1)(abc-1)-17	16,986,434	999,202	-	
Total	abcr-1=35	15270036	Not Significant		

STATISTICS - NO_x DATA AT 3000°F

	$\%N_2$	0	1	5	X_i
80%	Air	1140	2366	1898	5404
	Ar/O_2	2607	2811	1773	7191
		3747	5177	3671	12595
100%	Air	652	2458	1231	4341
	Ar/O_2	1391	5386	2053	8830
		2043	7844	3284	13171
120%	Air	557	1841	1098	3496
	Ar/O_2	2173	2126	1784	6083
		2730	3967	2882	9579
	$\Sigma\ Air_{ij}$	2349	6665	4227	13241
	$\Sigma\ Ar/O_{2ij}$	6171	10323	5610	22104
	$\Sigma\chi._j$	8520	16988	9837	35345

$X.. = 35345$

$\Sigma_y(\chi_y^2) = 88,812,169$

$r_1 = 2$

$t_1 = 18$

1. Correction term $C = \frac{(X...)^2}{r_1 t_1} = \frac{(35345)^2}{2(18)} = 34,701,917.4$

2. Total SS $= \Sigma_y(\chi_y^2) - C = 88,812,169 - 34,701,914.7 = 54.110,251.6$

3. Block SS $= \Sigma_y(\chi_{ij})^2/t_1 - C = \frac{8520^2+16998^2+9837^2}{18} - 34,701,917.4$

   $= 9,244,937.0$

4. Treatment SS $= \Sigma_y(\chi_y^2)/r_1 - C = \frac{88,812,169}{2} - 34,701,917.4 = 9,704,169.1$

5. Error SS = Total SS - Block SS - Treatment SS

   $= 54,110,251.6 + 0,244,937.0 - 9,704,169.1 = 53,631,019.5$

———o———

$r = 2,\ a = 3,\ b = 3,\ c = 2$

6. $SS(\%O_2) = \sum_i (\%O_2)_i/Rbc\text{-}C = \dfrac{12595^2+13171^2+13241^2}{2(3)(2)} - 34{,}701{,}917.4$

$= 7{,}584{,}194.8$

7. $SS(\%N_2) = \sum_j (\%N_2)_j/rac\text{-}C = \dfrac{8520^2+16988^2+9837^2}{2(3)(2)} - 34{,}701{,}917.4$

$= 3{,}460{,}508.7$

8. $SS(Air/Ar\text{-}O) = \sum_k (Ck)^2/rab\text{-}C = \dfrac{13241^2+22104^2}{2(3)(3)} - 34{,}701{,}917.4$

$= 2{,}182{,}021.3$

9. $SS(\%O_2\%N_2) = \sum_y (\%O_2\%N_2)^2/rc\text{-}C\text{-}SS(\%O_2) - SS(\%N_2)$

$= \dfrac{37472 + \cdots +2882^2}{4} - 34{,}701{,}917.4 - 7{,}584{,}194.8$

$- 3{,}460{,}508.7 = -5{,}171{,}537.7$

10. $SS(\%O_2Air/Ar\text{-}O_2) = \sum_k (Air(k)^2/rb\text{-}C\text{-}SS(\%O_2) - SS(Air/Ar\text{-}O_2)$

$= \dfrac{5404^2 + \cdots +6083^2}{6} - 34{,}701{,}917.4 - 7{,}584{,}194.8$

$- 2{,}182{,}021.3 = -6{,}642{,}836.4$

11. $SS(\%N_2Air\text{-}Ar/O_2) = \sum_s (A_j Ck)/(a\text{-}C\text{-}SS(\%N_2) - SS(Air\text{-}Ar/O_2)$

$= \dfrac{2269^2+ \cdots +5610^2}{6} - 34{,}701{,}917.4 - 3{,}460{,}508.7$

$- 2{,}182{,}021.3 = 309{,}756{,}8$

12. $$\text{SS}(\%\text{O}_2\%\text{N}_2\text{Air-Ar/O}_2) = \sum_{jk} \frac{(A_1 b_j Ck)^2}{r} - C - \text{SS}(\%\text{O}_2) - \text{SS}(\%\text{N}_2)$$

$$- \text{SS}(\text{Air-Ar/O}_2) - \text{SS}(\%\text{O}_2\%\text{N})$$

$$-\text{SS}(\%\text{O}_2\text{Air-Ar/O}_2 - \text{SS}(\%\text{N}_2\text{Air-Ar/O}_2$$

$$= \frac{1140^2 + \cdots + 1784^2}{2} - 34{,}701{,}917.4 - 7{,}584{,}194.8$$

$$- 3{,}460{,}508.7 - 2{,}182{,}021.3$$

$$+ 5{,}171{,}537.7 + 6{,}642{,}836.4$$

$$- 309{,}756.8$$

$$= 7{,}982{,}059.6$$

ANALYSIS OF VARIANCE

Source	Degrees of freedom	Sum of Squares	MSS	F	
Block	r-1=1	-9,244,937	-9,224,937	-2.92	6.04
$\%\text{O}_2$(A)	a-1=2	7,584,194.8	3,792,097.4	1.20	
$\%\text{N}_2$(B)	b-1=2	3,460,508.7	1,730,254.3	0.55	
Air-Ar/O_2(C)	c-1=1	2,182,021.3	2,182,021.3	0.69	
AB	(a-1)(b-1)=4	-5,171,537.7	-1,292,884.4	-0.41	
AC	(a-1)(c-1)=2	-6,642,836.4	-3,321,418.2	-1.05	
BC	(b-1)(c-1)=2	309,756.8	154,878.4	0.05	
ABC	(a-1(b-1(c-1)=4	7,982,059.6	1,995,514.9	0.63	
Error	(r-1)(abc-1)=17	53,631,019.5	3,154,765.8	-	
Total	abcr-1=35	54,110,249.6			

C-5 ADIABATIC FLAME TEMPERATURE

Basis: 1 lb.-mol of fuel oil (molecular weight 234.4 lb./lb.mol.)

Fule Oil Analysis:		
	Carbon	87.09%
	Hydrogen	12.81%
	Nitrogen	0.02%
	Sulfur	0.145%
	Oxygen	0.01%
	Water	0.00%
	Ash	0.01%

Basic Reactions are:

$$2C_{17}H_{30} + \frac{49O_2}{\text{Heat}} \rightarrow 34CO_2 + 30H_2O$$

$$(C + O_2 \longrightarrow CO_2)$$

$$(2H_2 + O_2 \longrightarrow 2H_2O)$$

$$(N_2 + O_2 \longrightarrow 2NO)$$

$$(S + O_2 \longrightarrow SO_2)$$

Carbon: 204.0 lbs = 17 moles ——— 17 moles of CO_2

Hydrogen: 30.0 lbs = 14.92 moles ——— 14.92 moles of H_2O

Nitrogen: 0.047 lbs = 0.0017 moles ——— .0034 moles of NO

Sulfur: 0.34 lbs = 0.0106 moles ——— .0106 moles of SO_2

Oxygen: 0.023 lbs = 0.0007 moles

Oxygen Required: 17 + 14.92 + 0.0034 + 0.0106 - 0.0007

= 24,4716 = 24.5 lb. moles

Air Required: $24.5\ (\frac{1.00}{0.21}) = 116.7$ lb. moles

Nitrogen Present: $24.5\ (\frac{.79}{.21}) = 92.2$ lb. moles

Helium Flow: $\frac{234.4 \text{ lb fuel}}{0.116 \text{ lb/min}} * \frac{825 \text{ cc}}{\text{min}} * \frac{0.0251}{0.1769} \text{ g/cc} * \frac{\text{lb}}{454\text{g}} * \frac{\text{lb-mole}}{416}$

$= 130$ lb. mole

$$(-\Delta H_c)_{net} = \sum_{i=1}^{n} (mCp)_i \Delta T$$

where $(-\Delta H_c)_{net} = 4.44 \times 10^6$ BTU

$\Delta T = T_2 - 530^{\circ}R$

mean $\overline{Cp}$: Water - 9.58 Btu/°R mole

Carbon dioxide - 11,42 Btu/°R mole

Nitric oxide - 7.81 Btu/°R mole

Oxygen - 7.88 Btu/°R mole

Sulfur dioxide - 11.65 Btu/°R mole

Nitrogen - 7.65 Btu/°R mole

Helium - 4.97 Btu/°R mole

$$b\ (4.44\text{x}10^6) = (T_2-530) \Big[17(11.42) + 14.92(9.58) + 0.0034(7.81) + 0.0106(11.65) + 130(4.97) + x(24.5)(7.88) + y(92.2)(7.65)\Big]$$

At 80 and 100% oxygen, x = 0.0; y = 0.8 and y = 1.0 respectively and b = 0.8 and 1.0 respectively

At 120% oxygen, x = 0.2, y = 1.2, b = 1.0

Results:

% Excess Oxygen	Adiabatic Flame Temperature (°R)
80	2825
100	3159
120	2906

C-6 HEAT BALANCE

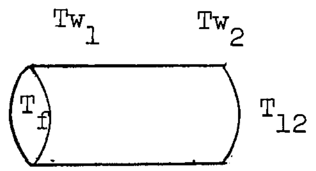
Flow

80% Oxygen: $21.60(0.067) + 825(\frac{0.010}{28312})60 = 1.4647$ lb/hr

100% Oxygen: $27.00(0.067) + 825(\frac{0.010}{28312})60 = 1.8265$ lb/hr

120% Oxygen: $32.40(0.067) + 825(\frac{0.010}{28312})60 = 2.1883$ lb/hr

Heat Balance



$$\begin{aligned} A &= \pi DL \\ &= \pi(1)(3/12) \\ &= 0.7854 \text{ ft}^2 \end{aligned}$$

T_a - ambient temperature

T_{w_1} & T_{w_2} - wall temperatures at flame height and 12 inches above

T_f - flame temperature

T_{12} - Temperature of gas 12 inches upstream

A - surface area

D - Diameter of combustor - 3 inches

L - length of combustor - 1 foot

m - flowrate

Heat change in reactor: $mCp(T_f - T_{12})$

Heat loss from reactor: $AU\left[(T_{w_1} + T_{w_2})/2 - T_a\right]$

Cp^* is specified heat ≈ 0.21 Btu/lb°R

U^* is heat transfer coefficient ≈ 4 Btu/°R ft^2

* from <u>Chemical Engineer's Manual</u> (Keys and Deem)

The following Table XXXIX presents temperature data, heat change in reactor (h_R), heat loss from reactor (h_o) and difference between the two, ($\Delta h = h - h$):

TABLE XXXIX

HEAT BALANCE DATA AND RESULTS

Run	Tf	T_{12}	Tw1	Tw2	Hr	Ho	ΔH
13	3027	1070	461	329*	899.3	989.6	-90.3
14	2754	677	355	279	796.7	744.6	52.1
15	2937	726	378	302	848.1	816.8	31.2
16	2773	575	355	377	676.1	898.5	-222.4
17	2884	689	345	289	1008.7	744.6	264.1
18	2782	685	366	330	645.0	841.9	-196.3
19	2806	693	358	342	649.9	848.2	-198.3
20	2959	765	332	333	841.5	793.2	48.3
21	3032	872	366	327	992.6	837.2	115.4
22	2522	684	310	265	565.3	651.9	-86.5
23	2884	762	361	275	813.9	747.7	66.2
24-25	2427	718	317	306	785.4	727.3	58.1
26	2555	605	339	358	599.8	843.5	-243.7
27	2695	773	381	397	883.2	970.8	-87.5
28	2298	687	369	349	617.9	876.5	-258.6
29	2198	764	389	393	550.0	977.0	-427.0
30	2532	616	338	372	589.3	863.9	-274.6
31	2829	700	369	433	654.8	1008.4	-353.6
32	2626	965	350	380	637.1	895.4	-258.2
33	2704	957	470	425	802.8	1154.5	-351.7
34	2460	612	306	363	462.3	779.5	-337.2
35	2920	772	348	426	843.1	964.5	-121.4
36	2861	876	354	390	912.2	917.3	-5.2
37	2939	977	366	338	744.9	854.5	-109.6
38	2774	929	363	356	567.5	878.1	-310.6
39	2752	962	352	317	686.6	799.5	-113.0
40	2852	1300	419	401	713.2	1036.3	-323.5

*Defective thermocouple, neglected zero readings.

APPENDIX D

APPENDIX D

RAW TEMPERATURE AND CORRECTED TEMPERATURE DATA, RUNS 8-40

The following tables contain all of the experimental (raw) temperature data and the corrected temperature data for experimental Runs 8 through 40. The tables for Runs 1 through 7 were presented in the chapter on results.

TABLE XL

RAW TEMPERATURE DATA (RUN 3)

RAW TEMPERATURE DATA

RUN	TIME MINS	1	2	3	4	5	6	7	8	9	10	11	12
					DEGREES F								
8	0	145	238	0	0	209	307	421	834	946	1513	2231	445
8	15	146	211	0	0	210	311	401	742	585	1408	2338	449
8	30	151	244	0	0	208	304	392	816	646	1784	2158	451
8	45	148	244	0	0	214	312	392	782	842	2095	2282	451
8	60	158	244	0	0	212	305	392	709	644	2140	2260	453
8	78	157	242	0	0	221	311	402	777	709	2211	2359	450
8	90	158	240	0	0	222	313	403	773	742	2190	2335	459
8	100	156	235	0	0	224	321	421	816	823	2179	2331	455
8	110	166	252	0	0	226	328	444	823	960	2225	2380	460
8	120	167	253	0	0	221	319	437	774	801	2205	2376	458
8	130	164	248	0	0	222	324	451	860	852	2186	2366	466
8	140	161	247	0	0	225	323	449	865	854	2197	2400	464
8	150	160	246	0	0	232	334	484	960	1240	2214	2409	462
8	160	162	256	343	412	234	334	482	954	1162	2230	2422	454
8	170	174	292	341	415	234	336	481	857	947	2214	2424	450
8	180	178	270	0	416	230	337	491	771	1042	2214	2407	452

CORRECTED TEMPERATURE DATA

RUN	TIME MINS	1	2	3	4	5	6	7	8	9	10	11	12
					DEGREES F								
8	0	145	238	0	0	269	408	570	1178	1315	2120	3139	604
8	15	146	211	0	0	270	414	541	1044	803	1971	3291	610
8	30	151	244	0	0	267	404	529	1151	889	2504	3035	612
8	45	148	244	0	0	276	415	529	1102	1167	2946	3211	612
8	60	158	244	0	0	273	405	529	997	886	3010	3180	615
8	78	157	242	0	0	286	414	543	1095	979	3110	3320	611
8	90	158	240	0	0	287	416	544	1089	1025	3081	3286	624
8	100	156	235	0	0	290	428	570	1151	1140	3065	3281	618
8	110	166	252	0	0	293	438	602	1162	1335	3130	3350	625
8	120	167	253	0	0	286	425	592	1091	1109	3102	3345	622
8	130	164	248	0	0	287	432	612	1215	1182	3075	3330	634
8	140	161	247	0	0	292	431	610	1222	1184	3091	3379	631
8	150	160	246	0	0	302	446	659	1360	1732	3115	3391	628
8	160	162	256	343	412	304	446	656	1351	1622	3137	3410	617
8	170	174	292	341	415	304	449	655	1211	1316	3115	3413	611
8	180	178	270	0	416	299	451	669	1086	1451	3115	3389	614

TABLE XLI

RAW TEMPERATURE DATA (RUN 9)

RAW TEMPERATURE DATA

RUN	TIME MINS	1	2	3	4	5	6	7	8	9	10	11	12
					DEGREES F								
9A	0	72	70	62	68	71	71	72	71	72	69	69	72
9A	0	106	167	316	255	146	234	468	113	1638	2380	2465	475
9A	130	156	211	311	323	147	238	379	737	1312	1962	2094	479
9A	150	148	209	328	319	146	264	461	829	1611	2336	2412	494
9A	165	148	224	377	338	139	251	450	731	1720	2290	2220	477
9A	180	148	232	377	340	141	253	483	731	1456	2089	0	0
9B	0	87	96	132	162	157	226	410	924	1460	2427	2576	421
9B	40	117	198	365	300	137	236	443	822	1456	2329	2502	470
9B	60	132	238	402	346	200	316	500	852	1320	2354	2485	476
9B	110	442	462	542	539	518	564	665	848	1206	2184	2240	674
9B	130	490	471	557	540	524	597	686	862	1228	2244	2279	662
9B	195	397	406	467	459	439	497	579	748	1005	2032	2041	618
9B	210	370	386	471	462	466	527	614	781	1150	2056	2261	485
9B	225	439	454	527	516	495	555	653	835	1216	2196	2217	693
9B	240	390	411	500	491	499	550	643	809	1182	2143	2197	675
9B	255	362	376	432	442	450	504	602	763	1109	2039	2067	624
9B	270	374	376	466	446	456	518	606	782	1105	2051	2080	630
9B	285	363	364	450	440	456	509	599	772	1092	2053	2093	638
9B	300	389	386	452	446	456	509	594	776	1061	2048	2054	619

TABLE XLII

CORRECTED RAW TEMPERATURE DATA (RUN 9)

CORRECTED TEMPERATURE DATA

RUN	TIME MINS	1	2	3	4	5	6	7	8	9	10	11	12
					DEGREES F								
9A	0	72	70	62	68	71	71	72	71	72	69	69	72
9A	0	106	167	316	255	177	302	634	131	2294	3348	3468	644
9A	130	156	211	311	323	178	307	507	1034	1832	2754	2942	649
9A	150	148	209	328	319	177	344	624	1167	2256	3285	3393	671
9A	165	148	224	377	338	167	326	608	1026	2411	3220	3120	647
9A	180	148	232	377	340	170	329	655	1026	2036	2935	0	0
9B	0	87	96	132	162	195	293	554	1308	2044	3417	3628	570
9B	40	117	198	365	300	167	307	601	1160	2039	3278	3523	639
9B	60	132	238	402	346	256	421	682	1204	1846	3313	3499	648
9B	110	442	462	542	539	707	773	916	1198	1684	3072	3152	929
9B	130	490	471	557	540	716	820	946	1218	1715	3157	3207	912
9B	195	397	406	467	459	595	678	794	1053	1399	2856	2869	849
9B	210	370	386	471	462	634	720	844	1101	1604	2890	3181	661
9B	225	439	454	527	516	675	760	899	1179	1698	3089	3119	956
9B	240	390	411	500	491	680	753	885	1141	1650	3014	3091	930
9B	255	362	376	432	442	611	688	827	1075	1546	2866	2906	858
9B	270	374	376	466	446	619	707	832	1102	1541	2883	2924	866
9B	285	363	364	450	440	619	695	822	1088	1522	2886	2943	878
9B	300	389	386	452	446	619	695	815	1094	1478	2879	2888	851

TABLE XLIII

RAW TEMPERATURE DATA (RUN 10)

RAW TEMPERATURE DATA

RUN	TIME	1	2	3	4	5	6	7	8	9	10	11	12
	MINS				DEGREES F								
10	0	82	112	198	140	101	158	316	634	1397	0	2195	375
10	30	90	158	271	197	114	184	361	621	1409	1834	2166	400
10	40	92	172	283	198	114	188	368	628	1433	1835	2207	405
10	55	93	178	288	202	117	196	380	652	1378	1865	2186	415
10	70	97	202	304	230	126	206	384	653	1386	1821	2192	434
10	85	100	206	304	232	126	210	384	655	1413	1787	2192	426
10	100	92	212	302	226	126	210	377	651	1392	1732	2195	420
10	115	113	212	304	246	124	211	985	644	1379	1739	2158	428
10	130	107	215	303	245	123	211	383	634	1375	1739	2150	432
10	145	110	215	302	247	123	214	372	640	1378	1787	2175	426
10	160	119	216	303	244	121	210	378	641	1363	1834	2215	431
10	175	117	220	306	260	125	216	375	649	1378	1773	2175	427
10	190	124	220	296	262	124	214	376	642	1373	1769	2192	435
10	205	123	218	291	257	121	212	376	637	1381	1769	2195	409
10	220	121	208	285	255	120	210	373	641	1400	1818	2158	414
10	235	120	214	288	248	120	209	371	642	1364	1782	2166	396
10	240	118	213	284	244	199	210	370	643	1364	1804	2130	410

CORRECTED TEMPERATURE DATA

RUN	TIME	1	2	3	4	5	6	7	8	9	10	11	12
	MINS				DEGREES F								
10	0	82	112	198	140	116	196	421	888	1955	0	3088	504
10	30	90	158	271	197	134	233	485	869	1972	2575	3047	540
10	40	92	172	283	198	134	239	495	879	2006	2577	3105	547
10	55	93	178	288	202	138	250	512	914	1928	2619	3075	561
10	70	97	202	304	230	151	265	517	916	1939	2557	3083	588
10	85	100	206	304	232	151	270	517	918	1978	2509	3083	577
10	100	92	212	302	226	151	270	507	913	1948	2431	3088	568
10	115	118	212	304	246	148	272	1370	903	1929	2440	3035	580
10	130	107	215	303	245	147	272	516	888	1924	2440	3024	585
10	145	110	215	302	247	147	276	500	897	1928	2509	3059	577
10	160	119	216	303	244	144	270	509	898	1907	2575	3116	584
10	175	117	220	306	260	150	279	504	910	1928	2489	3059	578
10	190	124	220	296	262	148	276	506	900	1921	2483	3083	590
10	205	123	218	291	257	144	273	506	892	1932	2483	3088	553
10	220	121	208	285	255	143	270	502	898	1959	2553	3035	560
10	235	120	214	288	248	143	269	499	900	1908	2501	3047	534
10	240	118	213	284	244	255	270	497	901	1908	2533	3066	554

TABLE XLIV

RAW TEMPERATURE DATA (RUN 11)

RAW TEMPERATURE DATA

RUN	TIME	1	2	3	4	5	6	7	8	9	10	11	12
	MINS				DEGREES F								
11	0	97	162	274	218	114	182	365	664	1504	0	2252	447
11	15	109	198	319	262	122	202	390	662	1457	0	2218	452
11	30	112	209	324	254	125	213	402	660	1433	0	2214	462
11	60	113	230	339	282	135	224	396	770	1268	0	2250	463
11	75	113	230	338	280	135	224	399	782	1272	0	2245	458
11	90	120	228	329	290	140	230	396	758	1118	0	2185	461
11	105	118	222	324	294	137	228	379	762	1098	0	2175	456
11	120	115	215	321	299	135	228	382	781	1050	0	2218	466
11	135	123	220	326	303	136	223	388	774	1032	0	2222	473
11	150	121	223	326	303	133	231	390	783	1040	0	2237	474
11	165	122	224	326	302	134	227	382	776	1048	0	2225	475
11	180	119	226	321	301	131	231	384	764	1081	0	2218	478

CORRECTED TEMPERATURE DATA

RUN	TIME	1	2	3	4	5	6	7	8	9	10	11	12
	MINS				DEGREES F								
11	0	97	162	274	218	134	231	490	931	2107	0	3169	607
11	15	109	198	319	262	145	259	526	929	2040	0	3120	614
11	30	112	209	324	254	150	275	543	926	2006	0	3115	628
11	60	113	230	339	282	164	290	534	1085	1772	0	3166	629
11	75	113	230	338	280	164	290	539	1102	1778	0	3159	622
11	90	120	228	329	290	171	299	534	1068	1559	0	3073	627
11	105	118	222	324	294	167	296	510	1073	1531	0	3059	619
11	120	115	215	321	299	164	296	514	1101	1463	0	3120	634
11	135	123	220	326	303	165	289	523	1091	1437	0	3126	644
11	150	121	223	326	303	161	300	526	1104	1448	0	3147	645
11	165	122	224	326	302	162	294	514	1094	1460	0	3130	646
11	180	119	226	321	301	158	300	517	1076	1507	0	3120	651

TABLE XLV

RAW TEMPERATURE DATA (RUN 12)

RAW TEMPERATURE DATA

RUN	TIME MINS	1	2	3	4	5	6	7	8	9	10	11	12
					DEGREES F								
12	0	116	173	275	257	142	244	409	894	1489	1804	1980	479
12	15	124	229	312	259	148	268	448	875	1377	1861	1981	485
12	30	128	230	318	272	168	284	457	841	1404	1836	1981	493
12	45	145	255	336	281	197	318	497	841	1410	1800	2106	501
12	80	142	244	320	301	180	295	471	756	1282	1817	2249	474
12	105	144	253	325	298	194	307	473	712	1302	1804	2258	479
12	120	157	265	335	302	224	335	491	710	1040	1719	2238	498
12	135	161	269	335	310	225	331	491	756	1056	1714	2254	503
12	150	167	270	328	310	230	332	480	722	1030	1770	2245	509
12	180	135	262	324	292	237	338	485	731	1150	1722	2253	506
12	195	160	259	321	295	234	332	475	703	1101	1705	2250	505
12	210	169	269	318	288	237	342	493	818	1090	1722	2256	505

CORRECTED TEMPERATURE DATA

RUN	TIME MINS	1	2	3	4	5	6	7	8	9	10	11	12
					DEGREES F								
12	0	116	173	275	257	174	319	553	1264	2086	2533	2783	652
12	15	124	229	312	259	182	353	608	1237	1927	2614	2784	661
12	30	128	230	318	272	211	375	621	1188	1965	2578	2784	672
12	45	145	255	336	281	252	424	678	1188	1973	2527	2961	683
12	80	142	244	320	301	228	391	641	1065	1792	2551	3164	645
12	105	144	253	325	298	248	408	644	1001	1820	2533	3177	652
12	120	157	265	335	302	290	448	669	998	1448	2412	3149	679
12	135	161	269	335	310	292	442	669	1065	1471	2405	3171	686
12	150	167	270	328	310	299	443	654	1015	1434	2484	3159	695
12	180	135	262	324	292	309	452	661	1028	1604	2416	3170	690
12	195	160	259	321	295	304	443	646	988	1535	2392	3166	689
12	210	169	269	318	288	309	458	672	1154	1519	2416	3174	689

TABLE XLVI

RAW TEMPERATURE DATA (RUN 13)

RAW TEMPERATURE DATA

RUN	TIME MINS	1	2	3	4	5	6	7	8	9	10
					DEGREES F						
13	0	62	66	69	60	68	70	70	71	65	0
13	30	108	112	150	162	142	594	601	867	1961	0
13	50	169	171	393	215	161	543	942	760	2096	0
13	65	209	216	437	242	183	638	752	665	1516	1998
13	80	227	237	441	278	204	704	711	659	1331	2095
13	90	239	249	452	282	201	690	765	658	1404	2105
13	105	267	274	457	305	241	722	706	658	1412	2091
13	120	278	287	454	318	254	711	698	656	1355	2084
13	135	283	292	449	321	260	693	693	640	1266	2107
13	150	285	295	463	326	275	734	741	663	1274	2140
13	195	288	306	480	330	284	736	705	956	1368	2072
13	210	302	309	469	328	294	743	736	800	1439	2077
13	225	294	306	459	319	289	741	749	780	1455	2071
13	240	0	0	454	0	289	738	750	779	1309	2107
13	255	302	312	453	327	287	738	741	759	1386	2081
13	270	0	0	465	0	302	777	726	738	1428	2069
13	285	0	0	452	0	302	758	705	842	1459	2071
13	300	0	0	460	0	302	734	771	1059	1247	2105
13	315	314	324	461	346	294	703	767	901	1244	2136
13	345	0	0	459	328	285	719	788	1140	1332	2174
13	360	0	0	462	0	273	724	769	1078	1244	2160
13	375	0	0	466	0	271	858	869	1194	1378	2173
13	390	0	0	486	0	276	917	924	1120	1442	2172
13	405	0	0	508	0	280	898	897	1042	1356	2167
13	420	0	0	512	0	286	918	913	1044	1290	2205
13	435	0	0	514	356	322	918	909	994	1434	2091
13	450	0	0	526	346	297	984	981	1202	1401	2165
13	465	330	341	520	410	296	955	980	1056	1232	2135
13	480	333	342	526	418	297	1017	1004	1043	1372	2160
13	495	339	350	526	428	302	1073	1053	1082	1542	2066
13	525	341	354	528	439	299	1021	1021	1108	1645	2129
13	540	0	0	490	373	316	1032	1033	1220	1468	2063
13	555	0	0	488	356	325	652	1294	1334	1411	2210
13	570	0	0	459	301	327	665	1425	1230	1660	2090
13	585	0	0	442	285	317	664	1094	1501	1620	2091
13	600	352	358	435	378	303	662	1262	1264	1692	2149
13	615	323	333	437	358	292	650	1227	1334	1638	2070
13	630	318	328	434	347	288	631	1258	1189	1668	2077

TABLE XLVI (Continued)

CORRECTED TEMPERATURE DATA

RUN	TIME MINS	1	2	3	4	5	6	7	8	9	10
					DEGREES F						
13	0	62	66	69	60	68	70	70	71	65	0
13	30	108	112	150	162	172	814	824	1224	2754	0
13	50	169	171	393	215	199	741	1308	1069	2946	0
13	65	209	216	437	242	230	876	1038	931	2122	2860
13	80	227	237	441	278	260	970	980	923	1860	3001
13	90	239	249	452	282	256	950	1056	921	1963	3015
13	105	267	274	457	305	313	995	973	921	1975	2995
13	120	278	287	454	318	331	980	961	918	1894	2985
13	135	283	292	449	321	340	954	954	895	1768	3018
13	150	285	295	463	326	361	1012	1022	928	1779	3066
13	195	288	306	480	330	374	1015	971	1352	1912	2968
13	210	302	309	469	328	388	1025	1015	1127	2013	2975
13	225	294	306	459	319	381	1022	1034	1098	2036	2966
13	240	0	0	454	0	381	1018	1035	1096	1829	3018
13	255	302	312	453	327	378	1018	1022	1067	1938	2981
13	270	0	0	465	0	399	1073	1001	1037	1997	2963
13	285	0	0	452	0	399	1046	971	1187	2041	2966
13	300	0	0	460	0	399	1012	1065	1501	1741	3015
13	315	314	324	461	346	388	968	1059	1273	1736	3060
13	345	0	0	459	328	375	991	1089	1619	1861	3115
13	360	0	0	462	0	358	998	1062	1529	1736	3095
13	375	0	0	466	0	355	1188	1204	1697	1926	3114
13	390	0	0	486	0	362	1272	1282	1590	2017	3112
13	405	0	0	508	0	368	1245	1244	1477	1895	3105
13	420	0	0	512	0	377	1274	1266	1480	1802	3160
13	435	0	0	514	356	428	1274	1261	1407	2006	2995
13	450	0	0	526	346	392	1367	1363	1708	1959	3102
13	465	330	341	520	410	391	1326	1362	1497	1719	3059
13	480	333	342	526	418	392	1414	1396	1478	1918	3095
13	495	339	350	528	428	399	1494	1465	1535	2159	2959
13	525	341	354	528	439	395	1420	1420	1572	2305	3050
13	540	0	0	490	373	419	1435	1437	1734	2054	2955
13	555	0	0	488	356	432	896	1807	1899	1973	3167
13	570	0	0	459	301	435	915	1993	1749	2327	2994
13	585	0	0	442	285	421	913	1523	2141	2270	2995
13	600	352	358	435	378	401	910	1762	1798	2372	3079
13	615	323	333	437	358	385	893	1712	1899	2296	2965
13	630	318	328	434	347	379	866	1756	1690	2338	2975

TABLE XLVII

RAW TEMPERATURE DATA (RUN 13 RADIAL)

RAW TEMPERATURE DATA

RUN	TIME MINS	X INCHES	1	2	3	4	5
				DEGREES F			
13	150	1.5	4955	3202	2953	1751	1152
13	150	2.1	1138	915	1558	2190	1271
13	150	3.6	1879	1236	1018	891	842
13	150	15.5	1796	1216	990	871	810
13	330	1.5	1144	2997	3065	1537	1067
13	330	2.1	1080	823	1681	2200	1234
13	330	3.6	4389	2677	1428	849	849
13	330	15.5	1980	1311	1023	902	819
13	510	1.5	1555	2689	3053	1845	1012
13	510	2.1	1862	1251	1738	2058	1288
13	510	3.6	4587	2381	1352	1007	974
13	510	15.5	2090	1481	1717	1206	1134

CORRECTED TEMPERATURE DATA

RUN	TIME MINS	X INCHES	1	2	3	4	5
				DEGREES F			
13	150	1.5	4955	3202	2953	1751	1152
13	150	2.1	1138	915	1558	2190	1271
13	150	3.6	1879	1236	1018	891	842
13	150	15.5	1796	1216	990	871	810
13	330	1.5	1144	2997	3065	1537	1067
13	330	2.1	1080	823	1681	2200	1234
13	330	3.6	4389	2677	1428	849	849
13	330	15.5	1980	1311	1023	902	819
13	510	1.5	1555	2689	3053	1845	1012
13	510	2.1	1862	1251	1738	2058	1288
13	510	3.6	4587	2381	1352	1007	974
13	510	15.5	2090	1481	1717	1206	1134

TABLE XLVIII

RAW TEMPERATURE DATA (RUN 14)

RAW TEMPERATURE DATA

RUN	TIME MINS	1	2	3	4	5	6	7	8	9	10
					DEGREES F						
14	0	71	73	74	74	74	74	73	74	67	41
14	15	104	117	200	137	147	384	722	878	1565	1982
14	30	150	157	308	204	170	451	937	516	1522	1968
14	45	193	202	386	249	180	510	1033	565	1380	1931
14	60	223	241	421	271	189	548	1094	574	1248	1908
14	75	249	265	438	304	199	569	1092	581	1387	1892
14	90	254	271	447	312	204	586	1041	600	1369	1852
14	105	274	287	449	314	202	566	936	536	1411	1859
14	120	277	285	427	329	208	554	848	818	1430	1896
14	135	277	284	418	339	271	564	996	837	1355	2120
14	150	278	283	387	329	297	560	974	840	1295	2036
14	165	269	274	357	311	283	510	968	592	1123	1955
14	180	240	244	311	286	265	462	846	557	948	1926
14	195	245	250	308	289	250	455	794	566	1058	1960
14	210	229	234	289	274	252	434	752	535	938	1895
14	225	218	221	273	264	238	414	714	512	805	1809
14	240	204	208	260	251	238	415	707	519	917	1820

CORRECTED TEMPERATURE DATA

RUN	TIME MINS	1	2	3	4	5	6	7	8	9	10
					DEGREES F						
14	0	71	73	74	74	74	74	73	74	67	41
14	15	104	117	200	137	178	514	994	1238	2190	2836
14	30	150	157	308	204	210	609	1299	714	2129	2815
14	45	193	202	386	249	225	693	1435	785	1928	2762
14	60	223	241	421	271	237	747	1522	798	1740	2729
14	75	249	265	438	304	252	777	1519	808	1938	2705
14	90	254	271	447	312	259	801	1447	836	1912	2648
14	105	274	287	449	314	256	772	1298	743	1972	2658
14	120	277	285	427	329	264	755	1173	1151	1999	2711
14	135	277	284	418	339	354	770	1383	1179	1892	3035
14	150	278	283	387	329	391	764	1352	1183	1807	2914
14	165	269	274	357	311	371	693	1343	824	1563	2797
14	180	240	244	311	286	345	625	1170	773	1315	2755
14	195	245	250	308	289	324	615	1096	786	1471	2804
14	210	229	234	289	274	327	585	1036	741	1300	2710
14	225	218	221	273	264	307	557	983	708	1112	2585
14	240	204	208	260	251	307	558	973	718	1271	2601

TABLE XLIX

RAW TEMPERATURE DATA (RUN 15)

RAW TEMPERATURE DATA

RUN	TIME MINS	1	2	3	4	5	6	7	8	9	10
					DEGREES F						
15	0	62	66	66	67	66	68	68	65	64	74
15	15	102	108	171	151	158	371	830	1480	1629	2070
15	30	176	182	316	220	199	482	999	1329	1730	2111
15	45	212	221	377	266	214	528	864	1179	1571	2108
15	60	260	267	413	312	231	560	962	1161	1594	2024
15	75	284	292	434	332	250	569	994	1124	1435	2024
15	90	291	300	470	346	272	610	1012	839	1547	2037
15	105	300	309	471	354	283	607	1056	1324	1475	2008
15	120	303	311	452	354	279	574	1226	1336	1438	2032
15	135	307	314	440	352	228	570	943	1384	1449	2023
15	150	301	309	430	347	288	564	890	1246	1329	2053
15	165	285	292	388	325	281	538	859	1280	1303	2093
15	180	278	282	367	316	273	518	862	1209	1310	2093
15	195	263	266	349	305	264	509	803	1177	1409	2083
15	210	258	263	333	299	254	500	802	1152	1452	2068
15	225	246	250	319	282	251	507	757	1142	1325	1988
15	240	243	247	322	269	268	502	624	1170	1329	1988

CORRECTED TEMPERATURE DATA

RUN	TIME MINS	1	2	3	4	5	6	7	8	9	10
					DEGREES F						
15	0	62	66	66	67	66	68	68	65	64	74
15	15	102	108	171	151	196	498	1150	2112	2284	2966
15	30	176	182	316	220	254	656	1390	1893	2427	3025
15	45	212	221	377	266	275	721	1198	1676	2202	3021
15	60	260	267	413	312	300	767	1337	1650	2234	2899
15	75	284	292	434	332	327	779	1383	1597	2008	2899
15	90	291	300	470	346	358	838	1408	1184	2167	2918
15	105	300	309	471	354	373	833	1471	1886	2065	2876
15	120	303	311	452	354	368	786	1712	1904	2013	2911
15	135	307	314	440	352	295	781	1310	1973	2028	2898
15	150	301	309	430	347	381	772	1235	1773	1858	2941
15	165	285	292	388	325	371	735	1191	1822	1821	2999
15	180	278	282	367	316	359	707	1195	1720	1831	2999
15	195	263	266	349	305	346	694	1111	1673	1972	2985
15	210	258	263	333	299	332	681	1110	1637	2033	2963
15	225	246	250	319	282	328	691	1046	1623	1852	2847
15	240	243	247	322	269	352	684	857	1663	1858	2847

TABLE L

RAW TEMPERATURE DATA (RUN 16)

RAW TEMPERATURE DATA

RUN	TIME MINS	1	2	3	4	5	6	7	8	9	10
					DEGREES F						
16A	0	243	247	322	271	268	502	624	1168	1329	1988
16A	15	234	238	322	268	234	489	752	1291	1211	2065
16A	30	231	236	320	263	230	480	695	1200	1271	2065
16A	45	221	226	299	253	226	468	652	1110	1017	1913
16A	60	222	227	310	258	212	456	602	1021	758	1945
16A	75	214	220	298	249	213	451	594	832	878	1884
16A	90	205	209	286	244	184	395	608	795	1166	1863
16A	105	188	192	259	233	156	383	558	792	976	1724
16A	120	178	180	239	224	137	306	549	822	1133	1450

CORRECTED TEMPERATURE DATA

RUN	TIME MINS	1	2	3	4	5	6	7	8	9	10
					DEGREES F						
16A	0	243	247	322	271	353	685	858	1661	1859	2848
16A	15	234	238	322	268	304	666	1040	1839	1691	2959
16A	30	231	236	320	263	299	654	959	1707	1776	2959
16A	45	221	226	299	253	293	636	898	1577	1416	2739
16A	60	222	227	310	258	273	619	827	1448	1048	2785
16A	75	214	220	298	249	275	612	815	1175	1218	2697
16A	90	205	209	286	244	233	533	835	1121	1627	2667
16A	105	188	192	259	233	194	516	764	1117	1358	2466
16A	120	178	180	239	224	167	407	751	1160	1580	2069

TABLE L (Continued)

RAW TEMPERATURE DATA

RUN	TIME MINS	1	2	3	4	5	6	7	8	9	10
					DEGREES F						
16B	0	68	70	67	68	66	74	65	68	75	82
16B	15	92	97	104	135	146	320	1082	1162	1501	1634
16B	30	193	198	210	232	176	444	1135	1220	1556	1876
16B	45	236	244	272	287	190	499	1048	1439	1510	1492
16B	60	290	298	316	336	199	531	1038	1332	1480	2000
16B	75	309	319	336	351	208	568	1096	1526	1463	2006
16B	90	336	345	363	372	227	580	1080	1400	1497	1980
16B	105	353	362	379	397	238	600	1061	1484	1463	1903
16B	120	364	374	388	414	245	600	1096	1630	1415	1673
16B	135	366	375	394	425	243	616	1259	1536	1538	2092
16B	150	378	388	406	428	250	636	1190	1582	1537	2029
16B	165	384	394	410	436	257	628	1105	1561	1532	1880
16B	180	384	396	408	426	262	634	1110	1580	1528	2060
16B	195	389	398	410	433	256	642	1120	1592	1514	2051
16B	210	392	402	412	430	249	637	1105	1556	1746	1994
16B	225	393	404	414	442	244	631	1088	1532	1648	2075
16B	240	387	399	410	432	241	614	1083	1532	1636	2065
16B	255	391	401	409	430	238	598	1058	1249	1641	2127

CORRECTED TEMPERATURE DATA

RUN	TIME MINS	1	2	3	4	5	6	7	8	9	10
					DEGREES F						
16B	0	68	70	67	68	66	74	65	68	75	82
16B	15	92	97	104	135	178	424	1506	1650	2101	2333
16B	30	193	198	210	232	220	600	1581	1734	2179	2684
16B	45	236	244	272	287	240	679	1458	2051	2113	2128
16B	60	290	298	316	336	253	724	1444	1896	2071	2863
16B	75	309	319	336	351	266	776	1526	2177	2047	2872
16B	90	336	345	363	372	293	794	1503	1995	2095	2834
16B	105	353	362	379	397	308	822	1476	2116	2047	2723
16B	120	364	374	388	414	318	822	1526	2328	1979	2390
16B	135	366	375	394	425	315	845	1757	2191	2153	2996
16B	150	378	388	406	428	325	873	1659	2258	2152	2905
16B	165	384	394	410	436	335	862	1539	2228	2145	2689
16B	180	384	396	408	426	342	870	1546	2255	2139	2950
16B	195	389	398	410	433	334	882	1560	2273	2119	2937
16B	210	392	402	412	430	324	874	1539	2220	2448	2854
16B	225	393	404	414	442	317	866	1515	2186	2309	2972
16B	240	387	399	410	432	312	842	1507	2186	2292	2957
16B	255	391	401	409	430	308	819	1472	1776	2299	3047

TABLE LI

RAW TEMPERATURE DATA (RUN 17)

RAW TEMPERATURE DATA

RUN	TIME MINS	1	2	3	4	5	6	7	8	9	10
					DEGREES F						
17	0	57	61	66	61	61	59	60	54	59	49
17	45	82	89	129	132	118	276	628	1244	1367	1909
17	60	133	138	231	196	178	388	363	1000	1112	1955
17	75	152	159	269	225	194	449	725	1032	1201	2068
17	90	201	209	342	269	211	490	810	1120	1316	2102
17	105	223	232	367	289	228	519	762	1181	1512	1993
17	120	235	244	372	303	238	524	796	1155	1418	2017
17	135	250	258	380	316	251	535	816	1156	1372	2014
17	150	255	263	387	320	255	541	845	1265	1350	1971
17	165	260	268	391	325	259	536	925	1310	1394	1963
17	180	268	276	391	329	262	542	926	1372	1404	1993
17	195	270	278	392	329	265	540	909	1233	1568	1944
17	210	267	273	389	329	263	546	998	1250	1480	2007
17	225	269	276	376	315	259	539	935	1350	1455	2036
17	240	260	268	360	32	255	532	908	1259	1502	2037
17	255	258	265	361	299	259	532	970	1329	1451	2099
17	270	259	266	372	308	255	531	945	1327	1413	2038
17	285	256	263	361	304	249	536	1006	1372	1596	2046

CORRECTED TEMPERATURE DATA

RUN	TIME MINS	1	2	3	4	5	6	7	8	9	10
					DEGREES F						
17	0	57	61	66	61	61	59	60	54	59	49
17	45	82	89	129	132	142	367	866	1774	1915	2736
17	60	133	138	231	196	228	526	490	1421	1553	2803
17	75	152	159	269	225	250	612	1004	1467	1680	2966
17	90	201	209	342	269	274	670	1125	1594	1843	3016
17	105	223	232	367	289	299	712	1056	1683	2121	2858
17	120	235	244	372	303	313	719	1105	1645	1988	2893
17	135	250	258	380	316	331	734	1133	1646	1922	2888
17	150	255	263	387	320	337	743	1174	1804	1891	2826
17	165	260	268	391	325	343	736	1288	1869	1953	2814
17	180	268	276	391	329	347	744	1289	1959	1968	2858
17	195	270	278	392	329	351	741	1265	1758	2200	2787
17	210	267	273	389	329	348	750	1391	1782	2076	2878
17	225	269	276	378	315	343	740	1302	1927	2040	2920
17	240	260	268	360	32	337	730	1264	1795	2107	2922
17	255	258	265	361	299	343	730	1352	1897	2034	3011
17	270	259	266	372	308	337	729	1316	1894	1980	2923
17	285	256	263	361	304	328	736	1403	1959	2240	2935

TABLE LII

RAW TEMPERATURE DATA (RUN 18)

RAW TEMPERATURE DATA

RUN	TIME	1	2	3	4	5	6	7	8	9	10
	MINS				DEGREES F						
18	0	256	262	361	304	249	536	1006	1372	1596	2046
18	15	253	259	361	305	211	514	938	1239	1486	1868
18	30	253	261	365	311	206	514	996	1340	1558	1872
18	45	258	267	378	325	230	529	1090	1498	1598	1868
18	60	256	264	376	328	228	516	1071	1470	1596	1946
18	75	255	264	380	329	233	518	1230	1201	1616	1960
18	90	255	263	380	334	235	515	1160	1508	1558	2000
18	105	259	267	379	328	232	506	1125	1540	1572	1957
18	120	254	261	376	339	228	503	1276	1481	1596	1967
18	135	254	261	373	340	229	494	1179	1448	1570	1913
18	150	252	259	369	340	228	484	1100	1374	1552	1918
18	165	257	264	367	339	226	478	1000	1396	1532	1949
18	180	255	262	360	338	223	485	1017	1390	1628	1950
18	195	254	260	359	341	219	486	970	1538	1636	1957
18	210	254	260	354	343	216	486	887	1422	1646	1965
18	225	250	257	342	335	214	479	879	1432	1609	1955
18	240	246	252	340	333	212	492	976	1452	1645	1937

CORRECTED TEMPERATURE DATA

RUN	TIME	1	2	3	4	5	6	7	8	9	10
	MINS				DEGREES F						
18	0	256	262	361	304	326	733	1400	1956	2237	2932
18	15	253	259	361	305	272	702	1304	1764	2081	2674
18	30	253	261	365	311	265	702	1386	1910	2184	2680
18	45	258	267	378	325	299	723	1519	2139	2240	2674
18	60	256	264	376	328	296	705	1492	2098	2237	2787
18	75	255	264	380	329	303	707	1718	1709	2266	2807
18	90	255	263	380	334	306	703	1619	2153	2184	2865
18	105	259	267	379	328	302	690	1569	2199	2203	2803
18	120	254	261	376	339	296	686	1783	2114	2237	2817
18	135	254	261	373	340	297	673	1646	2066	2201	2739
18	150	252	259	369	340	296	659	1534	1959	2175	2746
18	165	257	264	367	339	293	651	1392	1991	2147	2791
18	180	255	262	360	338	289	661	1416	1982	2283	2793
18	195	254	260	359	341	283	662	1349	2196	2294	2803
18	210	254	260	354	343	279	662	1231	2029	2308	2814
18	225	250	257	342	335	276	652	1220	2043	2256	2800
18	240	246	252	340	333	273	671	1358	2072	2307	2774

TABLE LIII

RAW TEMPERATURE DATA (RUN 19)

RAW TEMPERATURE DATA

RUN	TIME MINS	1	2	3	4	5	6	7	8	9	10
					DEGREES F						
19	0	88	89	79	92	84	84	77	83	84	95
19	10	99	102	127	144	130	306	913	1456	1660	1832
19	25	179	182	254	228	162	420	1102	1229	1614	1985
19	40	229	236	316	280	173	473	997	1431	1571	1847
19	55	266	272	347	316	184	493	1070	1286	1587	2003
19	70	299	305	354	351	195	539	1108	1417	1582	2032
19	85	310	318	364	362	198	530	1143	1320	1548	2054
19	100	317	322	388	368	208	531	1048	1361	1604	2023
19	115	326	330	388	370	214	535	1116	1486	1597	1965
19	130	327	333	391	375	218	525	1124	1383	1635	1956
19	145	324	330	399	372	214	521	1060	1344	1616	1870
19	160	317	322	390	362	214	520	1066	1424	1618	2037
19	175	325	332	392	373	220	544	1086	1420	1606	2004
19	190	330	336	394	379	218	543	1091	1349	1534	1946
19	205	337	345	398	385	230	558	991	1443	1613	1984
19	220	338	345	397	385	232	553	1018	1400	1634	1955
19	235	337	345	396	384	233	559	1003	1450	1645	1944
19	250	338	344	392	379	234	558	1015	1452	1602	1965

CORRECTED TEMPERATURE DATA

RUN	TIME MINS	1	2	3	4	5	6	7	8	9	10
					DEGREES F						
19	0	88	89	79	92	84	84	77	83	84	95
19	10	99	102	127	144	149	399	1261	2070	2321	2614
19	25	179	182	254	228	195	561	1529	1741	2256	2836
19	40	229	236	316	280	210	636	1380	2034	2195	2636
19	55	266	272	347	316	226	665	1484	1824	2217	2862
19	70	299	305	354	351	242	730	1538	2014	2210	2904
19	85	310	318	364	362	246	717	1587	1873	2162	2935
19	100	317	322	388	368	260	719	1452	1932	2242	2891
19	115	326	330	388	370	269	724	1549	2113	2232	2807
19	130	327	333	391	375	274	710	1560	1964	2286	2794
19	145	324	330	399	372	269	704	1469	1908	2259	2669
19	160	317	322	390	362	269	703	1478	2024	2261	2911
19	175	325	332	392	373	277	737	1506	2018	2244	2863
19	190	330	336	394	379	274	736	1513	1915	2142	2779
19	205	337	345	398	385	291	757	1372	2051	2254	2834
19	220	338	345	397	385	294	764	1410	1989	2284	2792
19	235	337	345	396	384	296	758	1389	2061	2300	2776
19	250	338	344	392	379	297	757	1406	2064	2239	2807

TABLE LIV

RAW TEMPERATURE DATA (RUN 20)

RAW TEMPERATURE DATA

RUN	TIME	1	2	3	4	5	6	7	8	9	10
	MINS				DEGREES F						
20	0	72	71	68	73	71	75	73	74	74	79
20	10	112	112	143	151	138	350	843	1455	1772	1801
20	25	156	159	186	201	156	408	910	1389	1659	2013
20	40	216	215	268	265	176	482	1004	1353	1677	1940
20	55	229	234	317	301	188	520	957	1503	1638	1983
20	70	258	264	339	332	201	586	1038	1492	1545	1984
20	85	268	274	350	344	208	596	1040	1466	1682	2042
20	100	285	288	358	361	213	591	991	1504	1651	2155
20	115	292	296	356	366	223	595	1013	1516	1740	2104
20	130	308	312	365	374	233	624	1100	1479	1733	2129
20	145	312	317	385	382	235	620	1093	1392	1750	2105
20	160	307	314	371	378	238	609	1091	1522	1704	2136
20	175	300	305	378	376	234	607	1098	1508	1701	2140
20	190	298	301	369	365	231	600	1171	1493	1628	2070
20	205	297	300	367	364	232	607	1278	1498	1667	2163
20	220	302	308	376	376	233	586	1159	1468	1686	2104
20	235	297	303	365	369	228	560	1110	1475	1728	2129
20	250	295	298	358	360	221	602	1224	1547	1650	2147

CORRECTED TEMPERATURE DATA

RUN	TIME	1	2	3	4	5	6	7	8	9	10
	MINS				DEGREES F						
20	0	72	71	68	73	71	75	73	74	74	79
20	10	112	112	143	151	165	465	1165	2073	2484	2573
20	25	156	159	186	201	190	548	1260	1977	2323	2880
20	40	216	215	268	265	219	653	1394	1925	2349	2774
20	55	229	234	317	301	236	707	1327	2142	2294	2837
20	70	258	264	339	332	254	800	1442	2126	2162	2838
20	85	268	274	350	344	264	815	1445	2088	2356	2922
20	100	285	288	358	361	271	808	1375	2143	2312	3086
20	115	292	296	356	366	285	813	1406	2161	2438	3012
20	130	308	312	365	374	299	854	1530	2107	2428	3048
20	145	312	317	385	382	302	849	1520	1981	2453	3013
20	160	307	314	371	376	307	833	1517	2170	2387	3058
20	175	300	305	378	376	301	830	1527	2149	2383	3064
20	190	298	301	369	365	297	820	1631	2128	2279	2963
20	205	297	300	367	364	298	830	1783	2135	2335	3097
20	220	302	308	376	376	299	800	1614	2091	2362	3012
20	235	297	303	365	369	292	764	1544	2101	2421	3048
20	250	295	298	358	360	282	823	1706	2206	2311	3074

TABLE LV

RAW TEMPERATURE DATA (RUN 21)

RAW TEMPERATURE DATA

RUN	TIME	1	2	3	4	5	6	7	8	9	10
	MINS				DEGREES F						
21	0	295	299	358	360	221	602	1224	1547	1650	2146
21	15	289	291	346	336	296	629	1020	1392	1591	2146
21	30	291	294	362	344	290	608	1232	1552	1714	2100
21	45	291	293	359	339	284	589	1313	1506	1730	2121
21	60	291	294	361	341	281	610	1312	1505	1572	1971
21	75	300	303	373	351	288	635	1203	1481	1744	2158
21	90	317	321	398	364	317	650	1278	1638	1710	2116
21	105	325	329	409	370	326	672	1301	1567	1767	2167
21	120	336	340	414	383	326	656	1309	1632	1676	2170
21	135	333	338	414	371	331	666	1277	1534	1750	2142
21	150	313	315	376	317	318	648	1259	1625	1836	2167
21	165	292	297	354	291	317	669	1294	1653	1830	2085
21	180	287	291	342	285	311	638	1281	1507	1792	2061
21	195	274	279	336	283	299	637	1249	1484	1740	2048
21	210	275	279	339	282	286	630	1214	1435	1652	2108
21	225	273	279	340	272	300	620	1225	1484	1564	2137
21	240	273	277	339	274	296	618	1228	1554	1740	2121

CORRECTED TEMPERATURE DATA

RUN	TIME	1	2	3	4	5	6	7	8	9	10
	MINS				DEGREES F						
21	0	295	299	358	360	286	827	1709	2209	2314	3076
21	15	289	291	346	336	392	865	1420	1985	2230	3076
21	30	291	294	362	344	384	835	1721	2217	2405	3010
21	45	291	293	359	339	375	808	1836	2150	2428	3040
21	60	291	294	361	341	371	838	1834	2149	2203	2823
21	75	300	303	373	351	381	874	1680	2114	2448	3094
21	90	317	321	398	364	422	895	1786	2341	2399	3033
21	105	325	329	409	370	435	926	1819	2238	2480	3107
21	120	336	340	414	383	435	903	1830	2332	2351	3111
21	135	333	338	414	371	442	918	1785	2191	2456	3071
21	150	313	315	376	317	424	892	1759	2322	2578	3107
21	165	292	297	354	291	422	922	1809	2363	2570	2988
21	180	287	291	342	285	414	878	1790	2152	2516	2953
21	195	274	279	336	283	397	876	1745	2118	2442	2935
21	210	275	279	339	282	378	866	1695	2047	2317	3021
21	225	273	279	340	272	398	852	1711	2118	2192	3063
21	240	273	277	339	274	392	849	1715	2220	2442	3040

TABLE LVI

RAW TEMPERATURE DATA (RUN 22)

RAW TEMPERATURE DATA

RUN	TIME MINS	1	2	3	4	5	6	7	8	9	10
					DEGREES F						
22	0	67	69	65	72	68	75	73	73	74	79
22	5	103	108	140	179	161	415	1072	1287	1431	1845
22	20	186	189	239	248	179	515	1229	1292	1431	1860
22	35	216	222	291	284	198	520	1038	1301	1396	1800
22	50	242	247	306	306	199	518	966	1254	1397	1745
22	65	245	250	305	310	200	508	960	1325	1435	1893
22	80	265	270	314	326	210	524	952	1306	1412	1930
22	95	272	276	321	348	211	525	910	1234	1466	1880
22	110	256	258	344	327	214	530	931	1197	1468	2029
22	125	194	198	294	212	197	472	936	1112	1376	1538
22	140	193	198	318	233	198	490	1012	1258	1420	1619
22	155	195	200	335	240	201	485	932	1194	1401	1666
22	170	223	226	334	256	202	507	1018	1291	1402	1760
22	185	226	230	335	251	202	511	994	1241	1380	1540
22	200	230	234	342	253	205	508	1016	1177	1460	1554
22	215	220	223	350	243	207	502	974	1301	1424	1656
22	230	221	223	354	254	208	515	1005	1255	1432	1821
22	245	227	230	341	242	208	515	1036	1267	1457	1876

CORRECTED TEMPERATURE DATA

RUN	TIME MINS	1	2	3	4	5	6	7	8	9	10
					DEGREES F						
22	0	67	69	65	72	68	75	73	73	74	79
22	5	103	108	140	179	198	558	1491	1830	2000	2637
22	20	136	189	239	248	223	700	1713	1837	2000	2659
22	35	216	222	291	284	250	707	1442	1850	1950	2572
22	50	242	247	306	306	252	704	1340	1782	1952	2493
22	65	245	250	305	310	253	690	1332	1885	2006	2707
22	80	265	270	314	326	267	713	1320	1857	1973	2760
22	95	272	276	321	348	269	714	1261	1753	2050	2688
22	110	256	258	344	327	273	721	1290	1699	2053	2904
22	125	194	198	294	212	249	639	1298	1576	1922	2193
22	140	193	198	318	233	250	665	1405	1788	1985	2310
22	155	195	200	335	240	254	657	1292	1695	1958	2378
22	170	223	226	334	256	256	689	1414	1836	1959	2514
22	185	226	230	335	251	256	694	1380	1763	1928	2196
22	200	230	234	342	253	260	690	1411	1671	2041	2216
22	215	220	223	350	243	263	682	1351	1850	1990	2364
22	230	221	223	354	254	264	700	1395	1783	2002	2603
22	245	227	230	341	242	264	700	1439	1801	2037	2682

TABLE LVIII

RAW TEMPERATURE DATA (RUN 23)

RAW TEMPERATURE DATA

RUN	TIME MINS	1	2	3	4	5	6	7	8	9	10
					DEGREES F						
23	0	227	230	341	242	208	515	1036	1266	1457	1878
23	15	252	255	335	257	233	566	1145	1450	1513	1914
23	30	254	258	363	273	240	576	1122	1427	1510	1921
23	45	262	267	369	270	240	564	1166	1476	1503	2003
23	60	253	257	381	262	240	572	1093	1442	1568	2010
23	75	262	265	367	270	236	568	1032	1454	1547	2017
23	90	256	258	376	267	238	560	1129	1439	1534	1992
23	105	264	267	373	287	227	551	1063	1442	1584	2046
23	120	267	272	351	283	226	535	972	1400	1618	2080
23	135	264	268	365	276	236	553	976	1418	1584	2104
23	150	270	270	350	274	238	552	1052	1446	1586	2031
23	165	287	291	356	281	244	563	975	1472	1525	1986
23	180	276	281	365	269	244	562	949	1471	1540	2017
23	195	285	289	362	285	248	561	921	1353	1576	2042
23	210	282	286	360	296	246	555	982	1382	1590	2015
23	225	282	286	357	286	247	557	957	1459	1611	2075
23	240	282	287	362	302	245	552	927	1410	1633	2086

CORRECTED TEMPERATURE DATA

RUN	TIME MINS	1	2	3	4	5	6	7	8	9	10
					DEGREES F						
23	0	227	230	341	242	267	703	1443	1803	2040	2689
23	15	252	255	335	257	303	776	1597	2069	2120	2741
23	30	254	258	363	273	313	790	1565	2036	2115	2751
23	45	262	267	369	270	313	773	1627	2107	2105	2869
23	60	253	257	381	262	313	784	1524	2057	2198	2880
23	75	262	265	367	270	307	778	1437	2075	2168	2890
23	90	256	258	376	267	310	767	1575	2053	2149	2854
23	105	264	267	373	287	294	754	1481	2057	2220	2932
23	120	267	272	351	283	293	732	1352	1997	2269	2981
23	135	264	268	365	276	307	757	1358	2023	2220	3016
23	150	270	270	350	274	310	756	1465	2063	2223	2910
23	165	287	291	356	281	319	771	1356	2101	2137	2845
23	180	276	281	363	269	319	770	1319	2099	2158	2890
23	195	285	289	362	285	324	768	1279	1929	2209	2926
23	210	282	286	360	296	321	760	1366	1971	2229	2887
23	225	282	286	357	286	323	763	1331	2082	2259	2974
23	240	282	287	362	302	320	756	1288	2011	2290	2990

TABLE LVIII

RAW TEMPERATURE DATA (RUN 24)

RAW TEMPERATURE DATA

RUN	TIME MINS	1	2	3	4	5	6	7	8	9	10
					DEGREES F						
24	0	65	66	66	67	65	66	64	65	70	68
24	25	238	240	207	385	570	690	1215	1267	1430	2594
24	40	322	275	302	512	524	741	1160	1262	1340	2691
24	55	406	399	420	536	678	842	1090	1270	1496	2881
24	70	243	250	284	297	178	485	1042	1218	1640	1941
24	85	244	265	301	333	190	504	1196	1260	1642	1968
24	100	259	263	331	338	197	517	1228	1299	1652	1919
24	115	248	253	334	343	198	504	1116	1253	1345	1937
24	145	261	266	316	321	218	512	1096	1339	1381	1614
24	160	283	267	320	332	214	503	1053	1253	1404	1743
24	175	292	295	326	329	219	520	1167	1203	1390	1708
24	190	290	296	358	353	222	521	1180	1282	1406	1672
24	205	303	309	345	345	223	530	1099	1257	1399	1599
24	220	312	316	336	348	225	539	982	1318	1474	1684
24	235	305	312	369	376	228	554	966	1327	1392	1632

CORRECTED TEMPERATURE DATA

RUN	TIME MINS	1	2	3	4	5	6	7	8	9	10
					DEGREES F						
24	0	65	66	66	67	65	66	64	65	70	68
24	25	238	240	207	385	781	951	1696	1804	2001	3724
24	40	322	275	302	512	716	1024	1618	1797	1874	3865
24	55	406	399	420	536	934	1167	1519	1808	2095	4140
24	70	243	250	284	297	224	660	1451	1733	2300	2779
24	85	244	265	301	333	241	687	1669	1794	2302	2818
24	100	259	263	331	338	251	706	1715	1850	2317	2747
24	115	248	253	334	343	253	687	1556	1783	1881	2773
24	145	261	266	316	321	281	699	1527	1908	1932	2306
24	160	283	287	320	332	276	686	1466	1783	1965	2493
24	175	292	295	326	329	283	710	1628	1711	1945	2442
24	190	290	296	358	353	287	711	1647	1825	1967	2390
24	205	303	309	345	345	288	724	1532	1789	1957	2284
24	220	312	316	336	348	291	737	1366	1878	2064	2407
24	235	305	312	369	376	295	758	1343	1891	1948	2332

TABLE LVIX

RAW TEMPERATURE DATA (RUN 25)

RAW TEMPERATURE DATA

RUN	TIME MINS	1	2	3	4	5	6	7	8	9	10
					DEGREES F						
25	235	305	312	369	376	228	554	966	1327	1392	1632
25	250	297	304	346	228	236	552	938	1372	1520	1745
25	265	303	308	317	226	232	548	913	1340	1500	1646
25	280	291	297	306	212	230	536	891	1336	1503	1649
25	295	289	296	303	220	231	546	936	1436	1398	1580
25	310	268	274	305	208	228	525	919	1400	1479	1649
25	325	278	282	291	219	226	532	939	1349	1422	1611
25	340	283	287	298	225	222	527	956	1274	1385	1615
25	355	276	281	301	241	218	522	966	1348	1400	1550
25	370	268	272	300	261	218	521	992	1454	1374	1723
25	385	277	282	310	268	218	523	996	1366	1308	1571
25	400	281	286	311	244	218	532	1003	1436	1310	1699
25	415	281	286	311	244	216	532	917	1393	1310	1582

CORRECTED TEMPERATURE DATA

RUN	TIME MINS	1	2	3	4	5	6	7	8	9	10
					DEGREES F						
25	235	305	312	369	376	296	759	1343	1891	1948	2332
25	250	297	304	346	228	307	756	1304	1956	2130	2496
25	265	303	308	317	226	302	750	1268	1910	2101	2353
25	280	291	297	306	212	299	733	1237	1904	2105	2357
25	295	289	296	303	220	300	747	1301	2049	1953	2257
25	310	268	274	305	208	296	717	1277	1997	2071	2357
25	325	278	282	291	219	293	727	1305	1923	1991	2302
25	340	283	287	298	225	287	720	1329	1814	1938	2308
25	355	276	281	301	241	282	713	1343	1921	1959	2214
25	370	268	272	300	261	282	712	1380	2075	1922	2464
25	385	277	282	310	268	282	715	1386	1947	1829	2244
25	400	281	286	311	244	282	727	1396	2049	1832	2429
25	415	281	286	311	244	279	727	1274	1987	1832	2260

TABLE LX

RAW TEMPERATURE DATA (RUN 26)

RAW TEMPERATURE DATA

RUN	TIME MINS	1	2	3	4	5	6	7	8	9	10
					DEGREES F						
26	0	72	72	72	72	69	73	65	70	73	82
26	15	98	99	122	165	107	296	824	1257	1450	1660
26	30	144	146	205	229	125	363	956	1356	1519	1808
26	45	178	182	248	272	129	387	954	1398	1562	1860
26	60	208	212	295	310	134	397	854	1380	1570	1880
26	75	239	245	333	337	140	413	826	1404	1571	1770
26	90	252	258	345	351	145	448	846	1394	1501	1872
26	105	265	270	355	377	156	445	798	1353	1406	1776
26	120	274	280	364	386	162	457	840	1346	1408	1751
26	135	279	285	365	395	166	458	813	1342	1386	1761
26	150	286	291	372	402	174	470	842	1327	1353	1780
26	165	285	291	377	409	174	486	860	1306	1348	1818
26	180	288	293	387	406	175	486	856	1311	1423	1805
26	195	290	295	388	409	174	498	1000	1353	1381	1765
26	210	299	304	401	408	180	502	980	1254	1415	1798
26	225	302	307	403	415	182	508	1000	1216	1329	1757
26	240	302	309	401	410	182	493	955	1253	1292	1755
26	255	305	310	399	408	184	494	974	1266	1382	1769

CORRECTED TEMPERATURE DATA

RUN	TIME MINS	1	2	3	4	5	6	7	8	9	10
					DEGREES F						
26	0	72	72	72	72	69	73	65	70	73	82
26	15	98	99	122	165	122	390	1140	1787	2028	2371
26	30	144	146	205	229	148	485	1327	1931	2126	2585
26	45	178	182	248	272	153	519	1324	1992	2187	2660
26	60	208	212	295	310	160	534	1182	1966	2198	2689
26	75	239	245	333	337	169	556	1143	2000	2200	2530
26	90	252	258	345	351	176	606	1171	1986	2101	2678
26	105	265	270	355	377	192	602	1103	1926	1966	2539
26	120	274	280	364	386	200	619	1162	1916	1969	2502
26	135	279	285	365	395	206	620	1124	1911	1937	2517
26	150	286	291	372	402	217	637	1165	1889	1890	2544
26	165	285	291	377	409	217	660	1191	1858	1883	2599
26	180	288	293	387	406	219	660	1185	1866	1990	2581
26	195	290	295	388	409	217	677	1389	1926	1930	2523
26	210	299	304	401	408	226	683	1361	1783	1978	2570
26	225	302	307	403	415	228	691	1389	1728	1856	2511
26	240	302	309	401	410	228	670	1326	1782	1804	2508
26	255	305	310	399	408	231	671	1353	1801	1932	2529

TABLE LXI

RAW TEMPERATURE DATA (RUN 27)

RAW TEMPERATURE DATA

RUN	TIME MINS	1	2	3	4	5	6	7	8	9	10
					DEGREES F						
27	0	305	310	399	408	184	494	974	1266	1382	1769
27	15	347	351	386	450	215	576	1230	1498	1507	1954
27	30	349	353	387	446	212	560	1095	1442	1516	2023
27	45	342	344	390	440	214	562	1140	1349	1681	2008
27	60	342	345	386	439	216	563	1133	1337	1713	1930
27	75	343	347	382	448	223	546	1092	1446	1702	1965
27	90	343	349	385	450	226	553	981	1555	1746	1892
27	105	337	344	383	408	234	573	1172	1486	1696	1858
27	120	321	326	395	389	232	577	1266	1558	1672	1884
27	135	312	316	382	381	221	574	1102	1532	1627	1876
27	150	314	320	387	385	217	577	991	1566	1622	1855
27	165	314	320	391	374	221	593	1227	1468	1600	1850
27	180	309	317	385	362	221	580	1092	1524	1614	1901
27	195	302	307	377	359	222	573	1006	1425	1613	1913
27	210	295	299	365	349	216	570	1040	1331	1606	1827
27	225	283	289	354	331	212	562	1014	1206	1604	1781
27	240	282	287	346	331	210	556	986	1148	1542	1712

CORRECTED TEMPERATURE DATA

RUN	TIME MINS	1	2	3	4	5	6	7	8	9	10
					DEGREES F						
27	0	305	310	399	408	233	673	1355	1803	1934	2531
27	15	347	351	386	450	277	790	1718	2139	2111	2799
27	30	349	353	387	446	273	767	1526	2057	2124	2898
27	45	342	344	390	440	276	770	1590	1923	2358	2877
27	60	342	345	386	439	279	771	1580	1906	2404	2764
27	75	343	347	382	448	289	747	1522	2063	2388	2814
27	90	343	349	385	450	293	757	1365	2221	2450	2709
27	105	337	344	383	408	304	786	1636	2121	2379	2660
27	120	321	326	395	389	302	791	1769	2225	2345	2697
27	135	312	316	382	381	286	787	1536	2188	2281	2686
27	150	314	320	387	385	280	791	1379	2237	2274	2655
27	165	314	320	391	374	286	814	1714	2095	2243	2648
27	180	309	317	385	362	286	795	1522	2176	2263	2722
27	195	302	307	377	359	287	786	1400	2033	2262	2739
27	210	295	299	365	349	279	781	1448	1897	2252	2615
27	225	283	289	354	331	273	770	1411	1716	2249	2548
27	240	282	287	346	331	270	761	1372	1632	2161	2448

TABLE LXII

RAW TEMPERATURE DATA (RUN 29)

RAW TEMPERATURE DATA

RUN	TIME	1	2	3	4	5	6	7	8	9	10
	MINS				DEGREES F						
28	0	71	72	73	74	72	74	73	74	75	82
28	10	92	95	123	138	128	323	1106	1197	1508	1708
28	25	146	148	206	216	128	373	908	1301	1443	1714
28	40	198	201	274	264	139	402	885	1313	1510	1614
28	55	226	229	320	302	148	448	887	1359	1494	1766
28	70	254	260	356	332	154	474	980	1408	1474	1792
28	85	273	271	380	354	160	511	1056	1447	1572	1675
28	100	283	291	422	354	168	529	998	1355	1566	1626
28	115	302	309	422	379	180	544	964	1396	1492	1668
28	130	316	324	428	390	187	554	1064	1382	1503	1650
28	145	324	331	436	395	189	555	1124	1324	1422	1531
28	160	327	334	441	394	197	567	1025	1325	1396	1527
28	175	330	337	440	402	200	563	1084	1512	1385	1547
28	190	342	349	418	414	198	562	965	1518	1360	1515
28	205	334	341	409	408	193	550	1055	1300	1318	1429
28	220	334	343	411	410	192	558	1057	1484	1384	1540
28	235	327	333	393	398	195	547	1068	1291	1342	1606
28	250	320	326	389	388	200	548	1027	1215	1478	1477

CORRECTED TEMPERATURE DATA

RUN	TIME	1	2	3	4	5	6	7	8	9	10
	MINS				DEGREES F						
28	0	71	72	73	74	72	74	73	74	75	82
28	10	92	95	123	138	150	427	1538	1699	2109	2439
28	25	146	148	206	216	150	498	1257	1850	2017	2447
28	40	198	201	274	264	166	539	1225	1867	2112	2303
28	55	226	229	320	302	179	604	1228	1934	2089	2523
28	70	254	260	356	332	187	641	1360	2004	2061	2560
28	85	273	271	380	354	196	694	1467	2061	2200	2391
28	100	283	291	422	354	207	719	1385	1928	2191	2320
28	115	302	309	422	379	224	741	1337	1987	2086	2381
28	130	316	324	428	390	234	755	1479	1967	2102	2355
28	145	324	331	436	395	237	756	1564	1883	1987	2182
28	160	327	334	441	394	248	773	1423	1884	1950	2177
28	175	330	337	440	402	253	768	1507	2155	1934	2206
28	190	342	349	418	414	250	766	1338	2164	1899	2159
28	205	334	341	409	408	243	749	1466	1848	1839	2035
28	220	334	343	411	410	241	761	1469	2114	1933	2195
28	235	327	333	393	398	245	745	1484	1835	1873	2291
28	250	320	326	389	388	253	746	1426	1725	2066	2104

TABLE LXIII

RAW TEMPERATURE DATA (RUN 30)

RAW TEMPERATURE DATA

RUN	TIME MINS	1	2	3	4	5	6	7	8	9	10
					DEGREES	F					
29	250	320	326	389	388	200	548	1027	1215	1478	1477
29	265	319	324	383	384	199	543	1063	1180	1419	1568
29	280	326	332	380	391	202	546	994	1193	1452	1527
29	295	321	326	378	397	206	544	1052	1210	1480	1529
29	310	321	321	385	385	210	555	1080	1360	1492	1563
29	325	321	324	394	395	211	560	1027	1317	1493	1565
29	340	321	320	401	388	206	550	1005	1298	1436	1511
29	355	319	322	396	389	201	553	1147	1306	1380	1491
29	370	322	327	397	395	202	557	1166	1346	1442	1526
29	385	324	326	394	397	215	553	980	1260	1341	1543
29	400	325	329	383	400	220	552	1021	1273	1454	1543
29	415	321	327	380	397	220	551	1044	1372	1432	1490
29	430	323	329	398	396	223	572	1090	1208	1516	1567
29	445	326	331	392	399	223	565	956	1148	1446	1490
29	460	321	328	382	393	223	569	1103	1124	1488	1575
29	475	322	328	391	395	223	582	1085	1238	1485	1548
29	490	327	327	389	398	224	579	1128	1166	1532	1647

CORRECTED TEMPERATURE DATA

RUN	TIME MINS	1	2	3	4	5	6	7	8	9	10
					DEGREES	F					
29	250	320	326	389	388	256	750	1430	1729	2070	2108
29	265	319	324	383	384	255	743	1481	1678	1986	2240
29	280	326	332	380	391	259	747	1383	1697	2033	2181
29	295	321	326	378	397	265	744	1465	1722	2073	2183
29	310	321	321	385	385	270	760	1505	1939	2090	2233
29	325	321	324	394	395	272	767	1430	1877	2091	2236
29	340	321	320	401	388	265	767	1399	1849	2010	2157
29	355	319	322	396	389	258	757	1600	1861	1931	2128
29	370	322	327	397	395	259	763	1627	1919	2019	2179
29	385	324	326	394	397	277	757	1363	1794	1876	2204
29	400	325	329	383	400	284	756	1421	1813	2036	2204
29	415	321	327	380	397	284	754	1454	1956	2005	2127
29	430	323	329	398	396	289	734	1519	1719	2124	2238
29	445	326	331	392	399	289	774	1329	1632	2025	2127
29	460	321	328	382	393	289	780	1538	1597	2084	2250
29	475	322	328	391	395	289	798	1512	1762	2080	2211
29	490	327	327	389	398	290	794	1573	1658	2147	2354

TABLE LXIV

RAW TEMPERATURE DATA (RUN 31)

RAW TEMPERATURE DATA

RUN	TIME MINS	1	2	3	4	5	6	7	8	9	10
					DEGREES F						
30	0	68	67	68	69	71	73	68	72	74	304
30	15	140	105	155	169	117	356	1094	1139	1306	1467
30	30	147	150	210	217	124	388	929	1230	1320	1610
30	45	227	230	268	300	136	460	936	1358	1488	1697
30	60	245	245	322	319	138	369	968	1443	1532	1697
30	75	289	295	318	353	147	431	1049	1440	1620	1727
30	90	308	314	337	382	155	467	990	1463	1606	1736
30	105	323	329	356	396	158	482	1040	1424	1556	1747
30	120	336	340	367	406	160	486	1025	1388	1600	1919
30	135	340	344	372	408	166	494	1079	1423	1522	1856
30	150	347	352	375	415	164	479	1105	1488	1591	1820
30	165	352	356	379	429	168	488	1094	1446	1588	1726
30	180	356	360	388	434	177	476	1078	1460	1579	1786
30	195	355	361	399	431	178	484	1089	1397	1522	1821
30	210	352	357	396	428	178	494	1176	1372	1528	1922
30	225	354	359	389	432	180	466	1240	1354	1532	1897
30	240	353	359	385	429	180	464	1093	1362	1452	1923

CORRECTED TEMPERATURE DATA

RUN	TIME MINS	1	2	3	4	5	6	7	8	9	10
					DEGREES F						
30	0	68	67	68	69	71	73	68	72	74	304
30	15	140	105	155	169	136	475	1522	1616	1823	2091
30	30	147	150	210	217	145	520	1288	1748	1843	2298
30	45	227	230	268	300	163	622	1298	1933	2081	2424
30	60	245	245	322	319	165	493	1343	2056	2144	2424
30	75	289	295	318	353	178	581	1458	2052	2269	2467
30	90	308	314	337	382	189	632	1375	2085	2249	2480
30	105	323	329	356	396	194	654	1446	2028	2178	2496
30	120	336	340	367	406	197	659	1424	1976	2240	2745
30	135	340	344	372	408	205	671	1501	2027	2130	2654
30	150	347	352	375	415	202	649	1538	2121	2228	2602
30	165	352	356	379	429	208	662	1522	2060	2223	2466
30	180	356	360	388	434	221	645	1500	2081	2211	2552
30	195	355	361	399	431	222	656	1515	1989	2130	2603
30	210	352	357	396	428	222	671	1639	1953	2138	2749
30	225	354	359	389	432	225	631	1729	1927	2144	2713
30	240	353	359	385	429	225	628	1521	1939	2030	2751

TABLE LXV

RAW TEMPERATURE DATA (RUN 31)

RAW TEMPERATURE DATA

RUN	TIME	1	2	3	4	5	6	7	8	9	10
	MINS				DEGREES F						
31	240	353	359	385	429	180	464	1093	1362	1452	1923
31	255	357	364	388	439	176	453	1092	1337	1507	1816
31	270	351	358	379	429	176	432	1032	1428	1481	1859
31	285	354	361	379	437	174	471	1046	1397	1508	1843
31	300	350	357	376	429	174	485	1040	1428	1489	1803
31	315	342	347	366	428	173	517	1010	1356	1710	1954
31	330	342	347	363	430	170	504	1000	1552	1685	1956
31	345	343	347	363	426	166	494	1004	1449	1725	1930
31	360	340	346	358	439	162	494	968	1488	1688	1931
31	375	340	346	357	427	167	476	924	1704	1776	1888
31	390	340	343	358	437	169	552	910	1690	1822	2046
31	405	340	343	359	432	170	558	940	1624	1749	2049
31	420	342	344	356	428	170	549	960	1762	1814	2083
31	435	340	344	368	432	167	549	982	1567	1692	2099
31	344	348	348	371	433	167	550	1021	1688	1781	2122
31	465	349	354	374	441	168	568	1034	1655	1728	2090
31	480	346	350	374	438	167	561	1063	1722	1867	2095
31	495	344	348	370	433	168	550	1074	1821	1867	2069

CORRECTED TEMPERATURE DATA

RUN	TIME	1	2	3	4	5	6	7	8	9	10
	MINS				DEGREES F						
31	240	353	359	385	429	228	631	1524	1942	2033	2754
31	255	357	364	388	439	222	615	1522	1906	2111	2599
31	270	351	358	379	429	222	585	1437	2037	2074	2661
31	285	354	361	379	437	219	641	1457	1992	2113	2638
31	300	350	357	376	429	219	661	1448	2037	2086	2560
31	315	342	347	366	428	218	706	1406	1933	2399	2799
31	330	342	347	363	430	214	688	1392	2217	2364	2801
31	345	343	347	363	426	208	673	1397	2068	2421	2764
31	360	340	346	358	439	202	673	1346	2124	2368	2765
31	375	340	346	357	427	209	648	1284	2437	2493	2703
31	390	340	343	358	437	212	756	1264	2416	2558	2932
31	405	340	343	359	432	214	764	1306	2321	2455	2936
31	420	342	344	356	428	214	751	1335	2521	2547	2985
31	435	340	344	368	432	209	751	1366	2238	2374	3008
31	344	348	348	371	433	209	753	1421	2414	2500	3042
31	465	349	354	374	441	211	778	1440	2366	2425	2995
31	480	346	350	374	438	209	768	1481	2463	2622	3003
31	495	344	348	370	433	211	753	1497	2606	2622	2965

TABLE LXVI

RAW TEMPERATURE DATA (RUN 32)

RAW TEMPERATURE DATA

RUN	TIME MINS	1	2	3	4	5	6	7	8	9	10
					DEGREES F						
32	0	62	65	56	64	56	66	64	60	63	78
32	15	111	113	112	181	94	451	984	1434	1329	1438
32	30	176	179	181	220	118	591	1084	1344	1532	1810
32	45	206	209	220	279	124	632	1134	1224	1588	1753
32	60	235	240	324	307	144	711	1086	1484	1564	1778
32	75	282	288	336	358	156	766	1057	1479	1612	1838
32	0	317	325	357	392	173	776	1085	1552	1598	1818
32	105	329	338	367	404	181	748	1079	1557	1648	1796
32	120	338	334	388	403	194	756	1103	1433	1581	1736
32	135	347	354	392	415	190	762	1049	1394	1525	1855
32	150	352	358	405	417	196	754	1068	1383	1552	1929
32	165	356	362	405	415	200	748	1114	1426	1480	1865
32	180	370	378	394	437	200	737	1109	1344	1534	1942
32	195	373	381	392	434	196	688	1104	1435	1664	1880
32	210	374	380	399	435	190	732	1076	1430	1594	1932
32	225	376	383	399	436	190	717	1062	1439	1592	1903
32	240	375	381	406	439	196	701	1060	1440	1558	1929
32	255	373	381	406	434	194	663	1084	1434	1575	1891
32	270	368	375	415	429	187	637	1102	1413	1656	1914

CORRECTED TEMPERATURE DATA

RUN	TIME MINS	1	2	3	4	5	6	7	8	9	10
					DEGREES F						
32	0	62	65	56	64	56	66	64	60	63	78
32	15	111	113	112	181	107	614	1370	2047	1860	2053
32	30	176	179	181	220	141	812	1512	1917	2148	2592
32	45	206	209	220	279	150	871	1583	1743	2227	2509
32	60	235	240	324	307	178	983	1515	2120	2193	2545
32	75	282	288	336	358	195	1061	1474	2112	2262	2632
32	0	317	325	357	392	219	1075	1514	2218	2242	2603
32	105	329	338	367	404	230	1035	1505	2225	2313	2571
32	120	338	334	388	403	249	1047	1539	2046	2218	2484
32	135	347	354	392	415	243	1055	1462	1989	2138	2657
32	150	352	358	405	417	252	1044	1489	1974	2176	2764
32	165	356	362	405	415	257	1035	1555	2036	2074	2671
32	180	370	378	394	437	257	1020	1548	1917	2151	2783
32	195	373	381	392	434	252	950	1541	2049	2335	2693
32	210	374	380	399	435	243	1013	1501	2042	2236	2768
32	225	376	383	399	436	243	991	1481	2055	2233	2726
32	240	375	381	406	439	252	969	1478	2056	2185	2764
32	255	373	381	406	434	249	915	1512	2047	2209	2709
32	270	368	375	415	429	239	878	1538	2017	2324	2742

TABLE LXVII

RAW TEMPERATURE DATA (RUN 33)

RAW TEMPERATURE DATA

RUN	TIME MINS	1	2	3	4	5	6	7	8	9	10
					DEGREES F						
33	0	368	375	415	429	187	637	1102	1413	1656	1914
33	15	378	385	460	431	183	736	1179	1442	1724	1911
33	30	388	398	481	441	193	737	1159	1485	1810	1927
33	45	363	373	494	386	195	730	1157	1475	1594	1796
33	60	374	384	484	436	210	724	1183	1440	1567	1854
33	75	372	382	448	428	216	768	1177	1494	1525	1836
33	90	374	382	486	418	216	763	1230	1542	1690	1844
33	105	377	387	485	423	217	752	1266	1523	1593	1889
33	120	380	390	485	418	219	744	1366	1494	1609	1879
33	135	389	399	483	428	218	691	1340	1529	1584	1943
33	150	391	402	488	414	227	699	1384	1473	1538	1930
33	165	398	409	471	428	223	675	1229	1332	1532	1843
33	180	387	396	463	427	208	648	1094	1312	1484	1832
33	195	390	398	462	425	205	616	1129	1466	1592	1929
33	225	396	406	465	430	212	618	1182	1412	1682	1957
33	210	392	403	463	430	210	624	1222	1449	1626	1851

CORRECTED TEMPERATURE DATA

RUN	TIME MINS	1	2	3	4	5	6	7	8	9	10
					DEGREES F						
33	0	368	375	415	429	238	876	1536	2016	2323	2741
33	15	378	385	460	431	232	1017	1646	2057	2419	2736
33	30	388	398	481	441	246	1018	1617	2120	2541	2759
33	45	363	373	494	386	249	1008	1614	2105	2235	2570
33	60	374	384	484	436	270	1000	1651	2055	2196	2654
33	75	372	382	448	428	279	1062	1643	2133	2137	2628
33	90	374	382	486	418	279	1055	1718	2202	2371	2639
33	105	377	387	485	423	280	1040	1769	2175	2233	2704
33	120	380	390	485	418	283	1028	1911	2133	2256	2690
33	135	389	399	483	428	282	953	1874	2183	2220	2783
33	150	391	402	488	414	294	964	1937	2102	2155	2764
33	165	398	409	471	428	289	930	1717	1898	2147	2638
33	180	387	396	463	427	267	892	1525	1869	2079	2622
33	195	390	398	462	425	263	847	1575	2092	2232	2762
33	225	396	406	465	430	273	849	1650	2014	2360	2803
33	210	392	403	463	430	270	858	1707	2066	2280	2649

TABLE LXVIII

RAW TEMPERATURE DATA (RUN 34)

RAW TEMPERATURE DATA

RUN	TIME	1	2	3	4	5	6	7	8	9	10
34	0	59	62	54	65	64	63	62	62	65	68
34	15	80	81	98	121	119	396	890	1075	1156	1584
34	30	114	117	179	209	130	348	806	897	1358	1564
34	45	158	161	252	262	142	386	893	939	1525	1582
34	60	231	236	247	375	154	442	981	1302	1570	1612
34	75	239	245	276	347	163	449	954	1165	1417	1860
34	90	261	267	306	372	167	474	986	1346	1554	1634
34	105	264	270	308	378	173	462	1005	1459	1564	1623
34	120	246	252	350	388	177	461	1027	1226	2480	1692
34	135	251	257	352	393	179	468	1037	1098	1428	1714
34	150	261	267	356	413	186	477	1042	1300	1494	1755
34	165	264	269	352	406	189	458	985	1438	1580	1882
34	180	264	268	351	396	194	479	960	1446	1523	1774
34	195	259	264	353	402	194	463	910	1346	1440	1823
34	210	262	267	352	428	198	481	944	1372	1554	1743
34	225	269	273	361	420	194	467	956	1402	1536	1785
34	240	272	278	368	433	198	480	955	1434	1552	1749
34	255	287	291	343	434	198	461	939	1461	1540	1860

CORRECTED TEMPERATURE DATA

RUN	TIME	1	2	3	4	5	6	7	8	9	10
34	0	59	62	54	65	64	63	62	62	65	68
34	15	80	81	98	121	142	535	1236	1499	1614	2264
34	30	114	117	179	209	158	467	1117	1246	1900	2235
34	45	158	161	252	262	175	521	1240	1306	2137	2261
34	60	231	236	247	375	192	600	1365	1821	2201	2304
34	75	239	245	276	347	204	610	1327	1627	1984	2663
34	90	261	267	306	372	210	646	1372	1883	2179	2336
34	105	264	270	308	378	219	629	1399	2044	2193	2320
34	120	246	252	350	388	224	627	1431	1713	3493	2420
34	135	251	257	352	393	227	637	1445	1531	2000	2452
34	150	261	267	356	413	237	650	1452	1818	2093	2511
34	165	264	269	352	406	241	623	1371	2014	2216	2695
34	180	264	268	351	396	248	653	1336	2025	2135	2539
34	195	259	264	353	402	248	630	1265	1883	2017	2610
34	210	262	267	352	428	254	656	1313	1920	2179	2494
34	225	269	273	361	420	248	636	1330	1963	2153	2555
34	240	272	278	368	433	254	654	1328	2008	2176	2503
34	255	287	291	343	434	254	627	1306	2047	2159	2663

TABLE LXIX

RAW TEMPERATURE DATA (RUN 35)

RAW TEMPERATURE DATA

RUN	TIME	1	2	3	4	5	6	7	8	9	10
35	0	287	291	343	434	198	461	939	1461	1540	1860
35	15	299	304	358	460	223	551	1010	1430	1575	1873
35	30	302	304	367	448	227	530	925	1300	1568	1868
35	45	281	285	363	402	224	532	964	1435	1816	2302
35	60	271	274	339	387	222	529	960	1576	1780	2235
35	75	360	365	336	394	218	532	901	1490	1718	2245
35	90	265	268	337	428	218	510	898	1492	1701	2177
35	105	271	275	344	444	218	539	931	1491	1556	2079
35	120	269	276	345	433	226	511	926	1436	1558	2129
35	135	269	271	339	445	222	492	882	1501	1640	2000
35	150	263	265	334	425	220	526	957	1522	1707	1941
35	165	264	267	336	431	234	557	997	1550	1670	1869
35	180	267	270	339	440	233	519	938	1552	1583	2011
35	180	267	270	339	440	233	519	938	1552	1583	2021
35	195	269	272	342	427	231	540	963	1533	1670	1972
35	210	268	271	342	419	230	542	951	1446	1616	1905
35	225	242	245	375	414	231	558	950	1369	1645	2189
35	240	245	249	370	415	234	553	913	1364	1596	1982

CORRECTED TEMPERATURE DATA

RUN	TIME	1	2	3	4	5	6	7	8	9	10
35	0	287	291	343	434	253	627	1305	2046	2158	2662
35	15	299	304	358	460	289	754	1406	2002	2208	2681
35	30	302	304	367	448	294	724	1285	1817	2198	2674
35	45	281	285	363	402	290	727	1340	2009	2550	3302
35	60	271	274	339	387	287	723	1335	2209	2499	3205
35	75	360	365	336	394	282	727	1251	2087	2411	3220
35	90	265	268	337	428	282	696	1247	2090	2387	3121
35	105	271	275	344	444	282	737	1294	2088	2181	2979
35	120	269	276	345	433	293	698	1287	2010	2184	3052
35	135	269	271	339	445	287	671	1224	2103	2300	2865
35	150	263	265	334	425	284	719	1331	2132	2395	2780
35	165	264	267	336	431	304	763	1387	2172	2343	2675
35	180	267	270	339	440	303	709	1304	2175	2219	2881
35	180	267	270	339	440	303	709	1304	2175	2219	2895
35	195	269	272	342	427	300	739	1339	2148	2343	2825
35	210	268	271	342	419	299	742	1322	2025	2266	2728
35	225	242	245	375	414	300	764	1321	1915	2307	3139
35	240	245	249	370	415	304	757	1268	1908	2237	2839

TABLE LXX

RAW TEMPERATURE DATA (RUN 36)

RAW TEMPERATURE DATA

RUN	TIME	1	2	3	4	5	6	7	8	9	10
36	0	245	249	370	415	234	553	913	1364	1596	1982
36	15	258	262	360	414	255	593	968	1462	1850	1980
36	30	264	269	353	435	264	607	1027	1434	1708	1872
36	45	284	290	340	400	267	613	985	1441	1951	2037
36	60	282	286	351	419	271	640	991	1342	1752	2163
36	75	292	297	339	408	270	634	969	1290	1532	1890
36	90	288	293	337	404	269	644	986	1320	1486	2061
36	105	297	301	354	404	273	681	1040	1468	2017	2137
36	120	287	292	358	387	276	656	1021	1589	2029	2145
36	135	286	292	356	371	278	649	1046	1490	1986	2061
36	150	272	280	359	395	279	658	1018	1397	1734	1972
36	165	271	277	359	399	278	656	995	1298	1788	1946
36	180	273	278	366	382	284	704	999	1328	1672	1863
36	195	271	278	367	357	282	680	1014	1388	1606	1802
36	210	267	276	360	360	274	634	968	1353	1602	1911
36	225	269	275	354	354	267	614	915	1378	1705	2112
36	240	260	266	342	321	264	612	903	1434	1604	2020

CORRECTED TEMPERATURE DATA

RUN	TIME	1	2	3	4	5	6	7	8	9	10
36	0	245	249	370	415	304	757	1268	1908	2237	2839
36	15	258	262	360	414	334	814	1346	2047	2598	2836
36	30	264	269	353	435	347	834	1430	2008	2396	2680
36	45	284	290	340	400	351	842	1370	2017	2741	2919
36	60	282	286	351	419	357	881	1379	1877	2459	3101
36	75	292	297	339	408	355	872	1348	1803	2147	2706
36	90	288	293	337	404	354	886	1372	1846	2081	2953
36	105	297	301	354	404	360	939	1448	2056	2835	3063
36	120	287	292	358	387	364	903	1421	2228	2852	3075
36	135	286	292	356	371	367	893	1457	2087	2791	2953
36	150	272	280	359	395	368	906	1417	1955	2433	2825
36	165	271	277	359	399	367	903	1384	1815	2510	2787
36	180	273	278	366	382	375	971	1390	1857	2345	2667
36	195	271	278	367	357	372	937	1411	1942	2252	2579
36	210	267	276	360	360	361	872	1346	1893	2246	2736
36	225	269	275	354	354	351	844	1271	1928	2392	3027
36	240	260	266	342	321	347	841	1254	2008	2249	2894

TABLE LXXI

RAW TEMPERATURE DATA (RUN 37)

RAW TEMPERATURE DATA

RUN	TIME	1	2	3	4	5	6	7	8	9	10
37	0	62	58	62	60	59	59	59	63	58	76
37	15	104	104	140	150	182	536	932	1176	1531	1847
37	30	159	162	254	223	210	636	1189	1274	1414	2027
37	45	214	219	279	273	233	762	1279	1406	1543	1986
37	60	238	242	344	293	244	723	1306	1448	1666	2019
37	75	253	258	359	307	245	690	1219	1286	1547	2058
37	90	287	291	359	330	260	725	1360	1467	1688	2059
37	105	283	289	389	342	265	706	1266	1360	1629	2069
37	120	297	302	405	353	279	728	1256	1454	1678	2072
37	135	305	309	411	361	288	752	1261	1384	1540	2094
37	150	306	310	410	364	290	731	1259	1492	1630	2076
37	165	310	315	405	374	295	752	1390	1496	1584	2083
37	180	307	309	417	378	290	733	1274	1461	1576	2046
37	195	310	316	416	388	291	736	1198	1415	1543	2063
37	210	322	328	405	404	290	780	1320	1497	1571	2067
37	225	329	336	394	393	284	746	1201	1514	1656	2088
37	240	330	336	418	399	299	769	1328	1421	1519	2094
37	255	330	335	418	406	296	746	1310	1393	1502	2096

CORRECTED TEMPERATURE DATA

RUN	TIME	1	2	3	4	5	6	7	8	9	10
37	0	62	58	62	60	59	59	59	63	58	76
37	15	104	104	140	150	233	735	1297	1644	2147	2646
37	30	159	162	254	223	273	877	1662	1783	1981	2907
37	45	214	219	279	273	305	1056	1790	1970	2165	2847
37	60	238	242	344	293	321	1001	1828	2030	2339	2895
37	75	253	258	359	307	322	954	1705	1800	2170	2951
37	90	287	291	359	330	344	1004	1905	2057	2370	2953
37	105	283	289	389	342	351	977	1771	1905	2287	2967
37	120	297	302	405	353	371	1008	1757	2038	2356	2972
37	135	305	309	411	361	383	1042	1764	1939	2160	3004
37	150	306	310	410	364	386	1012	1761	2092	2288	2978
37	165	310	315	405	374	393	1042	1947	2098	2223	2988
37	180	307	309	417	378	386	1015	1783	2048	2211	2934
37	195	310	316	416	388	388	1019	1675	1983	2165	2959
37	210	322	328	405	404	386	1082	1848	2099	2204	2964
37	225	329	336	394	393	378	1033	1679	2123	2325	2995
37	240	330	336	418	399	399	1066	1859	1991	2130	3004
37	255	330	335	418	406	395	1033	1834	1952	2106	3006

TABLE LXXII

RAW TEMPERATURE DATA (RUN 38)

RAW TEMPERATURE DATA

RUN	TIME	1	2	3	4	5	6	7	8	9	10
38	0	330	335	418	406	296	746	1310	1393	1502	2096
38	15	325	327	408	410	284	712	1178	1408	1519	1960
38	30	308	314	418	411	277	711	1364	1410	1458	1927
38	45	304	309	414	409	271	697	1250	1413	1534	1958
38	60	320	326	375	386	270	690	1208	1436	1538	1986
38	75	326	328	408	390	312	789	1293	1474	1582	1938
38	90	310	313	426	355	271	721	1208	1439	1562	1874
38	105	335	337	339	354	269	672	1171	1468	1562	1901
38	120	342	346	350	359	271	663	1381	1482	1556	1890
38	135	341	345	349	365	269	659	1435	1479	1545	1938
38	150	340	344	345	365	268	643	1166	1461	1566	1907
38	165	318	322	347	321	270	652	1415	1422	1620	1880
38	180	302	306	326	306	258	612	1184	1476	1570	1934
38	195	290	294	320	299	255	617	1258	1461	1595	1963
38	210	284	294	315	303	251	635	1418	1465	1614	1909
38	225	279	286	306	309	246	618	1268	1502	1633	1923
38	240	277	287	308	311	246	619	1132	1440	1642	1944

CORRECTED TEMPERATURE DATA

RUN	TIME	1	2	3	4	5	6	7	8	9	10
38	0	330	335	418	406	392	1031	1832	1949	2104	3004
38	15	325	327	408	410	375	983	1644	1971	2128	2807
38	30	308	314	418	411	365	981	1908	1973	2042	2759
38	45	304	309	414	409	357	962	1746	1978	2149	2804
38	60	320	326	375	386	355	952	1687	2010	2155	2845
38	75	326	328	408	390	415	1092	1807	2064	2218	2775
38	90	310	313	426	355	357	996	1687	2015	2189	2683
38	105	335	337	339	354	354	926	1634	2056	2189	2722
38	120	342	346	350	359	357	913	1932	2076	2181	2706
38	135	341	345	349	365	354	908	2009	2071	2165	2775
38	150	340	344	345	365	353	885	1627	2046	2195	2730
38	165	318	322	347	321	355	898	1981	1991	2272	2691
38	180	302	306	326	306	338	841	1653	2067	2201	2770
38	195	290	294	320	299	334	848	1758	2046	2236	2812
38	210	284	294	315	303	328	874	1985	2052	2263	2733
38	225	279	286	308	309	321	849	1772	2104	2290	2754
38	240	277	287	308	311	321	851	1579	2016	2303	2784

TABLE LXXIII

RAW TEMPERATURE DATA (RUN 39)

RAW TEMPERATURE DATA

RUN	TIME	1	2	3	4	5	6	7	8	9	10
39	0	62	61	57	66	64	64	62	62	62	62
39	15	123	124	157	171	207	554	1167	1337	1556	1749
39	30	197	198	213	232	224	626	1266	1396	1610	1787
39	45	200	204	328	244	236	677	1270	1434	1645	1871
39	60	236	242	352	280	237	650	1272	1418	1603	2043
39	75	247	253	386	299	244	642	1116	1424	1606	2012
39	90	254	258	386	302	252	652	1156	1421	1591	1971
39	105	282	284	393	333	258	658	1152	1403	1628	1958
39	120	290	296	388	342	264	652	1171	1423	1602	1955
39	135	289	297	395	333	268	668	1139	1394	1620	1909
39	150	292	299	390	306	277	699	1170	1444	1685	1936
39	165	289	295	391	342	274	704	1170	1454	1660	1890
39	180	286	301	392	350	273	720	1258	1440	1665	1955
39	195	294	299	359	362	275	742	1307	1437	1668	1942
39	210	319	325	367	364	278	762	1353	1453	1699	1916
39	225	321	326	368	371	279	796	1352	1454	1654	1938
39	240	340	347	360	381	295	848	1371	1437	1726	1938
39	255	338	344	351	377	286	789	1328	1415	1654	1896

CORRECTED TEMPERATURE DATA

RUN	TIME	1	2	3	4	5	6	7	8	9	10
39	0	62	61	57	66	64	64	62	62	62	62
39	15	123	124	157	171	267	759	1630	1871	2182	2503
39	30	197	198	213	232	291	862	1770	1955	2258	2558
39	45	200	204	328	244	308	934	1776	2008	2308	2679
39	60	236	242	352	280	310	896	1779	1986	2248	2928
39	75	247	253	386	299	319	884	1557	1994	2253	2883
39	90	254	258	386	302	331	899	1614	1990	2231	2824
39	105	282	284	393	333	339	907	1608	1964	2284	2805
39	120	290	296	388	342	348	899	1635	1993	2247	2801
39	135	289	297	395	333	354	921	1590	1952	2272	2734
39	150	292	299	390	306	366	965	1634	2023	2365	2773
39	165	289	295	391	342	362	972	1634	2037	2329	2707
39	180	286	301	392	350	361	995	1759	2017	2336	2801
39	195	294	299	359	362	363	1026	1828	2013	2341	2782
39	210	319	325	367	364	368	1055	1894	2035	2385	2745
39	225	321	326	368	371	369	1103	1892	2037	2321	2776
39	240	340	347	360	381	392	1177	1919	2013	2423	2776
39	255	338	344	351	377	379	1093	1858	1982	2321	2716

TABLE LXXIV

RAW TEMPERATURE DATA (RUN 40)

RAW TEMPERATURE DATA

RUN	TIME	1	2	3	4	5	6	7	8	9	10
40	0	338	344	351	377	286	789	1328	1415	1654	1896
40	30	347	355	392	396	340	900	1270	1535	1656	2031
40	45	352	360	390	397	340	938	1351	1531	1598	2017
40	60	346	354	414	397	345	951	1350	1541	1724	2058
40	75	351	357	415	395	347	976	1392	1558	1712	2037
40	90	352	359	424	403	350	926	1380	1600	1696	1988
40	105	362	366	429	400	358	959	1358	1582	1746	2000
40	120	363	370	435	407	357	930	1264	1591	1680	1926
40	135	364	375	436	419	362	934	1283	1635	1677	1974
40	150	366	372	434	409	365	944	1285	1572	1696	1988
40	165	370	377	440	413	367	965	1314	1561	1692	1982
40	180	379	386	438	427	371	948	1320	1640	1750	2000
40	195	368	378	425	409	369	942	1329	1494	1618	1998
40	210	349	357	418	390	340	915	1271	1545	1683	1985
40	225	343	354	427	388	366	961	1330	1620	1694	2012
40	240	351	358	440	396	374	994	1278	1583	1652	1959

CORRECTED TEMPERATURE DATA

RUN	TIME	1	2	3	4	5	6	7	8	9	10
40	0	338	344	351	377	378	1092	1857	1981	2320	2715
40	30	347	355	392	396	455	1250	1775	2151	2323	2910
40	45	352	360	390	397	455	1304	1890	2145	2240	2890
40	60	346	354	414	397	462	1322	1888	2159	2419	2949
40	75	351	357	415	395	465	1358	1948	2184	2402	2919
40	90	352	359	424	403	469	1287	1931	2243	2379	2848
40	105	362	366	429	400	480	1333	1900	2218	2450	2865
40	120	363	370	435	407	479	1292	1766	2230	2357	2758
40	135	364	375	436	419	486	1298	1793	2293	2352	2827
40	150	366	372	434	409	490	1312	1796	2203	2379	2848
40	165	370	377	440	413	493	1342	1837	2188	2374	2839
40	180	379	386	438	427	499	1318	1846	2300	2456	2865
40	195	368	378	425	409	496	1309	1859	2093	2269	2862
40	210	349	357	418	390	455	1271	1776	2165	2361	2843
40	225	343	354	427	388	492	1336	1860	2272	2377	2882
40	240	351	358	440	396	503	1383	1786	2219	2317	2806

VITA γ

Ryan DeLacy Moats, Jr.

Candidate for the Degree of

Doctor of Philosophy

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