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The Impact of Alcohol Fuels on Urban Air Pollution: Methanol Photochemistry Study

November 1984

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The Impact of Alcohol Fuels on Urban Air Pollution: Methanol Photochemistry Study

November 1984

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The work scope and funding for this project have been supplied as a result of Corporate interest in the project. In addition the Department of Energy has participated by providing the smog chamber and its instrumentation to the University as well as providing for the facility's maintenance.

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THE IMPACT OF ALCOHOL FUELS ON URBAN AIR POLLUTION: METHANOL PHOTOCHEMISTRY STUDY

Final Report
November 8, 1984

A. Summary

The past decade of research has clearly established methanol as one of the leading candidates from an environmental standpoint to replace petroleum in the ground transportation sector. Early studies, although limited (Ref.1,2,3), have indicated that in like operational circumstances methanol generated emissions can be as low as or lower than hydrocarbon emissions in photochemical reactivity. The following study, conducted by Systems Applications Inc. (SAI) and the University of Santa Clara (SCU), adds to that evidence. It has been co-funded by the ARCO Petroleum Products Co., E.I. DuPont de Nemours & Co., and the United States Department of Energy.

During the study the smog chamber facilities at the University of Santa Clara were used to conduct further validation studies of methanol's photochemistry. The facility consists of a 100 cubic foot aluminum and Pyrex^R chamber with an enclosed FEP Teflon^R bag. Eighty-four blacklights and eighteen sunlamps provide the solar simulation. The study primarily focused on neat methanol's exhaust emissions and the photochemistry of neat methanol. Methanol/gasoline blends were considered in an introductory way. Three series of photochemistry experiments were performed. The first series consisted entirely of hydrocarbon surrogates and methanol exhaust surrogates. The second series involved hydrocarbon surrogates and actual methanol vehicle exhaust. The third series compared exhaust and evaporative emissions from a base gasoline and a methanol/gasoline blend.

A baseline mixture of eight hydrocarbons was used to experimentally simulate the precursors of urban photochemical smog. A methanol exhaust simulation consisting of methanol and a formaldehyde surrogate (isobutene) was substituted for one-third of the baseline hydrocarbons in order to validate their chemical kinetic mechanism. A series of thirteen smog chamber experiments were performed at low (3:1), medium (9:1) and high (27:1) ratios of urban hydrocarbons (HC) to nitrogen oxides (NOx). SAI and SCU experimentally demonstrated that methanol exhaust has a significantly low ozone formation reactivity relative to the baseline mixture at moderate and especially at low HC/NOx ratios. Current emission control strategies will tend to lower the average urban HC/NOx ratio in the future and this should further enhance the benefit from methanol substitution.

The experimental results, which served as a validation for the model, did in fact compare favorably with results from a previous atmospheric modeling study (2) and indicate potential benefits from neat methanol substitution for gasoline. Based on these results the model predicts 18% or more improvement in ozone if all mobile sources in the Los Angeles region used neat methanol fuel in 1987. This important conclusion is supported by a series of experiments which covered a similarly wide urban range of HC/NOx ratios.

SAI has successfully modeled the hydrocarbon surrogate and the methanol exhaust surrogate substitution experiments. However, this task has required SAI to develop a significant extension to the previously used Carbon Bond Mechanism (CBM-III). The new extended CBM-III has just recently been applied to the previous atmospheric modeling study case. The extended CBM-III predicts a very similar reduction in ozone with neat methanol substitution for gasoline. It is important to note that the methanol photochemistry portion of the chemical kinetic mechanism, as used in both atmospheric modeling studies, was nevertheless validated in the form originally used.

The extended CBM-III mechanism includes a separate treatment of m-xylene's chemistry. m-Xylene was found to react rapidly and was consumed early during the photochemistry experiments. The extended CBM-III mechanism predicts greater ozone improvements for a fixed amount of hydrocarbon (with m-xylene) control than was predicted by previous CBM mechanisms. It suggests the possibility that previous urban modeling studies have overpredicted the amount of hydrocarbon controls needed to meet the ozone standard. The important effects of m-xylene's photochemistry require further study.

A series of almost neat (95% methanol + 5% isopentane) methanol vehicle exhaust substitution experiments was also conducted in order to validate the above use of methanol exhaust "surrogates". The dilute exhaust from a vehicle using this fuel was similarly substituted for one-third of the baseline hydrocarbon mix. Very similar reactivity effects were observed in the actual vehicle exhaust experiments when compared with the methanol/surrogate exhaust evidence, thus validating the use of methanol exhaust surrogates in the previous series of experiments. In effect, the experimental use of only methanol and formaldehyde emissions is sufficient to fully represent the reactive exhaust emissions from a neat methanol fueled vehicle.

In a subsequent series of vehicle exhaust and evaporative emissions photochemistry experiments, gasoline and a methanol/gasoline blend fuel (4.5% methanol and 4.5% GTBA) were compared. The two test fuels were blended to meet ASTM specifications for summer grade California gasoline (nine-pound Reid vapor pressure). The purpose of these reactivity comparisons was to identify any large and significant differences in exhaust and evaporative emissions reactivity between the two fuels.

Preliminary results from the evaporative and exhaust smog chamber studies for the methanol blend and base gasoline fuels showed no significant differences in peak ozone formation potential. Also the methanol blend did not show any negative synergisms compared to base hydrocarbon gasoline. A combination of modeling and experiments at low HC/NOx ratios indicated that the exhaust from the methanol blend was lower in reactivity than the base gasoline.

Further confirmation of this data base and additional experimental work should produce added insights into methanol's low reactivity. Further work is also needed to confirm the initial findings that methanol's benefit is further increased at low ppm carbon to NOx ratios.

B. Introduction

Methanol fuel appears to be an attractive supplement to gasoline for technical, economic and environmental reasons. This validation study of methanol's photochemistry was designed to assess the air quality impact of methanol emissions prior to the widespead commercial use of this alcohol as fuel. Methanol may produce an environmental impact directly or indirectly. The direct photochemical effects of methanol emissions are generally considered slight due to it low rate of reaction with hydroxyl radicals. However, methanol's indirect effects are deserving of careful study due to the possible increase in formaldehyde exhaust emissions associated with this alcohol and also due to the potential volatility increase and evaporative emissions effects which could result from blends.

The design of the program combined smog chamber experimentation with sophisticated computer modeling of the chemistry under study. This parallel approach of experimentation and computer modeling is a cost effective and powerful technique to validate chemical mechanisms used in predictive atmospheric models. The program consisted of a series of smog chamber experiments involving typical urban hydrocarbons and the oxides of nitrogen. These pollutants are widely recognized as the immediate precursors of photochemical smog or ozone. The effects of methanol plus formaldehyde substitution for conventional urban hydrocarbons was experimentally assessed in a photochemical smog chamber. The results of these experiments were then modeled in order to validate the theoretical chemical kinetic mechanism for their photochemistry. In addition, numerous vehicle exhaust experiments were conducted to further validate the simplified photochemistry of the hydrocarbon "surrogates" which were used in the earliest experiments.

The reactivities of exhaust and evaporative emissions produced by gasoline was also compared to those emissions from a methanol/gasoline blend. A series of exhaust only, evaporative only and combined exhaust plus evaporative emissions experiments was conducted with the two test fuels.

In the following sections the experimental results of the Tasks are discussed along with their modeling and comparative interpretations.

C. Results of Completed WORK STATEMENT

1. Subcontract Negotiation with Systems Applications, Inc., Task 1.*

The third and final revision of the Subcontract was sent to the Sponsors for their review on August 24, 1983. An informal consulting and working relationship between ourselves and SAI had existed since the January 1983 meeting at which verbal agreements had been reached to proceed with the work.

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* Tasks are defined in Contractual Agreement.

2. Review of Chamber Characterization Experiments with SAI, Task 2.
Review of Chamber Characterization Experiments with SCU, Task S1.

a. Problems with original data set (January to June 1983.)

A review meeting which was held June 13, 1983 was attended by all of the Program's participants. An analysis of the initial set of smog chamber characterization experiments was reported by SAI. A progressive bias in the recent set of experiments was evident since the chamber was last cleaned on May 9, 1983. An increase in the conversion rate of nitric oxide to nitrogen dioxide after one month of chamber use suggested that radicals from an extraneous source were substantially influencing the chemistry.

SAI was able to model these characterization experiments by assuming the presence of nitrous acid (HONO) as a source of radicals emitted from the chamber's walls. The magnitude of the assumed radicals was large and comparable to that produced by the chemistry under study. It was therefore necessary to modify the experimental hardware in order to minimize those wall effects.

b. Upgrading of smog chamber facilities to reduce contamination

Several modifications to the smog chamber were initiated to prevent the observed interference. An FEP Teflon^R bag was constructed and installed within the aluminum and Pyrex^R walls of the chamber. This technique has been used elsewhere (4) to provide an inert surface for containment of the hydrocarbons and NOx. The chamber's multiple sampling ports were consolidated into a single bag outlet from which all the instruments were supplied. A single bag inlet was also provided for the supply of clean dilution air and for recirculation mixing purposes prior to the start of an experiment.

It was also decided to carefully filter the clean air supply after the catalytic combustor in order to prevent ash from possibly entering the chamber. A high efficiency particulate air (HEPA) filter was installed for that purpose. An additional filter was installed on the outlet of the ozone instrument as a precaution to filter any manganese dioxide dust before recirculation into the chamber bag.

A fraction of the clean, filtered air was continuously routed into the "buffer-zone" air surrounding the Teflon^R bag, but within the aluminum and Pyrex^R chamber walls. This was a further precaution against the diffusion of hydrocarbon and NOx contaminants from the external laboratory air into the bag.

c. Repeated chamber characterization experiments and analyses

A repeat series of chamber characterization studies was performed next. These experiments were modeled by Systems Applications, Inc. in order to confirm the performance of the chamber against the knowledge of other chambers and the known chemistry of particular experiments. The most fundamental chamber characteristic to model was simple dilution of a hydrocarbon with a measured flowrate of clean air.

Given the chamber volume and the dilution flowrate one can readily calculate the theoretical decrease in initial concentration over time:

$$C(t) = C(init) * \exp(-dt)$$

$$\text{where } d = \frac{\text{dilution flowrate}}{\text{chamber volume}}$$

t = time elapsed since initial concent.: C(init)

Figure 2-1 shows the agreement between the theoretical and measured chamber dilution rates. A second fundamental chamber characterization involved the increase in chamber temperature within the bag and buffer-zone after the lights were turned on. Typical temperature profiles over time are presented in Figure 2-2. Some of the chemical kinetic rates are sensitive to temperature effects although these effects are relatively small in magnitude. The interpretation and modeling of the experimental results is enhanced by a knowledge of the temperature profile. Note that the decline from peak temperatures is due to the build up of natural convection currents.

A series of special experiments was designed with guidance from SAI to measure the reactivity contribution of the chamber's walls. These experiments involved the use of NOx, CO, and acetaldehyde. The acetaldehyde experiments used only acetaldehyde at about the one ppm level to determine the rate of NOx off-gassing from the chamber walls. Such off-gassing could be important to experiments limited by NOx concentrations. For example the ozone peak under high hydrocarbon to NOx ratio conditions is usually determined by the point when NOx approaches zero. If nothing is purposely added to the chamber and NOx measurements are made, very little if any NOx is measured because some small radical concentration is available to convert any residual NOx to NO2. Subsequently, hydroxyl radicals (OH) would rapidly convert the NO2 to nitric acid. Hence the NOx measurements would show only a trace steady-state sum of NO and NO2 (i.e. NOx) even though NOx might be off-gassing at a high rate. Acetaldehyde provides some radicals by photolysis and OH radicals produce peroxyacetyl radicals from acetaldehyde. Hence, any NOx off-gassing leads to peroxyacetyl nitrate (PAN) formation. Most chemiluminescent NOx measurements of NO2 include the NOx present in PAN. Hence any off-gassing of NOx in the presence of acetaldehyde and ultraviolet light would show a buildup of PAN which should be measured with a normal chemiluminescent NOx detector. Figure 2-3 shows the acetaldehyde experiments which were then modeled with acetaldehyde chemistry and an NOx off-gassing rate of only 0.04 ppb per minute. That rate was low enough as to not affect the results of this study and was consistent with other smog chambers.

Two types of experiments have been used to determine the organic and radical reactivity of the smog chamber. In the first experiment about 0.5 ppm of NO is the only precursor added to the chamber. Any conversion of NO to NO2 seen would be caused by trace organics reacting in the presence of some source of radicals. The second experiment is the same except 50-100 ppm carbon monoxide (CO) is added. The CO supersedes any trace organic reactivity because CO reacts with OH to generate CO2 and the hydroperoxy radical (HO2) which in turn reacts with NO to give NO2 and return the OH. Unlike most organics CO does not produce any products which can photolyze and provide radicals to sustain the smog chemistry associated with

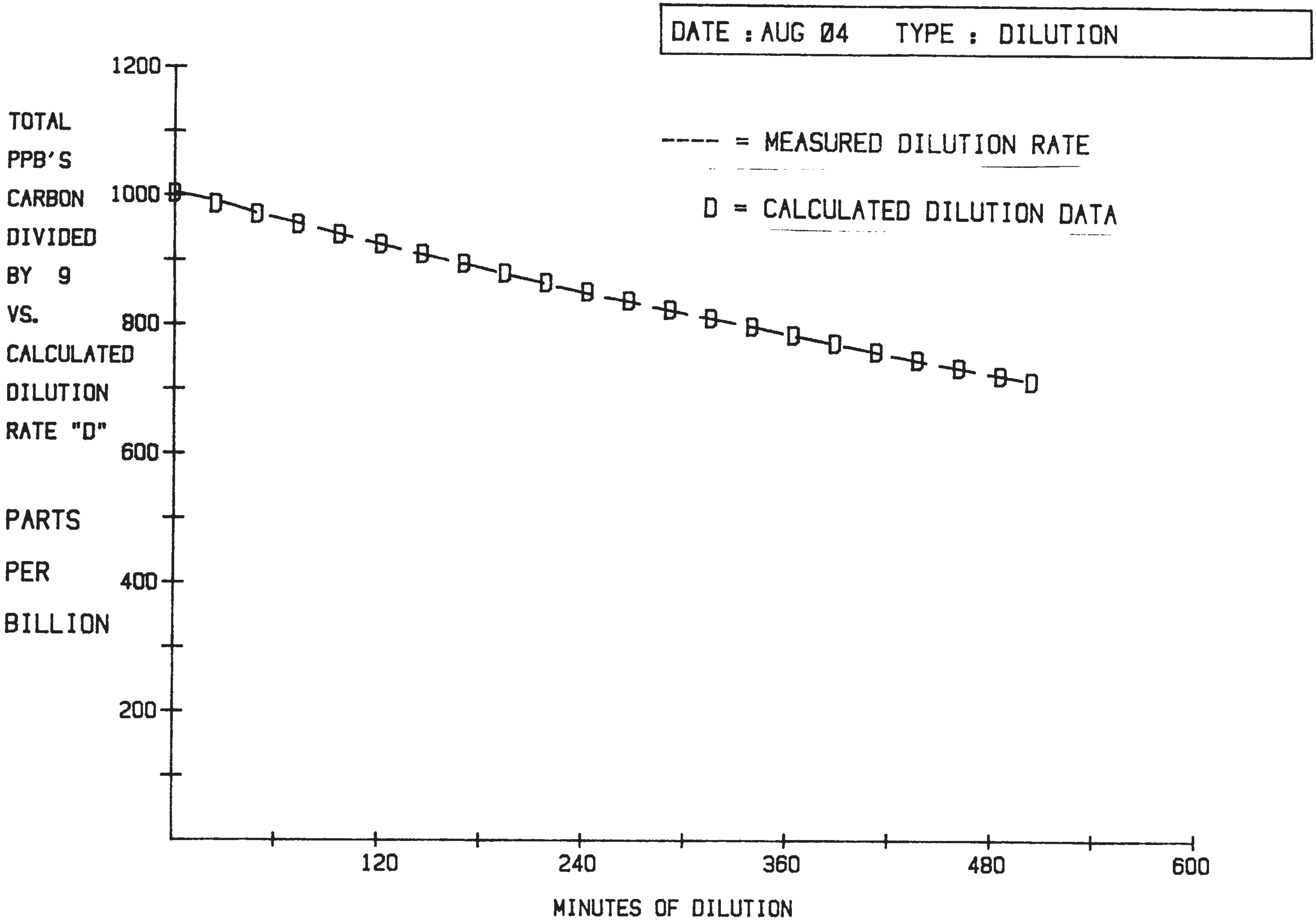

FIGURE 2-1 : EXPERIMENTAL VERSUS THEORETICAL SMOG CHAMBER DILUTION RATES

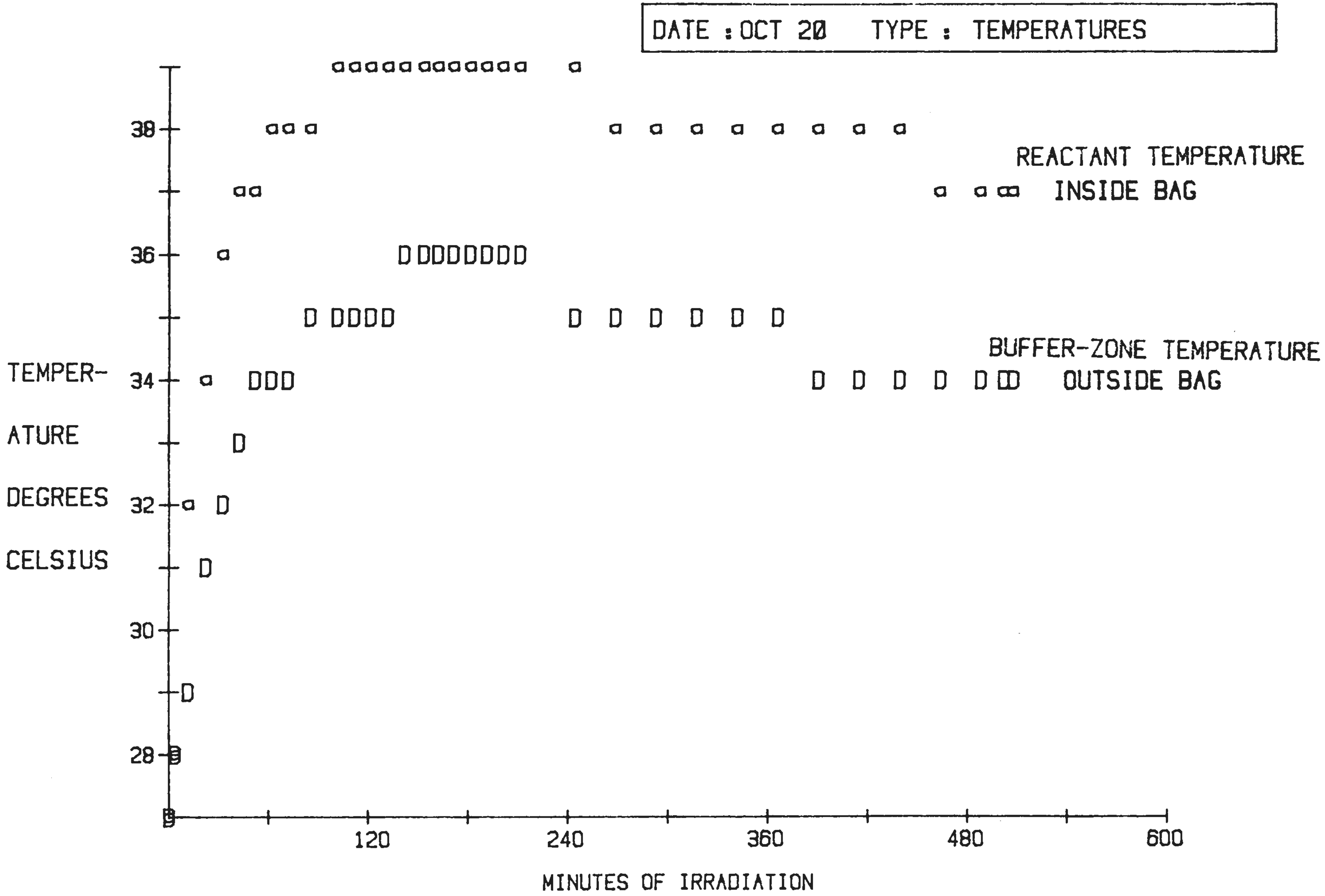

FIGURE 2-2 : TYPICAL TEMPERATURE PROFILE DURING SMOG CHAMBER EXPERIMENT

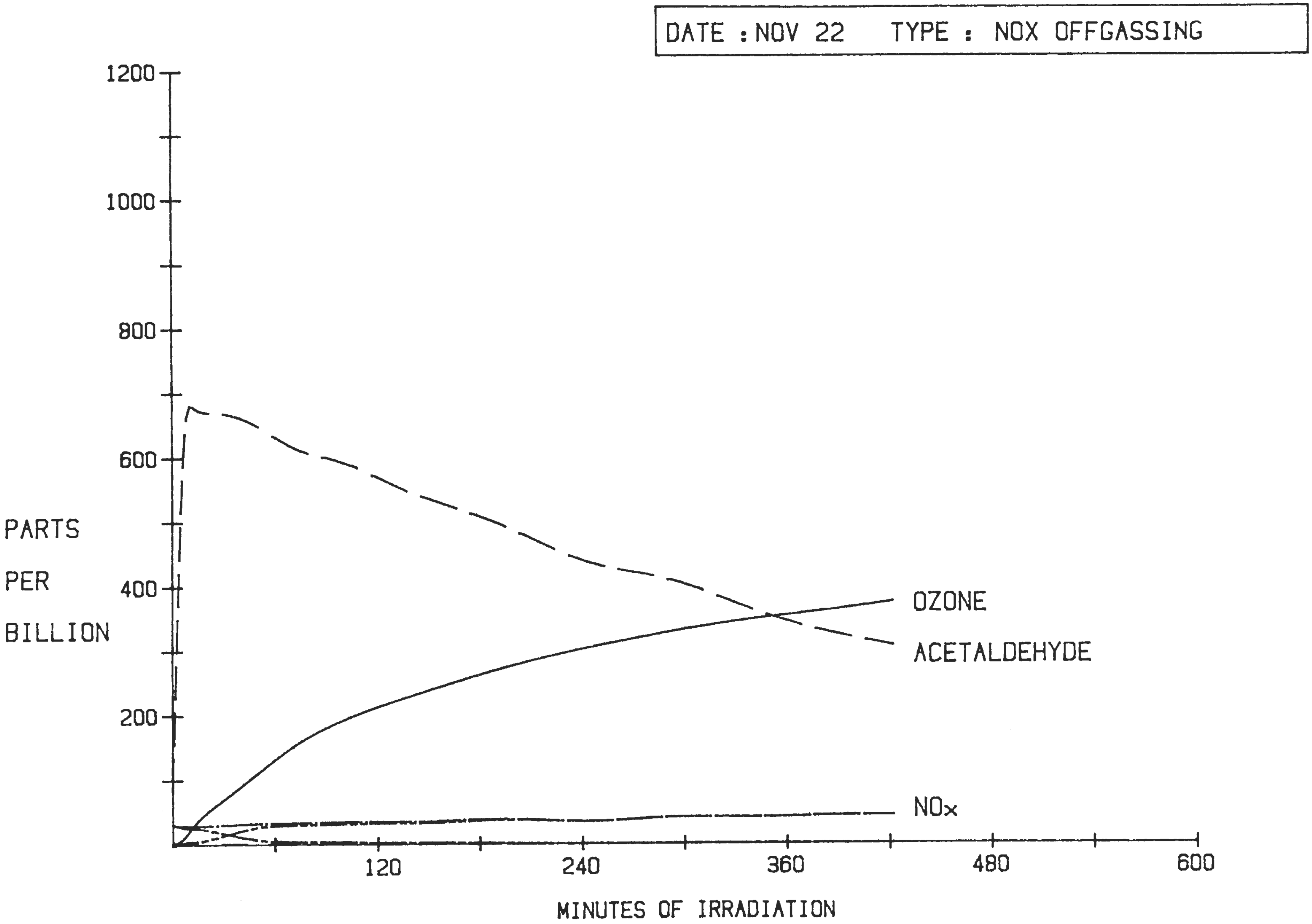

FIGURE 2-3 : ACETALDEHYDE CHARACTERIZATION TO MEASURE NOx OFFGASSING RATE conversion of NO to NO2. Hence the NO to NO2 conversion in the CO experiment amplifies the source of radicals in the chamber. The experiment without the added CO shows the result of both the chamber radicals and the organic reactivity.

Figures 2-4 and 2-5, respectively, show the NOx with clean air and NOx plus CO experiments which were fitted using an assumed background level of formaldehyde of 0.04 ppm initially plus a trace of formaldehyde coming off the walls at a rate of 0.0002 ppm per minute, plus a conversion of NO2 to nitrous acid (HONO) with a rate constant of 0.00024 per ppm per minute. This last value corresponds to a recently determined heterogeneous pathway studied by Sakamaki et al. (5). Such a reaction provides radicals from the subsequent fast photolysis of HONO to OH and NO. The use of assumed trace levels of formaldehyde is based on the work of Whitten, Killus, and Hogo (6). Such organic and radical levels as required to fit the chamber characterizations correspond to one of the lowest seen in smog chambers. For example, some recent data from a similar chamber at the University of California at Riverside required similarly low levels to simulate such experiments. The radical source strength corresponding to the formaldehyde off-gassing and heterogeneous NO2 to HONO conversions is about 0.05 ppb per minute, well below the typical 1 ppb per minute or greater generated from the organics and their products used in the regular experiments.

A very important characteristic of the smog chamber is its ultraviolet light intensity. The solar simulation was provided by 84 blacklights (F30T8/350 Bl) and 18 sunlamps (FS20). The lamps were individually replaced over an 840 hour life cycle in order to control aging effects. The light must pass through Pyrex^R glass windows which selectively attenuate the shorter wavelengths in the UV spectrum (6). The resulting spectral distribution of light intensity is analogous to that produced from sunlight after it passes through the earth's atmosphere.

Two photolysis reactions are of key importance in driving the photochemistry which produces urban ozone pollution. The first net reaction is formaldehyde photolysis to yield radical products:

$$\text{HCHO} \xrightarrow{hv} 2\text{HO}_2 + \text{CO}$$

These products initiate radical chain reactions which further oxidize other hydrocarbons and eventually convert nitric oxide into nitrogen dioxide.

$$\text{NO} + \text{HO}_2 \longrightarrow \text{NO}_2 + \text{OH}$$

A series of propene/NOx characterization studies was performed in order to better understand the formaldehyde photolysis rate constant. Past modeling experience by SAI has shown this to be the most important factor for achieving a close simulation of observed chamber data (8). Therefore, the formaldehyde photolysis constant was determined by fitting the propene experiments - these are shown in Figure 2-6. The key formaldehyde constant for photolysis to radicals so determined was 0.0025 per minute, a fairly high value but not inconsistent with the mixture of blacklights and sunlamps used in this chamber. The photolysis constant to stable products from formaldehyde is not important to smog chemistry, but the value of 0.0025 per minute was used to be consistent.

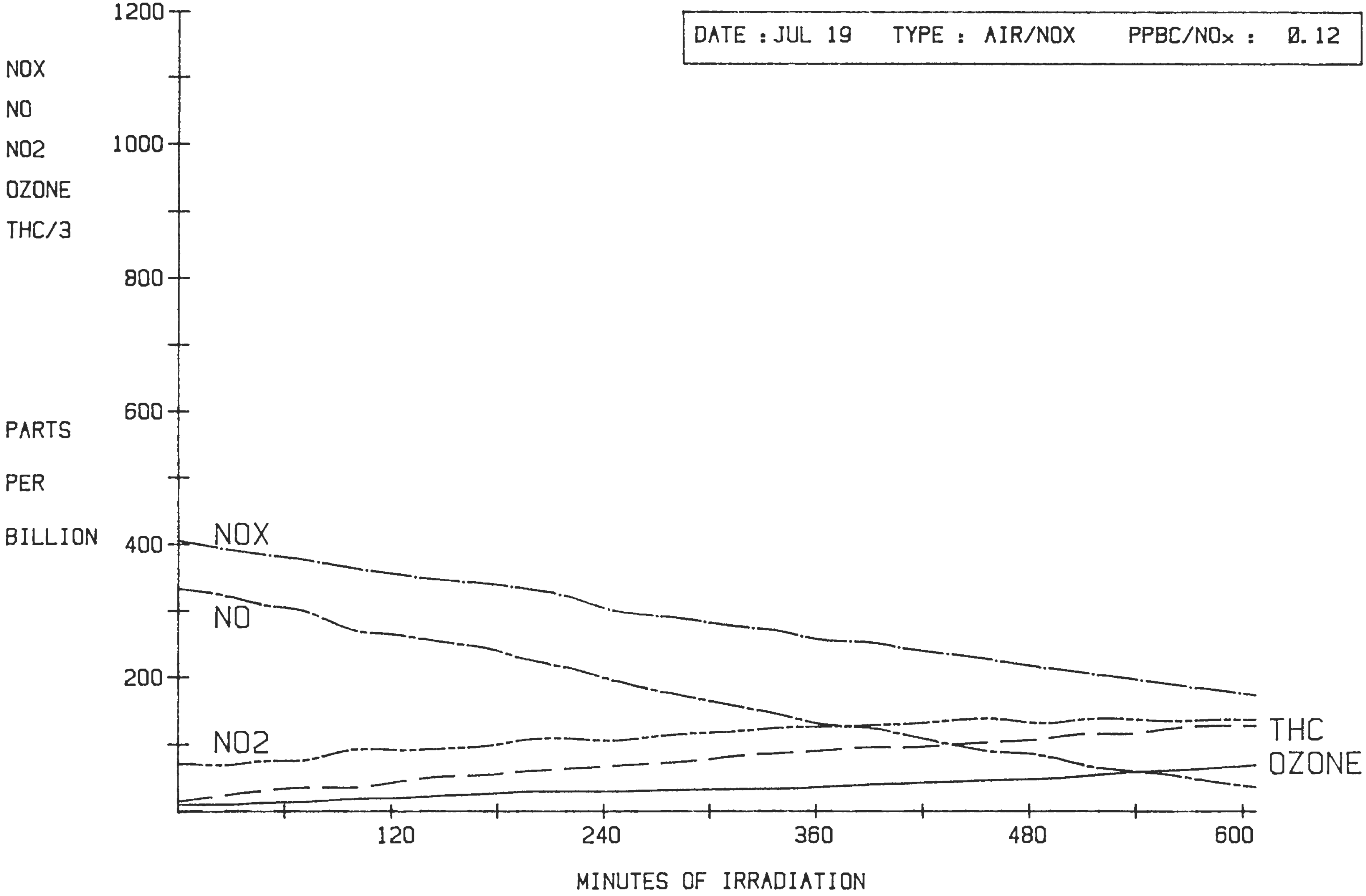

FIGURE 2-4 : CHARACTERIZATION EXPERIMENT USING CLEAN AIR AND NOX

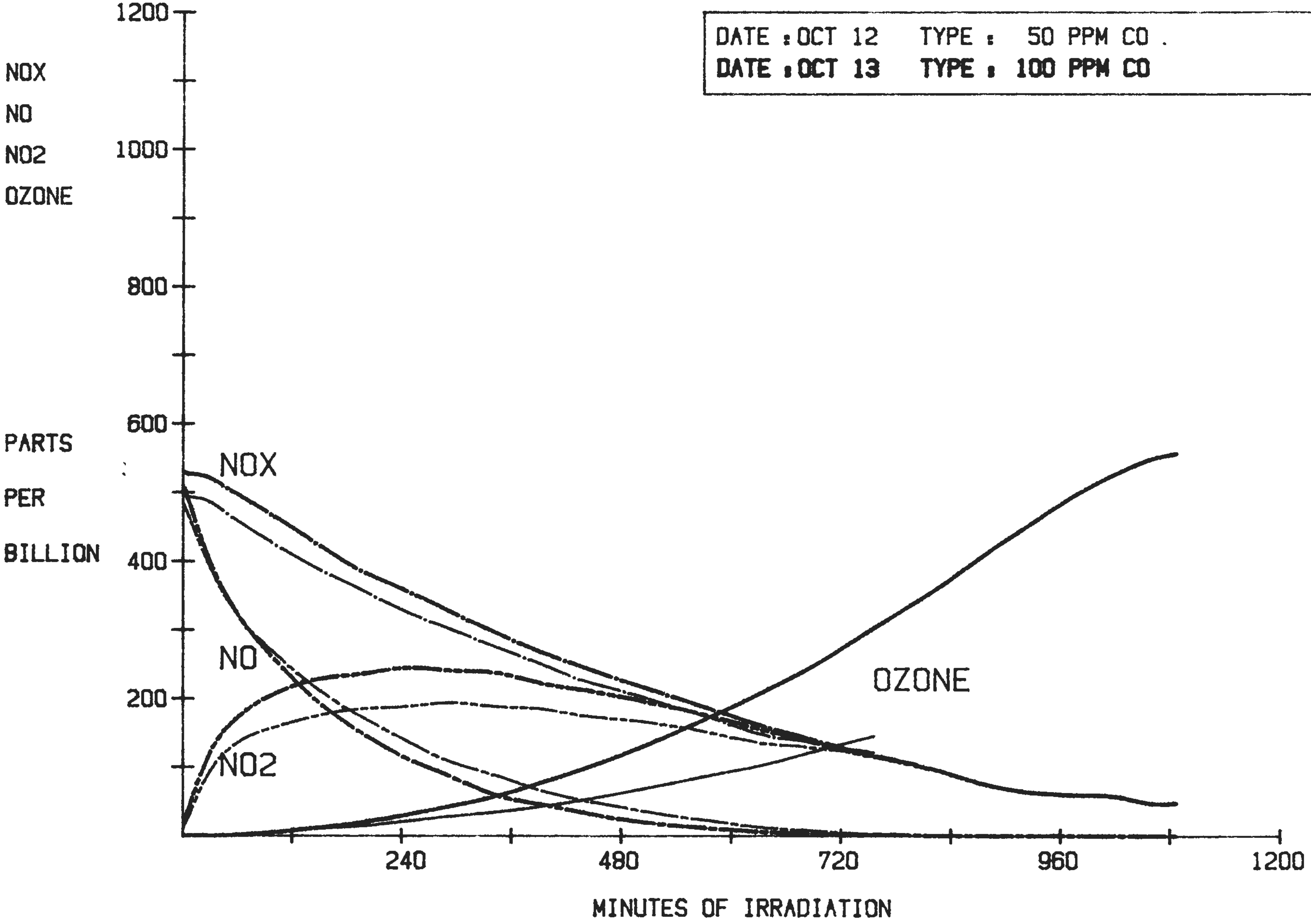

FIGURE 2-5 : CHARACTERIZATION EXPERIMENTS USING CARBON MONOXIDE AND NOX

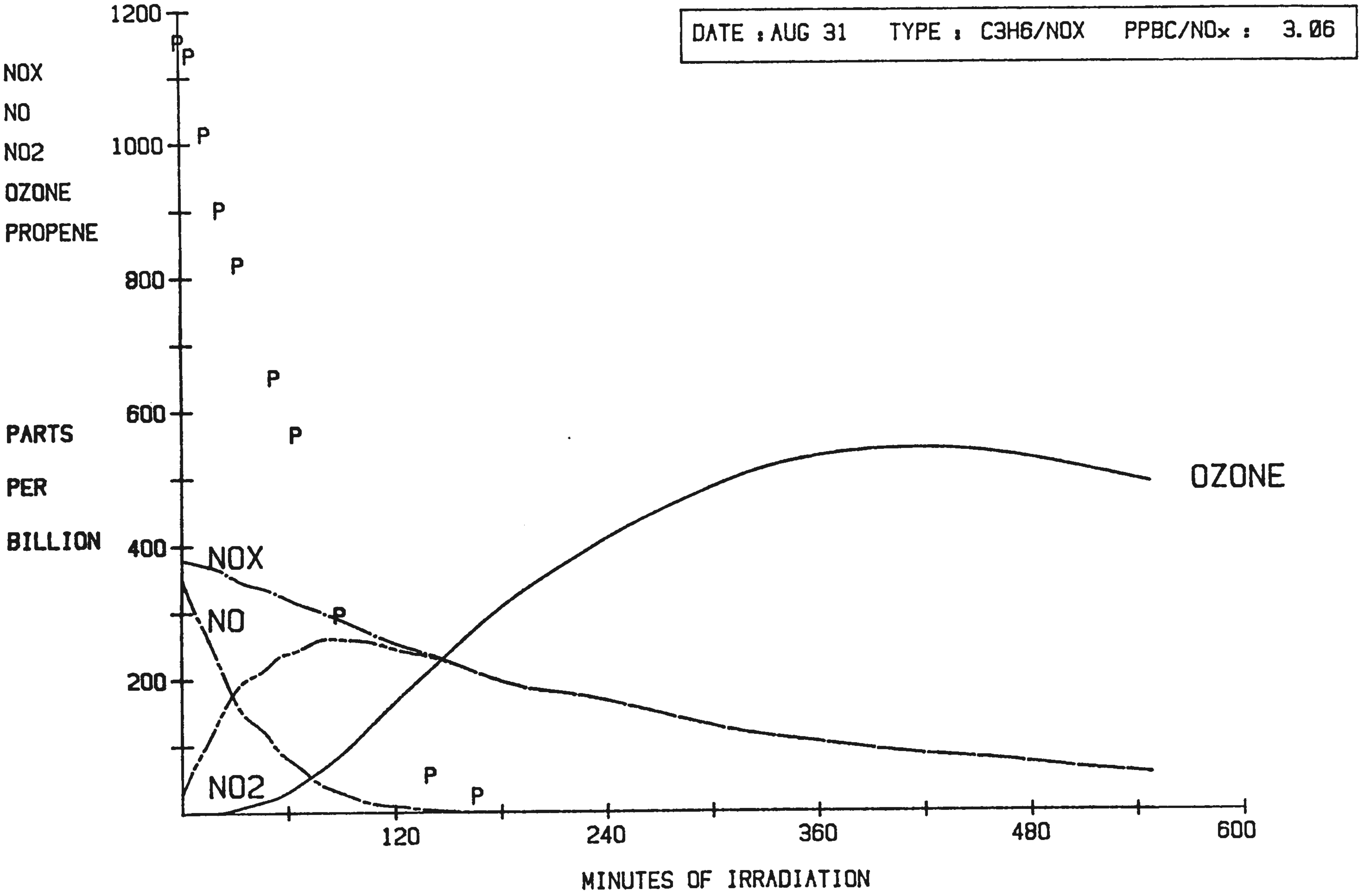

FIGURE 2-6 : PROPENE & NOX CHARACTERIZATION FOR FORMALDEHYDE PHOTOLYSIS

The second photolysis characteristic of key importance is the dissociation rate constant for nitrogen dioxide:

$$NO_2 \xrightarrow{hv} NO + O$$

The method of Wu and Niki (9) was used to determine the chamber's effective NO_2 dissociation rate. The measured value of 0.25 min^{-1} is about one half of the EPA's computed maximum solar value for Los Angeles on June 26th.(10) It is evident that the smog chamber's lights represent a reasonable approximation to average urban sunlight for the photolysis of NO_2.

3. Methanol Photochemistry Validation--Design Overview, Tasks 3, 4 and 5

The hydrocarbon surrogate mixture used in this study was designed to represent the current chemical classes of hydrocarbons observed in the South Coast Air Basin.(11) It includes a more representative group of <u>eight</u> surrogate species rather than the <u>two</u> or <u>four</u> hydrocarbon surrogate blends used in previous studies. Table 3-1 lists the organic compounds and their relative carbon percents within the surrogate mix.

TABLE 3-1: SURROGATES FOR URBAN HYDROCARBONS & METHANOL EXHAUST

HYDROCARBON SURROGATES	CARBON %
ethene	5.
propene	5.
isobutene	15.
n-butane	15.
n-pentane	20.
2,2,4-trimethyl pentane	15.
toluene	12.5
m-xylene	12.5
METHANOL SURROGATES	
methanol	69.
isobutene	31.

The experimental design is outlined in Table 3-2. The surrogate mixture of hydrocarbons was tested at three overall hydrocarbon (ppm carbon) to NOx ratios. Three sets of experiments were performed at each ratio: one with the full mixture, one with only two-thirds of the concentration (blank substitution), and one at two-thirds concentration with the remaining carbon concentraton substituted by a mixture of methanol and isobutene in a nine to one molar ratio.

Isobutene is believed to react rapidly to generate formaldehyde so the addition was equivalent to adding formaldehyde under reproducible conditions at the start of each experiment. The 10% molar isobutene concentration was selected to conservatively represent the formaldehyde emissions from combined exhaust plus vehicle fuel evaporation from neat methanol fueled vehicles.

An example of a complete set of measurements from one experiment is plotted in Figure 3-1. The initial reactant concentrations are shown at time zero on the left of the figure. Each of the eight urban surrogate hydrocarbons is represented by a letter symbol which is identified in the key at the upper right. Initial oxides of nitrogen (nitric oxide and nitrogen dioxide) are also plotted along with the photochemical products formaldehyde and ozone.

TABLE 3-2: EXPERIMENTAL DESIGN : INITIAL HYDROCARBON SURROGATES

		INITIAL SURROGATE CONCENTRATIONS, PPM		
Experimental Conditions	PPM Carbon to NOx Ratios	NOx	8-Surrogate Urban Blend	Methanol Exhaust Surrogates
Baseline	3	1.2	3.6	0
Hydrocarbons	9	0.4	3.6	0
(Task 3)	27	0.4	10.8	0
Two-Thirds	2	1.2	2.4	0
Baseline	6	0.4	2.4	0
(Task 4)	18	0.4	7.2	0
Methanol	3	1.2	2.4	1.2
Substitution	9	0.4	2.4	1.2
(Task 5)	27	0.4	7.2	3.6

The observed change in concentration of each species is the result of both controlled dilution and photochemical reactions. The purpose of the entire set of experiments is to validate an evolving chemical kinetic mechanism which describes in detail the chemical reactions and their rates within the system under study. The chemical kinetic mechanism is then incorporated into a model of the physical processes and emissions inventories of a specific urban setting for ozone modeling purposes. If the methanol substitution experiments produced results similar to the two-thirds baseline level without methanol then one would conclude that methanol was inert. If the substitution experiments were the same or more reactive than the full concentration experiments then one should conclude that the methanol was as reactive or more reactive than the urban surrogate mixture.

Task 3 A : Baseline Hydrocarbon Surrogate Reactivity at 3:1 Ratio
Task 4 A : Two-Thirds Baseline Hydrocarbon Reactivity at 2:1 Ratio
Task 5 A : Two-Thirds Baseline Plus Methanol Surrogate Reactivity

The comparative set of experimental results at the lowest ppm carbon to NOx ratios is presented in Figure 3-2. Due to an incorrect hydrocarbon calibration figure supplied by the vendor all of the ppm carbon to NOx ratios were 12% below experimental objectives. Only nitric oxide, nitrogen dioxide and ozone are plotted for these experiment overlay comparisons. The evidence in the lower right hand corner of the figure indicates that the methanol substitution experiment was very similar to the two-thirds baseline hydrocarbon reactivity experiment. Therefore, at this low ppm

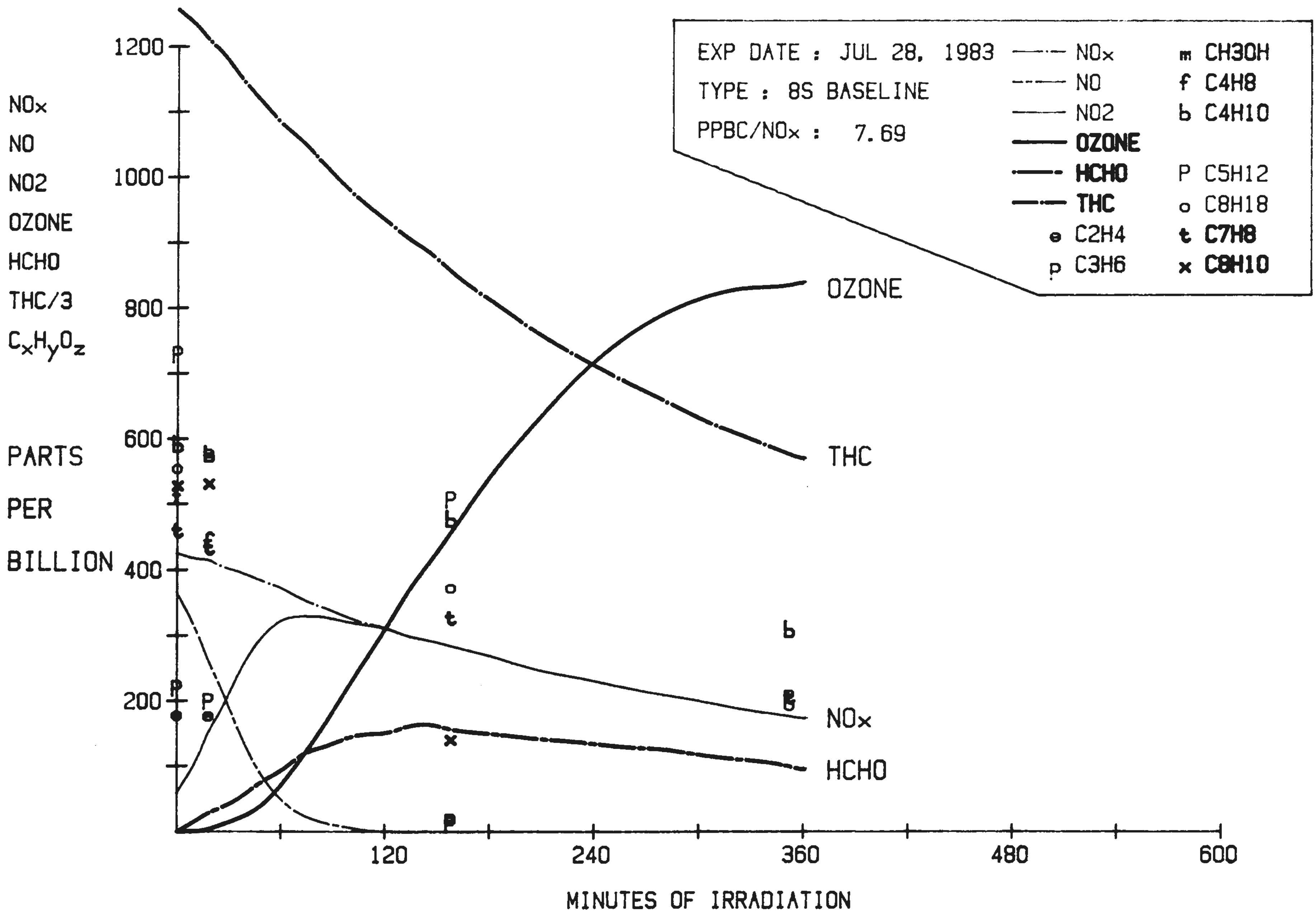

FIGURE 3-1 : REACTANT CONCENTRATIONS AND SMOG CHAMBER PRODUCTS OVER TIME

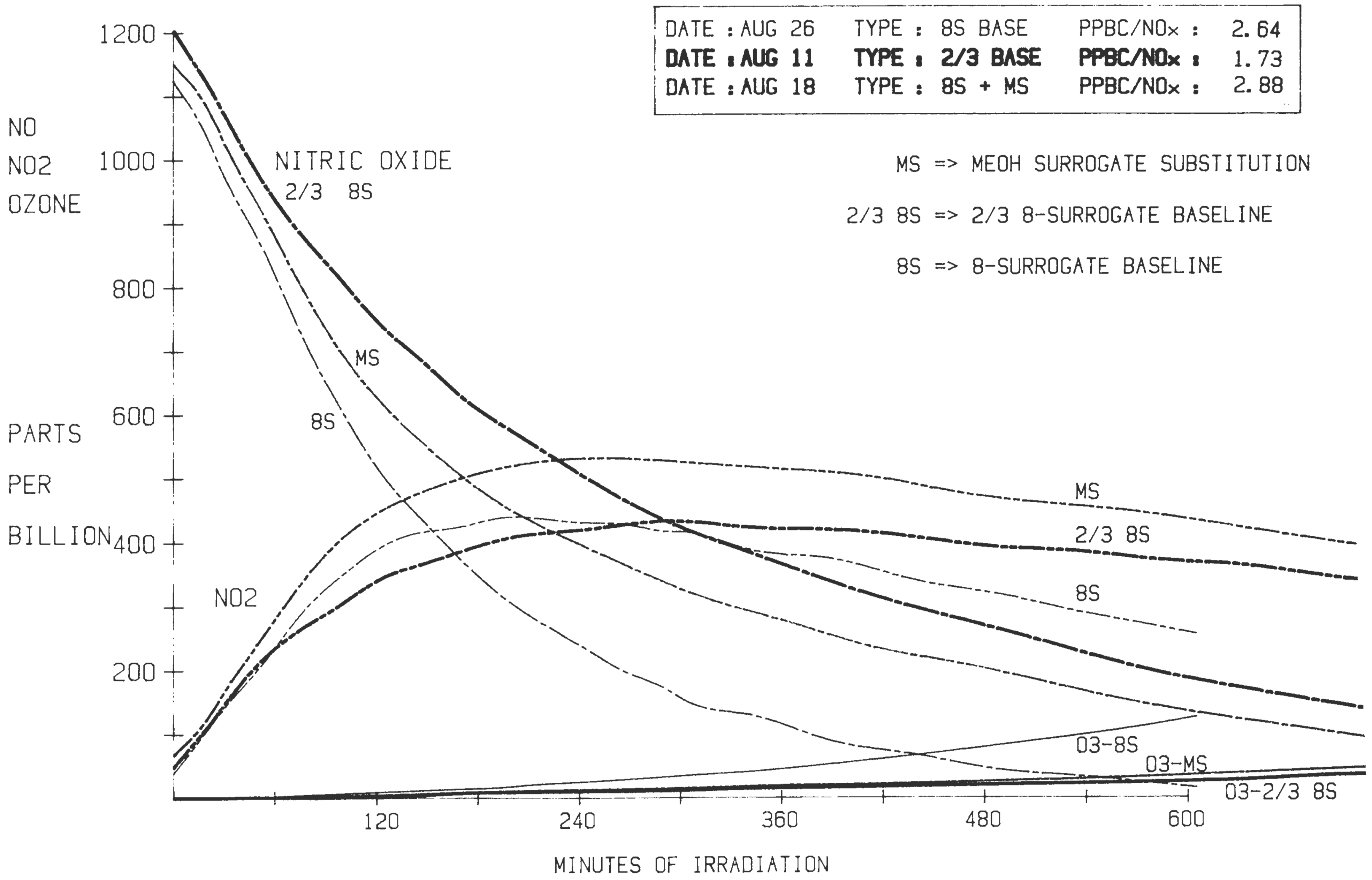

FIGURE 3-2: BASELINE SURROGATES, 2/3 BASELINE & METHANOL SUBSTITUTION AT 3:1

carbon to NOx ratio the methanol exhaust surrogates were relatively inert and contributed very little to ozone production.

The full baseline mixture produced over twice as much ozone after ten hours as the 2/3 baseline plus 1/3 methanol exhaust surrogate experiment. Hence, at this low ppm carbon to NOx ratio there is a substantial reduction in ozone production with methanol surrogate substitution. The complete set of experimental evidence for these three cases is presented in Appendix A.

Task 3 B : Baseline Hydrocarbon Surrogate Reactivity at 9:1 Ratio
Task 4 B : Two-Thirds Baseline Hydrocarbon Reactivity at 6:1 Ratio
Task 5 B : Two-Thirds Baseline Plus Methanol Surrogate Reactivity

The comparative set of experimental results at a nominal nine to one ppm carbon to NOx ratio is presented in Figure 3-3. The methanol substitution experiment was intermediate in reactivity at this ppm carbon to NOx ratio. The methanol emissions surrogate substitution contributed to the conversion of nitric oxide into nitrogen dioxide and subsequently yielded more ozone than the blank substitution case. However, the substitution of methanol and isobutene (formaldehyde) produced a less reactive mixture and less ozone than the baseline hydrocarbon surrogate case. Further experimental details are presented in Appendix A.

Task 3 C : Baseline Hydrocarbon Surrogate Reactivity at 27:1 Ratio
Task 4 C : Two-Thirds Baseline Hydrocarbon Reactivity at 18:1 Ratio
Task 5 C : Two-Thirds Baseline Plus Methanol Surrogate Reactivity

The nominal twenty-seven to one ppm carbon to NOx ratio experimental results are presented in Figure 3-4. A very rapid conversion of nitric oxide to nitrogen dioxide was observed for both the baseline and the methanol substitution cases. The ozone yield from the methanol emissions surrogate substitution experiment was essentially equal to that from the baseline condition. Therefore, methanol substitution exhibited comparable reactivity at this very high reactant ratio.

Reactivity of hydrocarbons is difficult to measure at high HC to NOx ratios unless the chemistry involves a special "NOx sink" as with toluene for example as shown by Killus and Whitten (12). Special NOx sinks would reduce the height of the ozone peak. The peaks for all three experiments in Figure 3-4 are essentially the same height. Hence, as expected, there is apparently no special NOx sink in the chemistry of methanol. Similar peak heights are also expected since EKMA ozone isopleth diagrams in general show that similar ozone peaks are generated at constant NOx for a wide range of HC concentrations as long as the HC/NOx ratio is high enough.

What is expected, as hydrocarbons are reduced in concentration or reactivity, is a lengthening in the time required to reach the ozone peak. The expected ozone peak delay for the 2/3 versus the full base case ozone curve can be seen in Figure 3-4. However, the methanol substitution case shows no apparent delay compared to the full base case experiment. Hence we must conclude that methanol (with 10 percent isobutene) is essentially equal in reactivity to the surrogate blend at high HC/NOx ratios. Further discussion of this change in blending reactivity with HC/NOx ratio is given in the next section where doubling the methanol substitution is reported.

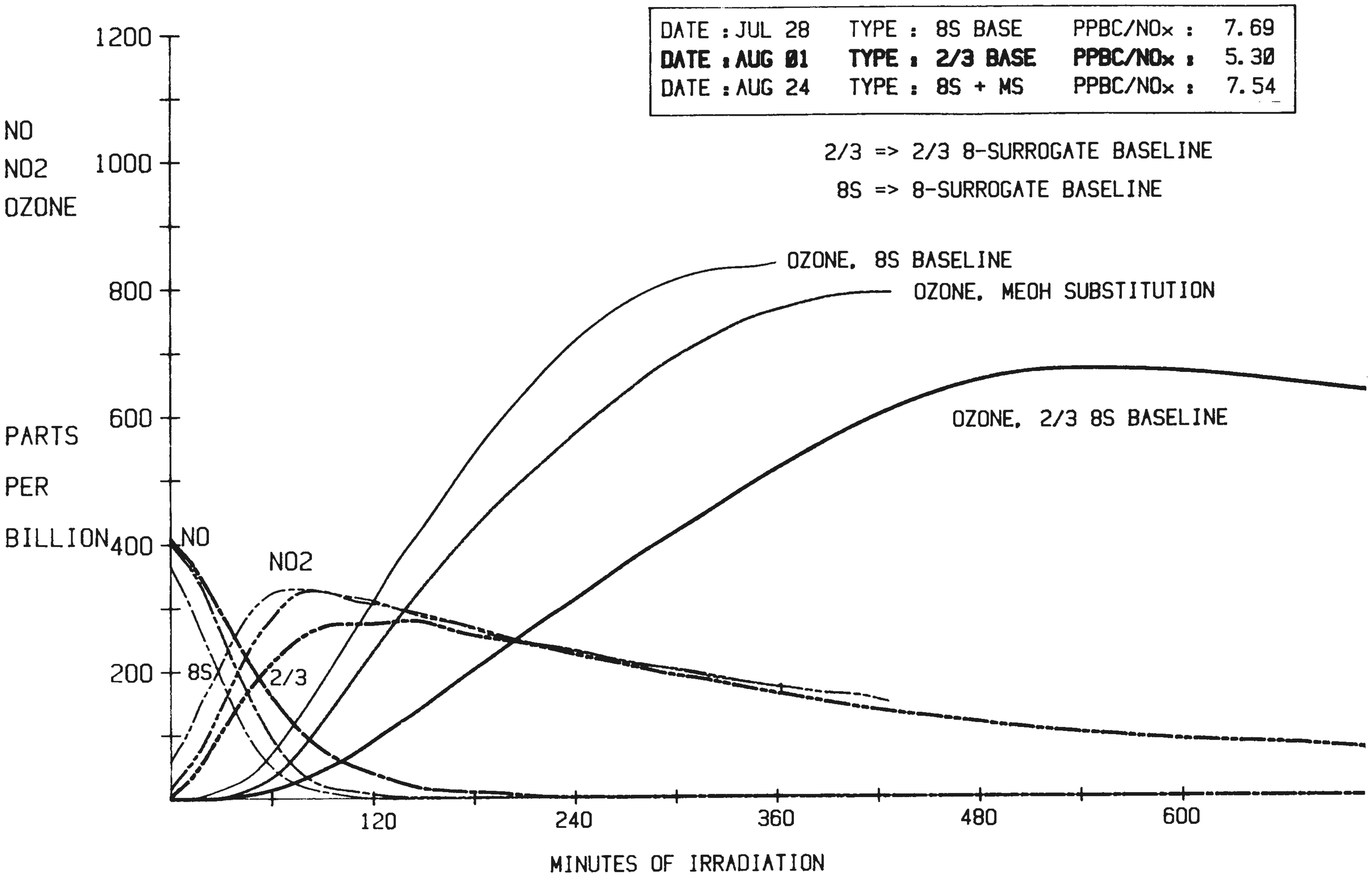

FIGURE 3-3: BASELINE SURROGATES, 2/3 BASELINE & METHANOL SUBSTITUTION AT 9:1

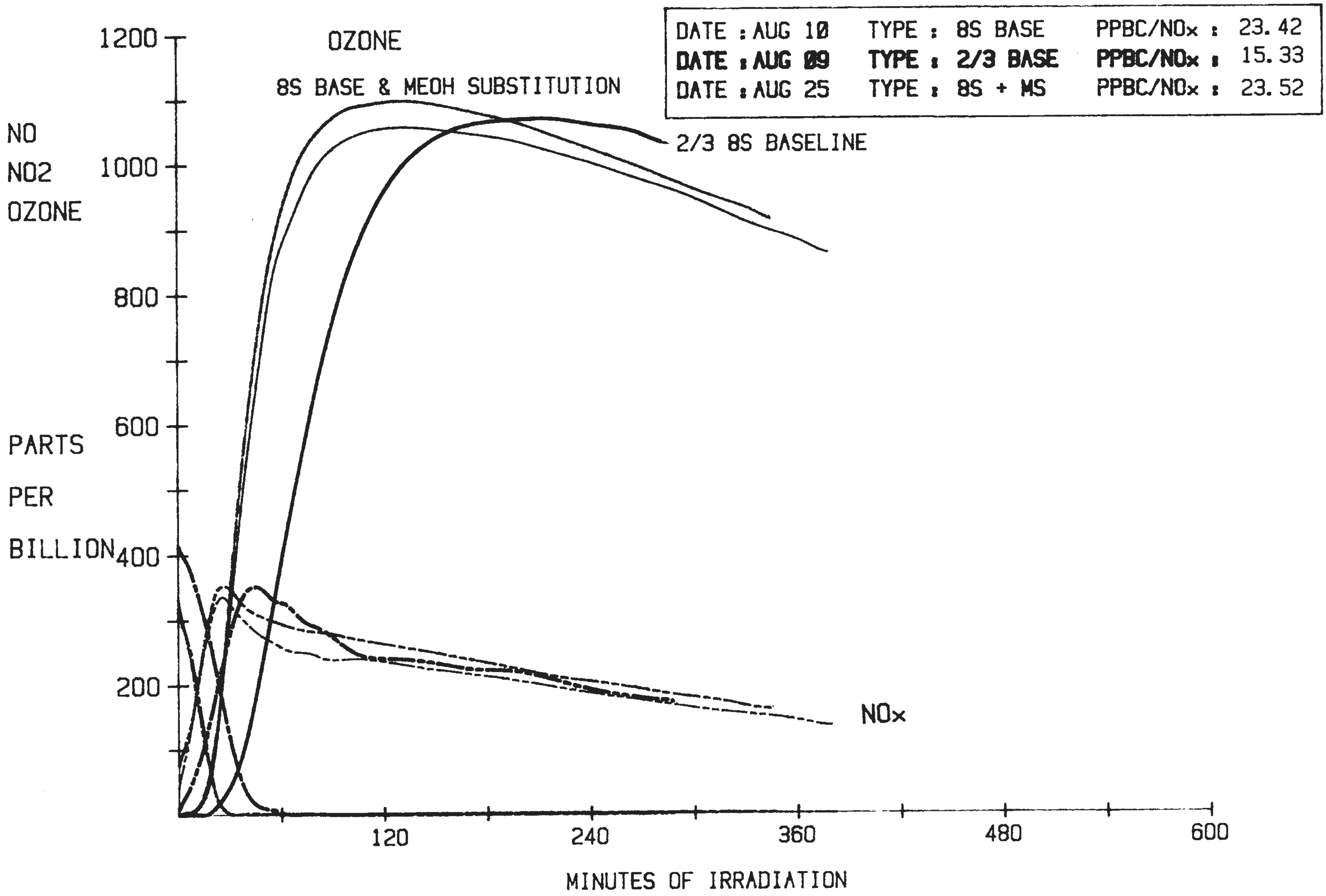

FIGURE 3-4: BASELINE SURROGATES, 2/3 BASELINE & METHANOL SUBSTITUTION AT 27:1

4. Methanol Exhaust Surrogates Increased to Produce Equal Effect, Task 6

The concentration of methanol exhaust surrogates was increased in Task 6 in order to produce a reactivity effect equal to or greater than the baseline case (Task 3 B). Two-thirds of the baseline hydrocarbon mixture (Task 4 B) plus an additional 2.4 ppm carbon of the methanol exhaust surrogates (assuming formaldehyde rather than isobutene) were photochemically tested during an experiment on March 6, 1984. The result is plotted in Figure 4-1. The evidence indicates a more rapid NOx conversion rate and a higher production of ozone for this experiment in comparison with the baseline hydrocarbon case.

It was seen in Figure 3-3 that an equimolar substitution of carbon (in the form of 90% methanol plus 10% formaldehyde) was lower in reactivity than the urban hydrocarbons replaced (at a nominal 9:1 ppm overall carbon to NOx ratio). However, doubling the moles of methanol plus formaldehyde produces a higher reactivity mixture than the hydrocarbon baseline as compared in Figure 4-1.

5. Methanol Vehicle Exhaust Substitution Experiments, Task 7

Three smog chamber experiments were conducted in which the exhaust emissions from a 1981 Ford Escort were combined with 2/3 of the baseline surrogate hydrocarbon mixture. The Escort was fueled with 94.5 %vol methanol and 5.5 %vol isopentane. The exhaust emission samples were pulled from the CVS sampling system while the Escort was being operated on the chassis dynamometer during the first 80 seconds of the Federal Test Procedure (FTP). In this manner a suitable ppm carbon to NOx ratio could be obtained which was representative of the vehicle's actual FTP emissions.

Three nominal HC/NOx ratio conditions were tested in the smog chamber. In each case two-thirds of the initial reactants consisted of the eight hydrocarbon surrogates used to represent baseline urban conditions. One third of the reactants was methanol/isopentane vehicle exhaust. Table 5-1 shows the test condition objectives.

TABLE 5-1. METHANOL VEHICLE EXHAUST SUBSTITUTIONS, TASK 7

		Initial Surrogate & Exhaust Concent., ppm		
Experiment Conditions	PPMC to NOx	NOx	Eight Surrogate Blend	Methanol Vehicle Exhaust
Methanol	3	1.2	2.4	1.2
Exhaust	9	0.4	2.4	1.2
Substitution	27	0.4	7.2	3.6

Experimental results for the 3 to 1 ppm carbon to NOx ratio conditions are shown in Figure 5-1. The vehicle exhaust substitution results obtained on September 16th (a high dilution rate experiment) are plotted along with previously reported methanol surrogate substitution results from August 18th. Nitric oxide conversion into nitrogen dioxide is plotted along with

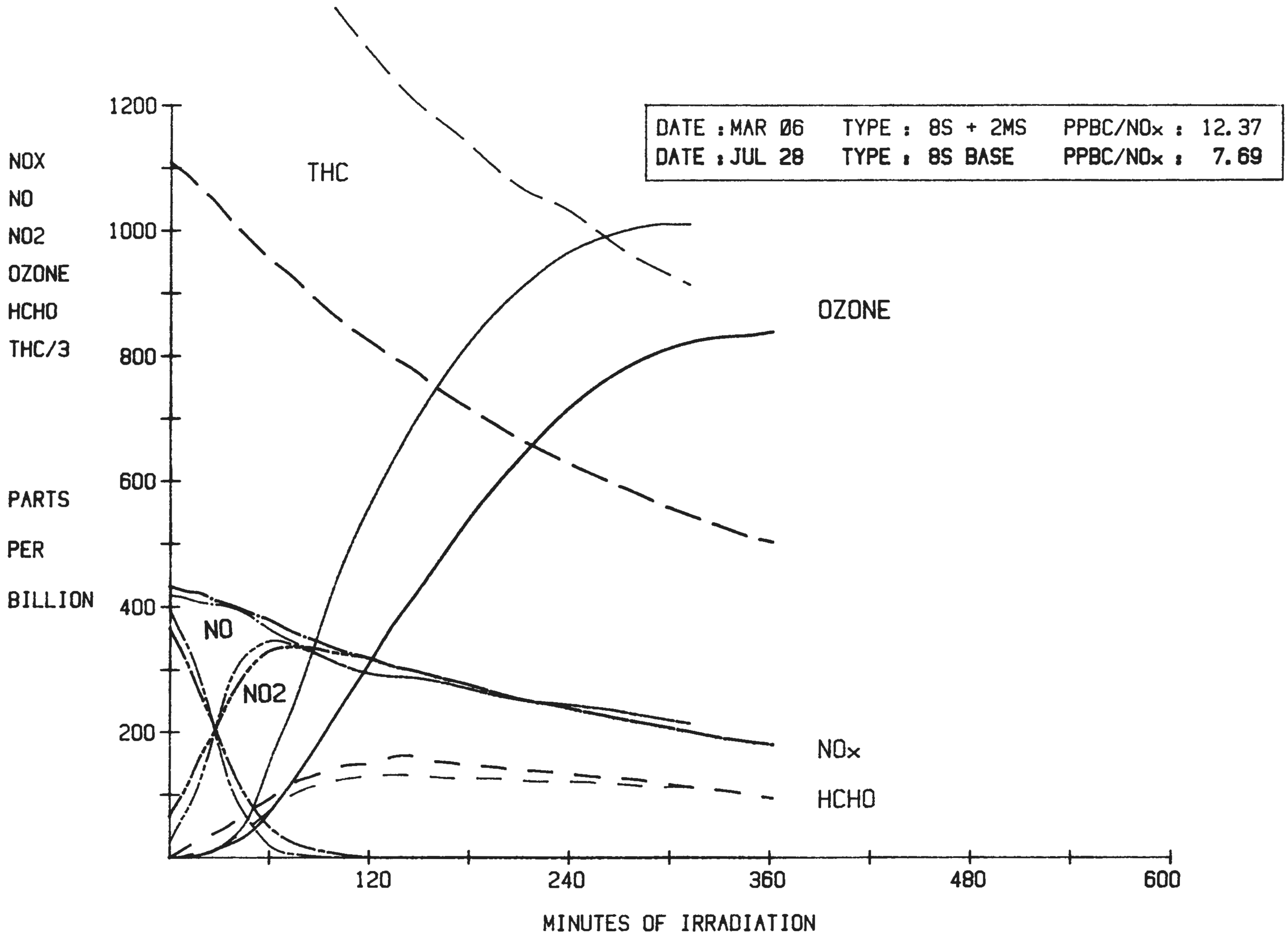

FIGURE 4-1 : SUBSTITUTION EXPERIMENT WITH DOUBLE METHANOL SURROGATES

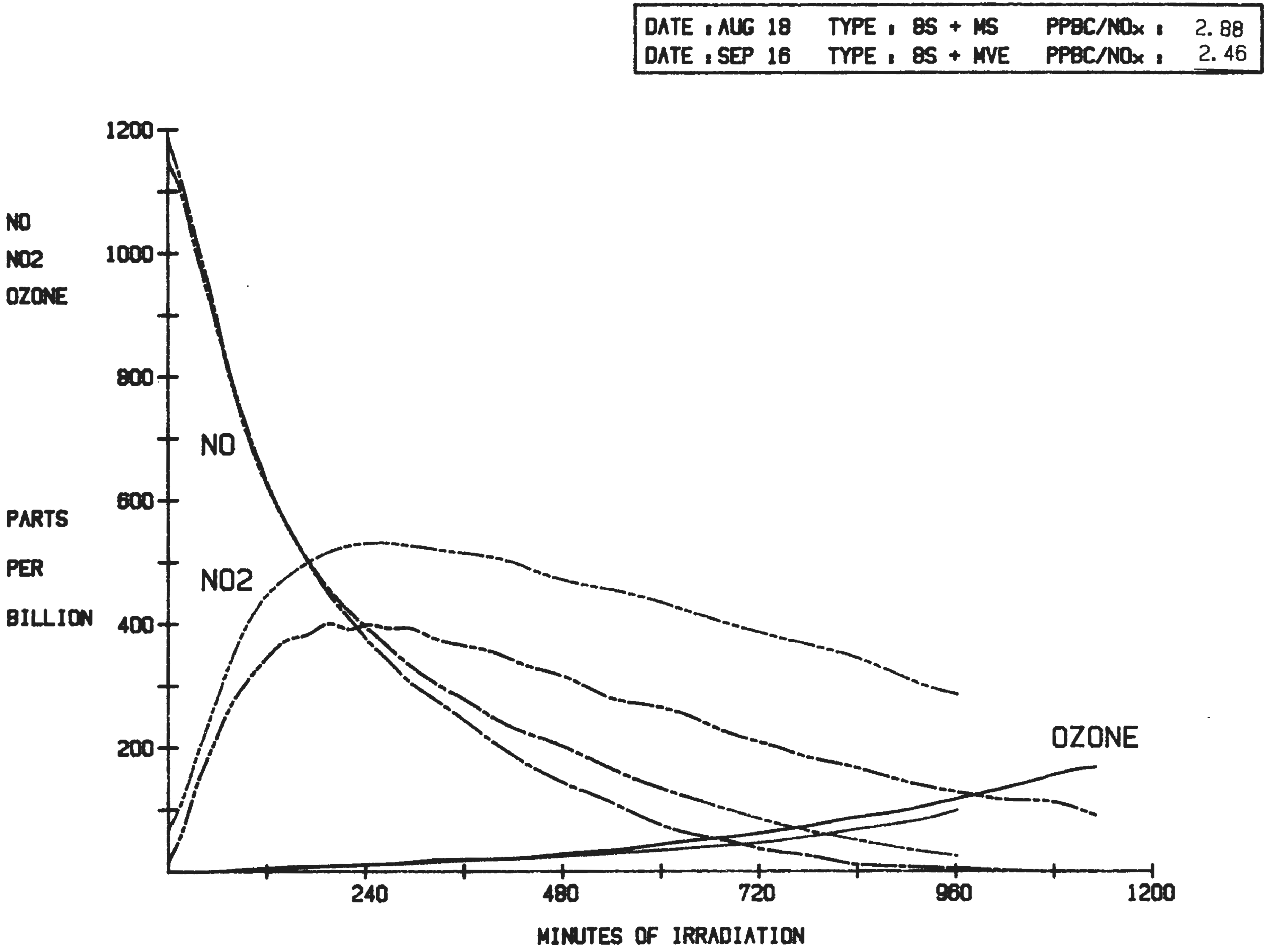

FIGURE 5-1 : METHANOL VEHICLE EXHAUST & SURROGATE COMPARISONS AT 3:1 PPMC/NOX

the formation of ozone. Both of these experiments started converting NO into NO_2 at about the same rate. Both also began to produce ozone at about the same time and at similar rates. The methanol vehicle exhaust (MVE) experiment was very comparable to the single methanol surrogate (MS) experiment at this 3 to 1 ppm carbon to NOx ratio.

It must be noted that experiments conducted from August 25th through November 3rd were diluted at a higher than normal rate with clean make-up air. This was established by measuring the dilution rates of a series of characterization experiments. The experimental data obtained during this period should not be visually or simply compared to experimental data from other times. The correct dilution rates have been used, however, for proper modeling of the experiments.

The above experiments, with two different dilution rates and slightly different initial conditions, have been modeled by SAI with no difficulty. The following MVE substitution experiments have also been modeled satisfactorily using the chemistry to be discussed later in this report.

Three experiments at a nominal 9 to 1 ppm carbon to NOx ratio are shown in Figure 5-2. The August 24th MS experiment is compared to the September 22nd MVE experiment; however, the higher dilution rate of the latter experiment is evident in the "total hydrocarbon" (THC) disappearance rate shown in the figure. A further comparison is provided with the November 7th experiment (at low dilution rate) in which only methanol was added to the two-thirds baseline case. The MVE experiment started out much faster converting NO into NO_2 than the MS experiment due to the greater formaldehyde present at its start. However, more ozone was produced by the MS experiment and at a higher initial rate than from the MVE experiment.

Two experiments at a nominal 27 to 1 ppm carbon to NOx ratio are shown in Figure 5-3. The August 25th MS (methanol surrogate) experiment started fast and produced ozone at a very fast rate. The September 13th MVE experiment was extremely fast in converting NO into NO_2. This was apparently caused by the higher formaldehyde concentration (157 ppb vs. 11 ppb) measured at the start of the MVE experiment. Formaldehyde is plotted in Figure 5-3 and indicates a similar peak value for the two experiments after an hour of irradiation. We note that the MVE contained a measured 5 carbon percent formaldehyde before it was blended with 2/3 hydrocarbon surrogate mix.

The conclusion drawn from these seven experiments is that the reagent grade methanol exhaust surrogates were fairly representative photochemically of actual methanol exhaust as obtained at the start of the FTP. In other words there was no evidence of any unexpected or highly reactive species being present in the exhaust experiments which would be of concern.

6. Gasoline & Blend Exhaust Using Dummy Catalyst, Tasks 8 and 9

One implicit experimental task has been to develop a protocol for obtaining a representative vehicle exhaust emissions sample from a light duty vehicle. Sampling during a segment of the Federal Test Procedure (FTP) was considered the best approach. It was also desired that the sample have a typically urban ppm carbon to NOx ratio of about 9:1 for comparison with the previous hydrocarbon surrogate experiments. In order to obtain an

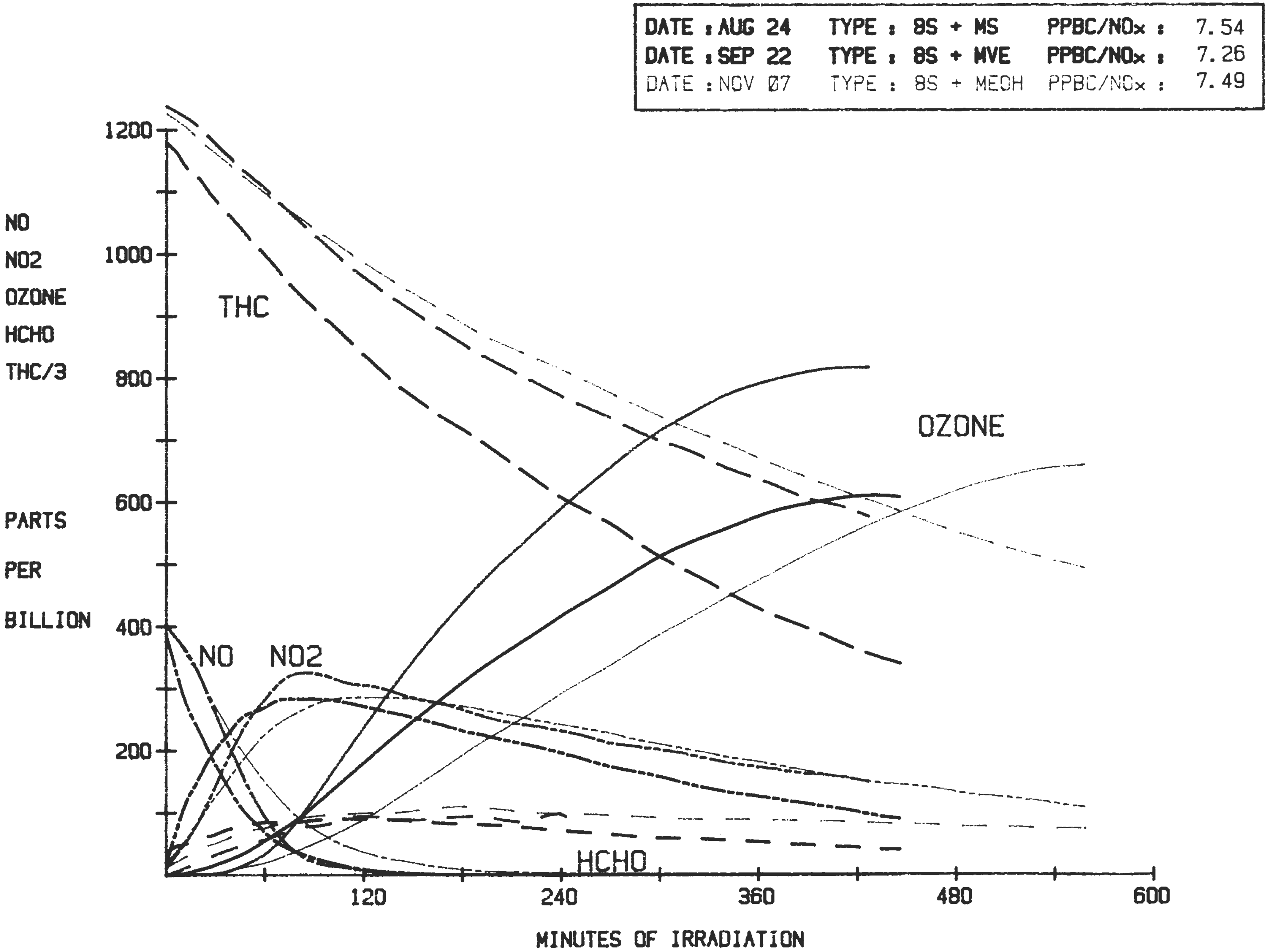

FIGURE 5-2 : METHANOL VEHICLE EXHAUST & SURROGATE COMPARISONS AT 9:1 PPMC/NOX

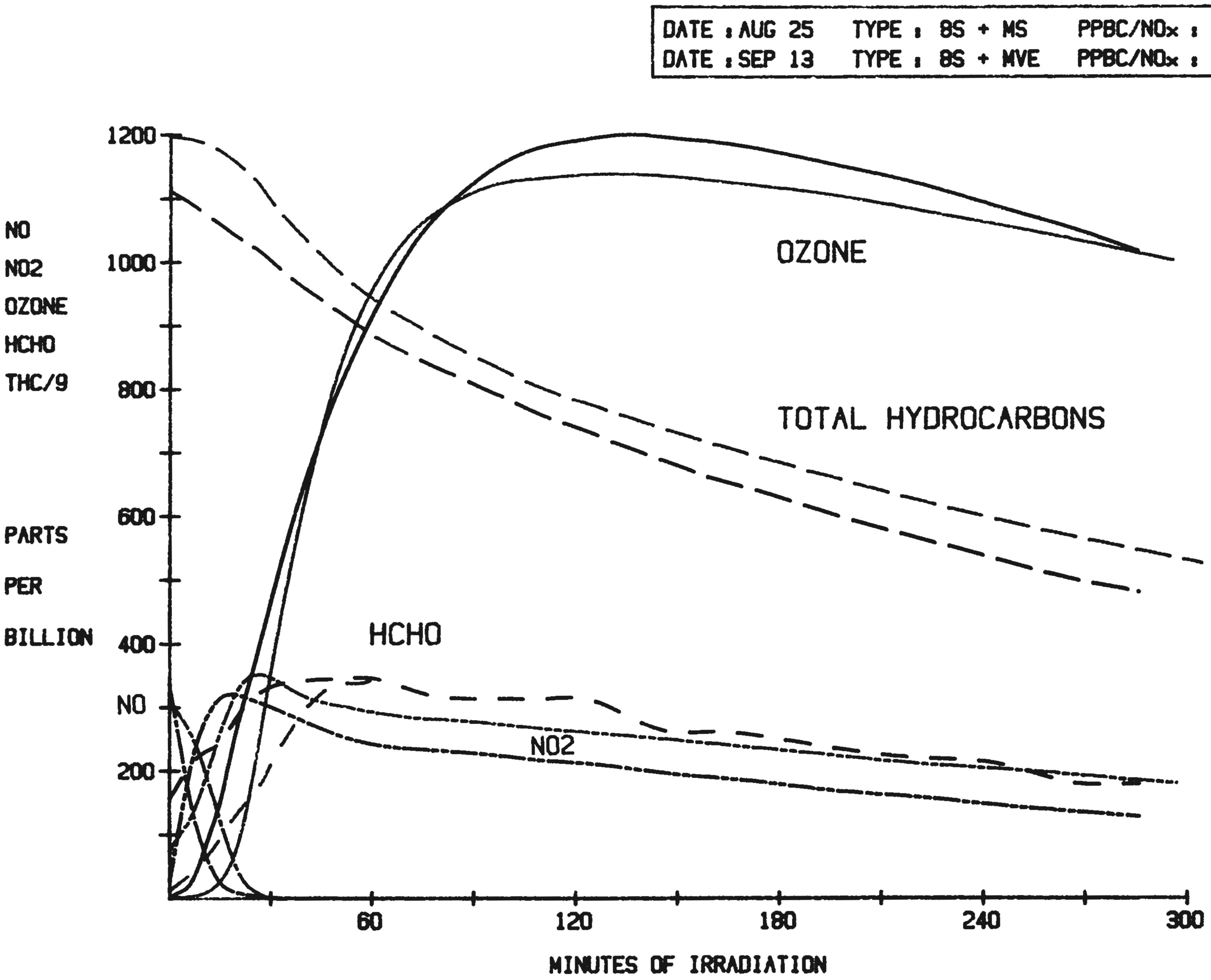

FIGURE 5-3 : METHANOL VEHICLE EXHAUST & SURROGATE COMPARISONS AT 27:1 PPMC/NOX

exhaust emission sample with this ratio it was necessary to sample during the first 80 seconds of the cold transient phase of the FTP. The emissions produced during this period are representative of emissions produced by ordinary vehicles with normal carburetor calibrations. However, the carburetor's choke was on during that time and the vehicle's catalyst had not yet reached its operating temperature. Therefore, due to the brief 80 second "cold catalyst" protocol used for sampling exhaust emissions the "dummy catalyst" sampling conditions proposed as Tasks 8 and 9 were omitted. Furthermore, due to the recognized importance of assessing the reactivity of purely evaporative emissions Tasks 12 and 13 were substituted in place of Tasks 8 and 9.

7. Mechanism Validation - Smog Chamber Modeling, Task S2

Systems Applications, Inc. has successfully modeled the hydrocarbon surrogate and also the methanol surrogate substitution experiments as will be discussed in this section. However, this task has required SAI to develop a significant extension to the previous Carbon Bond Mechanism (CBM-III). SAI's Phase I modeling study performed for ARCO ("Impact of Methanol on Smog: A Preliminary Estimate") utilized the CBM-III chemical kinetic mechanism. Part of that study has now been repeated using the more comprehensive chemical kinetic mechanism which has been validated as part of this study.

Modeling problems were not expected while extending the CBM-III to include methanol. However, problems arose while attempting to model the baseline hydrocarbon surrogate experiments. After review and repetition of certain characterization experiments it was determined that CBM-III did not adequately treat the chemistry of m-xylene over the HC/NOx range observed in the experiments. It was able to model the 9 to 1 ppm carbon to NOx ratio "mid-range" experiments. However, at very low ppm carbon to NOx ratios the experiments proceeded more slowly than the CBM-III model. Also at high ratios the experimental results showed higher ozone peaks than CBM-III predicted.

One reason for these discrepancies is the current use of an eight-surrogate hydrocarbon mixture. This was the first series of experiments to be conducted with this combination of surrogates. They were selected to best represent the hydrocarbons currently present in polluted urban air. A second reason for the discrepancy is the very wide range of experimental ppm carbon to NOx ratios used in the current study. Experiments were conducted with ppm carbon to NOx ratios ranging from 2 to 1 all the way up to 27 to 1. The CBM-III mechanism had previously been validated with a set of experiments covering a narrower reactant ratio range.

After some effort the specific problem with CBM-III was traced to the chemistry of m-xylene. In CBM-III toluene and m-xylene had been treated as one aromatic specie. The new extended CBM-III mechanism differs only in the separation of the aromatics into two species. The new extended mechanism successfully simulates the drastic reduction in ozone observed in the smog chamber experiments at low ppm carbon to NOx ratios. The mechanism further provides a good simulation at medium and high ppm carbon to NOx ratios.

A partial comparison of CBM-III and the extended CBM-III is presented in

8. Gasoline Emissions Assessment with OEM

Gasoline Exhaust Assessment with OEM Catalyst, Task 10A

The 1981 Ford Escort was used to supply a representative sample of exhaust emissions from the cold transient phase of the Federal Test Procedure. It was desired to irradiate the dilute vehicle exhaust at a controlled ppm carbon to NOx ratio of 9:1. That ratio would permit photochemical reactivity comparisons with the previously tested urban hydrocarbon surrogate mixture. However, the exhaust ratio of hydrocarbons to NOx was a dependent variable which was not to be manipulated beyond what was representative of the vehicle's actual exhaust. Therefore, the dilute sample was obtained during the first 80 seconds of the test in order to approach the desired 9:1 ratio. The 80 second sample was transferred directly to the smog chamber where it was analysed and further diluted prior to irradiation.

Three photochemical reactivity experiments were performed using the baseline gasoline to obtain exhaust emissions for irradiation. Two of these experiments approached the nominal 9:1 ppm carbon to NOx ratio as shown in Figure 8-1. The initial conditions were 0.44 ppm NOx in each experiment, however, 7% of the NOx was NO_2 and the ppmC to NOx ratio was 7.4:1 on February 7th while only 3% of the NOx was NO_2 and the ppmC to NOx ratio was 7.3:1 on February 8th. These differences in initial conditions may have contributed to the slight differences in peak ozone for these back to back experiments.

One experiment was performed with the baseline gasoline at a nominal 3:1 ppm carbon to NOx ratio. On January 26th the initial NOx concentration was 0.48 ppm of which 12% was NO_2. This vehicle exhaust experiment is compared in Figure 8-2 with the baseline hydrocarbon surrogate data presented previously in Figure 3-2. The time scale has been extended to cover the twenty hour duration of the gasoline exhaust experiment. Although the initial NOx concentrations were different between these two experiments their overall reaction rates appear similar as is expected for similar hydrocarbon to NOx ratio experiments (see Whitten et al, 1979).

Gasoline Exhaust Plus Evaporative Emissions with OEM Catalyst, Task 10 B

Two photochemical reactivity experiments were performed in which the baseline gasoline exhaust was combined with evaporative emissions at approximately the desired 9:1 ppm carbon to NOx ratio. The evaporative emissions for those experiments were collected in the adjacent Sealed Housing for Evaporative Determination (SHED) facility.

The 1981 Escort was driven until fully warmed and then was rolled into the SHED facility for the one-hour hot soak period. The mass of evaporative emissions was calculated in accordance with the Federal Test Procedure in 40 CFR Part 86.143-78. Four SHED tests were performed using the base gasoline. The mass of hot soak evaporative emissions are reported in Table 8-1.

Figures 7-1 and 7-2 respectively. The data points from the July 29th baseline experiment at a 3 to 1 ppm carbon to NOx ratio are plotted along with some of the CBM-III results in Figure 7-1. The experiment produced a low ozone peak after about twenty hours of irradiation. The "old" chemistry produced a higher ozone peak after only about ten hours of irradiation. The conversion rate of NO into NO_2 was experimentally much slower than the CBM-III mechanism produced.

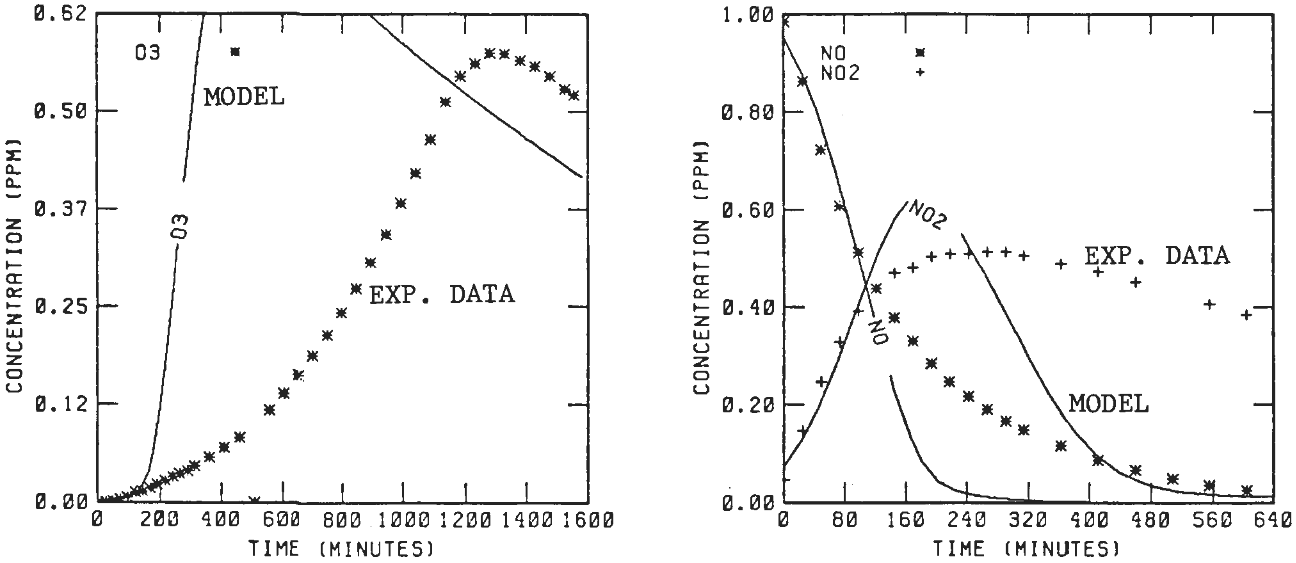

Figure 7-1. Experimental versus CBM-III NOx and ozone results at a low (3 to 1) ppm carbon to NOx ratio.

The extended CBM-III mechanism results are shown with the same experimental data in Figure 7-2. The ozone production and NOx conversion rates are in much closer agreement with the extended chemical kinetic mechanism.

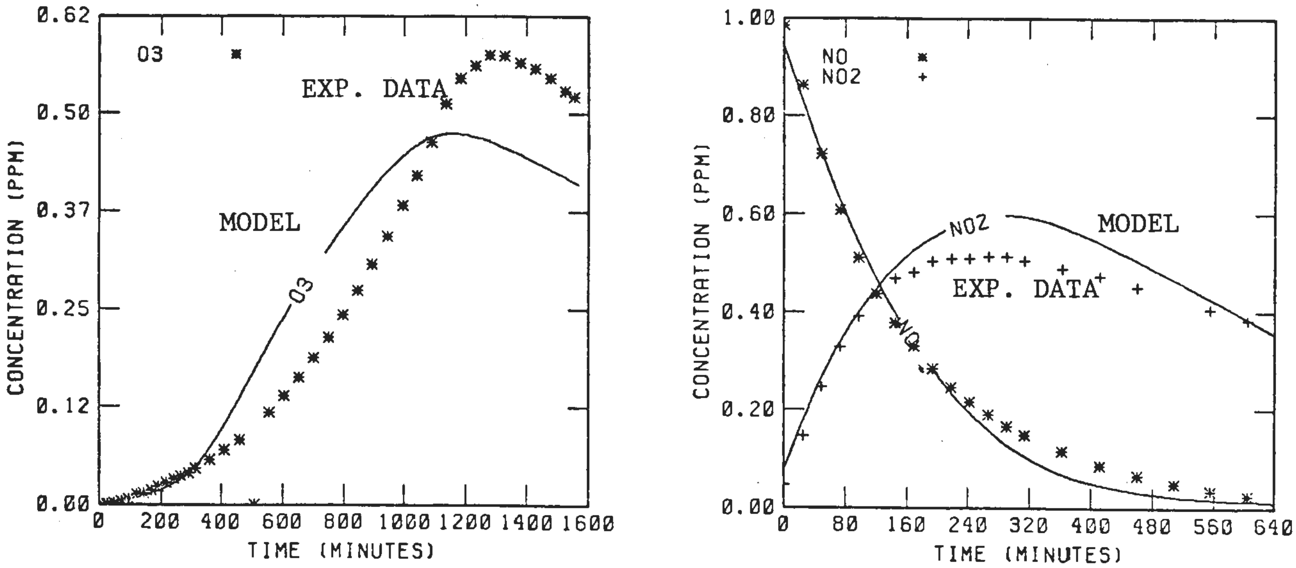

Figure 7-2. Experimental versus extended CBM-III NOx and ozone results at a low (3 to 1) ppm carbon to NOx ratio.

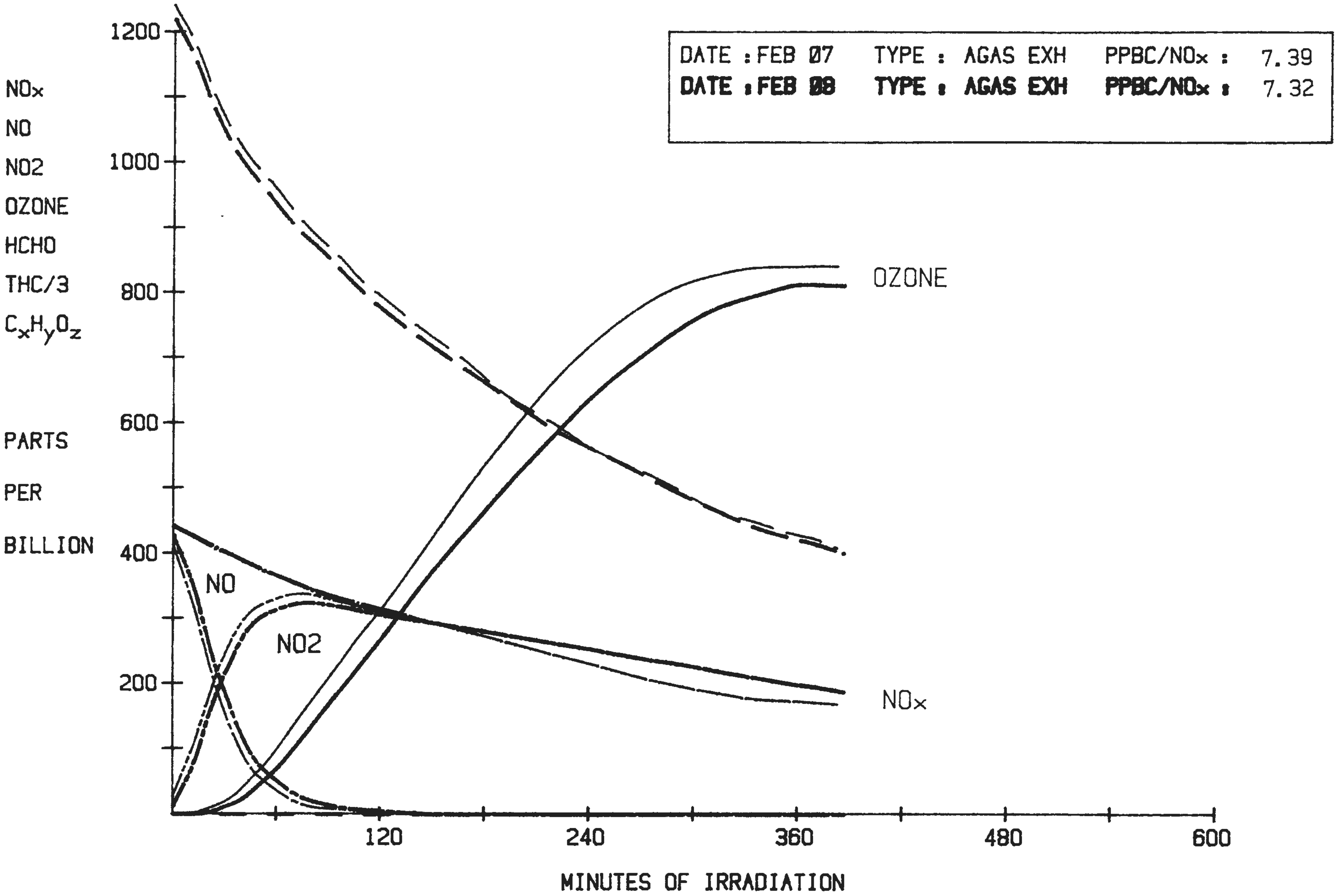

FIGURE 8-1 : GASOLINE EXHAUST SAMPLES FROM START OF FEDERAL TEST PROCEDURE

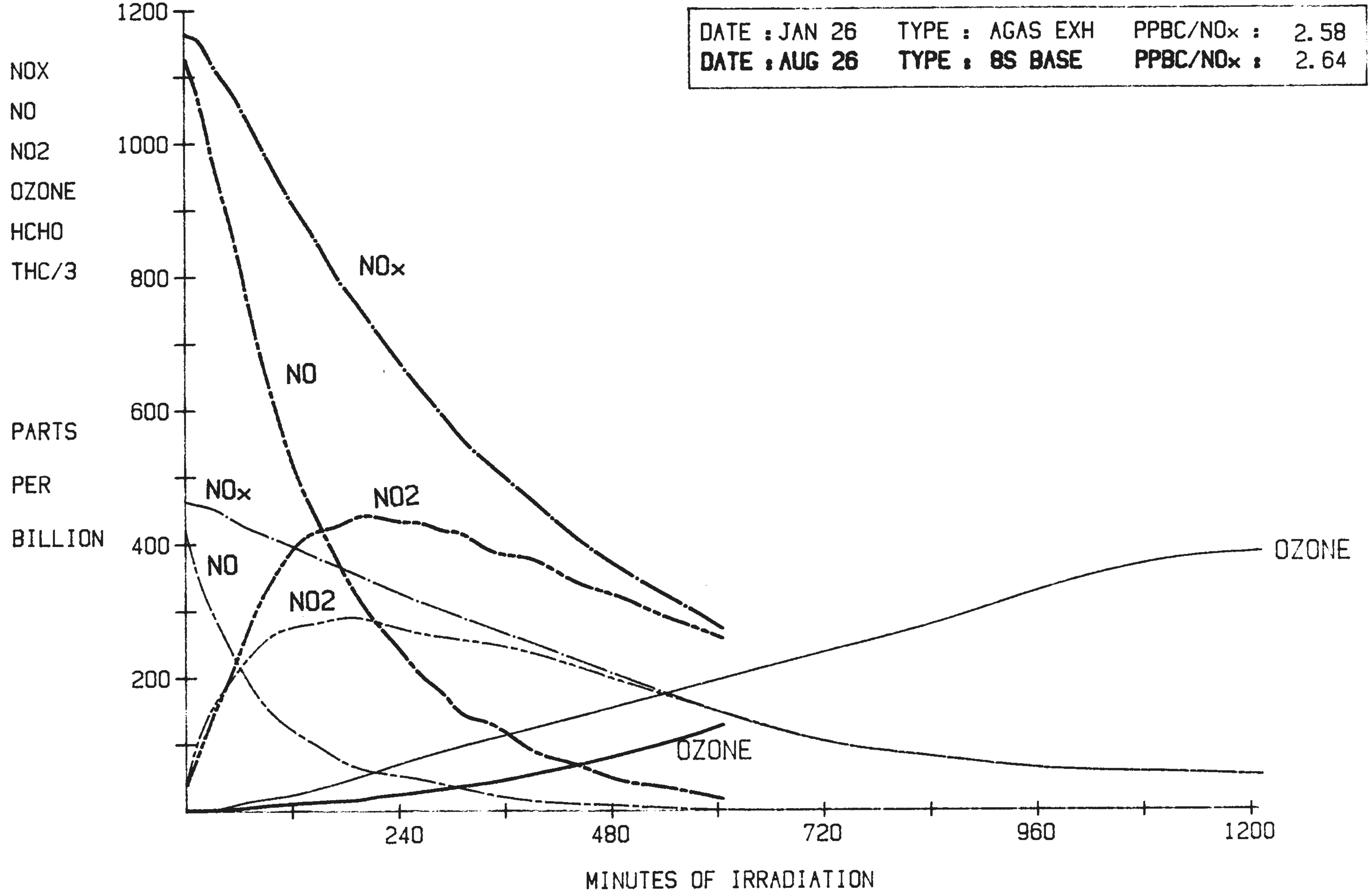

FIGURE 8-2 : GASOLINE EXHAUST SAMPLE FROM START OF FEDERAL TEST PROCEDURE

Table 8-1 : Hot soak evaporative emissions from baseline gasoline

FUEL	DATE	EVAPORATIVE MASS	AVERAGE
Baseline Gasoline	2/ 1/84	2.54 grams	
	2/21/84	1.45 grams	
	3/13/84	2.32 grams	
	3/15/84	1.93 grams	
			2.06 grams

After the final concentration measurement of evaporative emissions was completed, the evaporative emission sample was transferred directly to the smog chamber. This was done in a series of steps in order to produce the desired 9:1 ppm carbon to NOx ratio. The chamber contents were then diluted until the desired initial concentration of 0.40 ppm NOx was achieved. The combined gasoline exhaust and evaporative emissions smog chamber experiments are shown in Figure 8-3. The first, on February 21st, consisted of 48% exhaust hydrocarbons and 52% evaporative emission hydrocarbons. The ppm carbon to NOx ratio was 7.8:1. Its initial concentration of NOx was 0.41 ppm of which 6% was NO_2.

The second experiment, on March 13th, contained 67% exhaust hydrocarbons and 33% evaporative hydrocarbon emissions. Its ppm carbon to NOx ratio was 7.8:1 and its initial NOx was about 0.43 ppm of which 2% was NO_2. The latter experiment, with more NOx and a larger proportion of exhaust emissions, produced a higher ozone concentration as shown in Figure 8-3.

These two experiments have been modeled by SAI. However, there was no detailed information available on the species composition of the exhaust hydrocarbons. It was therefore necessary to assume that the composition of these exhaust hydrocarbons was equal to the measured composition seen in other smog chambers where automobile exhaust has been used. If the overall reactivity generated by such an assumed composition matched the reactivity seen in those other chambers and in this one, then these data suggest a consistent link between the chambers. That is, the same chemistry and modeling procedures show similar agreement with observed data of NO to NO_2 conversion, ozone generation and overall hydrocarbon decay in different smog chambers using auto exhaust from different vehicles burning different gasoline fuels. Indeed the model results show such agreement as indicated in Figures 8-4 and 8-5.

The chemical mechanism used to generate these simulations is currently being used to simulate auto exhaust smog chamber experiments performed at the University of North Carolina (UNC) outdoor facility under an SAI subcontract with the Environmental Protection Agency (EPA Contract No. 68-07-3735). The chemical mechanism used is called CBM-X for expanded Carbon-Bond Mechanism and is being published elsewhere (13).

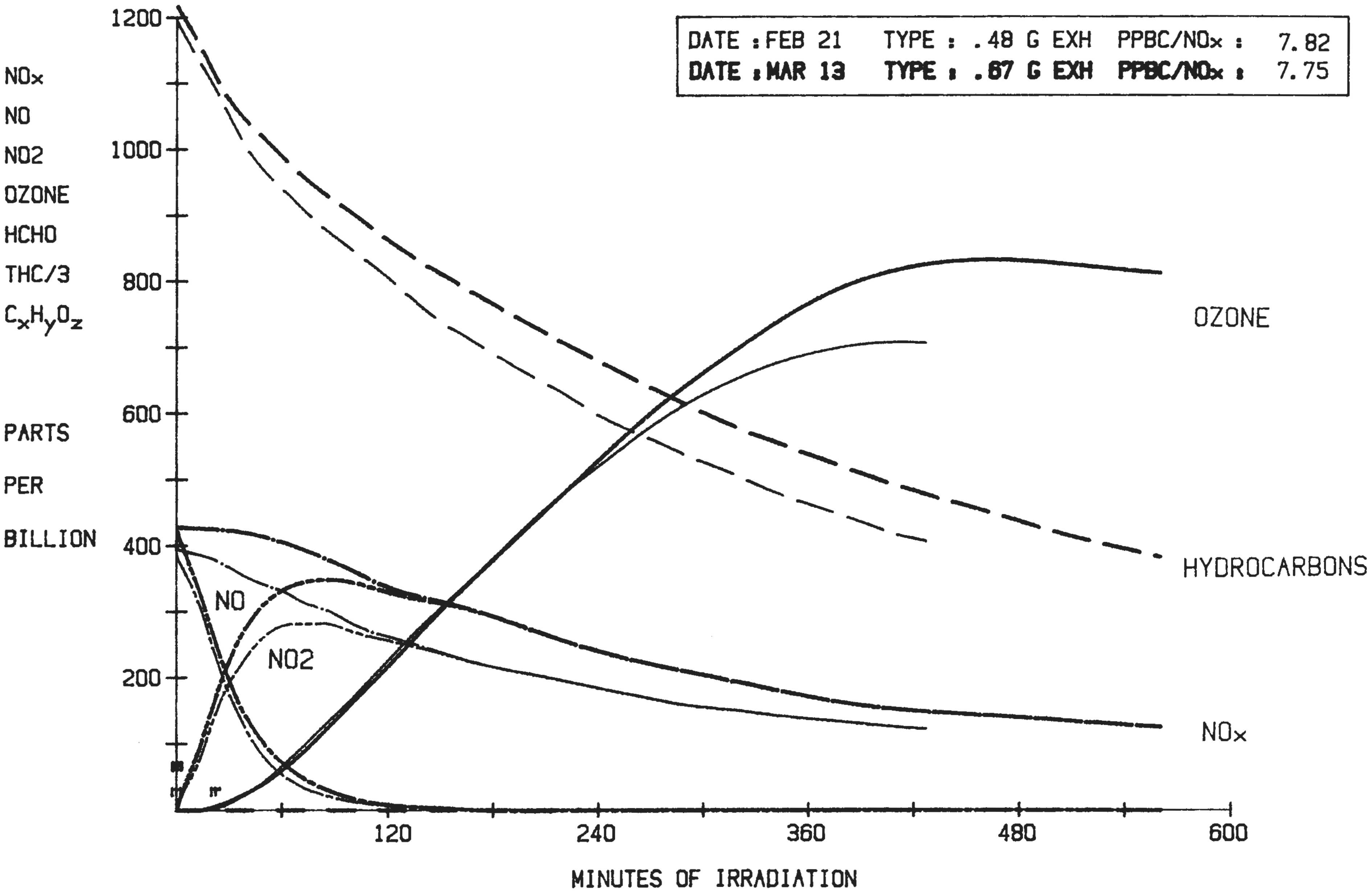

FIGURE 8-3 : GASOLINE EXHAUST PLUS EVAPORATIVE EMISSIONS SAMPLES

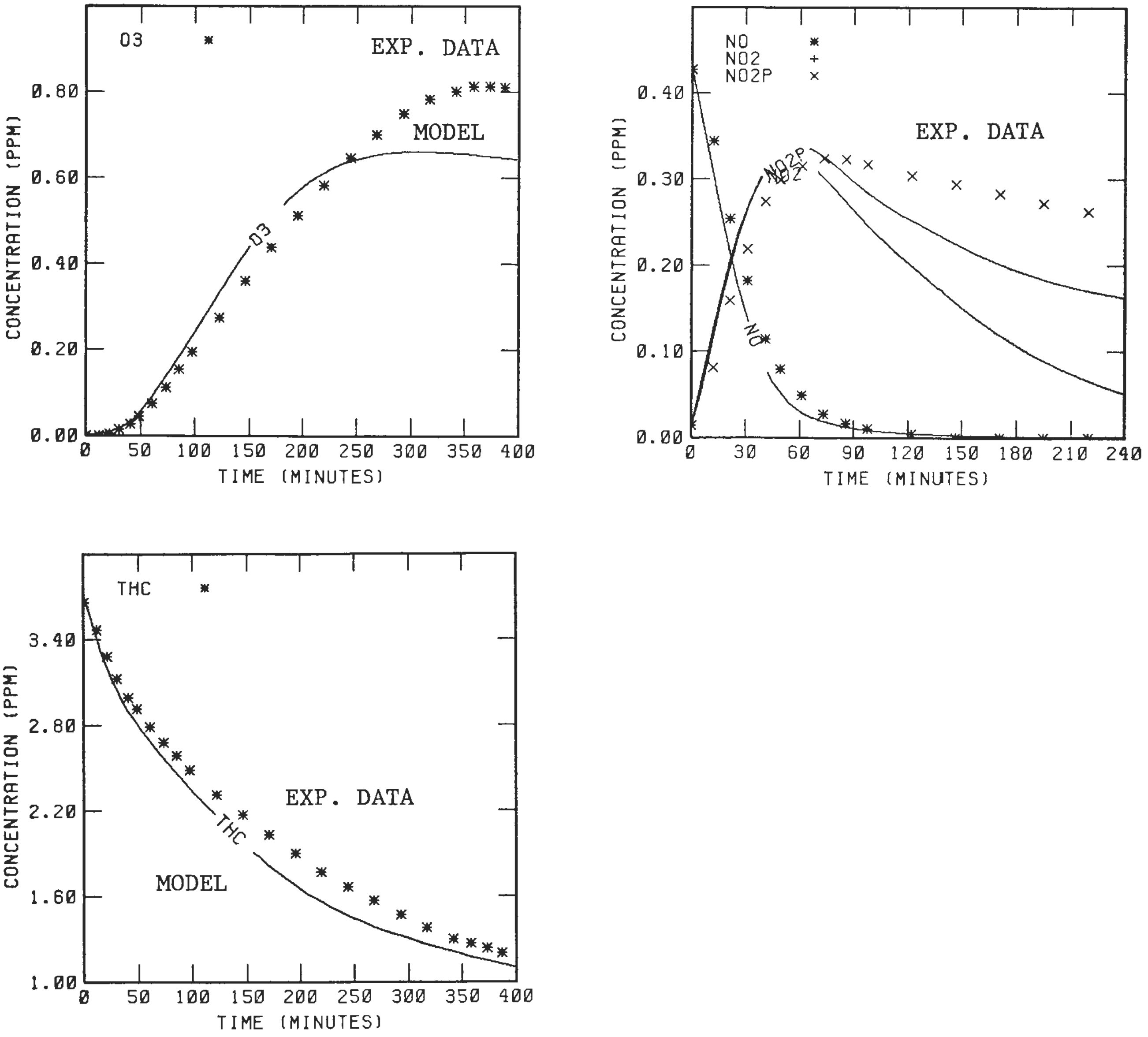

Figure 8-4: Simulation Results for Gasoline Exhaust Using UNC Auto Exhaust Reactivity in CBM-X Chemistry (7.3:1 ppmC to NOx on 2-8-84)

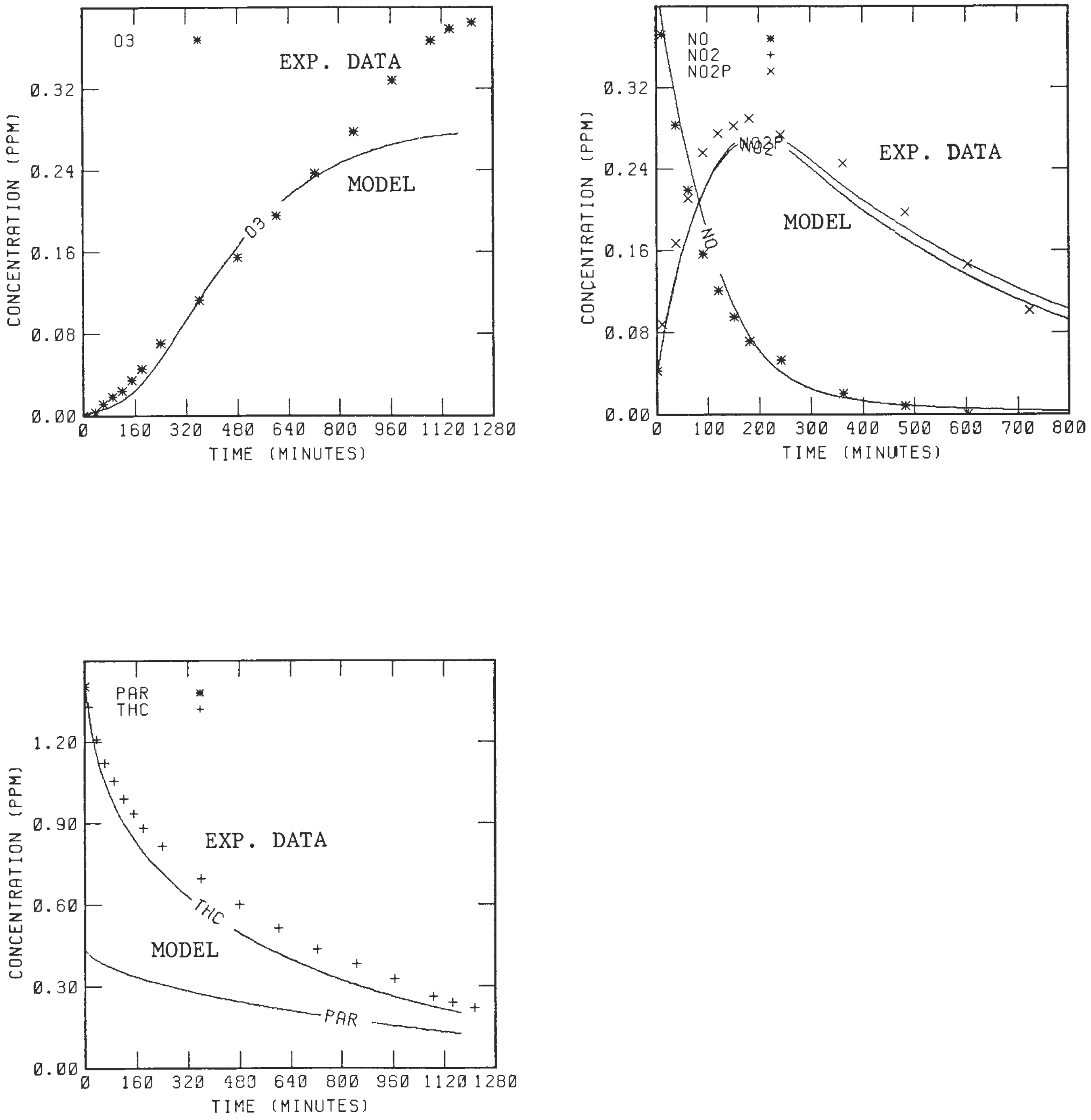

Figure 8-5 : Simulation Results for Gasoline Exhaust Using UNC Auto Exhaust Reactivity in CBM-X Chemistry (2.6:1 ppmC to NOx on 1-26-84)

9. Methanol Gasoline Blend Emissions Assesment with OEM Catalyst

Methanol Gasoline Blend Exhaust Assessment with OEM Catalyst, Task 11 A

Due to an apparent shift in fuel metering stoichiometry with the blend it was not experimentally feasible to produce the desired 9:1 ppm carbon to NOx ratio exhaust sample during the 80 second sampling period. It would have required an enrichment of the carburetor calibration in order to produce the higher 9:1 ratio. No data were obtained on the vehicle's mass emission rates of hydrocarbons and NOx. However, it is believed due to previous blend emissions studies that hydrocarbon emissions were decreased and NOx emissions increased slightly during the 80 second cold start sample period (14). The EKMA model would tend to produce lower urban ozone if all vehicle emissions were incrementally shifted in the same manner.

A photochemical reactivity experiment was performed using available emissions at a 3.9 : 1 ppmC to NOx ratio on March 21st (see Figure 9-1). The initial NOx concentration was 0.51 ppm of which 9% was NO_2. This experiment has been modeled for further comparison with the gasoline exhaust experiments reported earlier.

The gasoline exhaust experiments reported under Task 10 A were modeled by SAI using an assumed composition. Both the nominal 3 to 1 and 9 to 1 ppm carbon to NOx ratio experiments were consistent with the assumed exhaust species composition and reactivity. However, when modeling of the 3.9 to 1 ppmC to NOx ratio blend experiment was attempted, the assumed gasoline exhaust species reactivity was too great relative to the experimental data (see Figure 9-2).

Conversely, the 3.9 to 1 ppmC to NOx ratio blend experiment was modeled by assuming a lower reactivity for its hydrocarbons (see Figure 9-3). Reasonable agreement was achieved. However, when the Task 10 A gasoline experiments were modeled using the blend's assumed composition and reactivity the model underpredicted the reactivity of the gasoline exhaust experiments (see Figure 9-4). Hence, a combination of experiments and modeling have led to the conclusion that the methanol gasoline blend's exhaust reactivity per carbon atom is lower than that of the currently tested baseline gasoline.

However, the modeling exercises performed here and for the gasoline exhaust required assumed compositions to determine reactivity. Hence, no firm conclusions regarding the apparently lower reactivity for the methanol blend exhaust can be made at this time. If the differences in specific compounds were known between the gasoline and methanol blend exhausts, and if the overall reactivity difference seen could be explained by such differences, then a more firm conclusion would be possible. Such detailed measurements are an important part of the proposed future work. It would also be advantageous to know how representative the gasoline, the methanol blend, the particular automobile, and the operational procedures used in this study were compared to what might occur in a typical urban area.

Methanol Gasoline Blend Exhaust Plus Evaporative Emissions Case, Task II B

Two methanol gasoline blend emissions reactivity experiments have been conducted using a mixture of exhaust plus evaporative emissions. These

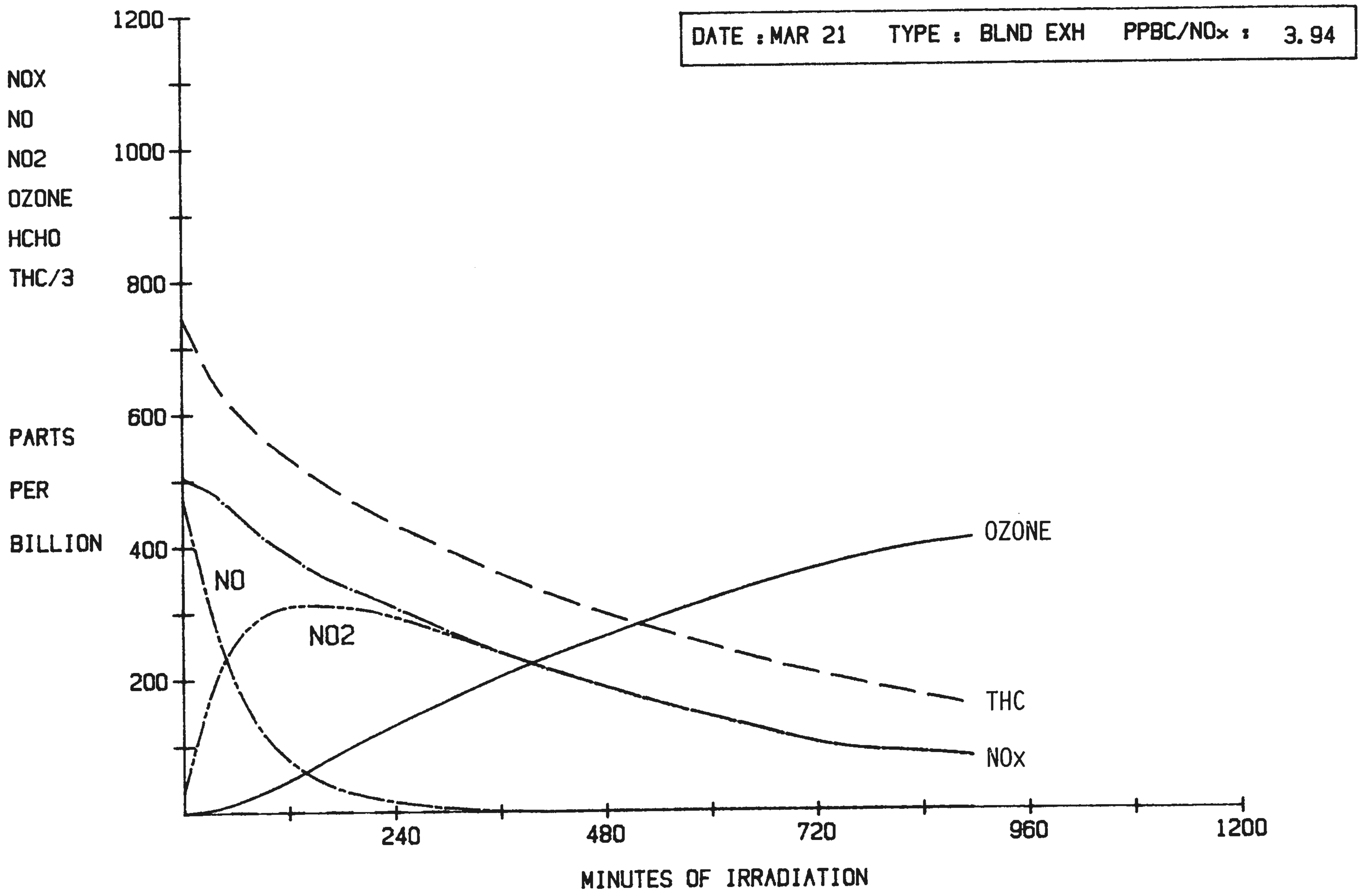

FIGURE 9-1 : METHANOL GASOLINE BLEND EXHAUST SAMPLE FROM START OF FTP

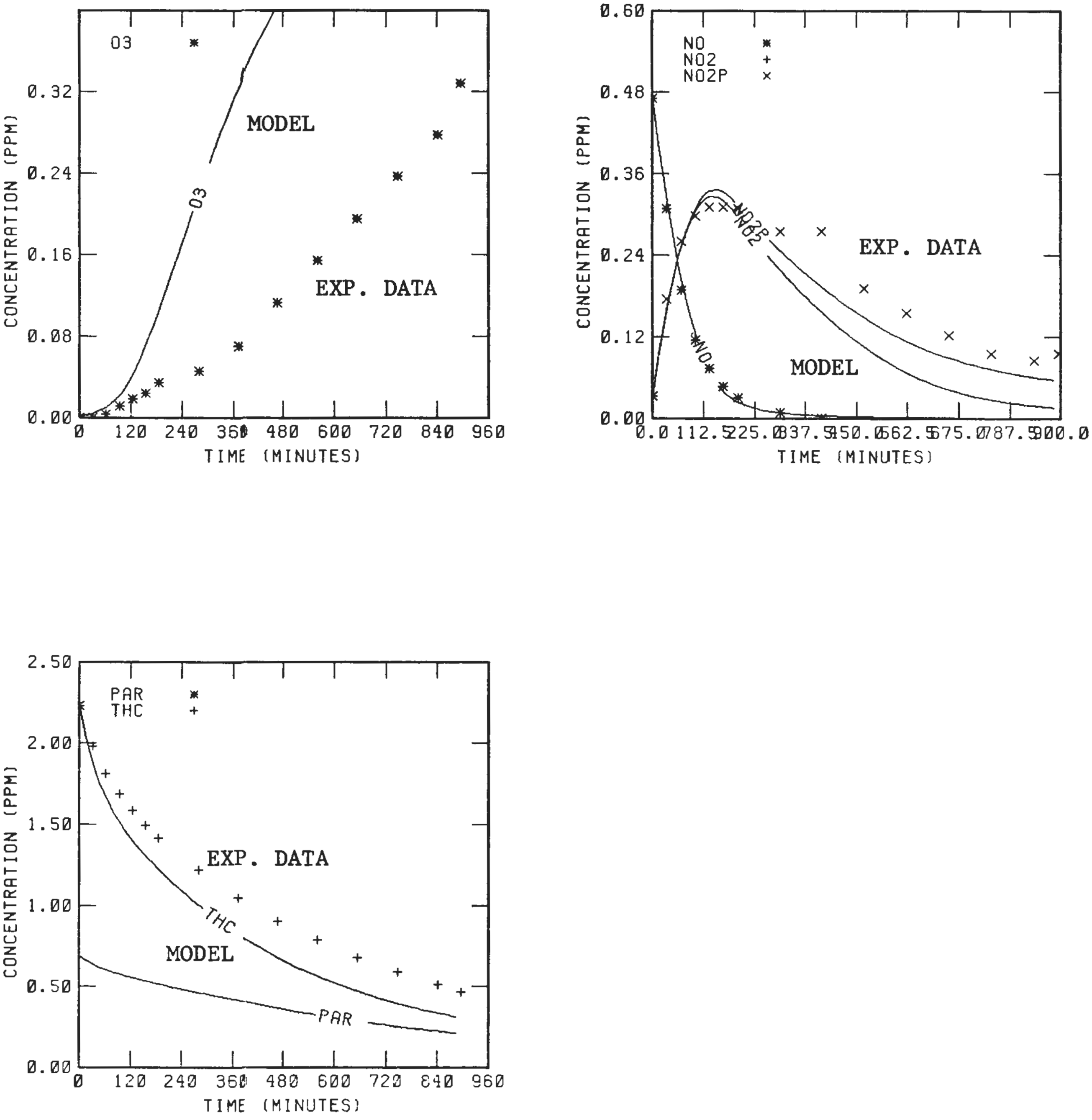

Figure 9-2 : Simulation Results for Blend Exhaust Experiment Using UNC Auto Exhaust Reactivity in CBM-X Chemistry.
(3.9 : 1 ppmC to NOx on 3-21-84)

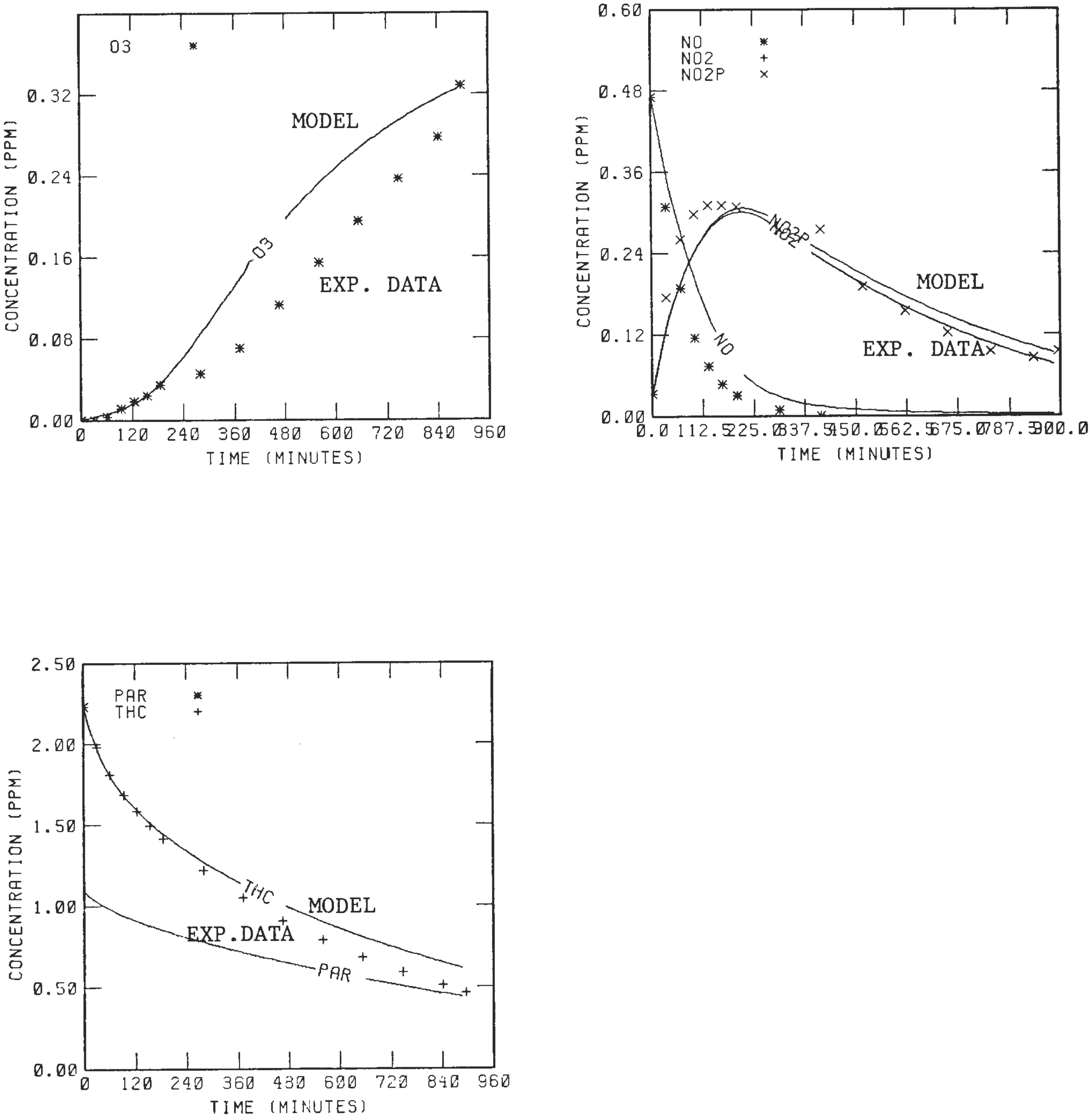

Figure 9-3 : Simulation Results for Blend Exhaust Experiment Using Lower Reactivity Exhaust in CBM-X Chemistry (3.9:1 ppmC to NOx ratio on 3-21-84)

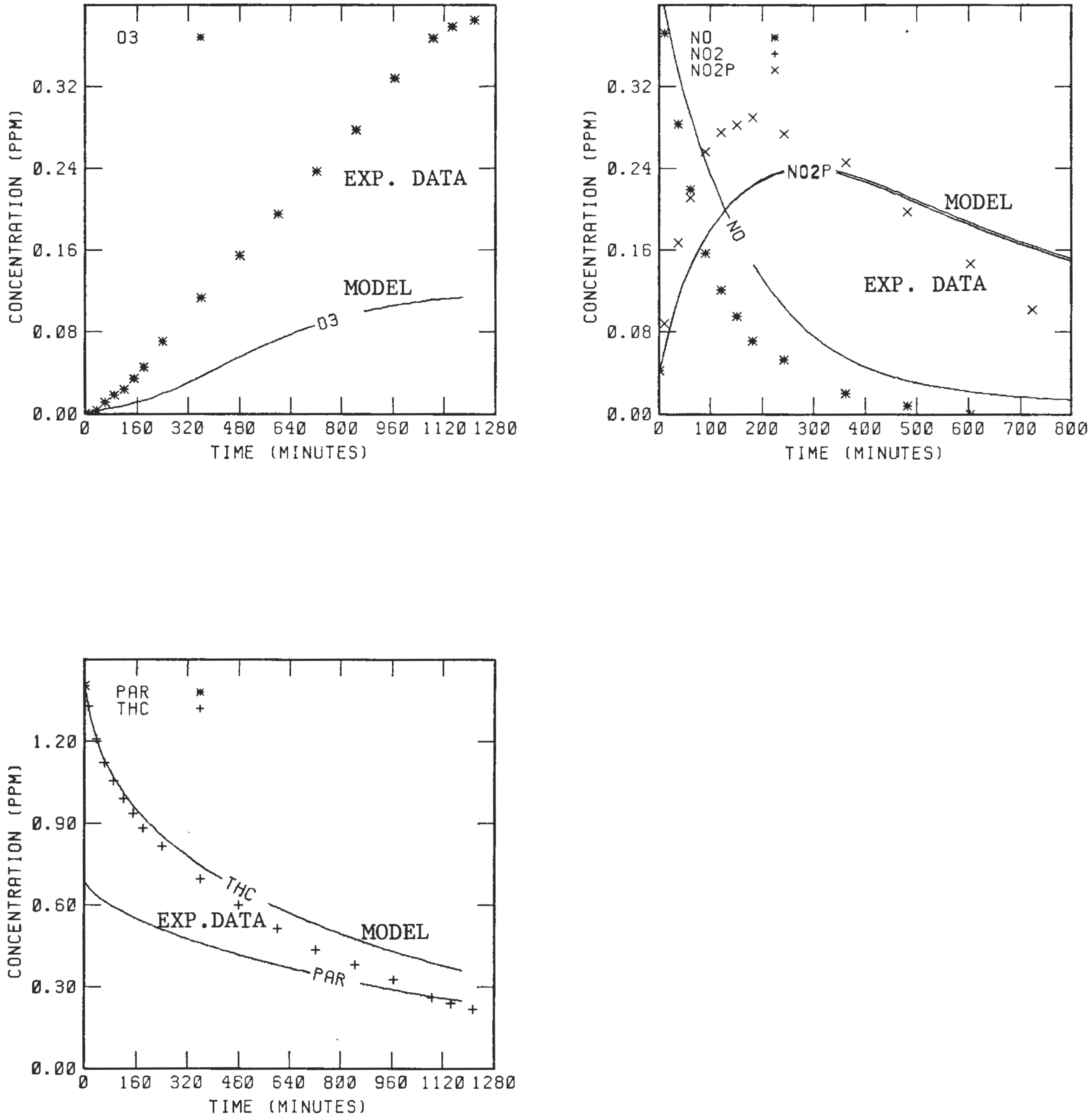

Figure 9-4 : Simulation Results for Gasoline Exhaust Experiment Using Low Reactivity Exhaust Composition as Needed to Simulate the Blend Exhaust Experiment of 3-21-84 were performed on February 27 and February 29, 1984 and are shown in Figure 9-5. Both reactivity experiments had about 0.43 ppm NOx for initial conditions. Their initial ppm carbon to NOx conditions were a ratio of about 7.7:1. The February 29th experiment started with about 17% of NO_2, while the February 27th experiment had only 9% NO_2 for initial conditions. Both experiments consisted of 58% exhaust hydrocarbons plus 42% evaporative emissions. The modeling of these experiments will be discussed further under subcontractor Task S3.

The evaporative emissions measurements from four methanol gasoline blend SHED (hot soak) tests are reported below in Table 9-1.

Table 9-1 : Hot soak evaporative emissions from methanol gasoline blend

FUEL	DATE	EVAPORATIVE MASS	AVERAGE
Methanol Gasoline Blend	2/27/84	2.29 grams	
	2/29/84	2.50 grams	
	3/1/84	1.73 grams	
	3/2/84	2.13 grams	
	3/8/84	1.86 grams	
			2.10 grams

A comparison of the mass average hot soak emissions from the gasoline (Table 8-1) and the methanol gasoline blend indicates no significant difference.

10. Gasoline Evaporative Emissions Reactivity Assessment, Task 12

The Escort was driven until fully warmed and then placed within the SHED facility. The evaporative emissions were measured during the one hour hot soak period as reported previously in Table 8-1. A sample of the evaporative emissions were immediately transferred to the smog chamber until the concentration reached the desired level, just over a nominal 3.6 ppm carbon. Dilute nitric oxide had previously been added to produce the initial condition of 0.41 ppm NOx of which 9% was NO_2. The hydrocarbon NO_2 composition of the sample was partially analysed prior to irradiation. A complete analysis was not possible due to the complex composition of gasoline and the gas chromatograph limitations. The results of the March 15th smog chamber experiment are shown in Figure 10-1.

The gasoline evaporative emissions experiment appears to be lower in reactivity relative to the two gasoline exhaust experiments reported in Figure 8-1. The two gasoline exhaust experiments started with lower ppmC to NOx ratios than the evaporative emission experiment and yet produced more ozone (840 ppb and 812 ppb respectively) after similar irradiation times (373 and 358 minutes respectively). The gasoline evaporative emissions experiment with an 8.1:1 ppmC to NOx ratio yielded 746 ppb ozone after 372 minutes.

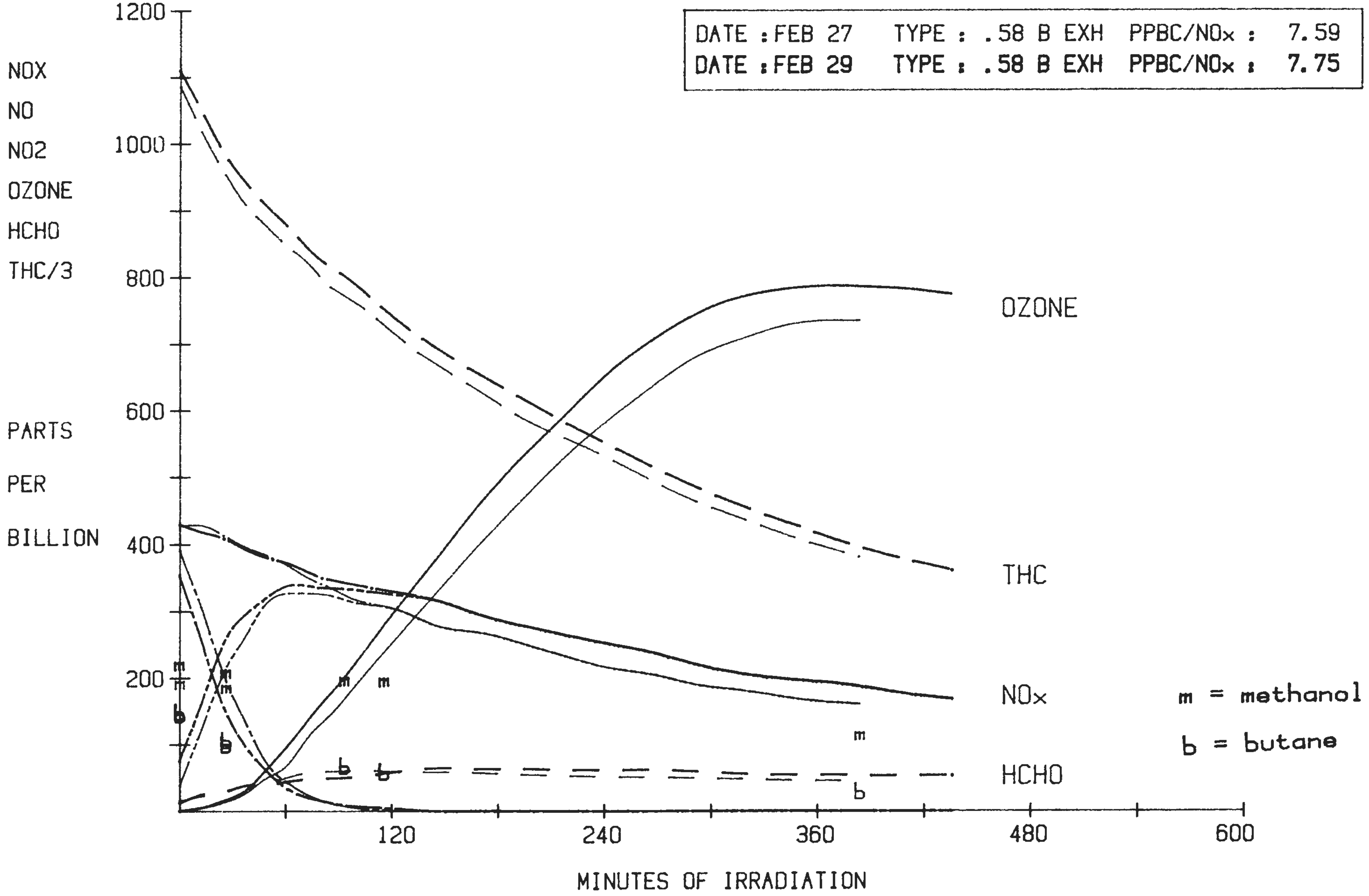

FIGURE 9-5 : METHANOL GASOLINE BLEND EXHAUST PLUS EVAPORATIVE EMISSIONS

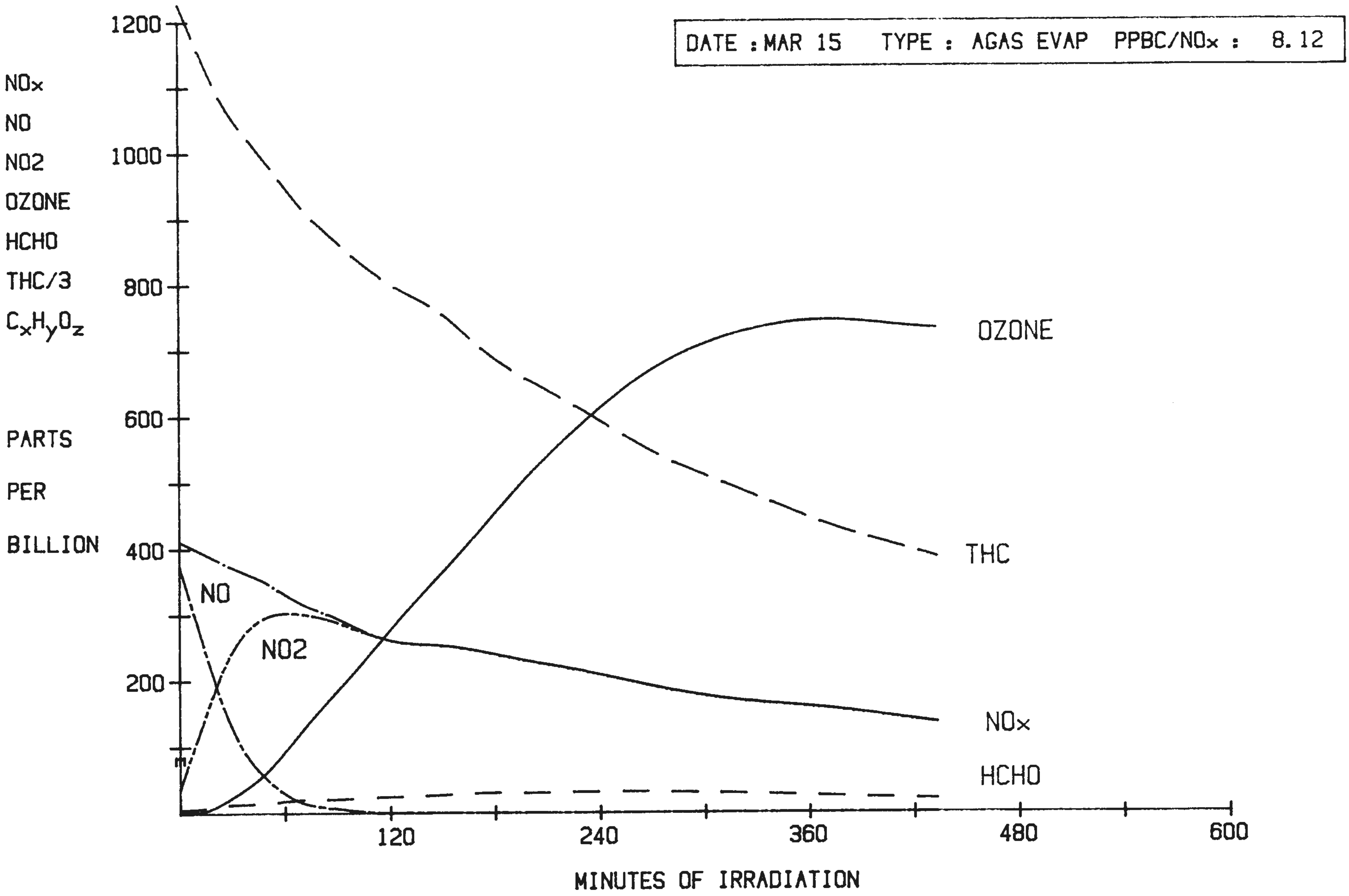

FIGURE 10-1 : GASOLINE EVAPORATIVE EMISSION SAMPLE FROM SHED HOT SOAK

11. Methanol Gasolinelend Evaporative Emissions Reactivity Cases, Task 13

The Escort was driven until fully warmed and then placed within the SHED facility for an evaporative emissions measurement. The March 2nd evaporative emissions result is included above in Table 9-1. Immediately after the final SHED concentration measurement, a sample of the evaporative emissions was transferred into the smog chamber until just over 3.6 ppm carbon was added. Dilute nitric oxide from a calibration gas supply had previously been added to produce the initial condition of 0.44 ppm NOx. The hydrocarbon composition of the evaporative emissions was also analysed to the extent possible with the instrumentation. The March 2nd smog chamber experimental results are shown in Figure 11-1.

The methanol gasoline blend evaporative emissions appear to be very comparable in reactivity to the evaporative emissions from the baseline gasoline. The higher initial NOx with a ppmC to NOx ratio of 7.7:1 produced an ozone peak of 770 ppb after 425 minutes of irradiation. The slight differences in experimental reactivity are small enough to require further evidence to determine if they are statistically significant differences.

12. Modeling of Blend Experiments Involving Evaporative Emissions, Task S3

Systems Applications, Inc. has modeled the gasoline and methanol gasoline blend experiments using a number of assumptions about composition. A limited analysis of composition has been completed using the packed column gas chromatography technique developed for analysis of the eight surrogate hydrocarbons plus methanol. Due to the lack of detailed species information the exhaust and evaporative emissions were arbitrarily assigned to reactivity classes based upon characterization studies performed recently at the University of North Carolina (15). The chemical kinetic mechanism used to model those emissions is also different from the CBM-III extended CBM-III mechanisms discussed above.

The results from modeling the available exhaust emissions experiments were previously discussed under Task 11 A. The modeling of the experiments indicated that the methanol blend's exhaust was lower in reactivity per carbon atom than exhaust from the baseline gasoline as discussed previously.

Pure Methanol Reactivity Estimate

The recent smog chamber and modeling study did not directly address the issue of pure methanol reactivity. The issue that was addressed assumed that some formaldehyde would always accompany the emissions of methanol which appears to be true if methanol is used as the primary fuel for transportation. However, the evaporative emissions from such vehicles and the evaporative emissions from vehicles using petroleum based fuel containing small amounts of methanol would not contain formaldehyde in their evaporative emissions. Hence it may be useful to estimate the atmospheric reactivity of pure methanol itself.

The main types of smog chamber experiments performed in the University of Santa Clara chamber were designed to test the reactivity of various compounds or mixtures of compounds under typical urban smog conditions.

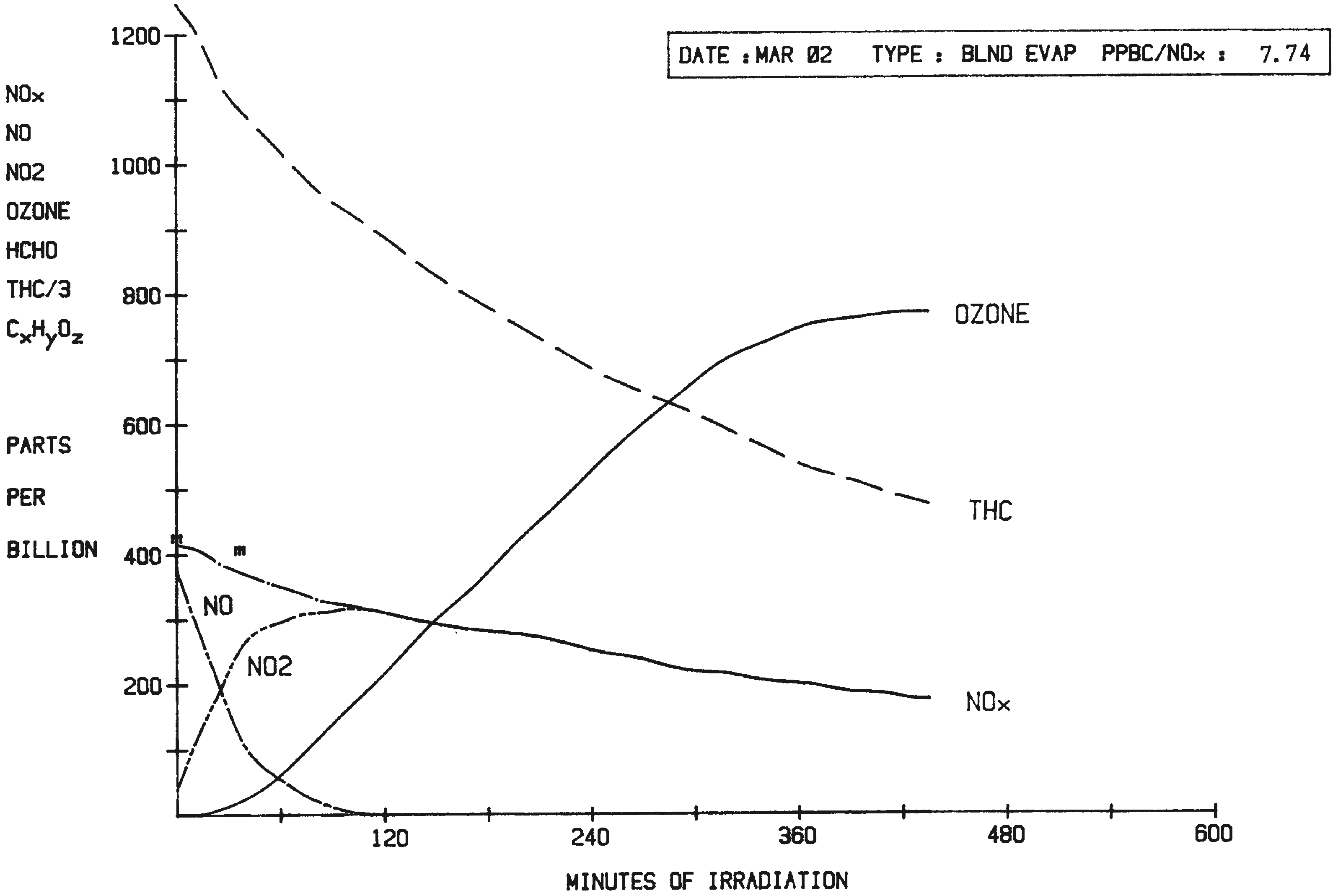

FIGURE 11-1 : METHANOL GASOLINE BLEND EVAPORATIVE EMISSION SAMPLE FROM SHED

These conditions were provided by a surrogate urban mixture of hydrocarbons and nitrogen oxides. Reactivity in this type of test was defined relative to the surrogate urban mixture of hydrocarbons by a series of three experiments. First was a base case experiment using only the surrogate mixture and NOx. Then a so called blank case experiment was performed using the same amount of NOx but only 2/3 of the concentration of the surrogate mixture. Finally a test case was performed by adding the hydrocarbon to be tested to the 2/3 concentration of the urban mixture until the full base case hydrocarbon concentration was reached.

The test case experiment was thus a substitution experiment where one third of the urban mixture had been replaced by the organic compound being tested. If the test case experiment produced results identical to the full base case experiment, then the reactivity of the test compound was said to be identical to the surrogate urban mixture. If the test case results were identical to the blank case experiment with only the 2/3 concentration of the urban mixture then the test organic was obviously inert because its presence had no effect. If the test case experiment produced intermediate results between the blank and base case experiments then the test compound was said to have a reactivity less than the urban mixture.

Another type of measure of reactivity is the substitution factor which is defined by adding just enough of the test organic to the 2/3 concentration of urban hydrocarbons to match the results of the full base case experiment. This factor can be found by first simulating the experiment on a computer and then confirming the results by performing the actual substitution experiment. At present only this computer estimate of reactivity is available for pure methanol.

Reactivity can vary with the overall hydrocarbon to NOx ratio so the substitution reactivity factor for methanol was determined at two ratios. However, there appeared to be little effect of overall hydrocarbon to NOx ratio within the range of 3 to 1 and 9 to 1. The relative reactivity of methanol compared to the reactivity per mole of carbon of the surrogate urban mixture was calculated. The substitution factor for methanol appeared to be near 2.5 moles of methanol per carbon mole of surrogate mix at the 9 to 1 ratio and near 3 moles per mole at the low hydrocarbon to NOx ratio of 3 to 1.

13. Atmospheric Simulations, Task S4

The photochemistry of methanol plus formaldehyde, as used in the Phase I modeling study prepared for ARCO, has been confirmed to be correct. However, the hydrocarbon surrogate chemistry, as used in that modeling study, was found to be inadequate to model the eight surrogate mix and the wide range of ppm carbon to NOx ratios in the current set of experiments. A large amount of time and effort was expended to model and understand the hydrocarbon surrogate chemistry so that methanol's photochemistry could be validated.

The principal cases of the Phase I modeling study have very recently been repeated using the extended CBM-III chemistry (see Table 13-1). As expected, the extended CBD-III chemistry applied to the 100% methanol vehicle substitution case produced a further reduction in urban ozone. However, the baseline urban case also produced a slight decrease in ozone so that the percentage improvement achieved by methanol substitution was slightly reduced.

Table 13-1 : Urban Ozone Predictions (ppm) by CBM-III and Extended CBM-III Mechanisms

	CBM-III Mechanism	Extended CBM-III Mechanism
Baseline Case	0.273	0.250
100 % Methanol Substitution	0.213	0.205
Percent Improvement	22 %	18%

Special attention has been given to ambient formaldehyde effects. The average and peak formaldehyde concentrations from the Phase I modeling study are presented in Table 13-2.

The model with CBM-III chemistry indicates that there would be no significant change in average ambient formaldehyde levels with 100% methanol substitution for all mobile sources. A small increase in peak ambient formaldehyde levels is predicted. This is not to say that curbside emissions of formaldehyde from neat methanol vehicles would not increase somewhat, but rather that diluted, areawide exhaust plus photochemically generated formaldehyde concentrations should not increase significantly. Under normal conditions (i.e., without methanol) formaldehyde is typically about half the total aldehydes (or carbonyls). The model using carbon bond chemistry does not separate the aldehydes. However, when the methanol chemistry was added, the extra formaldehyde (photochemically produced from methanol and directly accompanying the methanol exhaust was treated separately. Table 13-2 shows the difference between the base case and the zero mobile source case. A drop in the total average aldehydes of 10 ppb was calculated. Since the 100 percent methanol substitution case is 51 ppb total then the methanol adds 10 ppb of pure formaldehyde to the zero mobile case. Assuming that half of the zero mobile case is formaldehyde implies an additional 20 ppb from the non-mobile sources. Hence, the methanol substitution case appears to have an average total formaldehyde of about 30 ppb (10 ppb from methanol and 20 ppb from the non-mobile sources). If the base case is 50 percent formaldehyde the implication is that converting all mobile sources to methanol might change the average formaldehyde from 25 ppb to 30 ppb. However, this change is too small to be significant within the present analysis.

The following explanation describes why there was no significant change in average formaldehyde concentrations with a conversion to methanol fuel. The substitution of methanol for gasoline lowers the overall reactivity of the urban atmospheric mix of hydrocarbons (including methanol). Reacting mixtures of hydrocarbons generate a steady-state level of formaldehyde since it is a common intermediate in the chemistry.

Table 13-2 : Ambient Total Aldehyde (ppb) and Formaldehyde Effects of Methanol Substitution Using CBM-III Chemistry.

Total Aldehydes	Average	Peak	Estim. Avg. Formaldehyde
Base Case	51.	69.	26.
100% Methanol Substitution for Mobile Sources	51.	72.	31.
Zero Mobile Sources	41.	52.	20.

The steady-state level is determined by the reactivity of the mixture and the physical conditions such as temperature, solar intensity, and mixing depth. Higher reactivity generates more formaldehyde but the loss rate of formaldehyde is fairly independent of reactivity. Hence lower reactivity mixtures generate formaldehyde at a slower rate leading to a lower steady-state level of formaldehyde concentration.

On the other hand methanol is a special case because as it reacts it produces formaldehyde 100 percent of the time and some extra amount of formaldehyde is also emitted when methanol is used as a fuel. Hence the reduced reactivity of the atmosphere with methanol substitution for gasoline tends to reduce formaldehyde steady state levels while the high yield of formaldehyde combines with the extra formaldehyde emissions to result in a net formaldehyde level similar to the base case.

D. Conclusions and Proposed Future Work

Experimental evidence has been obtained to support methanol's low photochemical reactivity when substituted for typical urban hydrocarbons. This evidence supports a previous urban modeling study in which significant ozone reductions were predicted with large scale methanol substitution for gasoline. An improved (urban hydrocarbon) chemical kinetic mechanism has also been partially validated along with methanol's photochemistry.

It is important to confirm the experimental finding that m-xylene contributed very high reactivity to the urban mix recently studied. m-Xylene appeared to dominate the chemistry of the recent experiments more than any other compound. m-Xylene's effect was clearly a function of the ppm carbon to NOx ratio of the experiment. In effect, methanol substitution also produced a relative decrease in the ppm carbon to NOx ratio of the hydrocarbon surrogates and thereby also produced the independent effects of reducing m-xylene. It is important to repeat some of the methanol substitution experiments using an urban hydrocarbon surrogate mix which does not contain m-xylene and which is, therefore, not as sensitive to ppm carbon to NOx ratio effects.

The combined effects of replacing m-xylene with methanol in gasoline are also deserving of further study. Both experimental work and urban modeling studies are expected to show that significant ozone reductions could be achieved. Even m-xylene replacement by almost any other hydrocarbon should yield ozone reductions at moderate to low hydrocarbon to NOx ratios.

Neat methanol's ozone production reactivity should also be studied by experimentation accompanied by atmospheric modeling over a wider range of hydrocarbon to NOx ratios than was evaluated (3:1 to 9:1). Methanol's relative contribution to ozone formation per mole of carbon was found to be about one third that of the urban surrogate mix for the reactant ratio range studied.

A limited assessment of a methanol/gasoline blend (4.5% methanol plus 4.5% GTBA plus 91% unleaded gasoline) has been conducted during this research program. The mass of evaporative emissions (moles of carbon) was not increased with the use of this refinery produced methanol/gasoline blend relative to a gasoline of similar volatility. The photochemical reactivity of the evaporative emissions emitted during a one hour hot soak were not significantly different between the two test fuels. The photochemical reactivity of combined exhaust plus evaporative emission samples was also not significantly different between the two test fuels. The reactivity of exhaust emissions from the methanol/gasoline blend were computed from smog chamber evidence to be lower than the reactivity of the exhaust hydrocarbon emissions from the gasoline tested. This exhaust hydrocarbon reactivity comparison should be repeated along with a measurement of the blend exhaust's change in composition in order to achieve a consistent theoretical explanation.

Methanol/gasoline blends appear to be one of the most attractive interim uses for methanol as fuel. A more comprehensive assessment of their impact cannot be made without a more extensive analysis of the composition of the exhaust and evaporative emissions from those vehicles. Such a detailed analysis was beyond the scope of the present study. However, because of the low reactivity of the methanol in the emissions, it might be possible to permit blends to be more volatile than gasoline. The range of exhaust and evaporative emissions changes produced by various methanol/gasoline blends is of key importance for assessing their impact from otherwise unmodified vehicles. Given such a data base, the computer model could then apply hydrocarbon, methanol, cosolvent and NOx emission inventories to the environmental impact study.

Several cosolvents have been used to improve the water tolerance and material compatibility of methanol/gasoline blends. These have not yet been assessed for their photochemical reactivity characteristics. t-Butyl alcohol, iso-butyl alcohol and ethanol are three cosolvents which are proposed for vehicle fuel cosolvent use. We expect a wide range in ozone production reactivity among these proposed cosolvents.

Two improvements in chamber protocol are currently under development. First, the Teflon bag has been given added support to minimize any volume changes or dilution effects caused by temperature increases at the start of an experiment. Slight variations in NOx and hydrocarbon dilution conditions at the start of some experiments are believed to contribute to the variability observed in peak ozone concentrations.

Second, the sunlamps will be allowed to preheat before the chamber's reactants are exposed to any light. Window shades are being designed to cover all glass areas while the lights preheat. Some concern has been expressed about the higher intensity of ultraviolet light produced when the sunlamps are first turned on. These improvements in experimental technique are being evaluated as part of a separate contract now in progress.

The gas chromatograph used to measure the eight hydrocarbon surrogates plus methanol was satisfactory for that purpose. However, to properly characterize the species composition of the exhaust and evaporative emissions from gasoline and methanol blends, improved instrumentation is needed. It is important to relate changes in observed chamber reactivity to measured compositional changes in the hydrocarbons under study.

References:

1. Bechtold, R. and B. Pullman (1980), "Driving Cycle Economy, Emissions and Photo-chemical Reactivity Using Alcohol Fuels and Gasoline," SAE Paper 800260.

2. Whitten, G.Z. and H. Hogo (1983),"Impact of Methanol on Smog: A Preliminary Estimate," Report 83044 ,Prepared for ARCO Petroleum Products Co. by Systems Applications Inc.,San Rafael, California.

3. Whitten, G. and B. Pullman (1984), "Methanol Fuel Substitution Can Reduce Urban Ozone Pollution," VI International Alcohol Fuels Symposium, Ottawa, May 1984.

4. Carter, W. (1984) Private Communication. Univ. of Calif.,Riverside ;SAPRC

5. Sakamaki, F., S. Hatakeyama and Y. Akimoto (1983); "Formation of Nitrous Acid and Nitric Oxide in the Heterogeneous Dark Reaction of Nitrogen Dioxide and Water Vapor in a Smog Chamber," Int.J. Chem. Kinet. V.15, P1013-1029.

6. Whitten, G.Z., J.P. Killus and H. Hogo (1980), "Modeling of Simulated Photochemical Smog with Kinetic Mechanisms. Vol.1. Final Report," EPA-600/3-80-28a, U.S. Environmental Protection Agency, Office of Research and Development, Research Triangle Park, North Carolina.

7. Pyrex (#7740) spectral transmission reference from Corning Glass, Inc.

8. Whitten, G.Z. et al. (1979), "Modeling of Photochemical Smog with Kinetic Mechanisms," Vol. I, EPA-600/3-79-001a, Systems Applications, Inc., San Rafael, California.

9. Wu, C.H. and H. Niki (1975), "Methods for Measuring NO_2 Photolysis Rate," Environ. Sci. Technol., Vol. 14, pp 57-61.

10. Schere, K.L. and K.L. Demerjian (1977), "Calculation of Selected Photolytic Rate Constants over a Diurnal Range," EPA-600/4-77-015, U.S.E.P.A.

11. Grosjean, D. et al. (1982),"Captive Air Experiments in Support of Photochemical Kinetic Model Evaluations, Phase I.," ER&T Doc. No. P-A764-500, November, 1982, Environmental Research & Technology, Inc., Westlake Village, California.

12. Killus, J.P. and G.Z. Whitten (1983), "Comment on 'Photochemical Reactivity and Ozone Formation in 1-Olefin -Nitrogen Oxide-Air Systems'", Environ. Sci. Technol., Vol. 17, pp 760-762.

13. Killus, J.P. and G.Z. Whitten (1984), "An Expanded Carbon Bond Mechanism for Use in Atmospheric Simulation," in preparation.

14. Pefley, R.K. et al. (1978), "Characterization and Research Investigation of Methanol and Methyl Fuels Final Report", prepared for US EPA and US DOE and available from NTIS as report COO/W1258-01.

15. Jeffries, H. et al. (1984) Private Communication. Univ. of North Carolina.

APPENDIX A

The following Appendix contains detailed data from twenty-four smog chamber experiments. Initial conditions and ongoing reactant concentration data are supplied for four inorganics (NOx, NO, NO_2 and ozone), ten individual organics and a total FID hydrocarbon measurement.

Reactant temperature data were not obtained during the experiments from July through September of 1983. However, the typical temperature profile presented in Figure 2-2 of the text was often repeated during experiments from October, 1983 through March, 1984.

Dilution conditions within the chamber were known to have increased during the period from August 25 through November 3, 1983. A controlled dilution rate was established for experiments which began after the Teflon bag was installed in July 1983. Dilution air entered the 70 cubic foot bag at 1.34 liters per minute until a sample return line because disconnected prior to the August 25th experiment. The 2.0 liter per minute sample to the ozone instrument was normally routed back into the chamber along with the bypass flow from the total hydrocarbon analyzer. The sample return line (within the ozone instrument) became disconnected and the effective dilution rate was thereby increased to 3.6 liters per minute. The clean air supply routed inside the chamber's walls but outside the Teflon bag diluted the reactants. The experiments conducted from November 4, 1983 through March 15, 1984 were modeled with the previous low dilution rate.

Appendix A : Smog Chamber Experiment Summary

DATE	NOMINAL ppmC/NOx	REACTANTS		
		8 Surrogate Baseline Mix	Methanol Surrogates	Methanol Vehicle Exhaust
Aug 26	3:1	Baseline		
Aug 11	2:1	2/3 Baseline		
Aug 18	3:1	2/3 Baseline +	1/3 MS Substit.	
Jul 28	9:1	Baseline		
Aug 1	6:1	2/3 Baseline		
Aug 24	9:1	2/3 Baseline +	1/3 MS Substit.	
Aug 10	27:1	Baseline		
Aug 9	18:1	2/3 Baseline		
Aug 25	27:1	2/3 Baseline +	1/3 MS Substit.	
Mar 6	12:1	2/3 Baseline +	2/3 MS Substit.	
Sep 16	3:1	2/3 Baseline +		1/3 MV Exhaust
Sep 22	9:1	2/3 Baseline +		1/3 MV Exhaust
Sep 13	27:1	2/3 Baseline +		1/3 MV Exhaust
Nov 7	9:1	2/3 Baseline +	1/3 Methanol Only	

Date	ppmC NOx	Gasoline Exhaust	Gasoline Hot Soak Evap.	Blend Exhaust	Blend Hot Soak Evap.
Feb 7	9:1	Gas Exh.			
Feb 8	9:1	Gas Exh.			
Jan 26	3:1	Gas Exh.			
Feb 21	9:1	1/2 Gas Exh. +	1/2 GHS Evap.		
Mar 13	9:1	2/3 Gas Exh. +	1/3 GHS Evap.		
Mar 15	9:1		GHS Evap.		
Mar 21	3.9:1			Blend Exh.	
Feb 27	9:1			1/2 Blend Exh. +	1/2 BHS Evap.
Feb 29	9:1			1/2 Blend Exh. +	1/2 BHS Evap.
Mar 2	9:1				BHS Evap.

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THE   REDUCED   DATA   FILE   IS        : AUG263.DAT

THE INITIAL PPB CARBON TO NOX RATIO IS : 3128. TO 1186.  EQUALS :    2.64


MINUTES    NOX     NO      NO2  OZONE   HCHO    THC    C2H4    C3H6  CH3ONO  CH3OH  C4H8   C4H10  ACET   C5H12  224TMP C7H8   C8H10

    0.0 1185.8 1123.9    61.8    0.0    0.0 3127.8    197.    212.     0.     35.   396.   600.     0.   685.   521.   431.   495.  PPB'S
   12.1 1178.9 1077.2   101.7    0.0    1.9 3033.1    198.    204.     0.     36.   362.   616.     0.   680.   520.   422.   507.  PPB'S
   32.4 1135.7  964.6   171.1    1.0    7.5 2903.8    184.    186.     0.     37.   294.   597.     0.   647.   515.   409.   436.  PPB'S
   52.6 1097.0  864.7   232.3    2.0   16.8 2757.3    173.    160.     0.     34.   216.   579.     0.   584.   470.   430.   424.  PPB'S
   76.9 1037.8  722.4   315.4    5.1   28.0 2559.1    170.    147.     0.     35.   160.   596.     0.   584.   438.   379.   412.  PPB'S
  101.2  976.4  601.3   375.1    8.1   33.6 2378.2    147.    110.     0.     25.    94.   556.     0.   533.   417.   371.   318.  PPB'S
  121.4  928.6  514.2   414.4   10.1   50.4 2248.9      0.      0.     0.      0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  145.7  878.5  439.8   438.7   12.1   46.7 2093.8      0.      0.     0.      0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  170.0  821.6  373.9   447.7   14.1   46.7 1973.2      0.      0.     0.      0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  194.2  778.4  316.6   461.8   16.2   41.1 1852.6      0.      0.     0.      0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  212.5  744.2  282.6   461.7   20.2   37.3 1783.6     94.     45.     0.     26.     0.   390.     0.   305.   358.   280.   200.  PPB'S
  242.8  689.6  235.8   453.8   24.3   37.3 1654.4      0.      0.     0.      0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  267.1  648.6  197.6   451.1   28.3   37.3 1568.2      0.      0.     0.      0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  291.4  610.0  170.0   440.0   32.3   28.0 1482.1      0.      0.     0.      0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  303.5  589.5  150.9   438.6   34.4    0.0 1439.0     72.     26.     0.     25.     0.   329.     0.   266.   197.   198.   130.  PPB'S
  339.9  541.7  129.6   412.1   40.4    0.0 1335.6      0.      0.     0.      0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  388.5  487.1   89.2   397.8   52.5    0.0 1223.6      0.      0.     0.      0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  437.1  432.4   68.0   364.4   65.7    0.0 1120.2      0.      0.     0.      0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  485.6  386.9   44.6   342.3   80.8    0.0 1034.0      0.      0.     0.      0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  534.2  348.2   34.0   314.2   97.0    0.0  947.8      0.      0.     0.      0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  582.7  311.8   21.2   290.6  115.2    0.0  870.3      0.      0.     0.      0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  605.0  293.6   14.9   278.7  125.3    0.0  844.4      0.      0.     0.      0.     0.     0.     0.     0.     0.     0.    -9.  PPB'S
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THE   REDUCED   DATA   FILE   IS       : AUG113.DAT

THE INITIAL PPB CARBON TO NOX RATIO IS : 2185. TO 1263.  EQUALS :    1.73

MINUTES    NOX     NO      NO2  OZONE    HCHO    THC   C2H4   C3H6  CH3ONO  CH3OH  C4H8   C4H10  ACET  C5H12  224TMP C7H8  C8H10
                                                                                                                            
    0.0 1263.0 1202.6    60.5    0.0     3.7 2185.1   138.   149.     0.     0.   278.   421.    0.   486.   369.   302.   347.  PPB'S
   20.3 1242.7 1118.5   124.3    0.0    18.3 2116.2   139.   141.     0.     0.   227.   422.    0.   466.   362.   286.   327.  PPB'S
   40.5 1215.7 1021.7   194.0    1.0    40.3 2047.4   132.   127.     0.     0.   184.   426.    0.   452.   335.   287.   277.  PPB'S
   73.0 1163.9  891.4   272.5    1.0    64.2 1935.6     0.     0.     0.     0.     0.     0.    0.     0.     0.     0.     0.  PPB'S
   97.3 1130.2  817.8   312.4    2.0    77.0 1866.8     0.     0.     0.     0.     0.     0.    0.     0.     0.     0.     0.  PPB'S
  121.6 1098.7  744.2   354.4    3.0    88.0 1815.1     0.     0.     0.     0.     0.     0.    0.     0.     0.     0.     0.  PPB'S
  145.9 1064.9  687.5   377.4    5.1    91.7 1754.9     0.     0.     0.     0.     0.     0.    0.     0.     0.     0.     0.  PPB'S
  170.2 1026.6  628.6   398.0    8.1    93.5 1703.3     0.     0.     0.     0.     0.     0.    0.     0.     0.     0.     0.  PPB'S
  202.7  990.6  569.7   420.9    9.1    95.3 1643.1    72.    34.     0.     0.    14.   333.    0.   316.   217.   235.   115.  PPB'S
  243.2  934.3  502.5   431.8   10.1    95.3 1548.5     0.     0.     0.     0.     0.     0.    0.     0.     0.     0.     0.  PPB'S
  291.8  878.0  433.1   444.9   11.1    91.7 1462.4     0.     0.     0.     0.     0.     0.    0.     0.     0.     0.     0.  PPB'S
  340.5  819.5  384.7   434.8   14.1    84.3 1385.0     0.     0.     0.     0.     0.     0.    0.     0.     0.     0.     0.  PPB'S
  389.1  770.0  338.5   431.5   16.2    78.8 1307.6     0.     0.     0.     0.     0.     0.    0.     0.     0.     0.     0.  PPB'S
  437.8  718.2  298.5   419.6   18.2    75.2 1238.8     0.     0.     0.     0.     0.     0.    0.     0.     0.     0.     0.  PPB'S
  486.4  668.7  264.9   403.8   20.2    73.3 1178.6     0.     0.     0.     0.     0.     0.    0.     0.     0.     0.     0.  PPB'S
  535.0  625.9  229.2   396.7   22.2    69.7 1118.3     0.     0.     0.     0.     0.     0.    0.     0.     0.     0.     0.  PPB'S
  583.7  578.6  195.5   383.1   24.3    66.0 1066.7     0.     0.     0.     0.     0.     0.    0.     0.     0.     0.     0.  PPB'S
  632.3  544.8  170.3   374.5   27.3    62.3 1015.1     0.     0.     0.     0.     0.     0.    0.     0.     0.     0.     0.  PPB'S
  681.0  504.3  147.2   357.1   33.3    55.0  972.1     0.     0.     0.     0.     0.     0.    0.     0.     0.     0.     0.  PPB'S
  778.2  432.3  103.0   329.2   39.4    51.3  877.5     0.     0.     0.     0.     0.     0.    0.     0.     0.     0.     0.  PPB'S
  836.0  398.5   82.0   316.5   47.5    45.8  834.5     0.     0.     0.     0.     0.   161.    0.    80.    77.   149.    -9.  PPB'S
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THE   REDUCED   DATA   FILE   IS      : AUG183.DAT

THE INITIAL PPB CARBON TO NOX RATIO IS : 3566. TO 1237.  EQUALS :    2.88


MINUTES   NOX     NO      NO2   OZONE    HCHO    THC     C2H4    C3H6  CH3ONO  CH3OH   C4H8   C4H10   ACET   C5H12  224TMP C7H8   C8H10

    0.0 1237.4 1148.4    89.0     0.0     0.0 3565.6    142.    153.      0.   1285.   689.   433.      0.   465.   353.   292.    336.  PPB'S
   13.2 1233.0 1109.5   123.5     0.0     1.4 3546.6    135.    139.      0.   1239.   596.   404.      0.   438.   353.   305.    315.  PPB'S
   32.4 1211.0 1013.5   197.5     0.0    11.2 3442.3    138.    140.      0.   1286.   536.   419.      0.   492.   385.   268.    304.  PPB'S
   52.7 1189.1  915.4   273.6     0.0    33.6 3338.0    130.    120.      0.   1227.   418.   413.      0.   416.   276.   341.    294.  PPB'S
   70.9 1164.9  823.5   341.4     1.0    51.8 3233.7    122.    105.      0.   1190.   327.   400.      0.   378.   308.   331.    231.  PPB'S
   97.2 1127.5  705.0   422.6     3.0    74.1 3091.4      0.      0.      0.      0.     0.     0.      0.     0.     0.     0.      0.  PPB'S
  145.8 1057.2  557.8   499.3     6.1    86.7 2892.3      0.      0.      0.      0.     0.     0.      0.     0.     0.     0.      0.  PPB'S
  194.4  995.6  457.7   537.9     9.1    99.3 2712.1      0.      0.      0.      0.     0.     0.      0.     0.     0.     0.      0.  PPB'S
  243.0  945.1  392.3   552.8    11.1   104.9 2550.9      0.      0.      0.      0.     0.     0.      0.     0.     0.     0.      0.  PPB'S
  293.6  881.4  333.1   548.3    13.1   100.7 2418.2     73.     24.      0.    979.     0.   335.      0.   241.   238.   268.     95.  PPB'S
  311.9  859.4  314.7   544.7    14.1    99.3 2361.3     75.     23.      0.      0.     0.   336.      0.   235.   270.   219.     73.  PPB'S
  364.5  808.8  273.8   535.0    18.2    99.3 2238.0      0.      0.      0.      0.     0.     0.      0.     0.     0.     0.      0.  PPB'S
  413.1  758.3  235.0   523.3    20.2    95.1 2133.7      0.      0.      0.      0.     0.     0.      0.     0.     0.     0.      0.  PPB'S
  461.7  709.9  210.5   499.5    23.2    93.7 2038.8      0.      0.      0.      0.     0.     0.      0.     0.     0.     0.      0.  PPB'S
  558.9  624.2  153.3   470.9    30.3    83.9 1849.2      0.      0.      0.      0.     0.     0.      0.     0.     0.     0.      0.  PPB'S
  656.1  542.9  110.3   432.5    39.4    72.7 1678.5      0.      0.      0.      0.     0.     0.      0.     0.     0.     0.      0.  PPB'S
  753.3  470.3   73.6   396.8    50.5    61.6 1555.2      0.      0.      0.      0.     0.     0.      0.     0.     0.     0.      0.  PPB'S
  850.6  408.8   47.0   361.8    68.7    56.0 1413.0      0.      0.      0.      0.     0.     0.      0.     0.     0.     0.      0.  PPB'S
  947.8  338.5   26.6   311.9    90.9    53.2 1289.7      0.      0.      0.      0.     0.     0.      0.     0.     0.     0.      0.  PPB'S
  961.9  331.9   24.5   307.4    96.0    51.8 1280.2      0.      0.      0.      0.     0.     0.      0.     0.     0.     0.     -9.  PPB'S
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THE   REDUCED   DATA   FILE   IS       : JUL283.DAT

THE INITIAL PPB CARBON TO NOX RATIO IS : 3329. TO  433.  EQUALS :    7.69


MINUTES   NOX    NO     NO2   OZONE   HCHO   THC    C2H4   C3H6  CH3ONO  CH3OH  C4H8   C4H10  ACET   C5H12  224TMP C7H8   C8H10

   0.0  432.7  366.7   66.0    0.0    0.0 3328.5   210.   227.    0.     0.   424.   641.    0.   729.   554.   459.   527.  PPB'S
  12.1  424.3  303.2  121.1    1.0   18.8 3253.0     0.     0.    0.     0.     0.     0.    0.     0.     0.     0.     0.  PPB'S
  18.2  422.3  263.2  159.0    4.0   28.2 3202.7   209.   207.    0.     0.   367.   624.    0.     0.   578.   433.   530.  PPB'S
  24.3  415.0  227.4  187.6    9.1   35.2 3160.8     0.     0.    0.     0.     0.     0.    0.     0.     0.     0.     0.  PPB'S
  36.4  403.5  150.6  252.9   21.2   51.7 3051.8     0.     0.    0.     0.     0.     0.    0.     0.     0.     0.     0.  PPB'S
  48.6  391.0   88.1  302.9   39.4   75.1 2951.2     0.     0.    0.     0.     0.     0.    0.     0.     0.     0.     0.  PPB'S
  60.7  378.5   48.1  330.3   72.8   93.9 2859.0     0.     0.    0.     0.     0.     0.    0.     0.     0.     0.     0.  PPB'S
  72.8  361.8   25.6  336.2  115.2  117.4 2783.5     0.     0.    0.     0.     0.     0.    0.     0.     0.     0.     0.  PPB'S
  85.0  349.3   14.3  334.9  162.7  129.2 2691.3     0.     0.    0.     0.     0.     0.    0.     0.     0.     0.     0.  PPB'S
  97.1  336.8    8.2  328.6  213.2  140.9 2607.5     0.     0.    0.     0.     0.     0.    0.     0.     0.     0.     0.  PPB'S
 109.2  326.3    3.1  323.3  263.7  147.9 2532.0     0.     0.    0.     0.     0.     0.    0.     0.     0.     0.     0.  PPB'S
 121.4  318.0    1.0  317.0  314.3  150.3 2464.9     0.     0.    0.     0.     0.     0.    0.     0.     0.     0.     0.  PPB'S
 133.5  306.5    0.0  306.5  366.8  159.7 2397.9     0.     0.    0.     0.     0.     0.    0.     0.     0.     0.     0.  PPB'S
 145.7  299.2    0.0  299.2  411.3  162.0 2339.2     0.     0.    0.     0.     0.     0.    0.     0.     0.     0.     0.  PPB'S
 157.8  290.9    0.0  290.9  455.7  155.0 2263.7    18.    14.    0.     0.     0.   516.    0.   506.   371.   325.   138.  PPB'S
 182.1  274.2    0.0  274.2  546.7  147.9 2138.0     0.     0.    0.     0.     0.     0.    0.     0.     0.     0.     0.  PPB'S
 206.3  255.4    0.0  255.4  623.5  140.9 2020.6     0.     0.    0.     0.     0.     0.    0.     0.     0.     0.     0.  PPB'S
 230.6  242.9    0.0  242.9  693.2  136.2 1920.0     0.     0.    0.     0.     0.     0.    0.     0.     0.     0.     0.  PPB'S
 254.9  229.4    0.0  229.4  748.8  129.2 1827.7     0.     0.    0.     0.     0.     0.    0.     0.     0.     0.     0.  PPB'S
 279.2  216.9    0.0  216.9  789.2  124.5 1743.9     0.     0.    0.     0.     0.     0.    0.     0.     0.     0.     0.  PPB'S
 303.4  205.4    0.0  205.4  815.5  115.1 1660.1     0.     0.    0.     0.     0.     0.    0.     0.     0.     0.     0.  PPB'S
 327.7  192.9    0.0  192.9  829.6  108.0 1593.0     0.     0.    0.     0.     0.     0.    0.     0.     0.     0.     0.  PPB'S
 352.0  183.5    0.0  183.5  834.7   98.6 1525.9     0.     0.    0.     0.     0.   336.    0.   205.   192.   205.     0.  PPB'S
 362.1  180.4    0.0  180.4  838.7   93.9 1509.1     0.     0.    0.     0.     0.     0.    0.     0.     0.     0.    -9.  PPB'S
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THE   REDUCED   DATA   FILE   IS       : AUG013.DAT

THE INITIAL PPB CARBON TO NOX RATIO IS : 2241. TO  423.  EQUALS :    5.30


MINUTES   NOX     NO      NO2  OZONE   HCHO    THC    C2H4   C3H6  CH3ONO  CH3OH  C4H8  C4H10  ACET  C5H12  224TMP C7H8  C8H10

    0.0  422.9  407.6   15.3    0.0    0.0 2241.1   138.   149.     0.     0.   278.  421.    0.   500.   380.   315.   361.  PPB'S
   12.2  416.5  372.3   44.2    0.0    0.0 2182.8     0.     0.     0.     0.     0.    0.    0.     0.     0.     0.     0.  PPB'S
   24.3  411.2  319.8   91.4    0.0    0.0 2132.8     0.     0.     0.     0.     0.    0.    0.     0.     0.     0.     0.  PPB'S
   29.4  409.0  296.6  112.4    1.0    0.0 2107.8   133.   114.     0.     0.   153.  374.    0.   392.   318.   272.   350.  PPB'S
   48.6  395.1  205.8  189.3    7.1    0.0 2024.5     0.     0.     0.     0.     0.    0.    0.     0.     0.     0.     0.  PPB'S
   58.7  385.5  165.4  220.1   13.1    0.0 1974.5   116.    86.     0.     0.    93.  380.    0.   413.   345.   286.   259.  PPB'S
   72.9  372.7  117.0  255.7   25.3    0.0 1916.2     0.     0.     0.     0.     0.    0.    0.     0.     0.     0.     0.  PPB'S
   97.2  349.2   64.6  284.7   54.6    0.0 1824.5     0.     0.     0.     0.     0.    0.    0.     0.     0.     0.     0.  PPB'S
  103.3  341.7   56.5  285.2   62.7    0.0 1799.5    92.    37.     0.     0.    36.  363.    0.   384.   295.   259.   226.  PPB'S
  121.5  323.6   38.3  285.3   94.0    0.0 1741.2     0.     0.     0.     0.     0.    0.    0.     0.     0.     0.     0.  PPB'S
  145.8  307.6   18.2  289.4  136.4    0.0 1666.2     0.     0.     0.     0.     0.    0.    0.     0.     0.     0.     0.  PPB'S
  170.1  283.0   11.1  271.9  183.9    0.0 1599.6     0.     0.     0.     0.     0.    0.    0.     0.     0.     0.     0.  PPB'S
  194.4  268.1    8.1  260.0  229.4    0.0 1524.6     0.     0.     0.     0.     0.    0.    0.     0.     0.     0.     0.  PPB'S
  218.7  251.0    2.0  249.0  274.9    0.0 1466.3     0.     0.     0.     0.     0.    0.    0.     0.     0.     0.     0.  PPB'S
  243.0  234.9    1.0  233.9  317.3    0.0 1416.3     0.     0.     0.     0.     0.    0.    0.     0.     0.     0.     0.  PPB'S
  267.3  221.1    0.0  221.1  362.8    0.0 1358.0     0.     0.     0.     0.     0.    0.    0.     0.     0.     0.     0.  PPB'S
  291.6  206.1    0.0  206.1  404.2    0.0 1308.0     0.     0.     0.     0.     0.    0.    0.     0.     0.     0.     0.  PPB'S
  319.0  194.4    0.0  194.4  448.7    0.0 1258.0     5.     0.     0.     0.     0.  265.    0.   202.   153.   191.     0.  PPB'S
  340.3  182.6    0.0  182.6  485.1    0.0 1208.0     0.     0.     0.     0.     0.    0.    0.     0.     0.     0.     0.  PPB'S
  364.6  170.9    0.0  170.9  523.5    0.0 1166.4     0.     0.     0.     0.     0.    0.    0.     0.     0.     0.     0.  PPB'S
  413.2  148.4    0.0  148.4  591.2    0.0 1083.1     0.     0.     0.     0.     0.    0.    0.     0.     0.     0.     0.  PPB'S
  461.8  132.4    0.0  132.4  641.7    0.0  999.7     0.     0.     0.     0.     0.    0.    0.     0.     0.     0.     0.  PPB'S
  510.4  117.5    0.0  117.5  668.0    0.0  924.8     0.     0.     0.     0.     0.    0.    0.     0.     0.     0.     0.  PPB'S
  559.0  106.8    0.0  106.8  671.0    0.0  866.4     0.     0.     0.     0.     0.    0.    0.     0.     0.     0.     0.  PPB'S
  607.6   98.3    0.0   98.3  664.9    0.0  816.5     0.     0.     0.     0.     0.    0.    0.     0.     0.     0.     0.  PPB'S
  656.2   94.0    0.0   94.0  651.8    0.0  774.8     0.     0.     0.     0.     0.    0.    0.     0.     0.     0.     0.  PPB'S
  704.8   85.4    0.0   85.4  636.6    0.0  749.8     0.     0.     0.     0.     0.    0.    0.     0.     0.     0.     0.  PPB'S
  753.4   78.0    0.0   78.0  619.5    0.0  708.2     0.     0.     0.     0.     0.    0.    0.     0.     0.     0.     0.  PPB'S
  802.0   74.8    0.0   74.8  600.3    0.0  683.2     0.     0.     0.     0.     0.    0.    0.     0.     0.     0.     0.  PPB'S
  850.6   71.6    0.0   71.6  585.1    0.0  666.5     0.     0.     0.     0.     0.    0.    0.     0.     0.     0.     0.  PPB'S
  899.3   66.2    0.0   66.2  567.9    0.0  641.5     0.     0.     0.     0.     0.    0.    0.     0.     0.     0.     0.  PPB'S
  947.9   61.9    0.0   61.9  549.7    0.0  616.5     0.     0.     0.     0.     0.    0.    0.     0.     0.     0.     0.  PPB'S
  996.5   59.8    0.0   59.8  535.6    0.0  599.8     0.     0.     0.     0.     0.    0.    0.     0.     0.     0.     0.  PPB'S
 1039.0   58.7    0.0   58.7  517.4    0.0  591.5     0.     0.     0.     0.     0.    0.    0.     0.     0.     0.    -9.  PPB'S
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THE   REDUCED   DATA   FILE   IS        : AUG243.DAT

THE INITIAL PPB CARBON TO NOX RATIO IS : 3279. TO  435.  EQUALS :     7.54


MINUTES   NOX     NO      NO2  OZONE   HCHO    THC   C2H4   C3H6  CH3ONO  CH3OH  C4H8   C4H10  ACET   C5H12  224TMP C7H8  C8H10

    0.0  434.9  402.1    32.9    0.0    0.0 3278.8   135.   146.     0.    972.   766.   413.    0.    479.   364.   302.   346.  PPB'S
   14.2  431.6  352.2    79.4    0.0   13.1 3218.9   129.   132.     0.    928.   668.   412.    0.    445.   358.   294.   312.  PPB'S
   31.5  418.2  250.4   167.8    2.0   31.7 3107.6   122.   115.     0.    908.   525.   405.    0.    445.   341.   272.   243.  PPB'S
   50.8  404.8  137.1   267.6   19.2   46.7 2979.2   113.    90.     0.    887.   372.   400.    0.    428.   406.   264.   173.  PPB'S
   61.0  391.3   89.3   302.0   34.4   54.1 2919.2     0.     0.     0.      0.     0.     0.    0.      0.     0.     0.     0.  PPB'S
   73.2  383.5   48.8   334.7   64.7   65.3 2833.6     0.     0.     0.      0.     0.     0.    0.      0.     0.     0.     0.  PPB'S
   85.4  366.7   24.9   341.8  104.1   72.8 2756.6     0.     0.     0.      0.     0.     0.    0.      0.     0.     0.     0.  PPB'S
   97.6  351.1   14.5   336.5  147.5   76.5 2679.5     0.     0.     0.      0.     0.     0.    0.      0.     0.     0.     0.  PPB'S
  109.8  335.4   10.4   325.0  193.0   85.8 2602.5     0.     0.     0.      0.     0.     0.    0.      0.     0.     0.     0.  PPB'S
  122.0  326.5    5.2   321.3  237.5   87.7 2534.0     0.     0.     0.      0.     0.     0.    0.      0.     0.     0.     0.  PPB'S
  146.4  304.1    1.0   303.1  321.3   82.1 2414.1     0.     0.     0.      0.     0.     0.    0.      0.     0.     0.     0.  PPB'S
  170.8  288.5    0.0   288.5  397.1   85.8 2302.8     0.     0.     0.      0.     0.     0.    0.      0.     0.     0.     0.  PPB'S
  195.2  268.3    0.0   268.3  464.8   85.8 2200.1     0.     0.     0.      0.     0.     0.    0.      0.     0.     0.     0.  PPB'S
  219.6  256.0    0.0   256.0  523.5   80.2 2114.5     0.     0.     0.    632.     0.   304.    0.    171.   171.   189.   120.  PPB'S
  248.1  242.6    0.0   242.6  589.1   76.5 2011.8     0.     0.     0.    685.     0.   298.    0.    171.   188.   189.    72.  PPB'S
  267.4  229.2    0.0   229.2  629.6    0.0 1951.9     3.     0.     0.      0.     0.     0.    0.      0.     0.     0.     0.  PPB'S
  292.8  219.2    0.0   219.2  680.1    0.0 1866.2     0.     0.     0.      0.     0.     0.    0.      0.     0.     0.     0.  PPB'S
  317.2  209.1    0.0   209.1  716.5    0.0 1806.3     0.     0.     0.      0.     0.     0.    0.      0.     0.     0.     0.  PPB'S
  341.6  195.7    0.0   195.7  748.8    0.0 1729.3     0.     0.     0.      0.     0.     0.    0.      0.     0.     0.     0.  PPB'S
  366.0  186.7    0.0   186.7  769.0    0.0 1669.4     0.     0.     0.      0.     0.     0.    0.      0.     0.     0.     0.  PPB'S
  390.4  177.8    0.0   177.8  784.2    0.0 1600.9     0.     0.     0.      0.     0.     0.    0.      0.     0.     0.     0.  PPB'S
  414.8  171.1    0.0   171.1  790.2    0.0 1558.1     0.     0.     0.      0.     0.     0.    0.      0.     0.     0.     0.  PPB'S
  427.0  164.4    0.0   164.4  790.2    0.0 1523.8     0.     0.     0.      0.     0.     0.    0.      0.     0.     0.    -9.  PPB'S
  427.2  164.4    0.0   164.4  790.2    0.0 1523.8     0.     0.     0.      0.     0.     0.    0.      0.     0.     0.
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THE   REDUCED   DATA   FILE   IS        : AUG103.DAT

THE INITIAL PPB CARBON TO NOX RATIO IS : 8953. TO  382.  EQUALS :   23.42


MINUTES    NOX     NO      NO2  OZONE    HCHO    THC     C2H4    C3H6  CH3ONO  CH3OH  C4H8   C4H10  ACET   C5H12  224TMP C7H8   C8H10

    0.0  382.2  331.9    50.3    0.0     6.8 8953.0    563.    643.     0.      0.  1134.  1717.     0.  1915.  1456.  1205.  1384.  PPB'S
    6.1  378.9  256.7   122.2    4.0    32.4 8891.4     0.      0.      0.      0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
   12.2  375.7  156.7   219.0   17.2    73.3 8768.1     0.      0.      0.      0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
   16.2  368.0   94.8   273.2   44.5   104.0 8680.1    486.    526.     0.      0.   972.  1827.     0.  1848.  1546.  1168.  1399.  PPB'S
   24.3  357.2   14.4   342.7  170.8   185.8 8398.4     0.      0.      0.      0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
   32.4  326.7    1.0   325.6  362.8   277.9 8046.2    285.     66.     0.      0.   114.  1667.     0.  1512.  1258.   987.   896.  PPB'S
   36.5  313.6    0.0   313.6  463.8   323.9 7887.8     0.      0.      0.      0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
   48.6  284.2    0.0   284.2  711.4   431.3 7430.0     0.      0.      0.      0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
   54.7  275.5    0.0   275.5  815.5   465.4 7262.7     84.      0.      0.      0.     0.  1688.     0.  1501.  1189.   887.   676.  PPB'S
   64.8  261.3    0.0   261.3  903.4   496.1 7016.3     0.      0.      0.      0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
   77.0  257.0    0.0   257.0  978.2   497.8 6787.4     47.      0.      0.      0.     0.  1466.     0.  1442.  1065.   829.   571.  PPB'S
   85.1  249.4    0.0   249.4 1010.5   501.2 6646.5     0.      0.      0.      0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
   99.3  248.3    0.0   248.3 1039.8   496.1 6452.8     34.      0.      0.      0.     0.  1430.     0.     0.   959.   769.   414.  PPB'S
  129.7  239.6    0.0   239.6 1058.0   473.9 6100.7     0.      0.      0.      0.     0.  1430.     0.  1370.   983.   807.   352.  PPB'S
  170.2  224.3    0.0   224.3 1047.9   439.8 5704.6     0.      0.      0.      0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  194.5  215.6    0.0   215.6 1037.8   412.5 5502.1     0.      0.      0.      0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  218.9  204.7    0.0   204.7 1019.6   385.3 5308.4     0.      0.      0.      0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  243.2  193.8    0.0   193.8 1000.4   356.3 5141.1     0.      0.      0.      0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  267.5  184.0    0.0   184.0  978.2   337.5 4973.9     0.      0.      0.      0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  291.8  174.2    0.0   174.2  957.0   318.8 4815.4     0.      0.      0.      0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  316.1  165.5    0.0   165.5  929.7   294.9 4674.6     0.      0.      0.      0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  340.5  159.0    0.0   159.0  902.4   269.3 4533.7     0.      0.      0.      0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  364.8  149.2    0.0   149.2  879.2   260.8 4419.3     0.      0.      0.      0.     0.     0.     0.     0.     0.     0.   155.  PPB'S
  382.0  142.6    0.0   142.6  863.0   247.2 4331.2     0.      0.      0.      0.     0.   977.     0.   918.   579.   521.    -9.  PPB'S
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THE   REDUCED   DATA   FILE   IS        : AUG093.DAT

THE INITIAL PPB CARBON TO NOX RATIO IS : 6561. TO  428.  EQUALS :   15.33

                                                                                                                        C5H12 224TMP  C7H8   C8H10
MINUTES   NOX     NO     NO2  OZONE   HCHO    THC    C2H4   C3H6 CH3ONO  CH3OH  C4H8  C4H10  ACET
    0.0  427.9  412.3   15.6    0.0    0.0 6560.9   424.   457.    0.     0.   853.  1292.    0.  1457.  1107.   917.  1053.  PPB'S
    6.1  427.9  382.6   45.4    0.0    5.2 6517.1     0.     0.    0.     0.     0.     0.    0.     0.     0.     0.     0.  PPB'S
   12.2  420.3  332.3   88.0    0.0   17.2 6455.8     0.     0.    0.     0.     0.     0.    0.     0.     0.     0.     0.  PPB'S
   16.3  418.1  291.3  126.9    1.0   31.0 6394.5   422.   439.    0.     0.   729.  1294.    0.  1312.  1119.   954.  1060.  PPB'S
   24.4  410.5  188.7  221.8   21.2   69.0 6280.6     0.     0.    0.     0.     0.     0.    0.     0.     0.     0.     0.  PPB'S
   36.6  388.7   52.3  336.4   87.9  138.0 6114.2   402.   282.    0.     0.   383.  1334.    0.  1198.  1143.  1019.   851.  PPB'S
   48.9  362.6   10.3  352.3  233.4  189.7 5781.3     0.     0.    0.     0.     0.     0.    0.     0.     0.     0.     0.  PPB'S
   57.0  339.7    6.2  333.6  346.6  229.3 5606.1   125.    37.    0.     0.    46.  1217.    0.  1232.  1008.   968.   617.  PPB'S
   61.1  333.2    2.1  331.1  405.2  250.0 5509.7     0.     0.    0.     0.     0.     0.    0.     0.     0.     0.     0.  PPB'S
   73.3  303.8    1.0  302.8  566.9  319.0 5247.0     0.     0.    0.     0.     0.     0.    0.     0.     0.     0.     0.  PPB'S
   81.4  294.0    1.0  293.0  668.0  327.6 5080.5    39.     0.    0.     0.     0.  1117.    0.  1110.   836.   797.   465.  PPB'S
  101.8  255.9    0.0  255.9  854.9  344.9 4730.1    20.     0.    0.     0.     0.  1075.    0.  1051.   776.   765.   312.  PPB'S
  122.1  245.0    0.0  245.0  966.1  336.3 4467.4     0.     0.    0.     0.     0.     0.    0.     0.     0.     0.     0.  PPB'S
  146.6  239.6    0.0  239.6 1034.8  315.6 4230.9     0.     0.    0.     0.     0.     0.    0.     0.     0.     0.     0.  PPB'S
  171.0  228.7    0.0  228.7 1062.1  306.9 4029.4     0.     0.    0.     0.     0.     0.    0.     0.     0.     0.     0.  PPB'S
  195.4  225.4    0.0  225.4 1069.1  288.0 3863.0     0.     0.    0.     0.     0.     0.    0.     0.     0.     0.     0.  PPB'S
  219.8  211.2    0.0  211.2 1070.1  262.1 3705.3     0.     0.    0.     0.     0.   876.    0.   864.   592.   597.     0.  PPB'S
  244.3  194.9    0.0  194.9 1060.0  244.9 3573.9     0.     0.    0.     0.     0.     0.    0.     0.     0.     0.     0.  PPB'S
  268.7  184.0    0.0  184.0 1047.9  227.6 3442.5     0.     0.    0.     0.     0.     0.    0.     0.     0.     0.     0.  PPB'S
  287.0  179.7    0.0  179.7 1032.8  212.1 3363.7     0.     0.    0.     0.     0.     0.    0.     0.     0.     0.    -9.  PPB'S
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THE   REDUCED   DATA   FILE   IS       : AUG253.DAT

THE INITIAL PPB CARBON TO NOX RATIO IS : 9520. TO  405.  EQUALS :   23.52


MINUTES   NOX     NO      NO2  OZONE    HCHO    THC     C2H4    C3H6   CH3ONO  CH3OH   C4H8    C4H10   ACET    C5H12  224TMP  C7H8   C8H10

   0.0  404.8  312.7    92.0    0.0    11.2 9519.6    319.    395.      0.   3731.   2340.   1066.      0.   1304.    991.    821.    943.  PPB'S
   6.1  401.4  260.8  140.6     3.0    35.5 9476.8      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.  PPB'S
  14.2  399.2  136.1  263.1    21.2    82.1 9348.4    312.    339.      0.   3700.   1963.   1087.      0.   1249.    892.    805.    793.  PPB'S
  22.3  383.5   23.9  359.6   121.3   138.1 9091.5      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.  PPB'S
  26.3  375.7    7.3  368.4   232.4   160.5 8920.3      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.  PPB'S
  28.3  369.0    2.1  366.9   293.1   179.1 8800.5      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.  PPB'S
  36.4  343.3    0.0  343.3   515.4   250.1 8389.6      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.  PPB'S
  50.6  318.7    0.0  318.7   808.4   315.4 7807.4     25.     11.      0.   3289.     58.   1024.      0.   1039.    698.    607.    472.  PPB'S
  60.7  308.6    0.0  308.6   929.7   324.7 7465.0      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.  PPB'S
  72.8  299.7    0.0  299.7  1015.6   315.4 7148.2      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.  PPB'S
  83.0  296.3    0.0  296.3  1053.0     0.0 6908.5     14.      0.      0.   2796.      0.    909.      0.    906.    632.    582.    304.  PPB'S
  97.1  289.6    0.0  289.6  1083.3     0.0 6617.5      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.  PPB'S
 109.3  282.9    0.0  282.9  1091.4     0.0 6377.8      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.  PPB'S
 121.4  277.3    0.0  277.3  1096.4     0.0 6198.0      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.  PPB'S
 145.7  266.1    0.0  266.1  1094.4     0.0 5855.6      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.  PPB'S
 170.0  253.8    0.0  253.8  1081.3     0.0 5547.4      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.  PPB'S
 194.2  241.5    0.0  241.5  1066.1     0.0 5264.9      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.  PPB'S
 218.5  228.1    0.0  228.1  1043.9     0.0 4990.9      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.  PPB'S
 242.8  219.2    0.0  219.2  1020.6     0.0 4734.1      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.  PPB'S
 267.1  209.1    0.0  209.1   996.4     0.0 4494.4      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.  PPB'S
 291.4  197.9    0.0  197.9   970.1     0.0 4280.4      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.  PPB'S
 315.6  189.0    0.0  189.0   945.9     0.0 4066.4      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.  PPB'S
 339.9  176.7    0.0  176.7   920.6     0.0 3869.5      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.  PPB'S
 346.0  175.5    0.0  175.5   914.5     0.0 3818.1      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.     -9.  PPB'S
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THE   REDUCED   DATA   FILE   IS       : MAR064.DAT

THE INITIAL PPB CARBON TO NOX RATIO IS : 5171. TO  418.  EQUALS :   12.37


MINUTES   NOX     NO      NO2  OZONE    HCHO    THC     C2H4   C3H6  CH3ONO  CH3OH  C4H8   C4H10  ACET   C5H12  224TMP C7H8  C8H10

    0.0  418.1  394.4    23.7    0.0     0.0 5170.5    145.   157.      0.  1972.  1081.   443.     0.   498.   378.   313.   360.  PPB'S
    6.1  415.9  361.5    54.4    0.0     0.0 5160.3      0.     0.      0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
   12.2  411.4  328.6    82.7    1.0     4.5 5119.8      0.     0.      0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
   18.4  406.9  284.8   122.1    4.0     4.5 5069.1      0.     0.      0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
   24.5  404.6  230.1   174.6    7.1     9.0 4988.0      0.     0.      0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
   36.7  399.0  116.1   282.9   28.3    26.9 4856.2      0.     0.      0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
   48.9  384.4   54.8   329.6   69.7    49.3 4694.0      0.     0.      0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
   61.2  361.9   16.4   345.5  156.6    76.2 4531.8      0.     0.      0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB S
   73.4  345.1    5.5   339.6  234.4    98.6 4369.6      0.     0.      0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
   97.9  313.6    0.0   313.6  423.4   121.0 4075.6      0.     0.      0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  122.4  292.2    0.0   292.2  573.0   130.0 3832.2      0.     0.      0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  146.8  286.6    0.0   286.6  692.2   130.0 3619.3      0.     0.      0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB S
  171.3  274.3    0.0   274.3  791.2   125.5 3467.3      0.     0.      0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  195.8  258.5    0.0   258.5  870.1   125.5 3294.9      0.     0.      0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB S
  220.2  247.3    0.0   247.3  928.7   121.0 3163.1      0.     0.      0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  230.4  245.0    0.0   245.0  949.9   121.0 3132.7      4.    12.      0.  1467.     0.   322.     0.   376.   223.   250.     0.  PPB'S
  269.2  232.7    0.0   232.7  996.4   116.6 2919.8      0.     0.      0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  293.6  221.4    0.0   221.4 1009.5   112.1 2808.3      0.     0.      0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  312.0  213.6    0.0   213.6 1009.5   112.1 2737.3      0.     0.      0.     0.     0.     0.     0.     0.     0.     0.    -9.  PPB'S
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THE   REDUCED   DATA   FILE   IS       : SEP163.DAT

THE INITIAL PPB CARBON TO NOX RATIO IS : 2985. TO 1212.  EQUALS :    2.46


MINUTES   NOX     NO      NO2   OZONE    HCHO    THC     C2H4    C3H6   CH3ONO   CH3OH   C4H8    C4H10   ACET    C5H12   224TMP  C7H8    C8H10

    0.0 1212.3 1186.5    25.7    0.0    13.2 2984.7    143.    154.      0.    1006.    288.    436.      0.    471.    358.    296.    353.   PPB'S
   16.3 1191.9 1120.1    71.8    0.0    17.5 2921.4      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.   PPB'S
   34.5 1173.9 1025.9   148.0    0.0    21.9 2840.0    137.    133.      0.     992.    208.    446.      0.    410.    389.    296.    304.   PPB'S
   53.9 1140.0  929.5   210.5    1.0    26.3 2704.3    125.    110.      0.     945.    167.    419.      0.    393.    332.    257.    268.   PPB'S
   70.1 1099.4  837.4   262.0    2.0    26.3 2613.9    117.     96.      0.     904.    126.    408.      0.    334.    325.    271.    256.   PPB'S
   97.6 1036.2  715.3   320.8    5.1    26.3 2433.0      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.   PPB'S
  121.9  986.5  627.5   359.0    6.1    26.3 2315.4      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.   PPB'S
  146.3  943.6  556.8   386.8    8.1    26.3 2206.9      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.   PPB'S
  170.7  896.2  501.2   395.0    9.1    26.3 2089.3      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.   PPB'S
  195.1  862.3  449.8   412.6   10.1    26.3 1998.8      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.   PPB'S
  219.5  814.9  411.2   403.7   11.1    26.3 1917.4      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.   PPB'S
  243.9  783.3  372.7   410.7   12.1    30.7 1836.0      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.   PPB'S
  268.3  745.0  340.5   404.4   13.1    30.7 1745.6      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.   PPB'S
  292.7  713.4  308.4   404.9   15.2    30.7 1673.2      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.   PPB'S
  317.0  677.2  284.8   392.4   18.2    35.1 1609.9      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.   PPB'S
  338.4  647.9  265.6   382.3   19.2    39.5 1546.6     56.     16.      0.     544.      0.    200.      0.    136.    195.    222.    195.   PPB'S
  390.2  582.4  214.2   368.3   20.2    48.3 1410.9      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.   PPB'S
  439.0  514.7  171.3   343.4   23.2    43.9 1275.3      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.   PPB'S
  487.8  462.8  139.2   323.6   29.3    35.1 1166.7      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.   PPB'S
  536.5  406.3  113.5   292.8   33.3    30.7 1058.2      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.   PPB'S
  585.3  363.4   83.5   279.9   40.4    26.3  958.7      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.   PPB'S
  634.1  325.1   62.1   263.0   48.5    26.3  877.3      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.   PPB'S
  682.9  284.4   49.3   235.2   54.6    26.3  795.9      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.   PPB'S
  731.6  250.6   34.3   216.3   62.7    26.3  714.5      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.   PPB'S
  780.4  221.2   25.7   195.5   71.7    26.3  651.2      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.   PPB'S
  829.2  194.1   12.9   181.3   82.9    30.7  606.0      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.   PPB'S
  878.0  171.6    8.6   163.0   90.9    30.7  560.8      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.   PPB'S
  926.7  153.5    6.4   147.1  103.1    35.1  515.5      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.   PPB'S
  975.5  140.0    4.3   135.7  117.2    35.1  461.3      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.   PPB'S
 1024.3  128.7    2.1   126.5  131.4    35.1  434.1      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.   PPB'S
 1073.1  124.2    0.0   124.2  147.5    35.1  416.0      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.   PPB'S
 1121.9  106.1    0.0   106.1  160.7    35.1  352.7      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.   PPB'S
 1131.0  101.6    0.0   101.6  161.7    35.1  334.6      0.      0.      0.      0.      0.      0.      0.      0.      0.      0.     -9.   PPB'S
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THE   REDUCED   DATA   FILE   IS       : SEP223.DAT

THE INITIAL PPB CARBON TO NOX RATIO IS : 3124. TO  430.  EQUALS :    7.26


                                                                                                         224TMP  C7H8   C8H10
MINUTES   NOX    NO     NO2   OZONE   HCHO   THC    C2H4   C3H6  CH3ONO  CH3OH  C4H8  C4H10  ACET  C5H12

    0.0  430.2  387.5   42.7    0.0   36.6 3124.2   134.   145.    0.   1472.  270.  409.    0.   447.   340.   281.   323.  PPB'S
    6.1  422.2  330.1   92.1    1.0   46.9 3082.6     0.     0.    0.      0.    0.    0.    0.     0.     0.     0.     0.  PPB'S
   12.3  416.5  276.0  140.5    3.0   50.3 3015.9     0.     0.    0.      0.    0.    0.    0.     0.     0.     0.     0.  PPB'S
   18.4  410.8  241.4  169.4    7.1   59.4 2982.6   124.   111.    0.   1471.  179.  405.    0.   395.   292.   303.   253.  PPB'S
   24.6  408.5  206.7  201.7   11.1   61.7 2924.3     0.     0.    0.      0.    0.    0.    0.     0.     0.     0.     0.  PPB'S
   36.8  392.5  146.1  246.3   22.2   73.1 2824.3   120.    88.    0.   1487.  131.  388.    0.   405.   313.   264.   222.  PPB'S
   47.1  382.2  103.9  278.3   33.3   78.9 2741.0     0.     0.    0.      0.    0.    0.    0.     0.     0.     0.     0.  PPB'S
   57.3  365.0   75.8  289.2   48.5   84.6 2666.0   104.    49.    0.   1350.   83.  348.    0.   367.   292.   249.   162.  PPB'S
   67.5  355.9   52.0  303.9   65.7   84.6 2582.7     0.     0.    0.      0.    0.    0.    0.     0.     0.     0.     0.  PPB'S
   77.7  344.4   37.9  306.5   82.9   85.7 2499.4     0.     0.    0.      0.    0.    0.    0.     0.     0.     0.     0.  PPB'S
   96.2  327.3   21.6  305.6  121.3   90.3 2374.4    42.     0.    0.   1252.   45.  313.    0.   307.   261.   214.   171.  PPB'S
  118.7  303.2    8.7  294.6  170.8   90.3 2224.4    31.     0.    0.   1164.   27.  300.    0.   269.   250.   191.   152.  PPB'S
  147.3  279.2    2.2  277.0  232.4   86.9 2049.5     0.     0.    0.      0.    0.    0.    0.     0.     0.     0.     0.  PPB'S
  171.9  259.7    0.0  259.7  280.9   82.3 1932.8     0.     0.    0.      0.    0.    0.    0.     0.     0.     0.     0.  PPB'S
  178.0  255.2    0.0  255.2  293.1   82.3 1907.9    13.     0.    0.   1050.    9.  269.    0.   215.   156.   183.   101.  PPB'S
  196.4  243.7    0.0  243.7  327.4   80.0 1824.5     0.     0.    0.      0.    0.    0.    0.     0.     0.     0.     0.  PPB'S
  221.0  230.0    0.0  230.0  368.8   75.4 1699.6     0.     0.    0.      0.    0.    0.    0.     0.     0.     0.     0.  PPB'S
  245.5  214.0    0.0  214.0  409.3   69.7 1582.9     0.     0.    0.      0.    0.    0.    0.     0.     0.     0.     0.  PPB'S
  270.1  195.7    0.0  195.7  445.6   65.1 1491.3     0.     0.    0.      0.    0.    0.    0.     0.     0.     0.     0.  PPB'S
  294.6  183.1    0.0  183.1  484.0   59.4 1374.7     0.     0.    0.      0.    0.    0.    0.     0.     0.     0.     0.  PPB'S
  319.2  167.1    0.0  167.1  514.4   58.3 1283.0     0.     0.    0.      0.    0.    0.    0.     0.     0.     0.     0.  PPB'S
  343.7  154.5    0.0  154.5  538.6   54.9 1191.4     0.     0.    0.      0.    0.    0.    0.     0.     0.     0.     0.  PPB'S
  368.3  145.3    0.0  145.3  561.9   51.4 1108.1     0.     0.    0.      0.    0.    0.    0.     0.     0.     0.     0.  PPB'S
  392.8  135.0    0.0  135.0  576.0   46.9 1041.4     0.     0.    0.      0.    0.    0.    0.     0.     0.     0.     0.  PPB'S
  417.4  124.7    0.0  124.7  585.1   43.4  966.4     0.     0.    0.      0.    0.    0.    0.     0.     0.     0.     0.  PPB'S
  441.9  113.3    0.0  113.3  585.1   40.0  908.1     0.     0.    0.      0.    0.    0.    0.     0.     0.     0.     0.  PPB'S
  446.0  112.1    0.0  112.1  584.1   40.0  899.8     0.     0.    0.      0.    0.    0.    0.     0.     0.     0.    -9.  PPB'S
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THE   REDUCED   DATA   FILE   IS       : SEP133.DAT


THE INITIAL PPB CARBON TO NOX RATIO IS : 8836. TO  388.  EQUALS :   22.80



MINUTES   NOX    NO      NO2  OZONE   HCHO   THC     C2H4    C3H6  CH3ONO  CH3OH  C4H8   C4H10   ACET   C5H12  224TMP C7H8   C8H10

   0.0  387.5  336.1   51.4    0.0  156.9 8835.8    368.    397.     0.   4090.   741.  1122.     0.   1191.   905.   750.   861.  PPB'S
   6.1  381.5  156.8  224.8   21.2  209.2 8676.3      0.      0.     0.      0.     0.     0.     0.      0.     0.     0.     0.  PPB'S
  12.3  369.7   49.4  320.3  100.0  235.4 8490.2      0.      0.     0.      0.     0.     0.     0.      0.     0.     0.     0.  PPB'S
  15.3  362.6   22.5  340.0  147.5  245.8 8401.6    309.    225.     0.   3527.   470.  1166.     0.   1144.   905.   750.   654.  PPB'S
  18.4  356.7   11.8  344.9  218.3  272.0 8304.1      0.      0.     0.      0.     0.     0.     0.      0.     0.     0.     0.  PPB'S
  24.5  340.1    4.3  335.8  334.5  313.8 8144.6      0.      0.     0.      0.     0.     0.     0.      0.     0.     0.     0.  PPB'S
  34.7  314.0    0.0  314.0  526.5  340.0 7790.1     66.     29.     0.   3876.   169.  1055.     0.   1008.   905.   675.   459.  PPB'S
  49.0  282.0    0.0  282.0  741.7  345.2 7355.8      0.      0.     0.      0.     0.     0.     0.      0.     0.     0.     0.  PPB'S
  61.3  264.2    0.0  264.2  875.1  345.2 7001.3      0.      0.     0.      0.     0.     0.     0.      0.     0.     0.     0.  PPB'S
  73.5  257.1    0.0  257.1  979.2  324.3 6735.4      0.      0.     0.      0.     0.     0.     0.      0.     0.     0.     0.  PPB'S
  85.8  252.4    0.0  252.4 1043.9  313.8 6496.2      0.      0.     0.      0.     0.     0.     0.      0.     0.     0.     0.  PPB'S
  98.1  246.5    0.0  246.5 1089.3  313.8 6265.7      0.      0.     0.      0.     0.     0.     0.      0.     0.     0.     0.  PPB'S
 110.3  239.4    0.0  239.4 1114.6  313.8 6026.4      0.      0.     0.      0.     0.     0.     0.      0.     0.     0.     0.  PPB'S
 122.6  234.6    0.0  234.6 1125.7  313.8 5840.3      0.      0.     0.      0.     0.     0.     0.      0.     0.     0.     0.  PPB'S
 134.8  227.5    0.0  227.5 1132.8  287.7 5627.6      0.      0.     0.      0.     0.     0.     0.      0.     0.     0.     0.  PPB'S
 147.1  219.2    0.0  219.2 1127.7  261.5 5441.5      0.      0.     0.      0.     0.     0.     0.      0.     0.     0.     0.  PPB'S
 159.3  213.3    0.0  213.3 1121.7  261.5 5255.4      0.      0.     0.      0.     0.     0.     0.      0.     0.     0.     0.  PPB'S
 171.6  207.4    0.0  207.4 1112.6  256.3 5104.8      0.      0.     0.      0.     0.     0.     0.      0.     0.     0.     0.  PPB'S
 196.1  192.0    0.0  192.0 1087.3  235.4 4785.7      0.      0.     0.      0.     0.     0.     0.      0.     0.     0.     0.  PPB'S
 220.6  181.3    0.0  181.3 1059.0  219.7 4493.2      0.      0.     0.      0.     0.     0.     0.      0.     0.     0.     0.  PPB'S
 245.1  168.3    0.0  168.3 1022.7  209.2 4209.6      0.      0.     0.      0.     0.     0.     0.      0.     0.     0.     0.  PPB'S
 269.7  157.6    0.0  157.6  986.3  177.8 3943.8      0.      0.     0.      0.     0.     0.     0.      0.     0.     0.     0.  PPB'S
 286.0  150.5    0.0  150.5  958.0  177.8 3810.8      0.      0.     0.      0.     0.     0.     0.      0.     0.     0.    -9.  PPB'S
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THE   REDUCED   DATA   FILE   IS        : NOV073.DAT

THE INITIAL PPB CARBON TO NOX RATIO IS : 3244. TO  433.  EQUALS :    7.49

MINUTES   NOX     NO     NO2  OZONE    HCHO    THC   C2H4   C3H6  CH3ONO  CH3OH   C4H8   C4H10  ACET   C5H12  224TMP C7H8   C8H10

    0.0  433.1  401.1   32.0    0.0    12.2 3244.1   134.   145.    0.   1500.   270.   409.    0.    455.   346.   286.   328.  PPB'S
   12.8  428.5  351.1   77.4    0.0    30.4 3177.5   126.   122.    0.   1491.   214.   405.    0.    466.   337.   281.   322.  PPB'S
   24.4  423.9  296.6  127.3    1.0    45.6 3102.7     0.     0.    0.      0.     0.     0.    0.      0.     0.     0.     0.  PPB'S
   33.3  413.6  253.3  160.3    3.0    53.2 3052.7   121.   111.    0.   1571.   166.   393.    0.    434.   319.   265.   281.  PPB'S
   44.6  403.4  203.3  200.1   10.1    66.9 2986.2     0.     0.    0.      0.     0.     0.    0.      0.     0.     0.     0.  PPB'S
   56.4  398.8  160.0  238.8   16.2    73.0 2919.7   110.    82.    0.   1482.   104.   373.    0.    465.   262.     0.   259.  PPB'S
   79.5  375.9   92.2  283.7   38.4    89.8 2803.2   112.    68.    0.   1537.    76.   387.    0.    475.   262.   244.   235.  PPB'S
   96.2  363.4   61.1  302.3   57.6    95.8 2720.0    86.    42.    0.   1389.    43.   355.    0.    415.   243.   254.   235.  PPB'S
  123.8  338.2   31.1  307.1   95.0    98.9 2586.9    51.    18.    0.   1338.    19.   346.    0.    406.   215.   233.   197.  PPB'S
  144.3  325.7   20.0  305.7  129.3   100.4 2495.4    33.     0.    0.   1334.     0.   346.    0.    406.   215.   212.   101.  PPB'S
  164.4  309.7   11.1  298.6  163.7   106.5 2412.3    23.     0.    0.   1279.     0.   319.    0.    362.   215.   212.   156.  PPB'S
  185.9  294.8    5.6  289.3  202.1   108.0 2320.8    15.     0.    0.   1326.     0.   334.    0.    376.   206.   201.    79.  PPB'S
  219.2  274.2    2.2  272.0  255.7    98.9 2212.6     0.     0.    0.      0.     0.     0.    0.      0.     0.     0.     0.  PPB'S
  243.5  261.7    1.1  260.6  297.1    97.4 2137.8     0.     0.    0.      0.     0.     0.    0.      0.     0.     0.     0.  PPB'S
  267.9  249.1    0.0  249.1  333.5    94.3 2054.6     0.     0.    0.      0.     0.     0.    0.      0.     0.     0.     0.  PPB'S
  292.2  234.2    0.0  234.2  373.9    91.3 1971.4     0.     0.    0.      0.     0.     0.    0.      0.     0.     0.     0.  PPB'S
  316.6  222.8    0.0  222.8  409.3    88.2 1896.5     0.     0.    0.      0.     0.     0.    0.      0.     0.     0.     0.  PPB'S
  340.9  210.2    0.0  210.2  445.6    88.2 1830.0     0.     0.    0.      0.     0.     0.    0.      0.     0.     0.     0.  PPB'S
  365.3  200.0    0.0  200.0  480.0    86.7 1755.1     0.     0.    0.      0.     0.     0.    0.      0.     0.     0.     0.  PPB'S
  389.6  187.4    0.0  187.4  514.4    85.2 1688.6     0.     0.    0.      0.     0.     0.    0.      0.     0.     0.     0.  PPB'S
  414.0  176.0    0.0  176.0  545.7    83.7 1622.0     0.     0.    0.      0.     0.     0.    0.      0.     0.     0.     0.  PPB'S
  438.3  166.8    0.0  166.8  574.0    80.6 1563.8     0.     0.    0.      0.     0.     0.    0.      0.     0.     0.     0.  PPB'S
  462.7  161.1    0.0  161.1  599.2    79.1 1497.3     0.     0.    0.      0.     0.     0.    0.      0.     0.     0.     0.  PPB'S
  487.0  150.8    0.0  150.8  623.5    76.1 1439.0     0.     0.    0.      0.     0.     0.    0.      0.     0.     0.     0.  PPB'S
  506.1  146.3    0.0  146.3  636.6    76.1 1397.4     0.     0.    0.    809.     0.   169.    0.     95.   533.   164.     0.  PPB'S
  535.7  137.1    0.0  137.1  652.8    73.0 1339.2     0.     0.    0.      0.     0.     0.    0.      0.     0.     0.     0.  PPB'S
  554.0  130.3    0.0  130.3  656.8    73.0 1305.9     0.     0.    0.      0.     0.     0.    0.      0.     0.     0.     0.  PPB'S
  558.1  129.1    0.0  129.1  657.9    73.0 1297.6     0.     0.    0.      0.     0.     0.    0.      0.     0.     0.    -9.  PPB'S
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THE   REDUCED   DATA   FILE   IS       : FEB074.DAT

THE INITIAL PPB CARBON TO NOX RATIO IS : 3287. TO  445.  EQUALS :    7.39


MINUTES   NOX    NO     NO2  OZONE   HCHO   THC    C2H4   C3H6  CH3ONO  CH3OH  C4H8   C4H10  ACET   C5H12  224TMP C7H8   C8H10

    0.0  444.7  413.2   31.5    0.0    0.0 3287.3   0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
   12.0  428.3  319.0  109.4    2.0    0.0 3134.6   0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
   23.1  413.1  211.9  201.1   11.1    0.0 2931.1   0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
   36.1  397.8  115.6  282.2   29.3    0.0 2747.9   0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
   46.1  384.7   67.4  317.3   55.6    0.0 2646.1   0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
   54.1  376.0   47.1  328.9   77.8    0.0 2585.0   0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
   68.2  362.9   21.4  341.5  128.3    0.0 2462.9   0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
   82.2  348.8    8.6  340.2  178.9    0.0 2350.9   0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
   96.2  336.8    6.4  330.4  229.4    0.0 2259.4   0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  108.3  328.1    3.2  324.9  272.8    0.0 2167.8   0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  117.3  321.5    0.0  321.5  302.1    0.0 2116.9   0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  144.4  301.9    0.0  301.9  401.2    0.0 1964.2   0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  168.4  284.5    0.0  284.5  492.1    0.0 1842.1   0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  192.5  268.1    0.0  268.1  576.0    0.0 1699.6   0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  216.6  250.7    0.0  250.7  653.8    0.0 1597.8   0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  240.6  234.3    0.0  234.3  718.5    0.0 1485.9   0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  264.7  216.9    0.0  216.9  770.0    0.0 1404.5   0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  288.7  201.6    0.0  201.6  806.4    0.0 1323.0   0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  312.8  189.6    0.0  189.6  826.6    0.0 1231.4   0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  336.9  179.8    0.0  179.8  837.7    0.0 1180.6   0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  360.9  176.6    0.0  176.6  838.7    0.0 1129.7   0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  373.0  174.4    0.0  174.4  839.7    0.0 1109.3   0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  383.0  172.2    0.0  172.2  838.7    0.0 1078.8   0.     0.     0.     0.     0.     0.     0.     0.     0.     0.    -9.  PPB'S
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THE   REDUCED   DATA   FILE   IS        : FEB084.DAT

THE INITIAL PPB CARBON TO NOX RATIO IS : 3230. TO  441.  EQUALS :    7.32


MINUTES   NOX     NO     NO2  OZONE   HCHO    THC   C2H4  C3H6 CH3ONO CH3OH  C4H8  C4H10  ACET  C5H12 224TMP C7H8  C8H10
    0.0  441.4  427.3   14.1    0.0    0.0 3230.1    0.    0.    0.    0.    0.    0.    0.    0.    0.    0.    0.  PPB'S
   12.2  425.1  344.0   81.0    1.0    0.0 3063.2    0.    0.    0.    0.    0.    0.    0.    0.    0.    0.    0.  PPB'S
   21.3  413.1  254.2  158.8    4.0    0.0 2896.3    0.    0.    0.    0.    0.    0.    0.    0.    0.    0.    0.  PPB'S
   30.5  401.1  181.8  219.3   13.1    0.0 2758.8    0.    0.    0.    0.    0.    0.    0.    0.    0.    0.    0.  PPB'S
   40.7  388.0  113.6  274.4   25.3    0.0 2641.0    0.    0.    0.    0.    0.    0.    0.    0.    0.    0.    0.  PPB'S
   48.8  378.2   79.0  299.2   43.5    0.0 2572.3    0.    0.    0.    0.    0.    0.    0.    0.    0.    0.    0.  PPB'S
   61.0  364.0   48.7  315.4   73.8    0.0 2464.3    0.    0.    0.    0.    0.    0.    0.    0.    0.    0.    0.  PPB'S
   73.2  351.0   27.0  323.9  112.2    0.0 2366.1    0.    0.    0.    0.    0.    0.    0.    0.    0.    0.    0.  PPB'S
   85.4  339.0   16.2  322.7  153.6    0.0 2287.6    0.    0.    0.    0.    0.    0.    0.    0.    0.    0.    0.  PPB'S
   97.6  327.0    9.7  317.2  194.0    0.0 2199.2    0.    0.    0.    0.    0.    0.    0.    0.    0.    0.    0.  PPB'S
  122.0  308.5    4.3  304.1  274.9    0.0 2042.1    0.    0.    0.    0.    0.    0.    0.    0.    0.    0.    0.  PPB'S
  146.4  294.3    0.0  294.3  360.8    0.0 1914.5    0.    0.    0.    0.    0.    0.    0.    0.    0.    0.    0.  PPB'S
  170.7  283.4    0.0  283.4  437.6    0.0 1796.7    0.    0.    0.    0.    0.    0.    0.    0.    0.    0.    0.  PPB'S
  195.1  272.5    0.0  272.5  511.3    0.0 1678.9    0.    0.    0.    0.    0.    0.    0.    0.    0.    0.    0.  PPB'S
  219.5  261.6    0.0  261.6  581.1    0.0 1561.0    0.    0.    0.    0.    0.    0.    0.    0.    0.    0.    0.  PPB'S
  243.9  250.7    0.0  250.7  646.7    0.0 1472.7    0.    0.    0.    0.    0.    0.    0.    0.    0.    0.    0.  PPB'S
  268.3  238.7    0.0  238.7  700.3    0.0 1384.3    0.    0.    0.    0.    0.    0.    0.    0.    0.    0.    0.  PPB'S
  292.7  228.9    0.0  228.9  747.8    0.0 1296.0    0.    0.    0.    0.    0.    0.    0.    0.    0.    0.    0.  PPB'S
  317.1  216.9    0.0  216.9  781.1    0.0 1217.4    0.    0.    0.    0.    0.    0.    0.    0.    0.    0.    0.  PPB'S
  341.5  206.0    0.0  206.0  800.3    0.0 1148.7    0.    0.    0.    0.    0.    0.    0.    0.    0.    0.    0.  PPB'S
  357.8  198.4    0.0  198.4  811.5    0.0 1119.2    0.    0.    0.    0.    0.    0.    0.    0.    0.    0.    0.  PPB'S
  373.0  192.9    0.0  192.9  811.5    0.0 1089.8    0.    0.    0.    0.    0.    0.    0.    0.    0.    0.    0.  PPB'S
  386.2  186.4    0.0  186.4  810.4    0.0 1060.3    0.    0.    0.    0.    0.    0.    0.    0.    0.    0.   -9.  PPB'S
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THE   REDUCED   DATA   FILE   IS       : JAN264.DAT

THE INITIAL PPB CARBON TO NOX RATIO IS : 1241. TO  480.  EQUALS :    2.58

MINUTES   NOX     NO      NO2  OZONE   HCHO   THC    C2H4   C3H6  CH3ONO  CH3OH  C4H8   C4H10  ACET   C5H12  224TMP C7H8   C8H10
    0.0  480.4  421.1   59.3    0.0    0.0 1241.1    0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
   10.0  477.1  371.7  105.3    0.0    0.0 1173.8    0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
   36.2  466.9  282.9  184.0    3.0    0.0 1067.9    0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
   60.3  447.7  219.3  228.4   11.1    0.0  991.0    0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
   90.4  429.7  156.8  272.9   18.2    0.0  933.2    0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  120.5  412.8  120.6  292.1   24.3    0.0  875.5    0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  150.7  394.7   95.4  299.3   34.4    0.0  827.4    0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  180.8  377.8   71.3  306.5   45.5    0.0  779.3    0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  241.1  342.8   52.6  290.2   70.7    0.0  721.6    0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  361.6  281.9   19.7  262.2  113.2    0.0  615.8    0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  482.1  222.2    7.7  214.5  154.6    0.0  529.2    0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  602.7  163.5    0.0  163.5  196.0    0.0  452.2    0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  723.2  118.4    0.0  118.4  237.5    0.0  384.8    0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  843.8   95.9    0.0   95.9  278.9    0.0  336.7    0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  964.3   78.9    0.0   78.9  329.4    0.0  288.6    0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
 1084.8   73.3    0.0   73.3  368.8    0.0  230.9    0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
 1145.1   71.1    0.0   71.1  380.0    0.0  211.7    0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
 1213.0   67.7    0.0   67.7  386.0    0.0  192.4    0.     0.     0.     0.     0.     0.     0.     0.     0.     0.    -9.  PPB'S
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THE   REDUCED   DATA   FILE   IS      : FEB214.DAT

THE INITIAL PPB CARBON TO NOX RATIO IS : 3204. TO  410.  EQUALS :    7.82

MINUTES    NOX     NO      NO2  OZONE    HCHO   THC    C2H4   C3H6  CH3ONO  CH3OH  C4H8  C4H10  ACET   C5H12  224TMP C7H8   C8H10
                                                                                                                     
   0.0   409.7  384.4    25.2    0.0     0.0 3204.2     0.     0.     0.     28.    0.   220.    0.     0.     0.     0.     0.  PPB'S
  12.2   401.3  316.8    84.5    0.0     0.0 3048.8     0.     0.     0.      0.    0.     0.    0.     0.     0.     0.     0.  PPB'S
  22.4   392.9  231.5   161.5    3.0     0.0 2922.6     0.     0.     0.     28.    0.   210.    0.     0.     0.     0.     0.  PPB'S
  36.6   371.9  137.3   234.6   19.2     0.0 2728.4     0.     0.     0.      0.    0.     0.    0.     0.     0.     0.     0.  PPB'S
  48.8   357.3   82.4   274.9   40.4     0.0 2602.2     0.     0.     0.      0.    0.     0.    0.     0.     0.     0.     0.  PPB'S
  61.0   345.8   51.0   294.8   68.7     0.0 2514.8     0.     0.     0.      0.    0.     0.    0.     0.     0.     0.     0.  PPB'S
  73.2   327.9   31.4   296.6   99.0     0.0 2427.4     0.     0.     0.      0.    0.     0.    0.     0.     0.     0.     0.  PPB'S
  85.4   317.5   20.6   296.9  131.4     0.0 2349.7     0.     0.     0.      0.    0.     0.    0.     0.     0.     0.     0.  PPB'S
  97.6   299.7   12.7   286.9  162.7     0.0 2281.7     0.     0.     0.      0.    0.     0.    0.     0.     0.     0.     0.  PPB'S
 122.0   275.6    5.9   269.7  231.4     0.0 2145.8     0.     0.     0.      0.    0.     0.    0.     0.     0.     0.     0.  PPB'S
 146.4   255.6    2.0   253.7  296.1     0.0 2000.2     0.     0.     0.      0.    0.     0.    0.     0.     0.     0.     0.  PPB'S
 170.8   235.7    0.0   235.7  356.7     0.0 1893.4     0.     0.     0.      0.    0.     0.    0.     0.     0.     0.     0.  PPB'S
 195.2   222.1    0.0   222.1  419.4     0.0 1786.6     0.     0.     0.      0.    0.     0.    0.     0.     0.     0.     0.  PPB'S
 219.6   209.5    0.0   209.5  477.0     0.0 1689.5     0.     0.     0.      0.    0.     0.    0.     0.     0.     0.     0.  PPB'S
 244.0   195.9    0.0   195.9  527.5     0.0 1582.7     0.     0.     0.      0.    0.     0.    0.     0.     0.     0.     0.  PPB'S
 268.4   183.4    0.0   183.4  576.0     0.0 1505.0     0.     0.     0.      0.    0.     0.    0.     0.     0.     0.     0.  PPB'S
 292.8   171.8    0.0   171.8  617.4     0.0 1427.3     0.     0.     0.      0.    0.     0.    0.     0.     0.     0.     0.  PPB'S
 317.2   165.5    0.0   165.5  649.8     0.0 1359.3     0.     0.     0.      0.    0.     0.    0.     0.     0.     0.     0.  PPB'S
 335.5   159.3    0.0   159.3  670.0     0.0 1301.1     0.     0.     0.     22.    0.    73.    0.     0.     0.     0.     0.  PPB'S
 366.0   150.9    0.0   150.9  693.2     0.0 1223.4     0.     0.     0.      0.    0.     0.    0.     0.     0.     0.     0.  PPB'S
 390.4   144.6    0.0   144.6  704.3     0.0 1165.1     0.     0.     0.      0.    0.     0.    0.     0.     0.     0.     0.  PPB'S
 414.8   138.3    0.0   138.3  707.4     0.0 1106.9     0.     0.     0.      0.    0.     0.    0.     0.     0.     0.     0.  PPB'S
 427.0   136.2    0.0   136.2  706.4     0.0 1087.5     0.     0.     0.      0.    0.     0.    0.     0.     0.     0.    -9.  PPB'S
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THE   REDUCED   DATA   FILE   IS       : MAR134.DAT

THE INITIAL PPB CARBON TO NOX RATIO IS : 3314. TO  427.  EQUALS :    7.75


MINUTES   NOX     NO     NO2  OZONE   HCHO   THC    C2H4   C3H6  CH3ONO  CH3OH  C4H8   C4H10  ACET   C5H12  224TMP C7H8   C8H10

    0.0  427.4  420.5    6.9    0.0    0.0 3314.0    0.     0.     0.    67.     0.   158.     0.     0.     0.     0.     0.  PPB'S
   12.2  425.6  334.3   91.3    1.0    0.0 3161.0    0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
   24.3  423.9  234.4  189.5    9.1    0.0 2987.7    0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
   48.7  413.4  103.4  310.0   40.4    0.0 2773.6    0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
   73.0  392.4   46.5  345.8   92.0    0.0 2600.2    0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
   97.4  364.3   19.0  345.4  157.6    0.0 2467.7    0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  121.7  334.6    6.9  327.7  223.3    0.0 2335.1    0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  146.1  317.0    3.4  313.6  292.0    0.0 2222.9    0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  170.4  299.5    0.0  299.5  355.7    0.0 2121.0    0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  219.1  255.7    0.0  255.7  477.0    0.0 1927.2    0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  267.8  220.7    0.0  220.7  596.2    0.0 1743.7    0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  316.5  194.4    0.0  194.4  693.2    0.0 1580.5    0.     0.     0.    42.     0.    61.     0.     0.     0.     0.     0.  PPB'S
  365.2  168.2    0.0  168.2  774.1    0.0 1448.0    0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  413.9  150.6    0.0  150.6  819.5    0.0 1325.6    0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  462.6  141.9    0.0  141.9  832.7    0.0 1223.6    0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  511.3  133.1    0.0  133.1  824.6    0.0 1121.7    0.     0.     0.     0.     0.     0.     0.     0.     0.     0.     0.  PPB'S
  560.0  124.4    0.0  124.4  812.5    0.0 1040.1    0.     0.     0.     0.     0.     0.     0.     0.     0.     0.    -9.  PPB'S
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THE   REDUCED   DATA   FILE   IS        : MAR154.DAT

THE INITIAL PPB CARBON TO NOX RATIO IS : 3339. TO  411.  EQUALS :    8.12

MINUTES   NOX     NO     NO2   OZONE   HCHO   THC     C2H4   C3H6  CH3ONO  CH3OH  C4H8  C4H10  ACET  C5H12  224TMP C7H8  C8H10

  0.0   411.0  374.1   36.9    0.0     5.2 3339.2    0.     0.     0.     80.    0.   192.    0.    0.     0.    0.     0.   PPB'S
 12.4   394.8  266.2  128.6    3.0     7.9 3126.7    0.     0.     0.      0.    0.     0.    0.    0.     0.    0.     0.   PPB'S
 24.8   378.5  162.7  215.8   16.2    12.6 2934.4    0.     0.     0.     89.    0.   146.    0.    0.     0.    0.     0.   PPB'S
 37.2   363.7   91.7  272.0   36.4    14.2 2802.9    0.     0.     0.      0.    0.     0.    0.    0.     0.    0.     0.   PPB'S
 49.6   348.9   51.8  297.2   62.7    15.7 2691.6    0.     0.     0.      0.    0.     0.    0.    0.     0.    0.     0.   PPB'S
 68.8   317.9   16.3  301.6  121.3    21.0 2509.5    0.     0.     0.     74.    0.   150.    0.    0.     0.    0.     0.   PPB'S
 86.7   298.7    7.4  291.3  175.8    21.5 2377.9    0.     0.     0.      0.    0.     0.    0.    0.     0.    0.     0.   PPB'S
 99.1   282.4    3.0  279.4  212.2    23.1 2297.0    0.     0.     0.      0.    0.     0.    0.    0.     0.    0.     0.   PPB'S
123.9   258.7    0.0  258.7  289.0    25.2 2165.4    0.     0.     0.     67.    0.   152.    0.    0.     0.    0.     0.   PPB'S
148.7   252.8    0.0  252.8  360.8    27.3 2064.2    0.     0.     0.      0.    0.     0.    0.    0.     0.    0.     0.   PPB'S
173.4   242.5    0.0  242.5  433.5    30.4 1912.4    0.     0.     0.      0.    0.     0.    0.    0.     0.    0.     0.   PPB'S
198.2   229.2    0.0  229.2  507.3    30.4 1791.0    0.     0.     0.      0.    0.     0.    0.    0.     0.    0.     0.   PPB'S
223.0   217.3    0.0  217.3  572.0    31.5 1689.8    0.     0.     0.      0.    0.     0.    0.    0.     0.    0.     0.   PPB'S
272.6   189.2    0.0  189.2  675.0    31.5 1477.3    0.     0.     0.     66.    0.   128.    0.    0.     0.    0.     0.   PPB'S
322.1   168.5    0.0  168.5  728.6    28.8 1325.6    0.     0.     0.      0.    0.     0.    0.    0.     0.    0.     0.   PPB'S
371.7   156.7    0.0  156.7  745.8    24.6 1183.9    0.     0.     0.      0.    0.     0.    0.    0.     0.    0.    -9.   PPB'S
433.0   134.5    0.0  134.5  733.6    19.9 1052.4    0.     0.     0.     50.    0.    68.    0.    0.     0.    0.
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THE   REDUCED   DATA   FILE   IS      : MAR214.DAT

THE INITIAL PPB CARBON TO NOX RATIO IS : 2027. TO  515.  EQUALS :    3.94


MINUTES    NOX     NO      NO2   OZONE    HCHO    THC     C2H4    C3H6   CH3ONO   CH3OH   C4H8    C4H10   ACET    C5H12   224TMP C7H8    C8H10
    0.0  514.8  470.9    43.9     0.0     0.0 2026.5     0.      0.      0.      0.      0.      0.      0.      0.      0.      0.       0.  
   31.1  494.4  308.1   186.3     5.1     0.0 1798.6     0.      0.      0.      0.      0.      0.      0.      0.      0.      0.       0.   PPB'S
   62.2  459.7  188.4   271.4    16.2     0.0 1644.0     0.      0.      0.      0.      0.      0.      0.      0.      0.      0.       0.   PPB'S
   93.4  423.5  114.9   308.6    32.3     0.0 1530.1     0.      0.      0.      0.      0.      0.      0.      0.      0.      0.       0.   PPB'S
  124.5  395.2   73.4   321.7    51.5     0.0 1440.5     0.      0.      0.      0.      0.      0.      0.      0.      0.      0.       0.   PPB'S
  155.6  368.4   46.3   322.1    73.8     0.0 1359.2     0.      0.      0.      0.      0.      0.      0.      0.      0.      0.       0.   PPB'S
  186.7  349.5   30.3   319.2    96.0     0.0 1285.9     0.      0.      0.      0.      0.      0.      0.      0.      0.      0.       0.   PPB'S
  280.1  294.4    8.0   286.4   155.6     0.0 1106.9     0.      0.      0.      0.      0.      0.      0.      0.      0.      0.       0.   PPB'S
  373.4  242.5    0.0   242.5   210.2     0.0  952.2     0.      0.      0.      0.      0.      0.      0.      0.      0.      0.       0.   PPB'S
  466.8  201.5    0.0   201.5   257.7     0.0  822.0     0.      0.      0.      0.      0.      0.      0.      0.      0.      0.       0.   PPB'S
  560.2  165.3    0.0   165.3   301.1     0.0  716.2     0.      0.      0.      0.      0.      0.      0.      0.      0.      0.       0.   PPB'S
  653.5  133.8    0.0   133.8   340.5     0.0  618.5     0.      0.      0.      0.      0.      0.      0.      0.      0.      0.       0.   PPB'S
  746.9  105.5    0.0   105.5   373.9     0.0  537.2     0.      0.      0.      0.      0.      0.      0.      0.      0.      0.       0.   PPB'S
  840.2   96.0    0.0    96.0   399.2     0.0  463.9     0.      0.      0.      0.      0.      0.      0.      0.      0.      0.       0.   PPB'S
  895.0   89.7    0.0    89.7   408.3     0.0  423.2     0.      0.      0.      0.      0.      0.      0.      0.      0.      0.      -9.   PPB'S
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THE   REDUCED   DATA   FILE   IS      : FEB274.DAT

THE INITIAL PPB CARBON TO NOX RATIO IS : 3258. TO  429.  EQUALS :    7.59

MINUTES   NOX     NO     NO2  OZONE   HCHO    THC   C2H4  C3H6 CH3ONO CH3OH  C4H8  C4H10  ACET  C5H12 224TMP C7H8  C8H10
    0.0  429.4  391.1   38.3    0.0   15.0 3258.2    0.    0.    0.   190.    0.   145.    0.    0.    0.    0.    0.  PPB'S
   12.2  428.3  306.6  121.7    4.0   22.5 3055.9    0.    0.    0.     0.    0.     0.    0.    0.    0.    0.    0.  PPB'S
   26.4  411.4  195.6  215.8   14.1   30.0 2853.5    0.    0.    0.   184.    0.   106.    0.    0.    0.    0.    0.  PPB'S
   36.6  396.7  137.4  259.3   25.3   37.5 2732.1    0.    0.    0.     0.    0.     0.    0.    0.    0.    0.    0.  PPB'S
   48.7  384.3   74.0  310.3   48.5   42.7 2630.9    0.    0.    0.     0.    0.     0.    0.    0.    0.    0.    0.  PPB'S
   60.9  368.5   42.3  326.3   68.7   50.2 2539.8    0.    0.    0.     0.    0.     0.    0.    0.    0.    0.    0.  PPB'S
   73.1  349.4   23.3  326.1  112.2   57.7 2458.9    0.    0.    0.     0.    0.     0.    0.    0.    0.    0.    0.  PPB'S
   85.3  334.7   11.6  323.1  144.5   59.2 2357.7    0.    0.    0.     0.    0.     0.    0.    0.    0.    0.    0.  PPB'S
   97.5  318.9    5.3  313.7  181.9   60.7 2297.0    0.    0.    0.     0.    0.     0.    0.    0.    0.    0.    0.  PPB'S
  121.9  303.2    0.0  303.2  257.7   58.5 2145.2    0.    0.    0.     0.    0.     0.    0.    0.    0.    0.    0.  PPB'S
  146.2  277.2    0.0  277.2  330.4   57.7 2003.5    0.    0.    0.     0.    0.     0.    0.    0.    0.    0.    0.  PPB'S
  170.6  267.1    0.0  267.1  402.2   56.2 1882.1    0.    0.    0.     0.    0.     0.    0.    0.    0.    0.    0.  PPB'S
  195.0  250.2    0.0  250.2  468.9   54.0 1760.7    0.    0.    0.     0.    0.     0.    0.    0.    0.    0.    0.  PPB'S
  219.4  231.0    0.0  231.0  533.6   52.5 1669.6    0.    0.    0.     0.    0.     0.    0.    0.    0.    0.    0.  PPB'S
  243.7  214.1    0.0  214.1  588.1   51.0 1578.5    0.    0.    0.     0.    0.     0.    0.    0.    0.    0.    0.  PPB'S
  268.1  204.0    0.0  204.0  637.6   50.2 1477.3    0.    0.    0.     0.    0.     0.    0.    0.    0.    0.    0.  PPB'S
  292.5  189.3    0.0  189.3  681.1   48.7 1386.3    0.    0.    0.     0.    0.     0.    0.    0.    0.    0.    0.  PPB'S
  316.8  181.5    0.0  181.5  706.4   47.2 1315.4    0.    0.    0.     0.    0.     0.    0.    0.    0.    0.    0.  PPB'S
  341.2  171.3    0.0  171.3  726.6   45.7 1244.6    0.    0.    0.     0.    0.     0.    0.    0.    0.    0.    0.  PPB'S
  365.6  163.4    0.0  163.4  734.7   45.0 1183.9    0.    0.    0.     0.    0.     0.    0.    0.    0.    0.    0.  PPB'S
  383.9  160.0    0.0  160.0  734.7   45.0 1143.4    0.    0.    0.   112.    0.    29.    0.    0.    0.    0.   -9.  PPB'S
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THE   REDUCED   DATA   FILE   IS       : FEB294.DAT

THE INITIAL PPB CARBON TO NOX RATIO IS : 3332. TO  430.  EQUALS :    7.75


MINUTES   NOX    NO     NO2  OZONE   HCHO   THC    C2H4   C3H6  CH3ONO  CH3OH  C4H8   C4H10  ACET   C5H12  224TMP C7H8   C8H10
   0.0  430.1  355.5   74.6    0.0   12.6 3332.3    0.     0.     0.    219.    0.    149.    0.     0.     0.     0.     0.   PPB'S
  12.2  419.2  259.7  159.5    5.1   25.2 3153.3    0.     0.     0.      0.    0.      0.    0.     0.     0.     0.     0.   PPB'S
  26.4  408.3  149.4  258.9   17.2   30.3 2944.4    0.     0.     0.    207.    0.    100.    0.     0.     0.     0.     0.   PPB'S
  36.6  394.1  101.0  293.2   29.3   37.9 2835.0    0.     0.     0.      0.    0.      0.    0.     0.     0.     0.     0.   PPB'S
  48.8  381.1   61.8  319.2   60.6   40.4 2725.6    0.     0.     0.      0.    0.      0.    0.     0.     0.     0.     0.   PPB'S
  63.0  370.2   30.9  339.3  103.1   45.4 2616.1    0.     0.     0.      0.    0.      0.    0.     0.     0.     0.     0.   PPB'S
  77.2  353.9   17.5  336.3  150.6   49.2 2496.8    0.     0.     0.      0.    0.      0.    0.     0.     0.     0.     0.   PPB'S
  93.5  343.0    9.3  333.7  201.1   50.5 2407.2    0.     0.     0.      0.    0.      0.    0.     0.     0.     0.     0.   PPB'S
 115.9  332.1    5.2  326.9  278.9   56.8 2258.0    0.     0.     0.    195.    0.     68.    0.     0.     0.     0.     0.   PPB'S
 146.3  315.7    0.0  315.7  381.0   64.4 2079.0    0.     0.     0.    194.    0.     59.    0.     0.     0.     0.     0.   PPB'S
 170.7  294.0    0.0  294.0  461.8   63.1 1959.6    0.     0.     0.      0.    0.      0.    0.     0.     0.     0.     0.   PPB'S
 195.1  277.6    0.0  277.6  532.5   63.1 1850.2    0.     0.     0.      0.    0.      0.    0.     0.     0.     0.     0.   PPB'S
 219.5  263.5    0.0  263.5  596.2   61.8 1740.8    0.     0.     0.      0.    0.      0.    0.     0.     0.     0.     0.   PPB'S
 243.9  250.4    0.0  250.4  658.9   61.8 1641.3    0.     0.     0.      0.    0.      0.    0.     0.     0.     0.     0.   PPB'S
 268.3  237.4    0.0  237.4  707.4   61.8 1541.8    0.     0.     0.      0.    0.      0.    0.     0.     0.     0.     0.   PPB'S
 292.7  219.9    0.0  219.9  745.8   59.3 1452.3    0.     0.     0.      0.    0.      0.    0.     0.     0.     0.     0.   PPB'S
 317.1  206.9    0.0  206.9  770.0   55.5 1372.7    0.     0.     0.      0.    0.      0.    0.     0.     0.     0.     0.   PPB'S
 341.5  199.2    0.0  199.2  782.1   54.3 1303.1    0.     0.     0.      0.    0.      0.    0.     0.     0.     0.     0.   PPB'S
 365.9  193.8    0.0  193.8  787.2   54.3 1233.5    0.     0.     0.      0.    0.      0.    0.     0.     0.     0.     0.   PPB'S
 390.3  185.1    0.0  185.1  785.2   53.0 1173.8    0.     0.     0.      0.    0.      0.    0.     0.     0.     0.     0.   PPB'S
 414.7  174.2    0.0  174.2  781.1   53.0 1124.0    0.     0.     0.      0.    0.      0.    0.     0.     0.     0.     0.   PPB'S
 436.0  167.7    0.0  167.7  774.1   53.0 1084.3    0.     0.     0.      0.    0.      0.    0.     0.     0.     0.    -9.   PPB'S
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THE   REDUCED   DATA   FILE   IS       : MAR024.DAT

THE INITIAL PPB CARBON TO NOX RATIO IS : 3394. TO  439.  EQUALS :     7.74


MINUTES   NOX    NO     NO2   OZONE    HCHO   THC    C2H4   C3H6  CH3ONO  CH3OH  C4H8  C4H10  ACET   C5H12  224TMP C7H8   C8H10

    0.0  438.5  376.1   62.4    0.0    0.0 3394.1    0.     0.     0.    426.    0.    96.    0.     0.     0.     0.     0.   PPB'S
   12.2  429.5  286.4  143.1    1.0    0.0 3270.3    0.     0.     0.      0.    0.     0.    0.     0.     0.     0.     0.   PPB'S
   24.4  410.2  199.9  210.3    9.1    0.0 3074.3    0.     0.     0.      0.    0.     0.    0.     0.     0.     0.     0.   PPB'S
   36.6  395.5  118.9  276.7   21.2    0.0 2950.5    0.     0.     0.    407.    0.    96.    0.     0.     0.     0.     0.   PPB'S
   60.0  372.9   54.0  318.9   61.6    0.0 2775.1    0.     0.     0.    390.    0.    81.    0.     0.     0.     0.     0.   PPB'S
   73.2  361.6   30.3  331.4   95.0    0.0 2671.9    0.     0.     0.      0.    0.     0.    0.     0.     0.     0.     0.   PPB'S
   85.4  350.3   16.2  334.1  127.3    0.0 2589.4    0.     0.     0.      0.    0.     0.    0.     0.     0.     0.     0.   PPB'S
   97.6  344.7    5.4  339.3  159.7    0.0 2527.5    0.     0.     0.      0.    0.     0.    0.     0.     0.     0.     0.   PPB'S
  122.0  331.1    0.0  331.1  222.3    0.0 2403.7    0.     0.     0.      0.    0.     0.    0.     0.     0.     0.     0.   PPB'S
  146.4  316.4    0.0  316.4  291.0    0.0 2269.6    0.     0.     0.      0.    0.     0.    0.     0.     0.     0.     0.   PPB'S
  173.8  305.1    0.0  305.1  355.7    0.0 2145.8    0.     0.     0.    349.    0.    72.    0.     0.     0.     0.     0.   PPB'S
  195.1  299.5    0.0  299.5  414.3    0.0 2053.0    0.     0.     0.      0.    0.     0.    0.     0.     0.     0.     0.   PPB'S
  219.5  288.2    0.0  288.2  473.9    0.0 1949.8    0.     0.     0.      0.    0.     0.    0.     0.     0.     0.     0.   PPB'S
  243.9  271.2    0.0  271.2  537.6    0.0 1846.6    0.     0.     0.      0.    0.     0.    0.     0.     0.     0.     0.   PPB'S
  268.3  259.9    0.0  259.9  596.2    0.0 1764.1    0.     0.     0.      0.    0.     0.    0.     0.     0.     0.     0.   PPB'S
  292.7  243.0    0.0  243.0  648.8    0.0 1691.9    0.     0.     0.      0.    0.     0.    0.     0.     0.     0.     0.   PPB'S
  317.1  237.3    0.0  237.3  697.3    0.0 1609.4    0.     0.     0.      0.    0.     0.    0.     0.     0.     0.     0.   PPB'S
  341.5  226.0    0.0  226.0  725.6    0.0 1526.8    0.     0.     0.      0.    0.     0.    0.     0.     0.     0.     0.   PPB'S
  365.9  220.4    0.0  220.4  750.8    0.0 1444.3    0.     0.     0.      0.    0.     0.    0.     0.     0.     0.     0.   PPB'S
  390.3  209.1    0.0  209.1  760.9    0.0 1392.7    0.     0.     0.      0.    0.     0.    0.     0.     0.     0.     0.   PPB'S
  414.7  203.4    0.0  203.4  769.0    0.0 1330.8    0.     0.     0.      0.    0.     0.    0.     0.     0.     0.     0.   PPB'S
  424.8  197.8    0.0  197.8  770.0    0.0 1310.2    0.     0.     0.      0.    0.     0.    0.     0.     0.     0.     0.   PPB'S
  435.0  196.6    0.0  196.6  770.0    0.0 1289.6    0.     0.     0.      0.    0.     0.    0.     0.     0.     0.    -9.   PPB'S
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