THE UNIVERSITY OF CALIFORNIA, RIVERSIDE ENVIRONMENTAL CHAMBER DATA BASE FOR EVALUATING OXIDANT MECHANISMS

Indoor Chamber Experiments Through 1993

Volume 1
Backing Document and Data Base Description

by

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ABSTRACT

This document describes the data base of University of California, Riverside, environmental chamber experiments for use when evaluating photochemical mechanisms for urban and regional airshed models. This includes data obtained using the Statewide Air Pollution Research Center (SAPRC) Evacuable Chamber (EC), Indoor Teflon Chamber #1 (ITC), Indoor Teflon Chamber #2 (ETC), Dividable Teflon Chamber (DTC), and Xenon arc Teflon Chamber (XTC) between September of 1975 through November of 1993. This document provides backing information and data for that data set as well. This document lists and summarizes the experiments, summarizes the facility and procedures employed, documents the analytical and monitoring methods and their calibration data and associated uncertainties, assigns and documents the input data needed to conduct model simulations of the experiments in the present data base, and describes the format of the data sets which are distributed with this document on computer diskettes. Files are included in the distribution to permit modeling of the experiments in the present data base using the SAPRC-90 and the Carbon Bond IV chemical mechanisms, though a full mechanism evaluation procedure is beyond the scope of this report. Recommendations are made concerning the steps that need to be taken before using these data to evaluate chemical mechanisms.

This document consists of two volumes. Volume 1 contains the main body of the text documenting the data base, and Volume 2 contains the three appendices. Appendix A contains printouts of spreadsheets containing summaries of the runs in the data base. Appendix B contains tabulations of the NO_x and GC calibration data, which are too lengthy to include in the main body of the report. Appendix C describes how to install the distributed data files and software on a computer and how to conduct initial model simulations of the runs using the SAPRC modeling software and the SAPRC-90 and Carbon Bond IV mechanisms.

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Several other people besides the authors contributed substantially to the preparation of this report and the evaluation and corrections to this data base. Mr. James P. Killus made the major effort needed to make important corrections to the NO_x data for the runs in the present and future data base, made contributions to the planning of this data base and report, and provided helpful discussions. Dr. Harvey Jeffries at the University of UNC major contributions to the planning of the data base and report and provided helpful discussions during the initial period of this project. Dr. Ken Sexton of UNC discovered the problem with the NO_x data which were addressed by Mr. Killus, and also provided helpful discussions. Dr. Nelson Kelly of General Motors Research Laboratories took spectra of blacklights from our chambers which were highly useful in this work. Mr. Kurt Bumiller worked on the analysis of the formaldehyde calibration data, and Dr. John Pierce assisted in the summaries of the PAN and GC calibration data.

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1. INTRODUCTION

1.1 Background

Urban and regional oxidant models are important tools in the development and assessment of regulatory strategies aimed at reducing ground-level ozone formation. The gas-phase photochemical mechanism is an important component of such models because ozone is not emitted directly, but is formed from the gas-phase photochemical reactions of the emitted volatile organic compounds (VOCs) and oxides of nitrogen (NO_x) in air. The chemistry of ground level ozone formation is highly complex and nonlinear and has many uncertainties. Because of this, simple "rollback" models based on assuming ozone reductions are proportional to precursor reductions may result in inappropriate or counter-effective control strategies. Because the chemistry is complex and has uncertainties, no chemical model can be relied upon to give even approximately accurate predictions unless it has been evaluated by comparing its predictions with experimental data.

There are essentially two ways a photochemical oxidant model can be evaluated. The first is to compare the predictions of the complete model against data taken during a historic ozone pollution episode. Although this is the most comprehensive evaluation method in the sense that all components of the model are involved, it is rarely definitive because of the many uncertainties in the input data needed to represent any historic episode. Furthermore, because of the many components of any comprehensive model, it is rarely clear which component is the source of any discrepancy observed, or, if the model agrees with the data, whether there may be compensating errors among the different components.

The other approach for evaluating models is to evaluate each of the components separately. In the case of the gas-phase chemical mechanism, this means evaluating the predictions of the mechanism against results of environmental chamber experiments. In an ideal environmental chamber experiment, one knows precisely what pollutants are introduced and the conditions to which they are exposed and knows the results with a high degree of accuracy and precision. Based on this, one can use the results to evaluate how well the model can predict the transformations which occur under those conditions. If the chemical model (i.e., mechanism) cannot successfully predict these transformations under such controlled conditions, it certainly can not be relied upon for use in regulatory models. If the model can successfully predict the transformations under a range of chemical conditions which encompass the range of variability in the atmosphere, one has at least some basis to conclude that it may give reasonably accurate predictions of chemical transformations in the atmosphere, if provided with the appropriate input data.

Unfortunately, there is no such thing as an ideal environmental chamber experiment. Although not as difficult or uncertain as modeling ambient air data, input data for modeling environmental chamber experiments, or for evaluating the results, also have uncertainties which can be significant. Analytical methods for the reactants and products have inaccuracies and imprecisions which might introduce errors in the amount of initial or injected reactants assumed in the model, or in evaluating the extent to which the model can predict pollutant concentrations. Simulating a chamber experiment also requires knowledge of the temperature, light intensity, and spectrum of the photolyzing light, and how they vary with time. All of these have uncertainties that can result in errors in reaction rates when simulating the experiments. Characterizing the light intensity and spectra is particularly difficult in outdoor chamber experiments. Because of this, it is important that chamber experiments used to evaluate mechanisms have as high quality analytical data and as well characterized experimental conditions as possible, and that the sources of the uncertainties in these data be identified and quantified. With a knowledge of the range of uncertainty in the input or evaluation data, one can assess the extent to which a model can disagree with the data.

Perhaps the most serious problem is the existence of chamber wall effects (heterogeneous processes involving the walls) which are known to be non-negligible in all current-generation chamber experiments and can dominate the results of certain types of experiments (e.g., see Carter and Lurmann, 1990, 1991). Model simulation of characterization experiments, i.e., experiments which are designed to be especially sensitive to chamber effects but whose gas-phase chemistry are reasonably well understood, can be used to evaluate models for these "chamber effects". These chamber models can then be used when conducting model simulations of experiments where the gas-phase chemistry is being evaluated. However, chamber models will always have significant uncertainties since the physical and chemical basis for many of these effects is uncertain. Furthermore, some chamber effects vary from run to run in manners which are not always successfully predicted, and for many historic chamber data bases there are inadequate numbers of characterization runs. Because of this, one should not rely on data from a single chamber for evaluating mechanisms; the use of data from a variety of chambers is necessary to minimize the chance for errors in the chamber model causing errors in model simulations of experiments where the gas-phase chemistry is being evaluated.

With these problems in mind, the University of North Carolina (UNC), the Statewide Air Pollution Research Center (SAPRC) and several other research institutions initiated an effort that was sponsored by the U.S. Environmental Protection Agency to develop a standard data base and protocol for evaluating photochemical mechanisms for air quality simulation models. An overview of the many factors which must be considered when developing such a protocol is discussed in the document entitled "Protocol for Evaluating Oxidant Mechanisms for Urban and Regional Models" (Jeffries et al., 1992), which was prepared for this program. As discussed there, the specifics of the evaluation protocol will depend on the nature of the model being evaluated and the uses to which it will be put. However, regardless of these application-specific considerations, the data base of chamber experiments, and the comprehensiveness of its associated documentation, are critical to any evaluation. Sufficient information must be given concerning the experiments so the evaluator can represent them in the model appropriately, and can understand and document their uncertainties and variabilities. The report of Jeffries et al. (1992) gives standards for the necessary documentation of the data base.

This document is the result of SAPRC efforts to date on the development of the data base of environmental chamber experiments for mechanism evaluation. The data files distributed with this report provide the environmental chamber data themselves and the supporting information relevant to data quality. They also include programs and data necessary to use the data for mechanism evaluation. The data files do not cover all experiments carried out at SAPRC which are potentially useful for mechanism evaluation, being currently limited to indoor chamber experiments which were carried out through the end of 1993. The backing documentation is somewhat more comprehensive, including a discussion of most of the calibration data relevant to outdoor chamber experiments carried out during this same period, which will be included in future releases of the data base. The scope of the present release of the data base and the backing documentation is described in the following section.

1.2 Scope

1.2.1 Environmental Chamber Experiments Included

Coverage. To date, six different environmental chambers at SAPRC have provided data which are potentially useful for mechanism evaluation. These include the Evacuable Chamber (EC), the Indoor Teflon Chamber #1 (ITC), the Indoor Teflon Chamber #2 (ETC), the Dividable Teflon Chamber (DTC), the Xenon Teflon Chamber (XTC), and the Outdoor Teflon Chamber (OTC). These chambers are described in Section 3. The number of experiments which are included in the data base, or may be suitable for future inclusion, the time periods for these experiments, and our plans for releasing these data are summarized in Table 1. As indicated there, data from the indoor chambers are included in this release of the data base, and data from the outdoor chamber will be included in a later release. The DTC and XTC have since been moved to another location and are currently generating additional data. The data base will be updated to include these results as a part of the reporting of the results of those experiments.

Although the presently distributed data base has only indoor chamber data, the backing documentation in this report includes a description of all six chambers and their operating procedures, and discusses the analytical methods and calibration data applicable for all groups of runs listed in Table 1. However, the tabulations of run-specific information and the discussions of characterization data in this report are restricted to the sets of experiments in the presently distributed data base. This report will be updated to include this additional information when the future releases are distributed.

Table 1. Summary of experiments included in the SAPRC environmental chamber data base.

Chamber	Runs	Dates	Status [a]	Description
EC	095 - 930	09/29/75 - 11/18/83	1	5800-liter evacuable, thermostatted cylindrical chamber. FEP Teflon-coated aluminum walls. Quartz windows on both ends. 25 KW Xenon arc light "solar simulator" light source with pyrex filters to remove UV below ~290 nm. Generally operated at ~303 K and 50% RH.
ITC	428 - 1009 1547 - 1558	01/29/82 - 08/29/86 10/02/89 - 10/16/89	1 1	Replaceable ~6000-liter FEP Teflon bag in aluminum frame with banks of blacklights on either side. Generally operated at room temperature and 50% RH.
ETC	044 - 510	10/25/89 - 02/25/93	1	Replaceable ~4000-liter FEP Teflon bag in an aluminum frame with banks of blacklights on the top and bottom. All runs at room temperature and ~5% RH.
DTC	011 - 076	03/05/93 - 08/04/93	1	Dual replaceable ~5000-liter FEP teflon bags located next to each other, between banks of blacklights on either side. Allows for simultaneous irradiation of two mixtures. Has air exchange system for rapid mixing of common reactants. All runs at room temperature and all but 2 at ~5% RH.
XTC	081 - 121 [b]	08/23/93 - 11/17/93	1	Replaceable ~5000-liter FEP teflon bag located in a room with reflective walls and with 4 6.5 KW xenon arc lights on a wall 4’ from the bag. Uses same enclosure as DTC, and run numbering continues from that of DTC runs. All runs at room temperature and ~5% RH.
OTC	183 - 206 209 - 253 254 - 318	06/22/83 - 10/14/83 05/13/85 - 11/27/85 06/10/92 - 10/26/93	2 2 2	Replaceable ~50,000-liter pillow-shaped FEP teflon reaction bag located outdoors and irradiated with sunlight. Usually divided into two ~25,000-liter "sides" to allow simultaneous irradiation of two mixtures under the same conditions. Cover used during reactant injection and mixing, and irradiation begun by removing the cover. All runs at somewhat higher than ambient temperature and ~5% RH. Runs usually (but not always) carried out in summer.

[a] Data base status: 1 = included in this distribution; 2 = to be included in a future distribution.
[b] Numbering continues from that of DTC runs.

Selection Criteria for Inclusion of Runs. Not all environmental chamber experiments carried out in the chambers and periods summarized in Table 1 are considered appropriate for this data base. The process used in choosing the runs for inclusion consisted first of an initial screening, using the criteria listed below. All runs which passed this initial screening were then examined in more detail to determine if the quality and completeness of their data and run characterization information were sufficient for them to be potentially useful for modeling. The criteria used for the initial screening was as follows:

(1) The data from the experiment must be available in a form which can be read by CHADPRO, SAPRC's environmental CHAmber Data PROcessing program, or in a computer-readable form which can be converted to CHADPRO format using software available at SAPRC.

(2) The data from the EC must have been subsequent to the time when routine spectral measurements were made of the light source, because as discussed later the spectrum of this light source is not constant.

(3) The data from the ITC must have been subsequent to the time when the Teflon reactor was installed in that chamber. Previously, the ITC was the All Glass Chamber (AGC), which does not provide data suitable for mechanism evaluation because of insufficient wall characterization data, and because of exchange with laboratory air due to leaks.

(4) The data from the ETC must have been subsequent to the time when the blacklight-only light source was installed. Some early ETC runs were carried out using a mixture of blacklights and "vita-lights", but their intensity and spectrum were not well characterized. Early ETC runs which are not well characterized and documented are also excluded.

(5) Several sets of experiments were not included because they were considered to be exploratory in nature, and superseded by later experiments of similar types which were carried out in the same chamber using better established operating procedures. This included preliminary mini-surrogate runs carried out in the ITC in 1981, which were superseded by a more systematic and complete study in early 1982; the ETC experiments carried out prior to the start of the incremental reactivity study reported by Carter et al. (1993a); and the OTC experiments carried out in 1982, where poor chamber side equivalency was observed due to improper reactant injection methods (Carter et al, 1984a).

(6) The experiment must have been carried out for the purpose of oxidant mechanism evaluation or characterization of chamber effects, or be judged to be potentially useful for this purpose. This eliminated a large number of experiments conducted for specialized kinetic or product studies.

(7) All the chemical reactants injected in the experiment must be known and quantified. This eliminated a number of experiments using whole jet fuels, raw printing oils, or complex surrogates whose components were not all analyzed.

(8) The experiment must have been carried out under the standard temperature and pressure conditions utilized for that chamber. Although experiments at different temperatures and pressures are potentially useful for mechanism evaluation, it was judged that the present state of the chamber characterization models for these chambers is inadequate for inclusion of such experiments in the present release of this data base.

(9) The experiment must not be known to be missing important input data needed for modeling, or to have other known significant problems making them inadequately characterized for modeling.

During the preparation of the documentation of this data base, additional problems became evident with the data quality or completeness of the conditions for certain individual experiments which passed the initial screening. These experiments are included in the master run tabulations, but with the notation "reject" or "don’t model".

1.2.2 Data Evaluated or Corrected

The scope of this project was not sufficient to evaluate and document all of the measurements given in the data sets for all of the selected experiments. The run-specific data which were evaluated and which are documented in this report are sufficient for using the mechanism for evaluating its performance for predicting ozone formation, which is the main focus of this program. The data which were evaluated include the following:

NO and NO_2 Data. The calibration data for NO were completely re-evaluated, and NO calibration factors were re-computed and assigned for all experiments based on a global evaluation of the calibration data set. Note that the instruments employed do not actually measure NO_2; data reported as "NO_2" (or "NO2-UNC") are actually species which are concerted to NO by a heated catalyst which is referred to as the "NO_2 converter". In addition to NO_2, these include PAN, organic nitrates, and (under some conditions) HNO_3. The converter should be efficient under normal conditions, but if it is malfunctioning not all the NO_2 is converted to NO, and thus "NO_2" readings would be low. The NO_2 converter efficiency data were summarized and evaluated, and runs with potential problems in this regard were flagged. Information concerning zero errors in NO and NO_2 measurements were compiled and evaluated, and where possible corrections were made. Recommended initial NO and NO_2 concentrations are given for each experiment, along with their estimated uncertainties due to calibration or zero uncertainties or (for NO_2) uncertainties in converter efficiencies. Runs with NO_x analysis problems are identified in the master run tabulations.

Organic Reactant Data. The calibration data for all organic reactants which were injected into the experiments were summarized and evaluated, and recommended factors as indicated by these calibrations were derived, along with their associated uncertainties. Where possible and appropriate, the data base was corrected to incorporate the recommended factors. This was not possible for the earlier EC runs, since the analysis instrument and calibration factor were not identified in the data set, and entering this information from the raw data files was not possible given the time and personnel resources available. In those cases where the probable instrument could be identified, the relative uncertainty associated with the calibrations for reactant species around the time of the experiment was included in the data set for the experiment. Recommended initial concentrations for all injected organic reactants are given for each experiment, along with, wherever possible, its estimated calibration uncertainty. Runs with organic reactant analysis problems are identified in the master run tabulations.

Ozone Data. The ozone calibration data base was summarized and evaluated, and calibration correction factors were re-computed for all runs. Uncertainties due to variability in calibration data were included in the data base. All runs were examined for possible zero errors as indicated by nonzero ozone measurements in the presence of NO at the beginning of the run, and the data were corrected where appropriate. Runs with O_3 analysis problems are identified in the master run tabulations. Anomalous data points were flagged as questionable.

Light Intensity. The data base of the NO_2 actinometry experiments was tabulated and NO_2 photolysis rates were re-computed by direct model simulations using updated rate constants. The trends of actinometry results with time (for the ITC, ETC, DTC, and XTC) or with solar simulator power and radiometer measurements, and the relationships of these measurements with changes affecting the light source (for the EC) were evaluated. Based on this, NO_2 photolysis rates were re-assigned for each experiment. Uncertainties in these assignments were also included in the data base. Runs with light intensity characterization problems were identified and rejected from the recommended evaluation set.

Spectral Distribution (EC). The data base of EC spectral measurements was tabulated and evaluated. The calibration data for the instrument were evaluated, and a consistent method was used to calibrate all the data. Trends in spectral changes with time were determined to provide best estimates of spectra for individual runs. Since the spectral data base for the runs gives intensities at only a few wavelengths, complete spectra for the EC light source are given, and methods are developed to derive estimated complete spectra for all the experiments.

Spectral Distribution (Blacklight Chambers). The data base of measurements of blacklight spectra from various chambers using various spectrometers was compiled and evaluated. It is concluded that a single spectrum characterizes all runs with this type of light source. A recommended spectrum for modeling these experiments, which differs in some non-negligible respects from that used previously, was derived.

Temperature. The limited information concerning temperature calibrations was reviewed, and in a few cases corrections were made to the temperature data. The temperature data for each experiment were fit with a sequence of straight lines which approximated how it changed with time. These are needed as input in a model simulation of the run, so this sequence was included in the run data sets.

Humidity. The information concerning humidity in the experiments in the various chambers was reviewed, and recommendations are made concerning default humidities for most runs, and specific humidities for runs where humidity data are reported or with non-standard humidity conditions.

NO Oxidation and O_3 Formation. The change in $[O_3]$-[NO] is a measure of the processes responsible for ozone formation which is meaningful to mechanism evaluations even under conditions where excess NO suppresses O_3. This quantity was computed for all runs with valid O_3 and NO data, along with its maximum value, the time of its maximum, and its average rate of change at various times. Anomalous NO and O_3 data points were flagged and not used when computing these quantities.

Special Conditions. Any special run conditions associated with the experiment, such as subsequent reactant injections, turning the lights on and off in multi-day runs, or use of different humidities than standard for this chamber, were identified and included in the master run tabulations and the comments in the run's data set. Methods for representing them in model simulations were also included in the comments in the run's data set.

Because of the magnitude of this effort, we were not able to comprehensively evaluate all the data associated with all the runs in the data base. The following were evaluated to some extent, but not comprehensively as the data discussed above. Future releases of this data base may include a more comprehensive documentation and evaluation of these data, should they be judged to be sufficiently useful.

PAN. The calibration data for PAN was reviewed, and it was concluded that no major corrections are required in most cases. Probable uncertainties in the data are discussed. The data are probably suitable for mechanism evaluation, assuming that sufficient latitude is given for the uncertainties.

Formaldehyde. The problems and biases associated with the SAPRC formaldehyde data are discussed. Much of the earlier SAPRC formaldehyde data are not considered to be suitable for evaluating the ability of models to predict formaldehyde yields.

Other Organic Products. Many SAPRC EC and (to a lesser extent) ITC runs have concentration-time data for a variety of other reaction products, including acetaldehyde, acetone, individual organic nitrates, higher aldehydes, cresols, etc. Available calibration data for these products are summarized, recommended calibration factors are derived and applied to the data where appropriate and possible, and cases with obvious problems are identified. However, in many cases, particularly for the earlier EC runs where the instrument used was not identified in the data sets, it was not possible to make calibration corrections or estimate uncertainties. Mechanism evaluators can utilize the calibration summaries and other information in this report and the data sets to make conclusions concerning the data for individual runs of interest.

Chamber Effects Model and Model Parameters. As discussed by Jeffries et al. (1992), an important component of any protocol for mechanism evaluation is the model for chamber effects and chamber-dependent parameters (what Jeffries et al. [1992] term the "auxiliary mechanism"). A data base for mechanism evaluation is not complete without recommendations for appropriate inputs to chamber effects models which can be used when modeling specific runs. Although the development, evaluation, and documentation of chamber effects models is beyond the scope of this report, chamber effects models for the SAPRC EC and ITC have already been developed as part of the process of evaluating the SAPRC and RADM2 mechanisms (Carter and Lurmann, 1990, 1991), and portions of the model were recently revised and extended to the other chambers as part of our evaluation of effects of chamber and light source on mechanism evaluation results (Carter et al., 1994a). Recommendations are given for appropriate parameters in these models which can be used as a starting point when evaluating mechanisms using these runs. However, these parameters have not been optimized or fully evaluated against the set of characterization runs in this data set. This effort must be carried out as part of the mechanism evaluation process, which is beyond the scope of this report.

1.2.3 Computer Data Sets

This release of the data consists of two components, a series of computer files containing the experimental data and associated information, and this report, which documents these data. The data sets are distributed in compressed form on PC-compatible diskettes, and include an installation program which uncompresses the files and copies them to a hard disk in an appropriate directory structure. The data sets and an appropriate installation program are also available on the Internet for anonymous FTP at carterpc.ucr.edu in the directory "\chdata", or at cert.ucr.edu in the directory "\pub\carter\chdata". The format of the data sets are described in Section 2.3, and the procedure for installing the data (using diskettes or the Internet), and the associated software, are discussed in Appendix C. The data sets are as follows:

(1) Master Run Summary Spreadsheets. For each chamber whose data are included in this distribution, there is a series of files giving important summary information for each run in the data base. This

includes, for each run in the data base, the run descriptions and classification, initial reactant concentrations and their estimated uncertainties, notations where applicable of special run conditions or problems, notations where applicable of special problems with the run data, notations where applicable indicating runs judged not suitable for modeling, light intensity and (for the EC) spectral distribution assignments, and other data which might be of significance to the modeler. Printouts of these spreadsheets are given in Appendix A.

(2) Individual Experiments Data Sets. For each experiment, there is an ASCII file containing all the run-specific data. In addition to the experimental measurements as a function of time, it includes (where this information is available) identifications of instruments and calibration and zero corrections used, data flags, uncertainty estimates where available, recommended input data for modeling the runs, comments from the log book (for most but not all runs), comments documenting data corrections, and comments documenting special run conditions and input data to use when modeling. They contain all the information needed to model the run using the standard SAPRC chamber effects model and the initial default chamber model parameters, and to evaluate the results of the simulations either by comparing concentration-time plots for selected measured species, or by comparing ozone maxima or NO oxidation rates. Although these files are produced and read by FORTRAN programs when used at SAPRC, the measurement data are given in comma-separated-value (CSV) format so that they can be read by most spreadsheet or data base programs.

(3) Calibration Data Summary Files. For most (though not all) of the instruments used to monitor O_3, NO_x, or organics, there are calibration data files giving the calibration data and the times the instruments were calibrated, codes indicating how recommended calibration factors are to be computed, and relevant comments. Except where indicated to the contrary, or where the instrument employed or the original calibration factor used was not given in the data sets, (as was the case for most of the earlier EC runs) the chamber data were corrected to be consistent with the calibration data in these files. Computer programs (CALRUN for the O_3 and NO_x calibrations and GCALRUN for the GC data) read these files and produce output files giving: (1) a summary of the calibration data and recommended calibration assignments; (2) a summary of how the calibration assignments are associated with data in individual runs; (3) a file which can be used to create plots of calibration data and assignments as a function of time; and (4) files giving recommended calibration factors and uncertainty assignments for individual runs. These input and output files are included in computer-readable form.

(4) NO_2 Actinometry Results Data Files. The results of all the NO_2 actinometry experiments, from which the NO_2 photolysis rates were calculated, are included with the data sets. The modeler can use these to recompute the NO_2 photolysis rates if it is judged that the method or rate constants used in this work are inappropriate.

(5) Recommended Spectral Distributions. Data files giving results of light spectrum measurements of the blacklight source used in the ITC, ETC and DTC, of solar simulator used in the EC, and of the xenon arc lights used in the XTC are included. The appropriate spectra can be used to calculate the photolysis rates when modeling these experiments, as discussed in Section 5.

(6) Computer Programs. A number of FORTRAN computer programs which can read and process these files are included to assist the modeler in using these data. These are summarized in Table 7. These include the CALRUN programs discussed above and a program (SPL) which can be used to display plots of its output, a program which converts the run-specific data from ASCII to the binary format required by the other programs, programs which can be used to conduct model simulations of the experiments and plot and summarize the results, and several others. The source code and compile and link batch files are available as a separate distribution. These can be found on the Internet for anonymous FTP at carterpc.ucr.edu in the directory "\model", or at cert.ucr.edu in the directory "\pub\carter\model". PC-compatible diskettes containing these files can also be obtained from the EPA project officer or from William P. L. Carter upon request. All executable files require a 386 PC-compatible computer with a math co-processor or a 486DX or better. The programs are not documented here, but sample input files with comments and batch files giving examples of these are included.

(7) Chemical Mechanism Implementation Files and Software. Computer files implementing the SAPRC-90 (Carter, 1990) and a version of the Carbon Bond IV (Gery et al. 1988) mechanisms are included so example model simulations of the experiments can be carried out. Batch files showing examples of their use are included. The evaluator can use this software for mechanism evaluations, using the implementations of these mechanisms as guides, or, if other software is used, the evaluator can use this software and data files as guidelines for the necessary modifications. The modeling software and data files are summarized in Appendix C.

2. DESCRIPTION OF DATA BASE

2.1 Overview

The SAPRC environmental chamber data base consists of several components, all of which are either necessary or potentially useful for a modeler wishing to utilize these data for mechanism evaluation. These are summarized briefly below, and discussed in greater detail in the remainder of this document.

(1) This document. This describes the data base as a whole, discusses how the measurement and model input data were derived or assigned, and documents the structure and use of various computer data sets, which are the other components of this data base.

(2) Run Data Sets. For each experiment, there is a single computer file which contains all the measurement data for the run, and, for runs for which there is sufficient information for modeling, all the run-specific information needed for modeling. These files also contain run-specific documentation such as comments from the log book, lists of instruments used, uncertainty estimates where available, and in some cases notes indicating how certain parameters were assigned. Thus, these are the primary data files the modeler needs to simulate the individual experiments, and assess the model's ability to predict the results. However, these files do not contain model input information which is applicable for the chamber (or large groups of runs) as a whole, such as the spectral distributions for chambers where this is believed to be constant, or the chamber wall effects parameters. This information is contained in the Characterization Data Files, discussed below.

(2) The Run Spreadsheets. For each chamber, there is a series of "run spreadsheets" giving summary information of various types for all of the experiments in the chamber which are in the data set. Most but not all of the data in the spreadsheets are also in the run data sets, but the spreadsheets provide this information in a convenient format for summary purposes. The spreadsheets also contain classification and summary information which are not in the run data sets. The modeler may find these useful for assessing which runs are available and useful for a particular purpose, for obtaining an overview of which problems may be associated from them, and for obtaining uncertainty information in a more convenient format than the run data sets.

(3) Calibration Data Sets. Computer files are included which contain calibration information for most of the instrument used to produce measurement data of interest to the modeler. Although normally they may not be of interest to the modeler, they could be useful in cases where the modeler suspects problems might exist with the data. They contain information of potential utility for more detailed uncertainty analyses on critical data for assessing model performance.

(4) Characterization Data Files. As indicated above, the run data sets contain only run-specific model input data, and not all the information needed to simulate the experiments. These chamber-specific model input data sets contain the other input data needed to model the runs. These include recommended spectral distribution information which is applicable to all runs in a chamber and recommended or suggested values of input parameters used in our chamber effects model. The latter would obviously need to be modified if the modeler wishes to evaluate the chamber effects model, but they will be useful for serving as a starting point in this effort.

(5) Computer Programs and Example Chemical Mechanism Input Files. The distribution includes computer programs and example chemical mechanism input files which can be used to conduct model simulations of these experiments. There illustrate how these data can be used for mechanism evaluation, and demonstrate that the data base includes the necessary information for mechanism evaluation. Although in most cases the modeler will wish to use his or her own mechanism for this purpose, the input files for the example mechanisms should serve as a useful guideline in this effort.

In the remainder of Section 2, the computer data sets and spreadsheets are described in more detail. The rest of this volume serves as a backing document for these data, giving a description of the chambers and operating procedures (Section 3), the analytical methods and data corrections (Section 4), and the characterizations of lighting and other conditions (Sections 5 and 6). A brief discussion and recommendation section concludes this volume of this document. Volume 2 contains listings of the major run spreadsheets and calibration data, and instructions on installation of the computer files and software.

2.2 Run Spreadsheets

For each of the six SAPRC chambers whose data are or will be included in the data base, there is a series of spreadsheets which list the runs for each chamber in chronological order, and give various types of information or data summaries applicable to the runs. The types of spreadsheets and data they contain are summarized in Table 2, and printouts of cham-USE and merged cham-type spreadsheets are given in Appendix A. Note that the runs listed in the spreadsheets are those which passed the initial screening, and thus may include some runs which have subsequently been judged to be unsuitable for modeling. The runs judged to be unsuitable for modeling are indicated as such in the master run spreadsheet, which is discussed below.

As indicated in Table 2, for each chamber there is a master spreadsheet which gives a summary of the major information about the run, and its status in the data base. If the runs in the chamber have not yet been evaluated for the data base, the master spreadsheet is the only spreadsheet for the chamber, and includes only the run number, the run date, the 40-character run title which is in the data set, and a code indicating the most detailed project report available documenting the run. If the run is in the data

Table 2. Description of data on run spreadsheets.

Column Label	Description
	Spreadsheets Applicable to All Chambers:
	Spreadsheets = "cham-USE": Master Spreadsheets for Chamber (Printouts of these spreadsheets are given in Appendix A.)
RunID	Chamber ID and run number
Date	Date run carried out
Documentation	Code giving project report where run is discussed, where applicable. Table 3 lists and briefly summarizes reports associated with each code.
Title	Brief run description (as given in run data set)
Run Conditions	Summary of unusual run conditions or other relevant log book comments
Data Comments	Comments on unusual problems with analytical instruments, data quality, or missing data
Data Base Status	Comments on run from modeler's perspective. (Second column, which may be hidden, contains numerical code used when sorting runs.)
Action needed	Corrections needed to data sets before distribution. (For internal SAPRC use. Should be blank, but may not be in all cases.)
	Spreadsheets = "cham-TYPE": Modeler's Summary Spreadsheets (The data in these spreadsheets are merged into RUNSORT.XLS, which are then sorted by run type. A printout of RUNSORT.XLS is given in Appendix A.)
RunID	Chamber ID and run number
Classification	Modeler's classification. See Table 4 for description of codes. First column is species or mixture code. Second column is run type code.
Data Base Status	Comments for modeler. Copied from sheet "cham-USE".
Initial NO_x	Initial NO_x and uncertainty. Copied from sheet "cham-NOx".
Carbon	Initial added VOC in ppmC and uncertainty. Copied from sheet "cham-VOC".

Table 2 (continued)

Column Label	Description
OH React'y	OH reactivity of initial added VOCs in propene equivalents, and uncertainty. (Propene equivalents = $\Sigma_i[\mathrm{VOC}]_i^{\mathrm{init}}\mathrm{kOH}_i/\mathrm{kOH}_{\mathrm{propene}}$, units are ppm.). Uncertainty does not include uncertainties in rate constants. Copied from sheet "cham-VOC".
OHr/NOx	Ratio of initial OH reactivity to initial NO_x.
Run time	Number of minutes in the irradiation, or length of time for which useful data were taken.
MaxO_3	Maximum ozone concentration and time (in minutes after the start of the irradiation) of the O_3 maximum.
d(O_3-NO)/dt	$\Delta([O_3]-[NO])/\Delta$time for the first hour of the run and for the time from the start of the run to the time $\Delta([O_3]-[NO])$ reached half its maximum value.
Cond	Code indicating special run condition which may need to be taken into account when modeling the run. If blank, conditions of run is standard for the chamber. Details are in comments section of the run's data set.
Char set	Set of chamber effects parameters recommended for use as a starting point when modeling run. For EC runs this reflects temperature and humidity conditions. For ITC runs it is the reaction bag number. See Sections 2.4.5 and 6.4
Modelable	A blank in this column indicates that the run is sufficiently well characterized to be modeled using the distributed software and data files.
Inp File	A blank in this column indicates that there is sufficient information in the run data set to produce a model simulation input file for the run.
S90 Calc	A blank in this column indicates that a simulation of the run using the SAPRC-90 mechanism went to completion. (Applicable for EC and ITC only).
	Spreadsheets = "cham-NOx": Summary of NO_x data
RunID	Chamber ID and run number
Columns for total NO_x:	
Init	Sum of the initial NO and initial NO_2 recommended for modeling, and uncertainty in initial NO_x derived from uncertainties in initial NO and NO_2. (See below.)
Unc	Uncertainty in initial NO_x from uncertainties in initial NO and NO_2.

Table 2 (continued)

Column Label	Description
Columns for NO and NO_2:	
Inst	ID number for instrument used to measure NO or NO_2. If more than one NO_x instrument was used for a run, it is the instrument which was judged to have the best data, and which was used to derive data in the spreadsheet. In some cases, different instruments were considered best for NO and NO_2.
Fac., U.Fac	NO span factor and the uncertainty in the span factor derived from the calibration data for the instrument. For NO_2 the span factor is the product of the NO span factor and the NO_2 converter efficiency. See Tables B-1 and B-2.
Src	Code giving the source of the tabulated data. The code numbers used in this work are summarized in Table 10. The applicable source code for NO factors is "20", which means derived from calibration file (i.e., from Table B-1.)
Zero used	NO or NO_2 zero correction used when processing data.
Zero (init)	NO or NO_2 zero derived from readings prior to the injection of NO_x in the run. Source code of "21" means derived from strip chart data. If given as "zero used (init)", it means this was used to correct the data. Not applicable in all cases.
Zero (end)	NO zero derived from end of run, based on assumption that O_3 suppresses NO. This was not used to correct the data. Source code "1" means derived from data. See Section 4.2.5.
U.Zero	Uncertainty in the NO or NO_2 zero correction used. See text. Source code "29" means the uncertainty was the difference between the two derivation methods (initial vs end); "39" means a default uncertainty was assumed for the chamber.
NO2.Ef.	NO_2 converter efficiency used when processing the data. Source code "20" means derived from calibration data (Table B-2).
U.NO2.Ef (fit)	Uncertainty in NO_2 converter efficiency derived from consistency of results of converter efficiency checks (Table B-2).
U.NO2.Ef (used)	Uncertainty in NO_2 converter efficiency we recommend using for uncertainty estimates, and which were used to derive overall uncertainty in initial NO_2 and NO_x concentrations. Always $\geq$ U.NO2.Ef (fit).
Init Conc	Initial NO or NO2 concentration. Source code "1" means derived directly from first measurement before or after lights on; "2" means adjusted or estimated to fit data around the time the run started. Uncertainty derived from uncertainties in span factor and zero correction. For NO_2, the uncertainty in the converter efficiency was treated as an additional source of uncertainty in the span factor.

Table 2 (continued)

Column Label	Description
	Spreadsheets = "cham-Prds": Summary of O_3 and PAN data (EC and ITC) **Spreadsheets = "cham-O3": Summary of O_3 data** (ETC, DTC, XTC)
RunID	Chamber ID and run number
Inst	Instrument number used for O_3 or PAN. (If zero or blank, instrument ID is not in the data set.) Note, however, that instrument "2000" was almost certainty the instrument used in the earlier EC runs.
O_3 Zero	Zero correction for O_3. Source code of "23" means it was checked or derived by examining the O_3 data at the beginning of the run, in the presence of excess NO.
O_3 U.Zero	Uncertainty in O_3 zero correction. A source code of "27" means that if there is a nonzero correction, the uncertainty is assumed to be the same as the correction. A minimum uncertainty of 5 ppb is assumed.
O_3 Fac	Span factor for O_3 instrument. Source code of "20" means factor taken from calibration data (Table 7). Source code of "10" means the factor was in the original data file for the run, but the calibration data supporting it could not be found.
O_3 U.Fac	Estimated uncertainty for span factor for O_3 instrument. Source code of "20" means it was derived from precision of calibration data (Table 7). Source code of "38" means it was estimated for this group of runs.
Max O_3	Maximum O_3 concentration in run. O_3 data were examined and anomalous points flagged and not used when determining the maximum. The uncertainty in the O_3 maximum was based on estimated uncertainties in span factors and zero corrections.
PAN Cal	Calibration number for PAN (see Section 4.4) from original run data set. Calibration number of "0" means this information was not in the data set.
PAN nP	Number of data points for PAN during the irradiation.
PAN Max	Maximum PAN concentration in run. PAN data were examined and anomalous points flagged and not used when determining the maximum.

Table 2 (continued)

Column Label	Description
	Spreadsheets = "cham-VOC": Summary of Reactive Organics Injected. (Note: only VOC reactants present at the start of the irradiation at sufficient concentrations to affect model simulations are included in the summary. Initial CO is also included if it is greater than 10 ppm.)
RunID	Chamber ID and run number
InitC	Initial reactant concentrations in ppmC. Uncertainty is based on uncertainties for individual species. No uncertainty is given if uncertainty could not be determined for all the VOC reactants.
OH React	Initial OH reactivity measured as propene equivalents, computed as discussed above. The first line if the spreadsheet gives the OH rate constant used for propene ("Standard kOH"). The rate constant for the other VOCs are from the updated SAPRC mechanism (Carter, 1993).
Initial VOC i	The following information is given for each injected VOC in the run. The VOCs are listed in order of species type, i.e., in the order they appear in Table 5. All the injected VOCs are listed for the EC runs; the first 13 are listed for the ITC runs.
DMSname	Species name as it is used in the data sets. See Table 5 if the identity of the species is not obvious from the name.
Conc.	Initial concentration of the species in ppm. The injected VOC data was examined for all the runs, and the initial reactant concentrations were adjusted to be consistent with the data profile as a whole if the time = 0 concentrations in the data set appeared to be inappropriate.
Unc.	The uncertainty in the initial reactant concentration from the uncertainty in the GC calibration factor at the time it was measured. No value means the instrument used could not be identified, or the calibration factor for the species is unknown for the time of the measurement.
Note.	Note indicating the status of the calibration data and ability to estimate calibration uncertainty. The codes used are as follows: 20 — The applicable calibration data are available and the calibration factor and its uncertainty could be derived from it (see Table B-3). NoFac — The calibration factor actually used for the run is not known, but the probable instrument used was identified and the applicable calibration data are given in Table B-3. The relative uncertainty was estimated based on the uncertainty of the calibration factor from Table B-3. However, the data could not be corrected to be consistent with the current best estimate calibration factor.

Table 2 (continued)

Column Label	Description
	NoAsn The instrument used for the run could not be identified or the calibration factor at the time of the run is unknown. The data were not corrected and uncertainty is given.
	Ambig The instrument used for this measurement was not identified in the run’s data set, and more than one instrument or calibration factor was identified as possibly being used. The data were not corrected. The relative uncertainty in the calibration factor was estimated using the largest of the relative uncertainties of the possible calibration factors.
	Late The run was carried out too long after the last applicable calibration for this instrument for a reliable determination of the factor. The data were not corrected, but the uncertainty in the factor was used. The uncertainty estimate may be low.
	Spreadsheets = "cham-prms": Constants used in calculations
(various parameters)	See spreadsheets. These were used in calculations in the spreadsheets, as discussed in applicable sections in the text.
	EC Spreadsheets:
	Spreadsheet = "EC-Lite": Light Characterization Information for EC Runs
RunID	Chamber ID and run number
k1 Set	Grouping of runs for determining the light intensity. See Sections 5.1.1 through 5.1.3.
Note	Note on light characterization data for this run. See the bottom of the file for the explanation of the codes.
SSpower	Average solar simulator power (KW). "%sd" is percent standard deviation.
UVrad	Average UV radiometer readings. "%sd" is percent standard deviation.
Used for k1	"SS" means regression based on solar simulator power was used to estimate the NO_2 photolysis rate (k_1) for this run from results of actinometry experiments. "UV" means regression on UVrad was used. See Section 5.1.3
k1	Recommended NO_2 photolysis rate for modeling (min^{-1}).

Table 2 (continued)

Column Label	Description
unc k1	Uncertainty in recommended NO_2 photolysis rate based on the uncertainty in the estimate in the regression. See Section 5.1.3.
SD Set	Run grouping used do determine the smoothed spectral distribution recommended for use when modeling. See Section 5.1.4.
DayNo	Run day used when deriving smoothed spectral distribution. Number of days after 12/31/69.
WL Err	Estimated correction when deriving spectral distribution. The spectral data in the spreadsheet have not been corrected for wavelength errors, so this correction should be applied to these data before deriving the detailed spectrum to use for modeling.
Smoothed Spectral Distribution	Recommended spectral distribution derived from the regressions against DayNO for all spectral distributions in this "SD set". Relative values are given for the various wavelengths, where "SD 300" means relative spectral distribution at 300 nm, etc.
Corrected Spectral Distribution	Measured Spectral for run, with all corrections applied except for wavelength offset errors.
INST or Orig. Cal	"McPH" indicates McPherson instrument was used. "1976" or "1982" means the SPEX was used and data for run were originally processed using the 1976 or the 1982 calibration, respectively. See Section 5.1.4
Raw Spectral Distribution	Spectral data without any corrections.
	Spreadsheet = "EC-Misc": Miscellaneous information for EC Runs
RunID	Chamber ID and run number
Samp. Rate	Sampling rate (l/min) which was in the data set for the run. (These were not evaluated.)
Nominal RH	The intended or measured RH for the run. The wet/dry bulb RH is given if available, otherwise the intended RH is given.
Obs. RH	Wet/dry bulb RH. Taken from log book (not recomputed).
Brady RH	The first column is the RH measured by the Brady Array. The second is the difference between the Brady RH and the nominal RH. The wet/dry bulb RH is considered more reliable (see Section 6.2.1).

Table 2 (continued)

Column Label	Description
CO	The initial CO concentration in ppm.
Chart C0	The initial NO and NO_2 concentrations in uncalibrated units taken from the strip chart. These were used to derive the NO and NO_2 zero corrections as discussed in Section 4.2.5.
(data not printed)	The spreadsheet has additional columns with data which were used in processing the runs for the data base, but are probably not of direct utility for the modeler. They are retained in the data sets for internal SAPRC use.
	ITC Spreadsheets:
	Spreadsheet = "ITC-Misc": Miscellaneous information for ITC Runs
RunID	Chamber ID and run number
%Lts	Percent lights used
k1	NO_2 photolysis rate assigned to run. See Section 5.2.2.
Bag No.	Teflon reactor used for run. This may be useful in determining wall characterization parameters when modeling run. See Section 6.4
Nominal RH	The intended percent relative humidity for the run. "50" used for all ITC runs.
Dry Temp	Dry bulb temperature (degrees F).
Wet Temp	Wet bulb temperature (degrees F)
dr-wt	Difference between dry and wet bulb temperature, which is used to calculate RH.
Log Book RH	Relative humidity given in log book. In some cases it is computed from the wet/dry bulb temperatures, in other cases it is the nominal or desired RH. See Section 6.2.2.
Chart C0	Same as Chart C0 in "EC-Misc".

Table 2 (continued)

Column Label	Description
	ETC Spreadsheets:
	Spreadsheet = "ETC-misc": Miscellaneous information for ETC runs (Other columns, not listed below, were used internally when processing data.)
RunID	Chamber ID and run number
k1	NO_2 photolysis rate assigned to run. See Section 5.2.2.
CO	CO measurement made at the start of the run and entered in the log book. (In most cases, this information is in the comment records in the run data file.)
Dilution	Derivation of dilution rates for the individual runs. See Section 6.3.2
Chart C0	Raw initial NO and NO_2 concentrations derived from the strip charts. See Section 4.2.5
	Spreadsheet = "ETC-k1": Actinometry results. Contains data discussed in Section 5.2.2
	DTC Spreadsheets:
	Spreadsheet = "DTC-misc": Miscellaneous information for DTC runs (Other columns, not listed below, were used internally when processing data.)
RunID	Chamber ID and run number
k1	NO_2 photolysis rate assigned to run. See Section 5.2.2.
CO	CO measurement made at the start of the run and entered in the log book. (In most cases, this information is in the comment records in the run data file.)
	Spreadsheet = "DTC-dil": Dilution information Derivation of dilution rates for the individual runs. See Section 6.3.2.
	Spreadsheet = "DTC-k1": Actinometry results. Contains data discussed in Section 5.2.2

Table 2 (continued)

Column Label	Description
	XTC Spreadsheets:
	Spreadsheet = "XTC-misc": Miscellaneous information for XTC runs (Other columns, not listed below, were used internally when processing data.)
RunID	Chamber ID and run number
k1	NO_2 photolysis rate assigned to run. See Section 5.2.2.
Temperature	Average temperature for runs. Note that temperatures for runs XTC081 through XTC086 were rejected because of temperature probe problems. See footnotes in spreadsheet and Section 6.1.6. Plots of average temperatures against run number are given in the bottom of the spreadsheet.
Dilution	Derivation of dilution rates for the individual runs. See Section 6.3.2.
	Spreadsheet = "XTC-k1": Actinometry results. **Spreadsheet = "XTC-LiCo": Relative light intensities derived from LiCor.** **Spreadsheet = "XTC-LUni": Results of light uniformity tests.** Contains data discussed in Section 5.3.

base, it contains additional information, as summarized in Table 2. This includes the project report code, the classification of the run from the modeler's perspective, the run conditions and data quality, and its status in the data base. The project reports referenced by the codes in the spreadsheets are given in Table 3, and the modeling classification codes are given in Table 4. The master spreadsheets for the six chambers are given in Tables A-2 through A-7.

For each chamber there is also a modelers classification summary spreadsheet. This gives for each run the classification codes and data base status from the master spreadsheet, and the following additional information which may be useful to the modeler for assessing the potential role of the run in the evaluation project:

Initial NO_x and Estimated Uncertainty. The initial NO_x concentration is computed from the initial NO plus the initial NO_2. The uncertainty is estimated from the reproducability in NO span calibration data, uncertainties in zero corrections, and, where applicable, uncertainties in NO_2 converter efficiencies.

Table 3. Listing of original project reports documenting SAPRC chamber runs which are potentially useful for mechanism evaluation.

Code	Chambers	Reference	Description
EPA-79	EC	Pitts et al. (1979)	Documents earlier EC runs carried out specifically for mechanism evaluation. Most complete description of SAPRC instrumentation and laboratory procedures up to that date.
ARB-83a	EC, ITC	Pitts et al. (1983)	A series of tracer - NO_x air runs were carried out to evaluate the chamber radical source. Also describes alkane -NO_x and benzene - NO_x runs.
ARB-83b	ITC	Atkinson et al. (1983)	A series of incremental reactivity experiments were carried out at high ROG/NO_x ratios.
EPA-84	ITC, OTC	Carter et al. (1984a)	A series of multi-day surrogate - NO_x experiments were conducted to evaluate mechanisms' predictions of multi-day effects.
AF-84	ITC	Carter et al. (1984b)	A series of experiments were conducted to evaluate mechanisms for selected alkanes, alkylbenzenes, naphthalenes, and other components of jet fuels. Also experiments with synthetic fuels.
ARB-96	ITC, OTC	Carter et al. (1986)	A series of multi-day surrogate - NO_x experiments were conducted to evaluate the effects of methanol or methanol + formaldehyde substitutions.
AF-87	ITC	Carter et al. (1987)	A limited number of experiments were conducted to evaluate mechanisms for components of jet exhaust, including 1-alkenes, acrolein, and synthetic exhaust.
EPA-87	ITC	Carter (1987)	Experiments were conducted to evaluate the O_3-forming potentials of n-pentadecane and representative printing oils, relative to ethane. Consists primarily of high ROG/NO_x incremental reactivity runs.
DOW-92	ETC	Carter et al. (1992)	The incremental reactivities of several volatile silicone compounds were determined at high and low ROG/NO_x conditions.
EMIR-93	ETC	Carter et al. (1993a)	The incremental reactivities of a wide variety of compounds were determined at low ROG/NO_x conditions.
SOS-93	ETC	Carter et al. (1993b)	The incremental reactivity of isoprene was determined at low ROG/NO_x conditions. (Details of the procedures and data analysis are given in EMIR-93.)
CMA-93	ETC, DTC, XTC, OTC	Carter et al. (1993c)	Both incremental reactivity and single compound - NO_x experiments were conducted to evaluate mechanisms for acetone. Experiments involving formaldehyde and acetaldehyde are also described. (Details of the procedures and data analysis are given in EMIR-93.)
UNC	ITC	Jeffries et al. (1990)	This report primarily discusses work carried out at UNC, but includes a discussion of several ethene - NO_x, formaldehyde -NO_x and other experiments carried out in the ITC when Dr. Ken Sexton of UNC was visiting SAPRC.
ERCT-94	ETC, DTC,	Carter et al. (1994b)	Incremental reactivities of selected compounds were determined using various ROG surrogates and NO_x levels.
NREL-94	ETC, DTC, XTC, OTC	Carter et al. (1994a)	Experiments and model simulations were conducted to assess the effect of light source and chamber on mechanism evaluation results. New experiments for selected compounds and mixtures conducted in the ETC, DTC and XTC. EC and ITC runs also modeled. Radical source chamber effects assignments were re-evaluated for all chambers.

Table 4. Codes used in evaluation classification for runs in data base.

Code	Description
	Species or Mixture Code
(VOC name)	8-character detailed model species name used to designate single compounds. See Table 5 for list of species names.
CHAR-0	Pure air irriadiation
CHAR-1	Tracer - NOx - air
CHAR-2	Ozone dark decay
CHAR-3	Acetaldehyde-air
CHAR-4	Formaldehyde-air
CHAR-5	Tracer-NOx + CO
CHAR-6	Biacetyl irradiation
CHAR-6	Ozone light decay
MIX-A	Mixture of Alkanes
MIX-E	Mixture of alkEnes
MIX-R	MIxture of aRomatics
MIX-AE	Mixture of alkanes and alkenes
MIX-AO	Mixture of alkanes and oxygenates
MIX-EO	Mixture of alkenes and oxygenates
MIX-RO	Mixture of aromatics and oxygenates
MIX-AR	Mixture of alkanes and aromatics
MIX-ER	Mixture of alkenes and aromatics
SURG-7	Seven hydrocarbon mix used in EC runs.
SURG-4	Standard 4-component Mini-Surrogate #1 (ARB-83b)
SURG-4R	Mini-Surrogate #1 with VOC changed
SURG-8	"8-Component "SAI" surrogate"
SYNFUEL	Syntheticic Air Force jet fuel
SYNEXH	Synthetic Air Force jet exhaust
	Run type codes.
(blank)	Compound or mixture by itself in the presence of NO_x. No special conditions.
A	Compound added to NOx-air irriadiation
M	Compound in mixture with other compound (R1)
R3	Incremental reactivity — compound added to a 3-component surrogate
R4	Incremental reactivity — compound added to a 4-component surrogate
R	Incremental reactivity — compound added to a full surrogate
MD	Multi-day run

This is discussed in Section 4.2. In most cases, especially for the low NO_x runs, the zero correction is the major source of uncertainty.

Initial Reactive Organic (ppmC and OH Reactivity) and Estimated Uncertainty. The initial reactive organics concentration is given as ppm Carbon or as OH reactivity, the latter being expressed as propene equivalents (i.e., as the compound's concentration multiplied by its OH radical rate constant divided by the OH radical rate constant for propene). The OH rate constants used are based on current evaluations, and are given in a spreadsheet distributed with the data base. If the initial reactant columns are blank, the initial concentrations of one or more of the added organics could not be readily determined, and the run is either unmodelable, or, for certain complex mixtures such as the synthetic fuels, the initial reactants could be estimated as discussed in the original project report documenting the run. The uncertainties reflect calibration precision uncertainties only. In some cases footnotes are given if there are problems with the calibration data. The modeler should use prudence when modeling runs where numerical uncertainties are not given for initial organic reactants. However, for most EC runs prior to approximately EC400, instruments were not identified in the data sets, and in many cases we were unable to unambiguously identify which instrument was used for specific compounds. The calibration data have been of acceptable quality in most of those cases, but this could not be established. See Section 4.3 for a discussion of the GC measurements.

OH Reactivity / NO_x Ratio. The concentration ratio of reactive organics to NO_x is a useful indicator of the reactivity of the run in terms of rate of NO oxidation and ozone formation, and whether the run reaches an ozone maximum. However, this ratio is not particularly meaningful when comparing runs with different organics, unless some means is used to account for their differences in reactivity. Reactivity can be measured in a number of ways, but the simplest and to some extent the least controversial is to use the rate at which the VOC reacts, which for most VOCs is determined primarily by the OH radical rate constant. Thus the table includes the ratios of OH reactivities as propene equivalents to initial NO_x for the runs. In the case of propene, a ratio of 1 is usually not quite enough to achieve an O_3 maximum, while a ratio of 2 is. However, this varies among VOCs, because other factors also affect reactivity (Carter and Atkinson, 1989).

Duration of the experiment. The length of time of the irradiation, or the number of hours for which useable data were taken after the beginning of the irradiation, whichever is smaller. For O_3 decay experiments, the length of time for which O_3 decay data were taken is given.

Maximum O_3 concentration. The maximum ozone concentration in ppb. If this field is blank, it is not relevant in this type of experiment. (E.g, for CHAR-1 runs NO is always in excess and significant O_3 is not formed.) The time at which the O_3 maximum occurred is also shown. If this field is blank, the time of the maximum is the same as the duration of the experiment, i.e., the run did not achieve a "true" maximum. This information is useful for producing statistical summaries of ability of models to predict maximum ozone concentrations. The ozone data in each run were checked and data points which appeared to be anomalous were not used in deriving these quantities.

NO Oxidation Rates. The average rates of change of $[O_3]$-[NO] for the first hour of the run, and for the period of time between the start of the run and the time $[O_3]$-[NO] achieves half its maximum value. If half the maximum $[O_3]$-[NO] occurred during the first hour, the data in the first field is the average rate of change of $[O_3]$-[NO] up to the time of the half maximum. This information is useful for producing summaries of the ability of models to predict the rate of NO oxidation and ozone formation. The ozone data in each run were used to produce an $[O_3]$-[NO] data channel, and these data were then checked and data points which appeared to be anomalous were deleted before deriving these quantities.

Special Conditions. Code for special run conditions which must be taken into account when modeling the run.

Chamber Effects Characterization Sets. The classification of the run from the point of view of chamber effects characterization, where applicable. This is based on the approach used by Carter et al. (1994a), which the evaluator may wish to update. See Section 6.4.

Modelability. This column indicates cases where it was not possible to carry out a model simulation of the run using the data and software in the distributed data base. Codes in this column indicate that either there is some necessary information missing, or we do not have a recommended set of chamber-dependent parameters for modeling runs in this characterization set, or that some other problem was encountered. See Sections 2.4.5 and 6.4.

Inp File. Blank in this column indicates that the run data set has enough information to create a complete model simulation input file for the run. Note that the run does not necessarily indicate that the run is judged to be modelable.

S90 Calc (EC and ITC only). Blank in this column indicates that the run could be simulated (though not necessarily with acceptable performance) using the SAPRC-90 mechanism (Carter, 1990), updated as discussed by Carter (1994). Note that the mechanism may fail to simulate a run containing compounds, such as certain siloxanes, for which it has no mechanistic assignments.

A special spreadsheet has been prepared where the modeler’s spreadsheets are combined and then sorted by modeling classification code and data base status. This is useful for determining which runs have been given the various classification codes. A printout of this spreadsheet is given in Table A-1. This will be updated when runs from additional chambers are added to the data base.

As indicated in Table 2, a number of other spreadsheets have been prepared for the chambers whose runs have been prepared for the data base. These give summaries about ozone, NO_x, VOC, PAN, light characterization, run conditions, and other information. Table 2 gives the specific information available in each spreadsheet.

2.3 Types of Measurement Data

Most of the measurement data taken during a chamber run are given as arrays of values as a function of time. Such arrays, and the parameters associated with them, are referred to as "channels" of data in the subsequent discussion. (Spectral distributions in the EC are also included as "channels", though in this case the data are as functions of wavelength rather than time.) Each channel is identified by a species name indicating the measurement type, an instrument ID number indicating which instrument was used (or "0" if the instrument used is unknown), and, if the run is in a chamber which has more than one "side", the side number. (The latter is applicable only for the OTC and DTC.) In addition to the measurement data as a function of time, the data sets may have various other information concerning the channel, which are discussed below.

A consistent set of 8-character names is used to identify the various types of measurement data in the data base. These are listed in Table 5. Of course, not all runs have all the possible types of data which are listed, since not all types of measurements were made for each run. In addition, the table includes measurement types associated with SAPRC experiments which will be included in later releases of the data base, but are not on the runs in the current release.

Each instrument used to produce the measurement data listed in Table 5 are summarized in Table 6, along with the names of the species they are used to measure. Note that each instrument is identified by a 4-digit code, referred to as the "instrument ID number". This is how the instrument identification is keyed in the data base, and reference is given to the instrument ID number in the tables of calibration data and other discussions of the individual instruments.

For the EC runs prior to around EC400, the instrument identifications were not included in the data sets at the time the runs were carried out. Based on the comments in the log books, we were able to identify the instruments used to measure O_3 and the NO_x species, and these were entered into the data base as part of this program. Attempts were made to identify the GC instruments used, but the variety of GC instruments used at the time, with different instruments being capable of measuring the same species, made it difficult to make positive assignments in many cases. This is discussed further in Section 4.3. Channels with unknown instruments or whose instrument could not be unambiguously identified were given instrument ID numbers of 0, 1, or 2. The latter two were used if more than one unknown instrument was used for a particular type of measurement.

Table 5. Types of measurement data which are included with runs in the data base.

Name	Description
	Inorganic Species
O3	Ozone
NO	Nitric Oxide
H2O	Water
H2O2	Hydrogen Peroxide
HNO3	Nitric Acid
NO2-UNC	NO_2 from NOx-Box
NOX-UNC	NO_x from NOx-Box
CO	Carbon Monoxide
	Physical Parameters
T	Chamber Temperature
DEW-PT	Dew Point
REL-HUM	Relative Humidity
UV-RAD	UV Radiometer Reading (OTC runs)
TSR	Broadband Radiometer Reading (OTC and XTC)
SSPOWER	Solar Simulator Power (EC runs)
HCHO-VOL	Sampling volume for HCHO
Tmodel	Corrected chamber temperature fits recommended for modeling [a]
	Spectral Distributions [b]
Sdist	Corrected spectral distribution [c]
RawSdist	Uncorrected spectral distribution
ModSdist	Smoothed, corrected spectral distribution recommended for modeling [c].
Sd-hhmm	Measured chamber spectral distribution for clock time = hhmm. [d]
tSD-hhmm	Measured outdoor global (unshaded) spectral distribution for time = hhmm. [e]
sSd-hhmm	Measured outdoor shaded (diffuse) spectral distribution for time = hhmm. [e]
	Organic Species
METHANE	Methane
ETHANE	Ethane
PROPANE	Propane
N-C4	n-Butane
N-C5	n-Pentane
N-C6	n-Hexane
N-C7	n-Heptane
N-C8	n-Octane
N-C9	n-Nonane
N-C10	n-Decane
N-C14	n-Tetradecane
N-C15	n-Pentadecane
2-ME-C3	Isobutane
2-ME-C4	Iso-Pentane
22-DM-C3	Neopentane
23-DM-C4	2,3-Dimethyl Butane
224TM-C5	2,2,4-Trimethyl Pentane
CYCC6	Cyclohexane

Table 5 (continued)

Name	Description
ME-CYCC6	Methylcyclohexane
ET-CYCC6	Ethylcyclohexane
ETHENE	Ethene
PROPENE	Propene
1-BUTENE	1-Butene
1-HEXENE	1-Hexene
1-C9-OLE	1-Nonene
ISOBUTEN	Isobutene
T-2-BUTE	trans-2-Butene
C-2-BUTE	cis-2-Butene
13-BUTDE	1,3-Butadiene
ISOPRENE	Isoprene
A-PINENE	a-Pinene
B-PINENE	b-Pinene
D-LIMONE	d-Limonene
3-CARENE	3-Carene
SABINENE	Sabinene
BENZENE	Benzene
TOLUENE	Toluene
C2-BENZ	Ethyl Benzene
I-C3-BEN	Isopropyl Benzene
O-XYLENE	o-Xylene
P-XYLENE	p-Xylene
M-XYLENE	m-Xylene
135-TMB	1,3,5-Trimethyl Benzene
123-TMB	1,2,3-Trimethyl Benzene
124-TMB	1,2,4-Trimethyl Benzene
TETRALIN	Tetralin
NAPHTHAL	Naphthalene
ME-NAPH	Methyl Naphthalene
23-DMN	2,3-Dimethyl Naphth.
STYRENE	Styrene
ACETYLEN	Acetylene
MEOH	Methanol
ETOH	Ethanol
I-C3-OH	Isopropyl Alcohol
ME-O-ME	Dimethyl Ether
MTBE	Methyl t-Butyl Ether
ETO-ETOH	2-Ethoxy-Ethanol
CARBITOL	2-(2-Ethoxyethoxy) EtOH
ETOX	Ethylene Oxide
PROX	Propylene Oxide

Table 5 (continued)

Name	Description
FURAN	Furan
THIOPHEN	Thiophene
PYRROLE	Pyrrole
FORMALD	Formaldehyde
ACETALD	Acetaldehyde
PROPALD	C3 Aldehydes
BUTYRALD	Butyraldehyde
GLYCLALD	Glycolaldehyde
ACROLEIN	Acrolein
METHACRO	Methacrolein
BIACETYL	Biacetyl
VALERALD	Valeraldehyde
BENZALD	Benzaldehyde
M-TOLALD	m-Tolualdehyde
ACETONE	Acetone
MEK	C4 Ketones
2-C5-KET	2-Pentanone
3-C5-KET	3-Pentanone
2-C6-KET	2-Hexanone
3-C6-KET	3-Hexanone
MVK	Methyl Vinyl Ketone
NOPINONE	Nopinone
PHENOL	Phenol
O-CRESOL	o-Cresol
M-CRESOL	m-Cresol
P-CRESOL	p-Cresol
CONO2	Methyl Nitrate
C2ONO2	Ethyl Nitrate
1-C3ONO2	1-Propyl Nitrate
2-C3ONO2	2-Propyl Nitrate
C4ONO2	Butyl Nitrates
1-C4ONO2	1-Butyl Nitrate
2-C4ONO2	2-Butyl Nitrate
2-C5ONO2	2-Pentyl Nitrate
3-C5ONO2	3-Pentyl Nitrate
2-C6ONO2	2-Hexyl Nitrate
3-C6ONO2	3-Hexyl Nitrate
2-C7ONO2	2-Heptyl Nitrate
3-C7ONO2	3-Heptyl Nitrate
2-C8ONO2	2-Octyl Nitrate
3-C8ONO2	3-Octyl Nitrate
4-C80NO2	4-Octyl Nitrate

Table 5 (continued)

Name	Description
NO2-BENZ	Nitrobenzene
O-NO2TOL	o-Nitrotoluene
M-NO2TOL	m-Nitrotoluene
P-NO2TOL	p-Nitrotoluene
23-HNTOL	2,3-Hydroxy Nitrotoluene
25-HNTOL	2,5-Hydroxy Nitrotoluene
32-HNTOL	3,2-Hydroxy Nitrotoluene
43-HNTOL	4,3-Hydroxy Nitrotoluene
PAN	Peroxyacetyl Nitrate
PPN	Peroxypropionyl Nitrate
MA-PAN	Methacrolein PAN Analogue
CCL4	Carbon Tetrachloride
CL2IBUTE	3-(Cl-methyl)-3-Cl Propene
SI2OME6	Hexamethyldisiloxane
(SIOME)4	D4 Cyclosiloxane
(SIOME)5	D5 Cyclosiloxane
SI2OMEOH	Pentamethyldisiloxanol
	Measurements used to compute data
NO-K1	NO from k_1 Quartz Tube (OTC runs)
NO2-K1	NO_2 from k_1 Quartz Tube (OTC runs)
HCHOSAMP	Dasgupta Formaldehyde in sample mode
HCHOCAL	Dasgupta Formaldehyde in calibrate mode
HCHOZERO	Dasgupta Formaldehyde in zero mode
	Computed Quantities
TOT-NO3	Total Organic Nitrates [f]
NO2-CORR	NO2-UNC - TOT-NO3 [f]
K1	NO2 Photolysis Rate calculated from NO-K1 and NO2-K1 [f]

[a] Computed quantity which was derived in this work. See Section 6.1.2.

[b] Spectral distribution data are given as a function of wavelength in Angstroms rather than time. See Section 5.

[c] Computed quantity which was derived in this work. Both wavelength and instrument response corrections have been applied. Applicable to the EC only. See Section 5.1.5

[d] Applicable to the XTC. See Section 5.3.

[e] Applicable to the OTC. See Carter et al. (1994a). A discussion of the OTC light characterization data and procedures is beyond the scope of this document.

[f] Computed quantities which were derived previously and not evaluated in this work.

Table 6. Instruments used to produce measurement data for runs in the data base.

ID	Label	Description	Status [a]
		Ozone Monitors	
1070	D-1070	DASIBI O3 MONITOR; ID:1070	1
1140	D-1140	DASIBI O3 MONITOR; ID:1140	1
1212	D-1212	DASIBI O3 MONITOR; ID:1212	1
1413	D-1413	DASIBI O3 MONITOR; ID:1413	1
3378	D-3378	DASIBI O3 MONITOR; ID:3378	1
1790	D-1790	DASIBI O3 MONITOR; ID:1790	1
8410	MO3-8410	MONITOR LABS 8410 O3 ANALYZER (CHEMIL.)	-
4450	MEL-O3	MELOY O3 ANALYZER; SN 2C242	-
4900	B-O3-1	BENDIX O3 ANALYZER MD5513340-X SN32787-5	-
6120	REM-O3	REM O3 ANALYZER; CHAMP STATION	-
		NO$_x$ Monitors	
1510	T 14B-1	TECO 14B-1 NO-NOX ANALYZER	1
1520	T 14B-E	TECO 14B-E NO-NOX ANALYZER	1
1530	T 14B-3	TECO 14B-3 NO-NOX ANALYZER	1
1531	T14B3/N	TECO 14B-3 NO-NOX ANAL. W/NYLON FILTER	1 [b]
1540	TECO-42	TECO MODEL 42 NO-NO2-NOX ANALYZER	1
1625	C-1600A	COLUMBIA 1600 NO-NOX ANALYZER; SN 8581	1
1626	C-1600B	COLUMBIA 1600 NO-NOX ANALYZER; SN11506A	1
1627	C-1600C	COLUMBIA 1600 NO-NOX ANALYZER; SN11544A	1
1628	C-1600D	COLUMBIA 1600 NO-NOX ANALYZER; SN11903	1
4600	B-NOX-1	BENDIX 8101BX NOX ANALYZER; SN 300038-2	0
4150	B-NOX-2	BENDIX NOX ANALYZER MD5513802; SN 31157	0
		Light Monitors	
1244	EG&G	EG&G UV RADIOMETER	0
4130	EPPLEY-1	ARB TRAILER; EPPLEY 11692 UV RADIOMETER	0
4131	EPPLEY-2	EPPLEY 14290 UV RADIOMETER; CHAMP ROOF	0
4132	EPPLEY-3	EPPLEY TOTAL SOLAR RADIATION	0
4133	EPPLEY-4	EPPLEY TOTAL SOLAR RADIATION #2	0
		Humidity	
0880	EG&G-DP	EG&G DEW POINT HYGROMETER	0
		Temperature	2
3790	ANA-TEMP	ANALOGIC TEMP. MONITOR; SN1223790	
1900	KDAC-T0	KDAC TEMPERATURE CHANNEL #0	
1909	KT0-AMB	KDAC TEMP #0 - OUTSIDE SHADE (OTC-92 TLOC1)	
1910	KDAC-T1	KDAC TEMPERATURE CHANNEL #1	
1913	KT1-BNS	KDAC TEMP #1 - IN BAG W/O SHIELD (OTC-92 TLOC2)	
1915	KT1-NS	KDAC TEMP #1 - IN SAMPLE LINE (OTC-92 TLOC3)	
1920	KDAC-T2	KDAC TEMPERATURE CHANNEL #2	
1925	KT2-NS	KDAC TEMP #2 - IN SAMPLE LINE (OTC-92 TLOC3)	
1928	KT2-STAG	KDAC TEMP #2 - IN UNFLUSHED SAMPLE LINE (OTC-92 TLOC3)	

Table 6 (continued)

ID	Label	Description	Status [a]
1930	KDAC-T3	KDAC TEMPERATURE CHANNEL #3	
1932	KT3-BS	KDAC TEMP #3 - IN BAG WITH SHIELD	
1933	KT3-BNS	KDAC TEMP #3 - IN BAG W/O SHIELD	
1940	KDAC-T4	KDAC TEMPERATURE CHANNEL #4	
1941	KT4-LRM	KDAC TEMP #4 - LAB ROOOM AIR	
1944	KT4-FS	KDAC TEMP #4 - HCHO SAMPLE LINE	
1945	KT4-NS	KDAC TEMP #4 - O3/NOX SAMPLE LINE	
1946	KT4-CRM	KDAC TEMP #4 - CHAMBER ROOOM AIR (XTC)	
1950	KDAC-T5	KDAC TEMPERATURE CHANNEL #5	
1951	KT5-LRM	KDAC TEMP #5 - LAB ROOOM AIR	
1955	KT5-NS	KDAC TEMP #5- O3/NOX SAMPLE LINE	
1956	KT5-CRM	KDAC TEMP #5 - CHAMBER ROOOM AIR (XTC)	
1957	KT5-AP	KDAC TEMP #5 - ASPERATED TEMP PROBE.	
1800	DORIC-1	DORIC TEMPERATURE INDICATOR; SN 61479	
1805	DT1-NS	DORIC TEMP - O3/NOX SAMPLE LINE	
		Carbon Monoxide	
3003	D-3003	DASIBI ID# 3003 IR CO MONITER; SN 158	2
-		BECKMAN 6800 CO ANALYZER	[c]
		GC-FID	
2290	DMS-2	VAR-1400#8; DIMETHYLSULFOLANE; FID	1
2291	GSQ	VAR-1400#8; 30M GSQ MEGABORE; FID; TRAP	1
2200	DMS-1	VAR-1400#1; DIMETHYLSULFOLANE; FID	1
2920	10’C-600	VAR-1400#3; 10’ 10% CARBOWAX-600; FID	1
2922	5’C-600B	VAR-1400#3; 5’ 10% CARBOWAX-600; FID	-
2925	10’C600C	VAR-1400#4; 10’ 10% CARBOWAX-600; FID; TRAP	1
2930	5’ C-600	VAR-1400#2; 5’ 5% CARBOWAX-600; FID	1
1403	3-PART	VAR-1400#2; 3-PART; FID	1
1405	SP-1000	VAR-1400#5; SP-1000; FID; TENAX	2
2100	PN-1	VAR-1400#6; POROPAK-N; FID	1
2190	PN-2	RM-103; 5’ POROPAK-N GC; FID	-
2195	PN-3	VAR-1400#25; 5’ POROPAK-N; FID	1
2120	PQS-1	VAR-1400#1; POROPAK-QS; FID; TRAP	1
1400	C-20M	VAR-1400#7; C-20M/DC-703; FID; LOOP	1
1402	PN-1400A	VAR-1400#1; POROPAK-N; FID; LOOP	1
2701	SP C-20M	VAR-1400#5; C20M/KOH SUPERPAK; FID; TENAX	1
2702	SP C-II	VAR-1400#5; SUPERPAK-II; FID; TENAX	1
2703	SP 20M	VAR-1400#5; SUPERPAK 20m (SUPERPAK-II?)	0
2650	VAR3700	VAR-3700; SE-54; FID; LOOP	1
2750	SE-52C-2	HP5170A#2; 30M SE-52 QUARTZ CAP;FID;LOOP	1
2850	DB-5C-1	HP5771A#3; 30 M DB-5 QUARTZ CAP;FID;LOOP	1
2500	DB-5 TNX	HP5880; 15 M DB-5 MEGABORE; FID; TENAX	1
2600	HP1 DB5S	HP5890#1; 15 M DB-5 MEGABORE; FID	1

Table 6 (continued)

ID	Label	Description	Status [a]
2603	HP1 DB5L	HP5890#1; 30 M DB-5 MEGABORE; FID; LOOP	1
2601	HP1 DB5T	HP5890#1; ?? M DB-5 MEGABORE; FID; TEXAX	1
2800	HP2 DB5S	HP5890#2; 15M DB-5 MEGABORE; FID	1
2801	HP2 DB5L	HP5890#2; 30M DB-5 MEGABORE; FID	1
2802	HP2 GSQ	HP5890#2; 30M GSQ (PACKED); FID; LOOP	1
2310	TENAX	VAR-1400#6; 10'C-600; FID	[d]
2490	SP-1000	RM-103; SP-1000 GC; FID (TENAX SAMPLING)	-
2196	PN-1400	RM-103; POROPAK-N GC; FID LOOP	-
5710	DB-5C-2	RM-121; 30 M DB-5 QUARTZ CAP; FID #2	-
2110	[PN-1]	[PN-1 by peak height for testing.	0
2928	[C-600]	[10'C-600 by peak height for testing.]	0
		GC-ECD	[e]
2000	ECD-1	RM-121; 12" 5% CARBOWAX-400 GC; ECD	2
4000	ECD-3	RM-101; 24" 5% CARBOWAX-400 GC; ECD	2
2700	HP-ECD1	HP; 5 M HP-1; ECD; LOOP	2
2710	HP-ECD2	HP; DB-5; ECD; LOOP	2
		Formaldehyde	
3000	CA	CHROMOTROPIC ACID HCHO ANALYSIS	2
3001	UCR-DAS	SAPRC DASGUPTA FORMALDHYDE INST.	2
3002	UNC-DAS	UNC FORMALDEHYDE INSTRUMENT	3
		Spectrophotometers	[f]
7001	MC-PHER	MCPHERSON MONOCHROMATOR W. HAMAMATSU PM	
7002	SPEX	SPEX SPECTROMETER WITH 1P28 PM	
7010	LICOR	SAPRC LI-1800 PORTABLE SPECTROMETER	
7011	UNCLICOR	UNC LI-1800 PORTABLE SPECTROMETER	
		Calculated or synthesized	
9900	Corr'd	CORRECTED DATA FROM ANOTHER CHANNEL	
9990	Inj'd	CALCULATED FROM AMOUNT INJECTED	
9991	Est'd	ESTIMATED BASED ON OTHER RUNS WITH SAME INJECTIONS	

[a] Status codes:
- \- The log book for this instrument could not be found.
- 0 Calibration data not evaluated.
- 1 Calibration data for this instrument was evaluated and where appropriate corrections were applied to the data.
- 2 See text for a discussion of this instrument (or series of instruments).
- 3 See Jeffries et al (1990) for a discussion of this instrument.

[b] Uses calibration file of previous instrument

[c] This instrument was used only for earlier EC runs before instruments were identified in the data sets. No ID number or label was assigned. See Section 4.7

Table 6 (concluded)

[d] This may have been used in the earlier EC runs, but no runs were identified as using it.
[e] These instruments were evaluated only for PAN analysis.
[f] Data measured with these instruments are given as a function of wavelength (in Angstroms) rather than time. See Section 5.

Certain runs may also have data types which are not listed in Table 5. For example, many earlier tracer-NO_x runs (type CHAR-1) have a "HYDROXYL" channel, which is computed from the change inthe tracer concentrations in the time step, using the OH rate constants and dilution correction which was current at the time. A number of runs have special data types which were computed from other data types for particular purposes of data analysis. These were not re-evaluated. It is recommended that only data types listed in Table 5 be used for establishing run conditions or evaluating model fits. However, these special data types were not deleted from the runs, since in some cases they may contain information of relevance when the runs are examined on an individual basis.

In some cases more than one instrument was used to measure a particular species. In these cases the channel selected for use for modeling purposes (i.e., for determining run conditions or assessing model performance) is the one with the lowest "priority number" (see Section 2.4.2 and Table 9). (Note that the "priority number" refers to the status of the *data channel* in a run, *not* the run as a whole.) The data from the other channel is retained in the data set and is available for comparison purposes, but is not used in producing any of the summary data in the spreadsheets. The priority number gives an indication of our subjective estimates of the quality of the data in the channel. If there is no reason to suspect the data is more uncertain than usual for this type of measurement, it is given a priority number of "1". If the data have some problems, or if the channel is considered to be of somewhat lower quality than the data from another channel in the run measuring the same species, a priority number of "2" is used. Priority numbers of "3" are used for highly suspect data and "4" is used for data considered to be unusable. (Data with those priority numbers should not be used for modeling.) If there is no clear basis for suspecting problems with the data from either the instruments used to measure the same species, the channel given priority "2" is chosen based on our general judgements on the relative quality of the data from the two instruments. (The software used to prepare the summary data in the spreadsheets and to prepare the model input files will not process data from duplicate channels with equally low priority numbers.)

Not all measurements in the data base are given as a function of time. For example, for EC runs spectral measurements were made (usually) at one time in the run, and an array of relative intensities, given as a function of wavelength, is included in the data set for such runs (see the discussion at the beginning of Section 5, and Section 5.1.4). For many runs, humidity measurements were made only during the pure air fill, and measurements of CO were made only prior to reactant injections and not included as a separate data channel. In these cases, the relevant information is given in the "comments" section of the data sets. The more important of these types of data are also included in the spreadsheets. These are discussed in the relevant sections describing the various data types.

2.4 Distributed Data Files and Programs

The data base consists of various data files and associated utility and modeling programs, which are distributed on IBM-PC compatible diskettes. The files can be installed on any MS-DOS compatible computer with sufficient disk space, and the programs will run on any 386 or better computer with a 387-compatible math co-processor. (A plotting program which requires a VGA-compatible display is also included. See the README file on the first distribution disk for the hard disk space requirements.) The files are in a compressed format, and need to be installed using the installation procedure described in Appendix C. Because of the number and variety of types of files, the recommended installation procedure will place most of the files in various subdirectories. A listing and brief description of the distributed files and programs, and the subdirectories in which we recommend they be placed, is given in Table 7. The files and programs requiring more detailed explanations are described below.

2.4.1 Spreadsheet Files

Several different types of spreadsheet files are included in the distribution. These are distributed in three formats. All the spreadsheets were originally created using Microsoft Excel 5 for Windows, and the .XLS give these files in this format. The .XLS files include, where applicable, the formulas which calculate data which are dependent on (or copies of) other data in the spreadsheets. In general, one .XLS file may have several spreadsheets; for example, all the different types of summary spreadsheets for the EC chamber runs are in the file EC-USE.XLS. In addition, the spreadsheets are also available as ASCII files with comma separated value (CSV) format. In this case there is a single file for each spreadsheet (as indicated in Table 7), and with the formulas replaced by the calculated values. The different types of spreadsheets are summarized below.

Run Summary Spreadsheets. As discussed in Section 2.1, the spreadsheet files contain summary information for all the runs in the data base. The data contained in these spreadsheets are summarized in Table 2.

Actinometry Data Spreadsheets. The spreadsheet files ECK1.XLS and ITCK1.XLS are also in the distribution. These give the detailed data from the NO_2 actinometry experiments in the EC and ITC, respectively, and workups of these data as discussed in Section 5. Comparable information for the ETC, DTC, and XTC chambers are given in the ETC-k1, DTC-k1, or XTC-k1 spreadsheets in the ETC-USE.XLS, DTC-USE.XLS, and XTC-USE.XLS files. (The data are also given in .CSV format.)

Table 7. Description of files distributed with the data base. (See Appendix C for more information on the programs and modeling files.)

Name	Note	Description
Files in Directory = [ROOT]		
_README2 TXT		Summary and brief installation instructions.
INSTALL2 BAT		Batch file to install files on hard disk in this directory structure.
FILES2 TAB		This table in ASCII format.
FILES2 LIS		Listing of files on as they would be in the directory structure after a successful installation.
DISTRUNS LIS		List of RunID's for all runs in distribution.
chamUSE LIS		List of RunID's for all runs in a chamber, where "cham" is EC, ITC, ETC, DTC, or XTC.
DTCUSEAB LIS		List of Run and Side ID's for all DTC runs.
		The following are used for modeling only.
EXAMPLE2 BAT		Batch file to run example model simulations. See comments in file.
MODELING PRM		Defaults and locations of files used by modeling programs
CHA2CHD BAT		Batch file to create the chamber data binary (.CHD) files required by the modeling programs from the chamber data (.CHA) files in the distribution. Uses CHADCONV.
CB4 PRM		Parameters and locations of files for modeling runs using the CB4 mechanisms
SAPRC90 PRM		Parameters and locations of files for modeling runs using the SAPRC-90 mechanism
CB4 EXT	[b]	Listing of calculation numbers for runs modeled using the CB4 mechanisms. Produced by INTRUM. Required by SPL to plot modeling results.
SAPRC90 EXT	[b]	Listing of calculation numbers for runs modeled using the SAPRC-90 mechanisms.
ALLcham BAT		Batch file to run a selected program or batch file for all the runs in an undivided chamber, where "cham" is EC, ITC, ETC, or XTC (not DTC).
ALLDTC1 BAT		As above, program or batch file called for each DTC run.
ALLDTC2 BAT		As above, program or batch file called for each DTC run-side.
Files in Directory = [ROOT]\CHAFILES		
		These contain the chamber data files in ZIP format. Files for individual runs must be manually extracted using PKUNZIP.
ECCHA1 ZIP		Files for EC runs with numbers through 399.
ECCHA2 ZIP		Files for EC runs with numbers 400 and above.
ITCCHA1 ZIP		Files for ITC runs with numbers through 799.
ITCCHA2 ZIP		Files for ITC runs with numbers 800 and above.
ETCCHA1 ZIP		Files for ETC runs with numbers through 299.
ETCCHA2 ZIP		Files for ETC runs with numbers 300 and above.
DTCCHA ZIP		Files for all DTC runs
XTCCHA ZIP		Files for all XTC runs.
Files in Directory = [ROOT]\SHEETS		
RUNSORT XLS		Merged modeler's spreadsheets, sorted by run classification. Listed in Table A-1.
EC-USE XLS		Master Excel 5 spreadsheet file for EC runs. The spreadsheets in these files are as follows. (For this and the other chambers there is one .CSV file for each sheet, with the .CSV file name same as the sheet name.)

Sheet	Description
EC-USE	Master spreadsheet (Listed in Table A-2)
EC-TYPE	Modeler's spreadsheet
EC-PRDS	Summary of O_3 and PAN data
EC-NOX	Summary of NO_x data
EC-VOC	Summary of injected VOC data
EC-LITE	Summary of light characterization data
EC-MISC	Miscellaneous summaries
EC-PRMS	Constants and parameters used in the EC spreadsheets

Table 7 (continued)

<table>
<tr><th>Name</th><th>Note</th><th>Description</th></tr>
<tr><td colspan="3">Files in Directory = [ROOT]\SHEETS (continued)</td></tr>
<tr><td>ITC-USE XLS</td><td></td><td>Master Excel 5 Spreadsheet for the ITC runs. The spreadsheets are as follows:
<table>
<tr><th>Sheet</th><th>Description</th></tr>
<tr><td>ITC-USE</td><td>Master spreadsheet (Listed in Table A-3)</td></tr>
<tr><td>ITC-TYPE</td><td>Modeler’s spreadsheet</td></tr>
<tr><td>ITC-PRDS</td><td>Summary of O_3 and PAN data</td></tr>
<tr><td>ITC-NOX</td><td>Summary of NO_x data</td></tr>
<tr><td>ITC-VOC</td><td>Summary of injected VOC data</td></tr>
<tr><td>ITC-MISC</td><td>Miscellaneous summaries</td></tr>
<tr><td>ITC-PRMS</td><td>Constants and parameters used in the ITC spreadsheets</td></tr>
</table></td></tr>
<tr><td>ETC-USE XLS</td><td></td><td>Master Excel 5 Spreadsheet for the ETC runs. The spreadsheets are as follows:
<table>
<tr><th>Sheet</th><th>Description</th></tr>
<tr><td>ETC-USE</td><td>Master spreadsheet (Listed in Table A-4)</td></tr>
<tr><td>ETC-TYPE</td><td>Modeler’s spreadsheet</td></tr>
<tr><td>ETC-O3</td><td>Summary of O_3 and PAN data</td></tr>
<tr><td>ETC-NOX</td><td>Summary of NO_x data</td></tr>
<tr><td>ETC-VOC</td><td>Summary of injected VOC data</td></tr>
<tr><td>ETC-MISC</td><td>Miscellaneous summaries</td></tr>
<tr><td>ETC-K1</td><td>Summary of actinometry results and k_1 assignments.</td></tr>
<tr><td>ETC-PRMS</td><td>Constants and parameters used in the ITC spreadsheets</td></tr>
</table></td></tr>
<tr><td>DTC-USE XLS</td><td></td><td>Master Excel 5 Spreadsheet for the DTC runs. The spreadsheets are as follows:
<table>
<tr><th>Sheet</th><th>Description</th></tr>
<tr><td>DTC-USE</td><td>Master spreadsheet (Listed in Table A-5)</td></tr>
<tr><td>DTC-TYPE</td><td>Modeler’s spreadsheet</td></tr>
<tr><td>DTC-O3</td><td>Summary of O_3 and PAN data</td></tr>
<tr><td>DTC-NOX</td><td>Summary of NO_x data</td></tr>
<tr><td>DTC-VOC</td><td>Summary of injected VOC data</td></tr>
<tr><td>DTC-MISC</td><td>Miscellaneous summaries</td></tr>
<tr><td>DTC-DIL</td><td>Dilution information</td></tr>
<tr><td>DTC-k1</td><td>Summary of actinometry results and k_1 assignments.</td></tr>
<tr><td>DTC-PRMS</td><td>Constants and parameters used in the ITC spreadsheets</td></tr>
</table></td></tr>
<tr><td>XTC-USE XLS</td><td></td><td>Master Excel 5 Spreadsheet for the XTC runs. The spreadsheets are as follows:
<table>
<tr><th>Sheet</th><th>Description</th></tr>
<tr><td>XTC-USE</td><td>Master spreadsheet (Listed in Table A-6)</td></tr>
<tr><td>XTC-TYPE</td><td>Modeler’s spreadsheet</td></tr>
<tr><td>XTC-O3</td><td>Summary of O_3 and PAN data</td></tr>
<tr><td>XTC-NOX</td><td>Summary of NO_x data</td></tr>
<tr><td>XTC-VOC</td><td>Summary of injected VOC data</td></tr>
<tr><td>XTC-MISC</td><td>Miscellaneous summaries</td></tr>
<tr><td>XTC-K1</td><td>Summary of actinometry results and k_1 assignments.</td></tr>
<tr><td>XTC-LICO</td><td>Summary of light intensity information derived from LiCor.</td></tr>
<tr><td>XTC-LUNI</td><td>Summary of results of light uniformity tests.</td></tr>
<tr><td>XTC-PRMS</td><td>Constants and parameters used in the ITC spreadsheets</td></tr>
</table></td></tr>
<tr><td>ECK1 XLS</td><td></td><td>Excel 5 Spreadsheet of EC NO_2 actinometry data</td></tr>
<tr><td>ITCK1 XLS</td><td></td><td>Excel 5 Spreadsheet of ITC actinometry data. Contains the following sheets. (The "File" column gives the name for the corresponding CSV file.)
<table>
<tr><th>Sheet</th><th>File</th><th>Description</th></tr>
<tr><td>ITCK1</td><td>ITCK1-A</td><td>Main Summary</td></tr>
<tr><td>NOx Chk</td><td>ITCK1-B</td><td>Tables summarizing consistency of NO_x data</td></tr>
<tr><td>Curve Fit</td><td>ITCK1-C</td><td>Formula used to calculate k_1’s for runs, and comparisons of predicted vs experimental k_1’s.</td></tr>
</table></td></tr>
</table>

Table 7 (continued)

Name	Note	Description
Files in Directory = [ROOT]\SHEETS (continued)		
RUNTYPE XLS		Excel 5 spreadsheet giving classification codes for runs which were used in the modelers’ spreadsheets, and the code numbers to sort them for the MODELRUN.XLS file.
DMS XLS		Excel 5 spreadsheet giving SAPRC-90 detailed model species, their OH radical rate constants, number of carbons, etc.
Files in Directory = [ROOT]\SOURCE		
SUBS LIB		Utility subroutines needed to prepare executable files for a mechanism.
Files in Directory = [ROOT]\SOURCE\CHDATA		
CALRUN FOR		Source file for the CALRUN program.
GCALRUN FOR		Source file for the GCALRUN program.
CALSUBS FOR		Source file for subroutines used by CALRUN and GCALRUN.
CALBLD BAT		Compiles and links CALRUN and GCALRUN. Requires Lahey F77L.
Files in Directory = [ROOT]\SOURCE\INT		
INT LIB		Subroutines needed to prepare executable files for a mechanism.
Files in Directory = [ROOT]\PGMS		
PKUNZIP EXE		Program to extract files from the .ZIP files in the distribution diskettes.
GCALRUN EXE		Program to produce calibration assignments for species measured by GC. See text.
CALRUN EXE		Program to produce calibration assignments for other species. See text.
CHADCONV EXE		Converts chamber run files from .CHA to .CHD formats, and vise-versa. (Chamber data are distributed in ASCII format in the .CHA files, but most modeling programs require these data to be in the binary .CHD format.)
PRP EXE		Prepares a mechanism for model simulations.
PREP EXE		Used by PRP.EXE to prepare mechanisms for model simulations.
INTCL BAT		Used by the mechanism preparation program to compile the mechanism-specific subroutine and produce the mechanism-specific executable file.
RCHADINP EXE		Produces model input (.INP) files for a chamber run using data in the run’s CHD file.
INTRUN EXE		Does a model simulation of a chamber run for a specified model.
LUMPGEN EXE		Used by INTRUN.EXE to simulate runs using the CB4 mechanism.
LUMPINT EXE		Used by INTRUN.EXE to simulate runs using the SAPRC-90 mechanism.
DO3NO EXE		Creates O3-NO channels for model calculations. Used by INTRUN.EXE.
INTFILE BAT		Can be used to create a mechanism-specific input (.INT) file for a run.
INT EXE		Does a model simulation taking input from a mechanism-specific input (.INT) file
CDT2CSV EXE		Creates calculation results files in comma separated value format.
PLTSRUN BAT		Produces plots to screen of chamber data and (optionally) model simulations of these data for a run.
CHADSPL EXE		Produces a SPL plot input file for a chamber run and optionally a model simulation of the run. Used by PLTSRUN.BAT.
SPL EXE		Produces plots to the screen using data in .SPL files. Can be used to plot calibration .SPL files. Used by PLTSRUN.BAT.
SPL88 EXE		Same as SPL allows for output to go to a printer or a HPGL file.
SUMCALC EXE		Produces summary of calculation results in a .CSV file which can be read by spreadsheet programs to produce statistical summaries of model fits.
Files in Directory = [ROOT]\CHAR		
		Chamber-dependent model input parameters for a given chamber and characterization set.
EC-01 CHR		EC runs at ~50% RH and ~303°K.
EC-11 CHR		EC runs at ~5% RH and ~303°K.
ITC-bb CHR		ITC runs using reaction bag no "bb".
ETC-01 CHR		ETC runs before vacuum injection procedure implemented for NO_x. (HONO contamination)
ETC-02 CHR		ETC runs after vacuum injected NO_x implemented. First reaction bag.
ETC-03 CHR		ETC runs after vacuum injected NO_x implemented. Second reaction bag.

Table 7 (continued)

Name		Note	Description
Files in Directory = [ROOT]\CHAR (continued)			
DTC-02	CHR		DTC runs at ~50% RH
XTC-01	CHR		Conditions of all XTC runs in data set.
EC-1989	SDR		Detailed spectral distribution for the EC taken in 1989. Recommended spectrum for modeling EC runs is derived from this and the spectral distribution measurement data for the individual runs.)
ITCUSE	SDR		Recommended spectral distribution for modeling ITC runs.
TMP	SDR	[b]	Spectral distribution of the last EC run which was modeled. (Temporary file created by INTRUN by adjusting EC-1989.SDR to be consistent with the spectral distribution assigned for the individual run. Included as an example – can be deleted.)
Files in Directory = [ROOT]\INPFILES			
runid	INP	[c]	Input file for modeling run "runid". One for each run (or run+side) which has the necessary model input data defined. Created by RCHADINP.
Files in Directory = [ROOT]\MECH			
PLTNAMES	LIS		List of species to be plotted. Required by CHADSPL.EXE and PLTSRUN.BAT.
OLDNAMES	LPM		List of special channel names in runs which are not detailed model species in mechanism files.
DMS	PRM		List of SAPRC detailed model species. Used by some SAPRC modeling programs.
Files in Directory = [ROOT]\MECH\CB4			
CB4_621	PRP		Main mechanism preparation file for the UAM 6.21 version of the Carbon Bond mechanism.
CB4_621	RXC		Most of the reactions in the UAM 6.21 version of the Carbon Bond mechanism.
WALLS	RXC		Chamber-dependent model reactions.
*	PHF		Photolysis absorption cross sections and quantum yields for the Carbon Bond mechanism. Required by the mechanism preparation program. (These were derived to *approximate* the UAM 6.21 photolysis rates using an appropriate set of actinic fluxes. No documentation of the UAM photolysis rates actually used in the UAM exists, and we were unable to duplicate them exactly.)
CB4_621	PRO	[d]	Mechanism listing file output by the preparation program.
CB4_621	MOD	[d]	Mechanism data file output by the preparation program, and required when running CB4_621.EXE.
CB4_621	EXE	[d]	Program to do model simulations using the UAM 6.21 version of the Carbon Bond mechanism. Produced when running PRP.EXE to prepare the model.
CB4	LCC		Assignments of Carbon Bond species to detailed model species. Used by modules called by INTRUN when modeling runs with this mechanism. (This set was used by Systems Applications, Inc. for conducting UAM simulations for Phase 2 of the Auto/Oil Air Quality Improvement Program [Yarwood, private communication]).
Files in Directory = [ROOT]\MECH\SAPRC90			
FILES	DOC		Description of the files in this directory. (Also describes files which are needed for reactivity calculations, but are not on this distribution.)
PRPCHAM	BAT		Batch file to prepare the various mechanism files used for modeling chamber runs.
LMPA	PRP		Main model input file for simulating runs with no alkanes, aromatics, or alkenes.
LMPA01	PRP		Main model input file for simulating runs with only one alkene.
LMPA1	PRP		Main model input file for simulating runs with only one alkane or aromatic.
LMPA84	PRP		Main model input file for simulating mixture runs.
*	RXN		Reaction mechanism files. See FILES.DOC.
*	PHF		Photolysis absorption cross section and quantum yields.
LMPA*	MOD	[d]	Mechanism data files for the corresponding .EXE file
LMPA*	EXE	[d]	Programs to do model simulations for the different types of runs with this mechanism.
CHAMCALC	LPC		Lumping control file for use when modeling chamber runs using SAPRC-90 mechanism.
*	LPM		Assignment files for the SAPRC-90 mechanism which are referenced in CHAMCALC.LPM.

Table 7 (continued)

Files in Directory = [ROOT]\CHDFILES

Name	Note	Description
runid CHD	[b]	Chamber data files in binary format which are required for plotting the chamber data using SPL or for producing .INP files using RCHADINP. Produced from the corresponding .CHA file using CHADCONV.

Files in Directory = [ROOT]\CDTFILES

Name	Note	Description
CALCnnnn CDT	[b]	Model calculation results file, where "nnnn" is the calculation number. Produced by the model simulation program when running INTRUN. The calculation number is associated with the run in the model’s .EXT file.
CALC PRM	[b]	File containing the last calculation number used. If this file does not exist, the program creates it, and assigns "0001" to the first calculation.

Files in Directory = [ROOT]\CALCCSV

Name	Note	Description
CALCnnnn CSV	[b]	Calculation output files in comma separated value format. Produced by CDT2CSV.EXE.

Files in Directory = [ROOT]\ZIPFILES

Name	Note	Description
		Contains the folowing ZIP files, whose contents can be manually extracted using PKUNZIP.

Files in [ROOT]\ZIPFILES\INSFILES.ZIP [e]

Name	Note	Description
chamUSE INS		Channel and instrument summary file for the runs in a chamber, where "cham" is EC, ITC, ETC, DTC, or XTC. See Section 2.2.3

Files in [ROOT]\ZIPFILES\CALFILES.ZIP [e]

Name	Note	Description
Dnnnn CAL		Calibration files for the Dasibi O_3 instruments ("nnnn" is the instrument ID number).
NOnnnn CAL		NO span calibration files for where such information could be found.
CFnnnn CAL		Results of NO_2 converter efficiency checks, in calibration file format.
GCnnnn CAL		Calibration files for all of the GC instruments for which such data could be found.
DS-HCHO CAL		Calibration file for the diffusion scrubber (Dasgupta) formaldehyde monitor
* OUT	[a]	CALRUN or GCALRUN output showing how calibrations were assigned to runs.
* TAB	[a]	CALRUN or GCALRUN output giving summaries of the calibrations and their assignments.
* SPL	[a]	CALRUN or GCALRUN output which the SPL program can use to plot the calibration data.

Files in [ROOT]\ZIPFILES\CSVFILES ZIP [e]

Name	Note	Description
* CSV		Condensed archive file containing all the spreadsheets in comma separated value format. There is one such file for each of the spreadsheets in [root]\SHEETS.

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[a] These files can be created by running CALRUN or GCALRUN, but they are also in the distribution.
[b] These files are produced by the program indicated. They are not included in the distribution.
[c] These files can be created by the program indicated, but are also in the distribution in INPFILES.ZIP, and can be extracted manually from there using PKUNZIP.
[d] These files can be created by running PRP for each of the .PRP files, but are also in the distribution.
[e] These files are not copied to the directory structure by, INSTALL.BAT. They can be installed manually from the indicated ZIP file if desired.

DMS Spreadsheet. The spreadsheet DMS.XLS has a list of the model species in the current version of the SAPRC detailed mechanism, their OH radical rate constants, and other information. It is relevant to this distribution because the OH rate constants were used to calculate the OH reactivities in the summary spreadsheets. Most of the fields are obvious for "Cd." "Represent" and "Doc". The "Cd." field has a "*" if the compound is believed to react non-negligibly via processes other than with OH (though this was not taken into account in computing its OH reactivity). The other fields are applicable to the SAPRC mechanisms and are beyond the scope of this discussion.

RUNTYPE Spreadsheet. This spreadsheet contains the codes used to classify the runs for modeling purposes, and the sequence numbers associated with these codes which are used to sort the runs and produce the RUNSORT spreadsheet. The cham-TYPE.XLS spreadsheets have links to this RUNTYPE.XLS file to calculate the codes for sorting. (These links are lost in the RUNSORT.XLS and the .CSV files.)

2.4.2 Run Data Files

The major portion of the data base consists of the .CHA files, which contain all the measurement data and other run-specific information for the individual chamber runs. These are ASCII files which contain the data in a form which can be imported into spreadsheets and other data base programs which can recognize data in comma separated value (.CSV) format. The data are organized into five types of records: (1) primary records, (2) secondary records, (3) data records, (4) group termination records, and (6) blank records. Primary records consist of a keyword followed by various types of data or other information, separated by commas, which depend on the keyword. The primary record keywords, and the data they are used to input, are given in Table 8. As indicated in Table 8, the "CHAN" primary records, which are used to input the channel parameters and data, are followed by variable numbers of secondary records. Like primary records, these secondary records consist of a keyword followed by data or other information depending on the type of record, separated by commas The channel record keywords, and the data they are used to input, are given in Table 9. Some types of primary or secondary records are followed by variable numbers of data records, which consists of data or other information, separated by commas. Their formats are given in Tables 8 or 9 in conjunction with the description of the primary or secondary records they follow. Group termination record, which consists of a keyword starting with the characters "END", are used to indicate the end of secondary records or data records in those cases where the number of such records are not given explicitly. Blank records are output after major groups of records, but programs reading these files are expected to ignore them.

As shown in Table 8, there are five types of data which are contained in the .CHA files. The first is the set of run parameters, which are scaler values associated with the entire run. Each one is input in a single primary record. Not all types of parameters are defined in all runs, if such a parameter is not in the .CHA file, it is either not applicable to the run or not determined.

Table 8. Description of Chamber Run ASCII (.CHA) data files: 1. Primary record keywords and associated input

Keyword	Type[a]	Description
		Run Parameters
FILE	C8	Name of the .CHA file. Consists of a 2-3 character chamber ID followed by the run number.
FORMAT	Int	File format code. Should be 1.
RUNDATE	C16	Date the run was carried out
TITLE	C40	Run title or short description. Usually indicates the main reactant (s) used.
UPDATED	C16	The date of the last edit of this file.
TZERO	Int	The clock time of the start of the run. Format is HHMM, where HH is the hour and MM is the minutes. i.e., 1331 means 1:31 PM.
TEND	Int4	The clock time of the end of the run. Format is DHHMM, where D is the run day -1. I.e., 1631 means the run was a one-day run which ended at 4:31 PM, and 21500 means the run was a 3-day run which ended at 3:00 PM.
SIDES	Int	The number of sides for the run, i.e., the number of mixtures which were simultaneously irradiated. Applicable for divided chamber (such as OTC or DTC) runs only. If no such record present, the run is undivided. All EC, ITC, ETC, and XTC runs are undivided, and thus their CHA files do not contain this record.
CHARSET	Int	The classification of the run for chamber characterization purposes. Generally, it referrs to the reactor used (for Teflon chamber runs) or the humidity and or (for the EC) temperature range.
PSTPDT	Int	Time zone. 1 = PST, 2 = PDT. (However, the accuracy of this has not been verified, and some runs were found to have inappropriate codes given the time of year.) Not relevant to modeling indoor chamber runs.
IRUNID	Int	(Run ID used internally by some old SAPRC software. Retained for compatibility.)
ICOMP	Int	(Not defined in present data base — reserved for future use.) Should not be present in current version.
SDSTUS	Int	(Used internally by some old SAPRC software. Retained for compatibility.)
ITSPRT	Int	(Used internally by some old SAPRC software. Retained for compatibility.)

Table 8 (continued)

Keyword	Type	Description
K1	Real	NO_2 photolysis rate (in min^{-1}) assigned to run. Recommended for use when modeling. Should not be present in files for outdoor runs.
SRATE	Real	Instrument sampling rate in ml/minute. Given for earlier EC runs only. Not applicable to Teflon Bag chambers.
PR	Real	Pressure in atm. Applicable only to EC runs carried out at reduced pressure, which are not included in the present data base.
TEMP	Real	Average temperature for modeling classification purposes. (In the present data base, this is computed as the integral of Tmodel over time for the irradiation, divided by length of time.
H2O	Real	If negative, it is the percent relative humidity which was measured when the chamber was filled. Note that this is applicable for the fill temperature, which is usually ~300-305°K. If positive, it is the H_2O concentration in ppm.
SDFAC	Real	(Should be absent. Reserved for future use.)
		Instrument Descriptions (followed by instrument description data records)
INST	Int	Number of instruments. The "INST" primary record is then followed by one data record for each instrument.

The Instrument description data records consists of three fields of information concerning the instrument, separated by commas, as follows:

Field	Type	Description
1	Int	Instrument I.D. number
2	C8	Instrument label
3	C40	Instrument description

Keyword	Type	Description
		Channel Data and Parameters (followed by secondary records described on Table 9)
CHAN	Int	Number of channels whose data and parameters will be given in the immediately following set of subrecords or data records. The number of subrecords or data records which follow can vary, and they are terminated by an "ENDCHAN" record. In general, there will be more than one set of "CHAN" groups for any run, with a separate group being used for each set of channels for which measurement data were made at the same times (or, for spectral distribution data, the same wavelengths).

Table 8 (continued)

<table>
<tr><th>Keyword</th><th>Type</th><th>Description</th></tr>
<tr><td></td><td></td><td>Auxiliary Data Records (followed by auxiliary information data records)</td></tr>
<tr><td>AUX_DATA</td><td></td><td>Auxiliary data giving information concerning a channel which may be of use to the modeler. One set of AUX_DATA records is in the file for each channel which has such records. Besides the AUX_DATA keyword, the primary record contains the following additional fields of information, separated by commas:
<table>
<tr><th>Field</th><th>Type</th><th>Description</th></tr>
<tr><td>2</td><td>C8</td><td>Channel name</td></tr>
<tr><td>3</td><td>Int</td><td>Instrument ID number</td></tr>
<tr><td>4</td><td>Int</td><td>Side number (always "1" for undivided runs)</td></tr>
<tr><td>5</td><td>Int</td><td>number of auxiliary information data records to follow.</td></tr>
</table>
The auxiliary information data records, contain the following data or codes, which are separated by commas. These records are used to convey a variety of types of information, using special codes which are listed in Table 10.
<table>
<tr><th>Field</th><th>Type</th><th>Description</th></tr>
<tr><td>1</td><td>C8</td><td>The data type code. See Table 10 for a description of these codes.</td></tr>
<tr><td>2</td><td>Real</td><td>The data value, whose meaning or use depends on the type code.</td></tr>
<tr><td>2</td><td>C8</td><td>The derivation code, indicating how the data value was derived.</td></tr>
</table></td></tr>
<tr><td></td><td></td><td>Comment Records</td></tr>
<tr><td>COMMENT</td><td></td><td>Used to indicate that a variable number of comment records follow. The comments start in column 1, can be up to 80 characters long, and can consist of any textual material which is different from the termination record. Generally contains copies of entries from the log book made when the run was carried out. These continue until an "ENDCOMMENTS" termination record appears.</td></tr>
<tr><td>NOTES</td><td></td><td>Used to indicate that a variable number of note records follow. A note is defined as a comment with an associated 1-character "flag". The note records consist of the flag in column 1, followed by a comma, then the comment. As indicated in Table 9, a flag character can be associated with individual data points, and a note can be used to associate an 8-character explanation with the flag. In addition, notes with the flag "." were created when processing the run for the data base, and serve to document (in part) the updates and edits which were made. Furthermore, special notes with the flag "." and starting with the keywords "Model_Input" are used to indicate injections or changes in run conditions which need to be specified when modeling the run. These special comments contain the following fields of information, separated by spaces (not commas).</td></tr>
</table>

Table 8 (continued)

Keyword	Type	Description

Field	Type	Description
1	C11	The keyword "Model_Input"
2	Int4	The clock time where a change or reactant injection occurred. Must be greater than TZERO and less than TEND.
3	C8	The name of a species injected or the keyword "HV" to indicate a change in light intensity.
4	Int	The side number for the species. Always "1" for undivided runs.
4	Real	The amount of species injected (in ppm) or (if "HV" is in field 3) the factor the light intensity was changed, relative to the "K1" run parameter. (Factor = 0 means the lights were turned off; factor = 1 means they were turned on again.)

The notes input continue until an "ENDNOTES" termination record appears.

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[a] Data types: "Int" = integer, "Int4" = integer which may have values greater than 32767, "Real" = non-integer number; "Cn" = string of up to n characters.

The second group of input records are the instrument descriptions, which are input following a single INST data record. This group may be absent if there are no instruments defined for a run. "Unknown" instrument records are used when a given type of measurement is made by different instruments, but both instruments were not given in the original data file.

The third type of data input are the channel parameters and data, which are input using one or more "CHAN" groups. As indicated previously, a "channel" consists of data which is given either as a function of time or (for spectral distributions) a function of wavelength, and each channel has a number of parameters (such as the name, instrument ID, calibration factor, etc.) associated with it. A CHAN record group is used to input a set of up to 9 channels which share the same set of times or wavelengths. The number of channels input in the group is given on the CHAN record. Each of the secondary records following it have 2 x nChan + 1 fields of data, consisting of the secondary record keyword, followed by two fields for each channel. The keywords and the data corresponding to them are described in Table 9. The "DATA" subrecord, also described in Table 9, is used to give the data values and data flags for the channel. (A data flag is a character which can be used to place a footnote on a data point. These should be associated with "notes" which are input as comments as described in Table 8).

Table 9. Description of Chamber Run ASCII (.CHA) data files: 2. Secondary record keywords for CHAN input

Keyword	Type[a]	Description [b]
NAME	C8	The name of the species or parameter being measured. If it is not a name listed in Table 4, the channel probably should be ignored. "RT=nnn" means it is an unidentified GC peak with a retention time of nnn.
INST	Int	The instrument I.D. number. Must be one of the numbers in the first field of an "INST" data record. "0" means the instrument is unknown.
SIDE	Int	The side number. Present only in divided runs. "1" is data taken from Side "A"; "2" is data taken from side "B"; "0" is data associated equally with both sides (e.g., UV radiometer readings during an outdoor run); "3" is ambient air data taken during the run.
PRIORY	Int	Data priority number. "1" means normal priority; "2" means data judged to be of lower quality than measurements with priority of 1, "3" or a higher number means data of very low reliability or data with known problems. If there are measurements of the same species using different instruments, only the measurement with the lowest priority number is used for modeling. Data with priority numbers of "3" or higher should not be used.
STATUS	C4	Channel status. "OK" means the factors and zero corrections have been applied, or there are no available factors or zero corrections available to apply. "RAW" means there are factors and zero correction data, but they have not been applied to the data in the channel. This is used internally in data processing programs at SAPRC, since the status values should always be "OK" in the distributed data files. (Calibration factors and zero offset corrections have been applied to all data in the .CHA files wherever this information is available. If no calibration information is available, this is indicated by the "UNITS" code either being blank or referring to some raw instrument output such as "mv".)
DATA	2 Int	Channel data records will follow. The first integer is the number of data records which will follow. The second is the "time set" number, which can be used internally by the program reading the data, or can be ignored. If channels read in subsequent "CHAN" groups have the same time set number as this, then they can share the same time array, and are given in separate "CHAN" groups only because there is a maximum of 9 channels per group. The data records which follow have two fields of data for each channel, plus a field for the time or wavelength. The format is as follows:

Field	Type	Description
1	Int	Clock time in DHHMM format (see TEND description in Table 8 for an explanation of this format.) If the channel is a spectral distribution (has a UNITS code of --1), it is the wavelength in angstroms.

Table 9 (continued)

Keyword	Type	Description
		2 C1 The flag for the data point for the first channel for the given time or wavelength, or blank if no flag. 3 Real The data value for the time or wavelength.
CALFAC	Real	The calibration or correction factor for the channel data. The data are corrected using: (corrected data) = ZEROCOR x [(Raw data)-ZERCOR]. This correction has already been applied if the channel status is "OK".
ZERCOR	Real	The zero offset correction for the channel. See "CALFAC".
PRTORD	Real	(Print order. Used internally by some old programs at SAPRC. Ignore.)
DIGITS	Real	(Digits for printouts. Used internally by some old programs at SAPRC. Ignore.)
UNITS	Int	Data Units code. Codes presently used are as follows: 1) ppm 2) Deg C 3) % 4) liters 5) volts 6) KW 7) mw/cm2 8) none 9) ppmC 10) ppb 11) deg F 12) deg K 13) volts 14) raw data 15) minutes 16) mv 17) min-1 18) n.m. 19) 10^{-4} m^{-1} 20) counts 21) factor 22) 10^3/cc 23) um^2/cc 24) um^3/cc 25) part/cc 26) cal/cm^2/min 27) ppt 28) area 29) mph 30) deg 31) langley 32) millilangley 33) relative 34) psia -1) Relative Spectral Distribution ("time" array is angstroms)
CHNKOD	Int	(Reserved for future use. Should not be present. Ignore.)
INIT	Real	Initial concentration of reactant. (Note: The initial concentration given in the AUX_DATA should be used for modeling.)
AVG	Real	Average concentration of reactant. (Note: for temperature, the TEMP run parameter or the Tmodel data should be used for modeling.)
SDEV	Real	Standard deviation of average
ENDCHAN		Termination record used to indicate end of the CHAN group

[a] The data types can be as follows: "Int" = integer, "Int4" = integer which may have values greater than 32767, "Real" = non-integer number; "Cn" = string of up to n characters; "2 Int" = two integer values, separated by a comma.

[b] For all of the records described above except for those with the "DATA" keyword, the data format is as follows. The first field is always blank except for the "DATA" input. The second field gives the data corresponding to the keyword.

The fourth type of data input are the auxiliary channel data, which consists of special information concerning selected channels which may be of use to the modeler or the data evaluator. These data were not originally part of the run files, but derived as part of the process of preparing these runs for this data base. These include, for example, codes indicating whether the channel data refers to an injected reactant, and if so what is its initial concentration and uncertainty, codes indicating the maximum value of the channel if it is a product of interest to the modeler (such as O_3), codes indicating the availability of the calibration data and its uncertainty, etc. The codes used in the auxiliary channel input, and the data associated with them, are given in Table 10. This information is given using "AUX_DATA" groups, with one such group for each channel which has such parameters.

The fifth type of data which are input are the comments. There are two types of comments: unflagged comments and "notes". The unflagged comments are input using the "COMMENTS" group, and consist of entries from the log book made when the run was carried out, or during the time when the run data were originally processed. "Notes" are comments which have flag characters associated with them. The flag character could be either a character which was used to flag one or more data points, with the associated comment being used to explain what the flag means. The special character "&" is used to indicate that the comment is a continuation for the comment from the previous flag. In addition, the special flag "." is used to designate comments which were added as part of the preparation of the run for the data base. This includes documentation of when edits and assignments were made, and the "Model_input" notes, which are present in runs where reactants were injected or the lights were turned off and on during the course of the experiment. The latter give the recommended model input to use when simulating these runs (see Table 9.)

2.4.3 Calibration Data and Output Files

The primary calibration information for the O_3, NO_x, Dasgupta formaldehyde, and GC instruments are given in calibration (.CAL) files which serve as inputs to the CALRUN and GCALRUN programs. These programs output several files, which, with their input files, are included in the distribution. The programs determine which runs and channels need to be updated by reading the run channel/instrument summary (.INS) files which are discussed in the following section. The .CAL files and the CALRUN and GCALRUN output files are summarized below. Note that the recommended calibrations have already been applied to all the data where applicable in the calibration data files, so the modeler does not need to apply these calibrations when using these data. The only uncalibrated data in the run data files are those for which no reliable calibration information is available. In those cases, the data units ("UNITS" parameter, Table 5) for the channel in the run data file is either blank, "raw data", "volts", or some such, and not concentration units such as "ppm".

General calibration files. General calibration files are processed using the CALRUN program and are used for O_3, NO, NO_2 converter efficiencies, and formaldehyde measured by the dasgupta

Table 10. Codes used to define auxiliary channel data.

Code	No [a]	Description
		Data Type Codes
		The following depend on the data and are updated if the factor and zero are changed.
INIT	1	Initial value of species which must be specified when modeling run.
AVG	2	Average value of species
MAX	3	Maximum value of species. (Can be used for performance evaluation statistics)
LAST	4	Final value of species.
		The following give information about the data characterization.
CAL.F	20	Calibration factor used. Should be same as the CAL channel parameter.
ZERO	23	Zero offset correction used. Should be the same as the ZERO channel parameter.
NO2.F	22	NO_2 converter efficiency estimated from converter efficiency checks around the time of the run. Unless indicated otherwise in the run's comments, the NO_2 data will not be corrected for non-unit converter efficiencies.
CH-C0	21	The uncalibrated initial concentration of the species taken from the strip charts. (Used to derive zero corrections for NO_x data.)
CAL?1	30	Unknown calibration factor (used to enter estimated relative uncertainty). If there is a CAL?2 parameter, then the instrument used for the measurement is ambiguous. **The derivation code gives the instrument ID number for this factor.**
CAL?2	31	Unknown calibration factor #2 (used to enter estimated relative uncertainty when the actual instrument used for the run is ambiguous). **The derivation code gives the instrument ID number**.
RAW.F	33	Factor the "uncalibrated" data was changed by to change the basis for the factor. (This was used primarily to convert uncorrected temperature data from °C or °F to °K.)
CAL?T	32	Calibration factor derived from an assignment when the only calibration(s) applicable to this run were done too long ago to be reliable.
Kd0nn	nn	Undefined code.
		The following refer to uncertainties or other information regarding the above data types. "code" indicates the code for the data type, and "x" indicates the number.
U-code	100+x	The uncertainty in the data type (one σ basis). (E.g., "U-INIT", or code number 101, refers to the uncertainty in the initial concentration.)
M-code	200+x	The maximum likely value for the data type. (Used if the data are expected to be biased or have a non-normal uncertainty distribution.)
N-code	300+x	The minimum likely value for the data type.
C-code	400+x	The corrected value for the data type. Used where the applicability of the correction is uncertain, and the correction not implemented in the data set.
W-code	800+x	Warning message about the data type.

Table 10 (continued)

Code	ID	Description
I-code	900+x	Information about the data type. Generally used when different methods are available for deriving the same parameter; these give the values for the other methods which are not implemented in the data. (For example, can give values of factors which were in the data set before corrections were made.)
		Data Derivation or Information Codes
	The following indicate that the parameter depends on measured data in the channel, and should be updated if the values, factor, or zero change.	
DATA	1	Derived from the data without adjusting
ADJDAT	2	Derived from the data after manual adjusting (visually deriving a fit to scattered data, or ignoring "noise" points.)
COMPUT	3	Derived from the data by a computer algorithm (similar to "DATA")
FACZER	4	Uncertainty derived from uncertainties in factor and zero offsets. (Used for U-code data types only.)
	The following are for parameters which affect data characterization.	
ORIG	10	The value originally in the run file. Used primarily when factors were updated based on re-assessments of the calibration data for preparation of the data base.
CALFIL	20	Derived from the .CAL file by CALRUN or GCALRUN.
CHART	21	Derived from the strip chart.
LASTDT	22	Derived from data at the end of the run. (For example, an NO zero derived from the data at the end of the run in the presence of excess O_3.)
INITDT	23	Derived from data at the beginning of the run (or pre-t=0 data). (For example, an O_3 zero derived at the start of the run in the presence of excess NO.)
ADJ2	24	Initial value estimated or adjusted using primarily final values. (May be used for slower reacting species.)
EQVAL	27	Uncertainty estimated to be equal to the value. Used for U-code data types only. (For example, the uncertainty in a zero offset correction may be estimated to be of the same magnitude as the correction.)
DIFF	29	Derived from different methods. Specific meaning depends on context. (For example, the uncertainty may be derived from discrepancies between two different methods for deriving the value.)
CALINJ	30	Calculated from the number of moles or volume injected.
EST.1	37	Estimated for this run.
EST.2	38	Estimated for this group of runs.
EST.G	39	Estimated for all runs in this chamber or with this instrument.
#nnnn	nnnn	Instrument ID number (if nnnn > 1000). Undefined code if nnnn < 1000.
KD0nn	nn	Undefined code.

Table 10 (continued)

Code	ID	Description
		Special Uncertainty Values
	The following negative numbers may be used in place of uncertainties to indicate special conditions which prevent deriving quantitative uncertainty estimates.	
-1.		There is only one calibration (or other) value available to derive the value for the channel.
-2.		The parameter was estimated by a linear regression using only two points.
	The following may be output by GCALRUN. The program code can be examined if the circumstances need to be known.	
-21.		No assignment.
-22.		The factor in the run file is a different magnitude from any of the factors in the calibration file.
-23.		The method used for the analysis in this channel could not be determined unambiguously from the magnitude of the factor in the run file.
-24.		No assignment
-25.		Program error
-26.		No assignment.
-27.		No assignment
-28.		This run was carried out too long after the last calibration to derive a reliable assignment.

[a] The ID number used for the data type or derivation method in the binary (.CHD) files and internally in the CHADPRO programs.

instrument (see Sections 4.1, 4.2, and 4.6, respectively.) A separate file is used for each species which is being measured by a particular instrument. The first record in such files gives the name of the species, the instrument ID number, the 8-character (max) instrument label, and, optionally, the minimum percent uncertainty to be used when outputing calibration factor uncertainty estimates. (If no minimum uncertainty is given, the programs used in processing these chamber data used 2% as the minimum.) The subsequent records are treated as comments until a record with a "." in column 1 appears. In addition, records with a "!" in the first column are also treated as comments regardless of where they appear. Following the "." record, the calibration records are input, in chronological order. The format of the calibration records is as follows.

Cols.	Type	Data
1	C2	Code indicating how to use these data to estimate factors for runs (see below)
3+	Int.	Date of the calibration, given as number of days after December 31, 1969.
next	Real	Calibration factor (can be blank if the code is "-")
next	Real	Standard deviation of the calibration, if known. (Not used in computing the factors for the runs.)

The code must be in column 1; column 2 must be blank, but the factor and the standard deviations can appear in any columns after that, separated by a space, tab, or comma. Text following a "!" on the record are ignored by programs processing these files for the data base.

As indicated above, a code is used to determine how the calibration factors are used to determine how the input calibration data are to be used when deriving calibration factors for the runs. The codes are as follows:

Code	Use
A	Average all factors starting with this one until the next record with a non-blank code
L	Fit the factors starting with this one, up to the next record with a non-blank code, to a linear regression line against day number (see below)
X	Reject this factor (i.e., don’t use it in the regression or average, but include it in the tabulation in the report)
(blank)	This factor is to be used in the average or regression with those input above. If the first calibration record does not have a code, an "A" is assumed
-	The instrument becomes "uncalibrated" as of this date, and factors input previously cannot be applied to runs after this time. This is used if there is a change to the instrument (such as a span adjustment) which makes previous calibrations inapplicable to subsequent experiments, but there is no new calibration factor available.
A-	Same as "A", except this factor is to be used in the average or line fit for the immediately previous group as well as the new one that this starts. Note that this results in the calibration result being given twice in the corresponding tabulation of the calibration data in Section 4 or Appendix B.
L-	Same as "L", except this factor is to be used in the average or line fit for the immediately previous group as well as the new one that this starts.

These codes are also used for the GC calibration files, though their position in the input records is somewhat different.

GC Calibration Files. GC calibration files differ from general calibration files in that they can contain calibration factors for the multiple species which can be measured by a particular instrument. The first record of this file contains the keyword "GC" followed by the instrument ID number, the 8-character (max) instrument label, and (optionally) the minimum percent uncertainty to be output. If a minimum uncertainty is not given, 2% is used. (This can be over-written by inputs of minimum uncertainties for individual species, as shown below.) As with general calibration files, subsequent input records are ignored (treated as comments) until a record with a "." in column 1 is encountered, and records with a "!" in column 1 are also treated as comments. After the "." record, the calibration data for the various species are input. These are initiated by a record giving the species name (starting in column 1), the analysis or quantification method (i.e., loop, trap, or Tenax cartridge sampling, height or area quantification, etc.) for which the factors apply, and optionally the minimum uncertainty to be output if different than 2% or the value input on the first record. The factors for this species and analysis method are then input using the following format:

Cols.	Type	Data
1-2		Must be blank
3-6	Int.	Date of the calibration, given as number of days after December 31, 1969.
7-16	Real	Calibration factor (blank if code is "-")
17-24	Real	Standard deviation of the calibration, if known.
25-43		Data in these columns are ignored by the processing program. (Generally contain the retention time and the date of the calibration in a yymmdd format.)
44-45	C2	Code for determining how calibration is to be used to derive factor for the runs. Same as for general calibration files.

Before any calibration data are entered, there may optionally be a special set of input records indicated by the keyword "CHANGES" instead of the name of a species. Records following that contain (in columns 3-6, with columns 1 and 2 blank) day numbers (dates as number of days after 12/31/69) where changes were made to the GC instrument which results in all calibration factors becoming inapplicable. Any characters after column 6 are treated as comments, and generally contain a brief explanation of what the change was. The effect of this input is the same as including a code "-" record for that date for all the species and methods whose factors are input.

Calibration Tabulation (.TAB) Files. Both the CALRUN and GCALRUN programs produce tabulation files summarizing the calibration data and assignments in a form suitable for a report. They serve as a basis for the calibration summary tables in Section 4 and Appendix B, and are discussed in detail in Section 4.1.

Calibration Summary Output (.OUT) Files. The programs also produce output files which indicate how the calibrations were assigned to individual runs, and where the runs are (in time) relative to the dates of the calibrations. The DayNo column refers to the day number (see above); the Set column refers to the calibration assignment set as indicated on the tabulation file; the RunID column refers to the run number; F(old) refers to the factor in the .INS file which was input, which may or may not need to be updated; F(new) is the new recommended calibration; "diff" is the difference between F(old) and F(new); "Unc" is the uncertainty assigned to F(new); and "Days(run-cal)" is the number of days since the start and the end of the assignment set. (See Section 4.1 for a discussion of assignment sets and how calibrations are assigned.) If channels are recognized as being for the relevant instrument and species but cannot be assigned a factor, indicates this, and gives an indication of the nature of the problem. The .OUT files produced by GCALRUN and CALRUN have slightly different formats, but contain essentially the same information.

Calibration Assignment Plotting (.SPL) Files. The programs also output files which can be used as input to the SPL plotting program which is included in the distribution. (This program requires a VGA or compatible display to operate). When the program is run using this input file, the calibration data and the assignments will be displayed (with symbols also showing where the runs are) for the species being calibrated. For CALRUN output, the data are plotted as soon as the program is run; for GCALRUN a menu is displayed allowing the user to chose the species and measurement whose calibration data are to be plotted (unless there is only one). See Appendix C for instructions on how to install and run the distributed programs.

EDCHAD Input (.CPO) Files. The run files can be edited using a program called EDCHAD, and the CALRUN and GCALRUN programs output .CPO files which serve as input to this program to update the calibration factors in the run files. The .CPO files and the EDCHAD program are not included in the distribution (because the modeler should not be editing the run files), but are mentioned here to indicate the relationship between the calibration and run data files.

2.4.4 Run Channel/Instrument Summary (.INS) Files

The files chamUSE.INS are ASCII files which contain a summary of all the measurement channels for all the distributed runs in a chamber. They are used as input in the CALRUN and GCALRUN programs to determine which runs have data for the instrument and specie(s) whose calibration data are being processed. They are also useful for determining which runs have certain types of measurements, or used certain instruments.

The first records in this file contain a listing of the instruments and the instrument labels. Following that, the channels of data for each instrument are summarized. All the channels for a given instrument are summarized together, and the data for different instruments are separated by form feeds. The first record in a group gives the instrument label, name of the species, and the instrument ID number. Then, there is a record for each run which has a channel for that species measured using that instrument. The records give the run ID, the run date, the day number (days after 12/31/69), the calibration factor, the zero offset correction, the channel priority (corresponding to FAC, ZERO, and PRIORY, respectively, in Table 8), the approximate initial concentration (not necessarily the value recommended for modeling), and, for some channels, codes "I" and "M". An "I" code means the channel has an auxiliary data record giving the initial concentration of an injected reactant which must be specified when modeling the run, and an "M" code means the channel has an auxiliary data record giving the maximum concentration.

2.4.5 Characterization Data Files

There are three types of characterization data files in the distribution. The first are the ECK1.XLS and ITCK1.XLS spreadsheet files which, as indicated above contain the results and analysis of the NO_2 actinometry experiments for the EC and ITC chambers, respectively. (The spreadsheets giving the results and analyses of the actinometry data for the other chambers are incorporated in the run spreadsheet files for the respective chambers. For example, the actinometry data for the ETC runs are in the "ETC-k1" spreadsheet in the file ETC-USE.XLS.) The second are the EC-1989.SDR and ITCUSE.SDR files, which contain the relative spectral distributions which we recommend using when modeling EC and blacklight chamber runs (see Section 5). These consist of a title record, comments which are indicated by a "!" in column 1 which document the data contained therein but are ignored by the program, and records containing a wavelength (in microns) and a relative intensity for that wavelength (in quanta per unit wavelength). The spectral distributions are normalized so they will give an NO_2 photolysis rate of 1 x 10^{-20} min^{-1} using the NO_2 absorption cross sections and quantum yields in the SAPRC-90 mechanism (Carter, 1990). Note that the spectrum in the EC-1989.SDR file is strictly speaking only appropriate for the time it was measured; the spectra for the other runs should be adjusted based on the measured spectrum as discussed in Section 5.1.4. (The recommended spectral distributions for modeling the XTC runs are derived from the spectral measurements in the run data files, as discussed in Section 5.3.)

The third set of characterization files are the modeling input files we recommend using as a starting point for representing chamber-dependent effects when modeling these experiments. They are named cc-nn.CHR, where ’cc" is the chamber ID (EC, ITC, ETC, DTC, or XTC), and "nn" is the characterization set number (CHARSET — see Table 8). These contain the chamber-specific input we recommend as appropriate for initial modeling of runs with that chamber and characterization set. The input is in a format required for the SAPRC modeling programs (see following section and Appendix C), but its conversion to other programs should be straightforward for those who understand the parameters contained therein. These parameters and the assignment of characterization set numbers to the runs are discussed in Section 6.4. In most cases, the input consists of a keyword naming the parameter, followed by its value. The files also contain comment records, which are indicated by a "!" in column 1. The characterization files also contain references to the spectral distribution (EC-1898.SDR or ITCUSE.SDR) files recommended as appropriate for modeling runs in the chamber.

2.4.6 Example Modeling Input Files and Programs

Although not strictly speaking a part of the data base, the distribution also contains programs and files necessary to conduct model simulations of these runs using our currently recommended characterization model and parameters, and to examine the output. The files and programs are summarized in Table 7 and discussed in slightly more detail (though not comprehensively documented) in Appendix C. The programs and files will permit model simulations using the version of the SAPRC-90 mechanism (Carter, 1990) which was used to calculate the reactivity scales given by Carter (1994), and using the Carbon Bond

IV mechanism (Gery et al, 1988) as incorporated in version 6.21 of the UAM (CARB, 1994; Gery, private communication, 1993; unpublished results from this laboratory). Not all the runs in the data base are sufficiently well characterized for modeling, and the run spreadsheets indicate those runs for which a simulation could be successfully carried out. (Note that in this context a "successful" simulation means that there was enough input information contained in the run’s file and its associated characterization file that the software was able to complete the simulation. The results may not necessarily agree with the data to an acceptable extent. Evaluation of mechanisms, or even of mechanism evaluation protocols, is beyond the scope of this document.) These preliminary simulations, and general issues and recommendations regarding use of these data for mechanism evaluation, are discussed further in Section 7.

3. DESCRIPTION OF CHAMBERS AND OPERATING PROCEDURES

3.1 Facility Descriptions

3.1.1 Evacuable Chamber and Solar Simulator

The SAPRC evacuable chamber-solar simulator facility in its present configuration is shown schematically in Figure 1. Its design and construction have been described in detail elsewhere (Pitts et al., 1979 and references therein). The major features of this chamber and its light source are discussed below.

Chamber. The SAPRC evacuable chamber is a cylindrical, aluminum alloy cell, 1.37 m in diameter and 3.96 m long (surface-to-volume ratio 3.41 m^{-1}), with the interior coated in FEP Teflon. The ends of the chamber consist of Teflon-coated grid structures, each of which holds sixteen 33 cm x 33 cm quartz windows. Each window is individually Viton O-ring sealed to the grid, and the grids in turn are bolted to the ends of the chamber through O-ring sealed flanges. Thermal fluid passages welded to the exterior of the chamber permit wall temperature control (to ± 1-2° C) over the temperature region employed in most experiments by means of an ethylene glycol-water mixture circulated through the passages from a remotely located heat exchanger and refrigeration system. The exterior of the chamber is insulated with fiberglass (1 inch) and polyurethane (2 inches) and covered with an aluminum sheath. The volume of the chamber was experimentally determined to be 5774 liters (Pitts et al, 1979), in good agreement with the calculated volume of 5860 liters.

The chamber is equipped with a total of 23 flanged ports, with openings ranging from 2 to 16 inches in diameter. Small ports were fitted with Swagelock O-seal connectors (0.5 or 1 inch) to allow insertion of glass tubes for injections and sampling. As seen in Figure 1, two large, diametrically-opposed ports are used to install multiple reflection optics for in-situ IR analyses. Because the sensitivity of this IR system is not sufficient to provide data in concentration regimes relevant to ambient models, and because the runs with IR usually were not conducted for mechanism evaluation, only limited IR data are included in the data base, These data were not evaluated. However, the optical mirrors were in place in the chamber during most of these experiments. For some later runs, multipass optics for a differential optical absorption spectrometer were installed along the long axis of the chamber, blocking part of the solar simulator light beam (not shown in the figure).

For most experiments the chamber was evacuated by means of a three-stage, hydrocarbon-free pumping system to ~10^{-5} torr in four hours or less. However, before run EC120, the pumping system consisted of a liquid (water) ring roughing pump and air ejector pump which evacuated the system to ~10 torr, and three cryosorption pumps, two of which, when used sequentially, further reduced the

Figure 1. Diagram of SAPRC Evacuable Chamber (EC) and Solar Simulator.

pressure to 10^{-3} to 0.02 torr. For runs after EC120, a 25.4 cm diffusion pump employing a perfluorinated oil ("Fomblin" polyether) as a working fluid was added to the system, and the chamber is now routinely pumped to, and maintained overnight, at $<10^{-5}$ torr.

Solar Simulator. The 25 KW solar simulator (Beauchene et al., 1973) was designed to provide a collimated beam of light with an overall light intensity uniform to ±10% and with spectral fidelity to the deep-space solar spectrum, particularly in the 300-450 nm region. The output of a 25 KW xenon arc lamp (Hanovia or Durotest) is collected and projected by a collector mirror via a 45° flat mirror onto an optical integrator. The beam then passes on to the collimating optics which are over-coated with magnesium fluoride for peak reflectivity at 300 nm. A compact optical system was obtained at the cost (due to the secondary mirror) of a "hole" in the beam whose diameter ranges from 25 to 11 cm over the length of the chamber. The beam is collimated to a collimation half-angle of ±1.1°. Although this collimation angle requires a larger clearance between beam and chamber walls (beam diameter is 1.2 m) to minimize surface photochemistry, it also reduces the effect of shadows caused by the secondary mirror and the window grid structures.

The output of the solar simulator passes through at least one, and sometimes two, light filters before reaching the chamber. A trichroic spectral filter, designed to remove some of the energy in the near-infrared portion of the spectrum, was used in some of the earlier runs. It was not used for most experiments in this data base. More importantly, for all experiments reported here a Pyrex pane was placed between the simulator to filter out the UV radiation below approximately 300 nm. The Pyrex pane was changed several times during these runs, and these changes can significantly effect the spectrum of the light entering the chamber. The same 0.25" thick pane was used for a large period of time during this program, and solarization of this pane was found to cause a gradual decrease in UV intensity with time during the course of these runs. A change in this pane probably caused the significant depression in U.V. intensity which occurred for a number of experiments in 1982, as discussed in Section 5.1.4.

The light from the simulator enters the chamber through 0.8-inch thick quartz windows which are supported by the grid structure. (The grid structure shown in Figure 1 is the same on the end of the chamber near the solar simulator.) These quartz windows are rarely changed, being replaced only when broken. At no time were the quartz windows changed all at once. The end of the chamber opposite the solar simulator also had quartz windows, though most had aluminum panels on the outside to reflect the light back into the chamber. A few windows opposite the simulator were broken and replaced with Teflon coated plates. One of the quartz windows on the opposite the simulator was used so light can pass through the chamber and out through the window so its spectrum and intensity can be measured. Data concerning effects of the quartz windows on spectral characterization measurements are discussed in Section 5.1.4.

The xenon lamps used in this system have a limited lifetime, and are changed after approximately 400 hours of use. The flat, primary, and secondary mirrors (Figure 1) also degrade with time and have to periodically re-coated. On two occasions the lamp exploded, necessitating refurbishment of the optical system as well as a lamp change. The pyrex panes were also changed from time to time. These events are noted in the run spreadsheets and the EC actinometry tabulations, and are taken into account when assigning light intensities and spectral distributions for the EC runs (see Section 5.1).

The power used by the solar simulator can be varied to control the light intensity. The power required to achieve a given intensity depends on the age of the lamp and the condition of the reflectors, though for a given run series it can give an indication of the relative light intensity. The power used by the solar simulator is recorded at least once a run, and usually more than once, as the run is carried out. Unless it is deliberately changed, it does not fluctuate by more than about 5% during an experiment (see following section).

chamber consisted of a reaction bag which was constructed of 2-mil thick FEP Teflon panels heat-sealed together using a double-lap seam and externally reinforced with Mylar tape. The reaction bag was fitted

Figure 2. Diagram of SAPRC Indoor Teflon Chamber #1 (ITC).

inside an aluminum frame of dimensions of 8 ft x 8 ft x 4 ft. One edge was hinged to allow the bag to collapse to less than one-fifth of its maximum volume. Teflon flanges were used for the sampling ports. The chamber had a stirring fan, with feed-throughs designed for high vacuum applications, which was used to mix the contents during reactant injections, but was usually turned off during irradiations.

The light source for this chamber consisted of two diametrically opposed banks of 40 Sylvania 40-W BL blacklamps backed by arrays of Alzak-coated reflectors. The light intensity could be controlled

3.1.2 Indoor Teflon Chamber #1 (ITC)

The ~6400-liter SAPRC indoor Teflon chamber #1 is shown schematically in Figure 2. The by switching on or off sets of lights as previously described (Darnall et al. 1981). For most experiments in the data base the light intensity was held constant at 70% of its maximum, though some experiments used 100% of the lights. This is noted in the ITC run spreadsheets. The intensity and spectral characteristics of this light source are discussed in Section 5.2.

3.1.3 Fawcett Laboratory Pure Air System

Pure air for the SAPRC EC and ITC experiments was provided by an air purification system which has been described in detail by Doyle et al. (1977). In this system, ambient air was drawn through Purafil beds (to remove NO_x), compressed by a liquid (water) ring compressor to 100 psig, and passed successively through a heatless dryer, a Hopcalite tower (to remove CO) and a second heatless dryer packed with activated coconut charcoal. The latter acts as a pressure-swing adsorption unit and routinely reduced the hydrocarbon levels (as measured in the chamber) to ~800 ppb methane, <5 ppb of C_2 hydrocarbons and propane and <1 ppb of all higher hydrocarbons. The dry, purified air stream is then filtered to remove any charcoal dust. For unhumidified runs, the air is passed directly to the chamber(s). However, most EC and ITC runs in the data base were humidified to approximately 50% RH. In this case, the dry air stream was heated and then divided into two metered streams, one of which passes through a spray tower supplied with heated distilled water. The streams are recombined in the appropriate relative amounts to give the desired humidity. The humidity was measured by placing a wet bulb/dry bulb thermometer in the air stream when the chamber is being filled or flushed.

3.1.4 Indoor Teflon Chamber #2 (ETC)

The ~3000 liter SAPRC indoor Teflon chamber #2 is shown schematically in Figure 3. This chamber is referred to as "Ernie's Teflon Chamber" (ETC), after Ernesto Tuazon, who originally designed it. Except for its smaller volume and the orientation of the lights, it is very similar in design to the ITC, discussed above. The chamber consisted of a 2-mil thick FEP Teflon reaction bag fitted inside an aluminum frame of dimensions of 8 ft x 4 ft x 4 ft. The light source for the chamber consisted of two diametrically opposed banks of 30 Sylvania 40-W BL blacklamps, one above and the other below the chamber. Pure dry air for these experiments prior to January 1992 was provided by the Fawcett Laboratory air purification system discussed above. After January 1992, an AADCO air purification system was employed. The air was not humidified for these experiments, and is estimated to have a relative humidity of approximately 5%. Dry air was used because it tends to reduce chamber wall effects and improve reproducability. The temperature in the chamber when the lights ranged from 298 to 304° K.

3.1.5 Dividable Teflon Chamber (DTC)

The Dividable Teflon Chamber (DTC) is shown schematically in Figure 4. It consists of two ~5000-liter reaction bags located adjacent to each other, and fitted inside an 8' cubic framework. The light source consisted of two diametrically opposed banks of 32 Sylvania 40-W BL blacklights, whose intensity can be controlled by 16 switches, each of which operates 2 blacklights. The lights are backed by aluminum-coated plastic reflectors which are molded into the same shape as the Alzak reflectors in the ITC. The roof, floor and the two end walls are covered with polished aluminum panels, except for a window in the middle of one of the end walls where the sampling, reactant injection, and air fill probes were located. The light intensity in this system turned out to be so high that to achieve light intensities

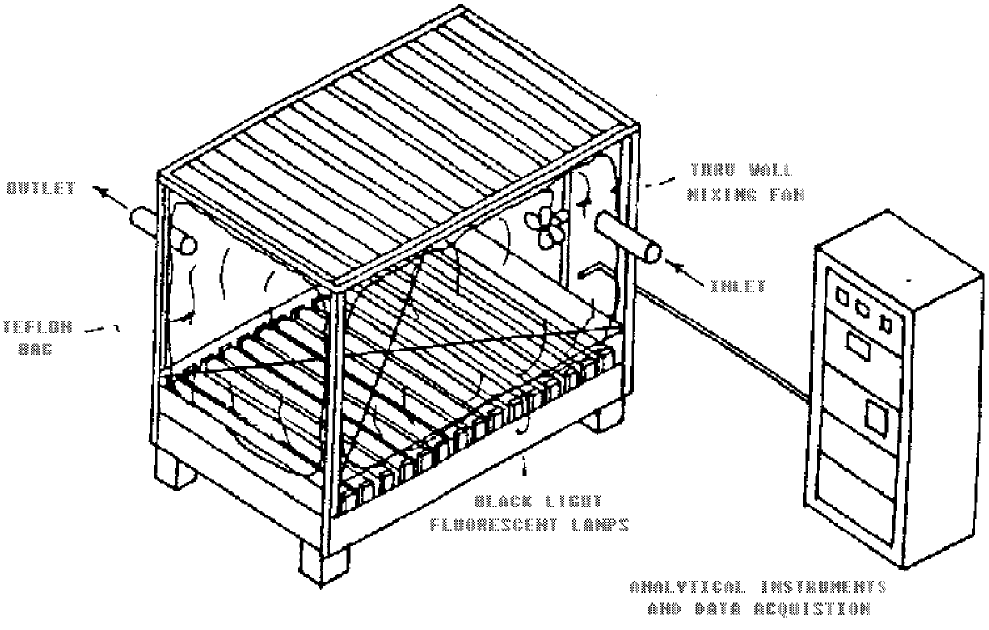


Figure 3. Diargram of SAPRC Indoor Teflon Chamber #2 (ETC).

comparable to ambient conditions all the runs in the data base were carried out with 50% of the maximum light intensity. Dry purified air was provided by the same AADCO air purification system as employed for the ETC after January, 1992. All runs were carried out at ~5% RH, except for a few runs where water vapor was manually injected to yield ~50% RH.

The dual reaction bag design allowed for simultaneous irradiation of two mixtures. It was designed primarily to conduct incremental reactivity experiments, to determine the effect of adding a reactant to a standard mixture. A specially constructed system of two Teflon-coated fans and blowers (see Figure 4) was used to rapidly exchange and mix the contents of the two reaction bags. Each blower forces the air from one reaction bag into the other, and the fans mix the air in the bags. This results in equal concentrations of common reactants in both reaction bags. The valves connecting the two bags can be closed to isolate the two chambers, and the fans can then be used to mix reactants in each of the sides separately.

The sampling to the continuous monitoring instruments are controlled by two computer-activated solenoid valves, which select the chamber side where air is withdrawn for analysis. One of these valves

Figure 4. Diagram of SAPRC Dividable Teflon Chamber (DTC).

controls the sampling for the O_3 and NO_x analyzers, where the sides being sampled are usually alternated every 10 minutes. The other valve is used to control sampling for formaldehyde, which usually had a 15 minute sampling time for each reaction bag. The data acquisition system controlled the sampling valves and kept track of which reaction bag is being monitored when the data are being collected.

The two reaction bags are designated as sides "A" and "B". Because two separate mixtures are being irradiated simultaneously, each DTC run consists of two separate experiments. These are designated as runs DTCnnnA and DTCnnnB, where nnn is the run number.

3.1.6 Xenon Teflon Chamber (XTC)

A schematic diagram of the Xenon Teflon Chamber (XTC) is shown in Figure 5. The XTC was set up in the space previously occupied by the dividable Teflon chamber (DTC), discussed above, with the fluorescent lights removed and with the reflective wall opposite the sampling window replaced by the sliding panel shown in the figure. The reactor consists of a single 5000-liter FEP Teflon reaction bag constructed in the same manner as the ITC, ETC, and DTC. The light source consisted of four 6.5 KW xenon arc lamps (Atlas model RM-65) which were evenly spaced on the wall of the chamber room

Figure 5. Diagram of SAPRC Xenon Teflon Chamber (XTC).

approximately 5’ from the chamber. A sliding panel is used to keep the chamber from being irradiated while the lights are warming up. All surfaces in the chamber enclosure are covered with reflective material to maximize the light intensity and dispersion. The floor, ceiling, and walls behind and opposite the lights are covered with polished aluminum panels, and the side walls had the aluminum-coated molded plastic reflectors which backed the fluorescent lights in the DTC. The chamber temperature was controlled to within ± 1 C by means of a temperature control system with a dedicated air conditioner. The air purification system was the same as for the DTC. Dry (~5% RH) air was used for all XTC runs in the data base. The construction and characteristics of this chamber are discussed in greater detail by Carter et al. (1994a).

3.1.7 Outdoor Teflon Chamber (OTC)

The SAPRC Outdoor Teflon Chamber (OTC) in the configuration employed during 1985-1993 is shown schematically in Figure 6. The configuration employed in the 1983 runs is similar, except a slightly different framework design was used (Carter et al., 1984a). The chamber consists of a ~30,000-50,000-liter, 2-mil thick FEP Teflon, pillow-shaped reaction bag located outdoors. The reaction bag is

Figure 6. Diagram of SAPRC Outdoor Teflon Chamber (OTC).

supported by nylon ropes on a framework and held 2.5 feet off the ground to allow air circulation under the chamber. A green indoor-outdoor carpet is located under the chamber. When the chamber contents are not being irradiated, the reaction bag is covered by an opaque tarp which is removed to begin the irradiation. An AADCO air purification system supplies pure dry air for this chamber. All OTC runs employed dry (~5%) air. The OTC chamber is described in more detail elsewhere (Carter, et al., 1984a, 1986a).

This chamber can be operated in a dual mode to allow two parallel experiments under the same lighting and temperature conditions. This division of the chamber into two separate reactors, which is made after reactants common to both chamber sides are injected and mixed, is accomplished by means of three 1 1/4-in diameter cast-iron pipes, which are surrounded by foam to protect the Teflon reactor. The reaction bag is divided by raising the lower pipe and placing it tightly between the upper pipes, then rotating them by 180 degrees. Previous tests have shown that this forms a tight seal, with the exchange between the chamber sides being less than 0.1% per hour (Carter et al., 1981). The chamber is oriented such that the pipes dividing the chamber run in a north-south direction, with side A, by convention, always being on the eastern half of the chamber. Most but not all OTC experiments were conducted with the chamber in the divided mode.

3.2 Typical Operating Procedures

3.2.1 EC

Preparation of the Chamber. Prior to each photochemical run the chamber was usually evacuated (at ambient temperature) for at least 12 hours at pressures of <5 x 10^{-2} torr (Runs before EC120) or <10^{-4} torr (Runs after EC121). From time to time the chamber walls were further cleaned by an evacuated bakeout at >200 F, followed by ozone conditioning at 10-20 ppm (minimum of 12 hours). (On a few occasions the walls were also washed with water or solvents, as described in the master run spreadsheet.) After Run EE261, the chamber was further conditioned from time to time by performing "dummy" propene-NO_x-air irradiations (initial propene ~0.5 ppm, NO_x ~0.5 ppm) for at least four hours, following evacuated bakeouts and actinometry experiments. This was done so that the condition of the chamber following actinometry or evacuated bakeouts would resemble that following a regular photochemical run. Experience has shown that this is required to assure high reproducability of replicate runs.

Pure Air Fill. Except as noted in the run spreadsheets or the comments with the runs. the chamber was filled with air prior to injection of the reactants. To achieve the desired temperature and humidity of the matrix air for each experiment, the pure air system was turned on at least 30 minutes prior to use and the chamber temperature controller was set to the desired gas phase temperature. The humidified air stream was brought via a heating wire-wrapped pipe to a manifold at one of the chamber ports, and allowed to by-pass the chamber through a flow meter into a tube equipped with both a Brady array humidity sensor and wet-dry bulb thermometer set. This arrangement allowed adjustment of both the humidity and temperature of the air stream to the desired levels before diverting the flow into the chamber.

The chamber was filled to a pressure of about 760 torr (about 25 torr above atmospheric pressure at Riverside) to allow installation of all sampling probes under positive pressure. Prior to Run EC197, the chamber was then opened to the atmosphere via a filter canister filled with equal volumes of Purafil, charcoal and indicating Drierite throughout the experiment. (Before each experiment, the canister was backflushed with pure air.) Beginning with Run EC197, the makeup air was provided from a Teflon bag which was filled with purified air at the same temperature and humidity as used in filling the chamber. After filling the chamber but before addition of the reactants, background levels of all species were determined. The total nonmethane hydrocarbon level was generally less than 80 ppbC.

Reactant Injections. In most cases, similar reactant injection methods were used for all chambers, and these are discussed in a separate section below. For run EC-230 and those following, the system for injection of reactants was modified to include a 1.6 cm (I.D.) Teflon disperser tube which runs the length of the chamber. Employing this system reduced mixing times to ~10 minutes. However, it also resulted in some formaldehyde loss in runs where formaldehyde was a reactant, as indicated by low measured formaldehyde compared to the calculated amounts injected (see EC run spreadsheet).

In some cases, formaldehyde, acetaldehyde or benzaldehyde were expanded into the evacuated chamber prior to the pure air fill. These cases are noted in the run spreadsheets or comments in the run data sets.

Irradiation Procedure. The solar simulator was brought to the desired power level with the douser (light barrier) in place at least 5 minutes prior to the start or irradiation. The chamber wall temperature control was switched to refrigerate at a setting of about 5 F below the desired gas phase temperature ~5 minutes before the run was begun in order to minimize the variation of the gas phase temperature due to the solar simulator heat load. During an experiment, a radiometer (EG & G Model 550) located at the far end of the chamber facing the solar simulator is maintained within ±0.02 mw/cm^2 of the value determined in the actinometry. Beginning with Run EC106, the relative spectral distribution of the photolyzing light was determined at least once at approximately the middle of the run.

Sampling. The sampling methods were usually similar regardless of which chamber was used, and are discussed in a separate section below. Some of the EC runs included sampling for H_2O_2, where the sampling method was essentially the same as described for formaldehyde, except that sampling times were 30 minutes. (The H_2O_2 data are now believed to be subject to interferences, have not been evaluated, and are not recommended for use in mechanism evaluation.) Since the EC is rigid, make-up air must be introduced into the chamber during the run to make up for sampling losses. Because of this, the sampling rates for the continuous monitoring were measured periodically, and, for runs prior to EC407, are given in the data sets with each experiment, and included in the run spreadsheets. The contribution of the GC sampling to the total sampling rate was generally negligible.

Procedures for Actinometry Experiments. The light intensity in the EC was measured by conducting NO_2 actinometry experiments by photolyzing NO_2 in N_2 according to the method of Holmes et al. (1973). These experiments are discussed in detail in Section 5.1.2. Before Run EC324, the solar simulator was brought up to the approximate desired power level before filling the chamber, and then was unshuttered briefly to allow adjustment of power to give the desired radiometer value. For Run EC324 and those following, the solar simulator power was held at the set value used for the associated photochemical runs and the radiometer value was not adjusted. The solar simulator was shuttered and the chamber was filled with nitrogen of ≥99.995% stated purity level. Approximately 20 torr of vacuum-distilled NO_2 (<1% NO) in a 500 ml bulb was then flushed into the chamber with nitrogen.

After mixing was completed and constant initial values for NO and NO_2 were obtained, the solar simulator was unshuttered and a one or two minute irradiation carried out. Radiometer readings (with a

330 nm interference filter of 80 nm full-width at half maximum) were taken every 10 seconds during the irradiation, and solar simulator power settings (product of current and voltage panel meter readings) were recorded, at least initially and at the end of the irradiation. During this brief irradiation period, the light intensity did not vary significantly (<0.01 mw/cm^2). The final NO_2 concentration was allowed to stabilize (~20 min) after the end of irradiation. The calculation of NO_2 photolysis rates from the results of these experiments is discussed in Section 5.1.2.

3.2.2 ITC

Before each experiment, the chamber was typically flushed with purified air for at least three hours with the lights on and then for at least two hours with the lights off. For the final flush purified air humidified to ~50% relative humidity (RH) was employed. Prior to any reactant injections, background samples were analyzed using all of the gas chromatographic instruments to be employed during the run. NO, NO_2 and the various organic reactants were then injected individually, as described below. Gas chromatographic (GC) samples were then taken on all instruments prior to the beginning of the irradiations, which, as noted above, were all carried out at 70% of the maximum light intensity.

The reactants were injected into the chamber using several methods, as discussed below. The procedures during the irradiation depended on the type of experiment being conducted. Most runs were 6-hour irradiations, where the light intensity was held constant at either 70% or 100% of maximum. GC and formaldehyde samples were taken at least hourly during these experiments, though for many runs more frequent GC samples were taken. Data from the continuous monitoring instruments were collected every 15 minutes during the entire experiment using a computer-based data acquisition system.

Several experiments were multi-day runs, in these cases the light intensity was held constant for 12 hours and the lamps were then turned off for 12 hours. GC and formaldehyde samples were taken hourly during the initial six hours of each simulated "day" day in multi-day runs, and also immediately prior to turning off the lights. In some multi-day experiments NO was injected into the chamber one hour after the resumption of the irradiation on the second or subsequent "days" of the irradiation.

The procedures for the various conditioning, characterization and control runs were similar, except that they were generally carried out for shorter periods of time; the details are usually indicated in the comments for each run which are included with their data sets, and where applicable are summarized in the master ITC run spreadsheet. See also the reports referenced in Table 3.

3.2.3 ETC

The procedures for runs in this chamber are similar to those for the ITC. Before each experiment, the chamber was flushed with purified air for at least 6 hours with the lights on and then for at least 3 hours with the lights off. The NO/NO_x monitors were zeroed with zero air prior to being connected to the chamber. The monitors for ozone and NO/NO_x were connected to the chamber approximately 1.5 hours before the start of the irradiation. Temperature was monitored prior to as well as during the experiments. Space heaters were turned on prior to the experiments to bring the chamber to the approximate temperature attained when the lights are on. The reactants were injected as described below, with the NO and NO_2 being injected last, approximately 15 minutes before the lights are turned on. Samples were then analyzed on the appropriate gas chromatograph (GC) before irradiation began. A measurement for CO was also taken. The irradiation began by turning on both banks of blacklights. Most irradiations lasted for 6 hours. Data from the continuous monitoring instruments (ozone, NO, NO_x, and temperature) were recorded every 15 minutes using a computer data acquisition system. GC samples were taken hourly for monitoring organic reactants.

3.2.4 DTC

The procedures for runs in this chamber are similar to those for the ETC. Before each experiment, the chamber was flushed with Aadco purified air for at least 6 hours with the lights on and then 3 hours with the lights off. The NO-NO2-NOx monitors and CO monitor were zeroed with zero air and instrumental zero, respectively and calibrated with span gases prior to being connected to the chamber. The monitors for ozone and NO-NO2-NOx were connected to the chamber approximately 1 hours before the start of the irradiation. A measurement of CO in the chamber was also taken only before the start of irradiation. Three temperature sensors were employed to monitor the temperature inside of each bag and of room air prior and during the experiments. The reactants were injected as described below, with the VOC reactants common to both sides being injected first, the NO and NO2 being injected next, and the reactants specific to one side or the other being injected last after the valves connecting the sides are closed. Two mixing blowers were turned on in the chamber to insure proper mixing when the reactants were injected, and to assure equal concentrations of the common reactants on both sides. After the common reactants were injected and mixed the valves connecting the sides were closed, but the fans continued operating to mix the reactants in the individual sides. The fans were turned off prior to the start of irradiation. Samples were then analyzed on the appropriate gas chromatograph (GC) before irradiation began.

The irradiation began by turning on half of both banks of blacklights. Most irradiations lasted for 6 hours. Data from the continuous monitoring instruments (ozone, NO-NO2-NOx and temperature) were recorded every 10 minutes using a computer data acquisition system. GC samples were taken approximately hourly for monitoring organic reactants for each side.

3.2.5 XTC

The procedures for runs in this chamber are similar to those for the DTC. The chamber was flushed with Aadco purified air for at least 6 hours before the experiment. The monitors were zeroed and calibrated and the CO was sampled as described for the DTC runs. The reactants were injected as described below, with the VOC reactants being injected first, and the NO_x being injected approximately 30 minutes before the start of the run. The reactants were mixed by a fan in the chamber which was turned off prior to the irradiation. Samples were then analyzed on the appropriate gas chromatograph before irradiation began.

The lights were turned with the shutter closed and allowed to stabilize for approximately 10 minutes before the start of the irradiation. A power level was set to read 4.0 KW at the beginning of the run, and was not adjusted during the course of the run. (Its variation during the course of the run was small.) The 4.0 KW power setting was used for all runs carried out thus far. The irradiation of the chamber began when the sliding panel was moved out of the path of the light. The light intensity was monitored continuously using a broadband radiometer, and the spectrum and intensity of the lights were measured using a LiCor LI-1800 spectroradiometer at least three times during each experiment. A shelf was cut out of one of the side walls to hold the spectrometer in the same position when it was used for all the runs. Most irradiation lasted for 6 hours. Data from the continuous monitoring instruments (ozone, NO-NO2-NOx and temperature) were recorded every 10-15 minutes using the same computer data acquisition system as employed for the DTC. GC samples were taken at least hourly.

3.2.6 OTC

The procedures for outdoor chamber runs varied somewhat with the program and are described in previous reports (Carter et al., 1984a, 1986a). Generally, the chamber was filled with dry, pure air in the morning before the run began. Background samples were taken prior to injection of the reactants. The reactants were injected using the procedures described below. Reactants common to both sides of the chamber were injected first, with the contents of the chamber being mixed by manually agitating the sides of the bag. The chamber was then divided and the reactants which are different on the various sides are injected and mixed. Samples were taken for analysis from both sides prior to the start of the irradiation. The reaction bag was then uncovered to begin the irradiation. This generally occurred between 9 and 10 AM. For single day runs, the run was terminated after 6 hours of irradiation. For multi-day runs, the chamber was generally covered after 6 hours of irradiation, and then uncovered the next day around 9:00 AM. This was done to avoid preferential irradiation of the western side of the chamber (side B) in the evenings and the eastern side (side A) in the mornings. GC samples were taken at least hourly.

3.2.7 Reactant Injections

Injections of reactants were generally made 45-60 min prior to the beginning of the irradiation, although in a number of cases, small supplementary injections for fine-tuning were made up to 30 min prior to the irradiation. The reactants were injected into the chamber using several methods, depending on the compound or group of compounds being injected. In the case of NO, the calculated volume of gaseous NO was taken from a cylinder of Matheson, C.P. grade nitric oxide and a 20-ml gas-tight, all-glass syringe (with a stainless steel tip), and diluted to 100-ml with N_2 using a separate 100-ml syringe. The NO_2 was prepared in a similar manner, except that the NO was diluted with an excess of O_2 to yield NO_2. The calculated amounts of other gaseous reactants (e.g., propene for the propene-NO_x-air irradiations, or propene and n-butane in the tracer-NO_x-air runs) were also measured using gas-tight syringes, and diluted to 100-ml in a syringe. The contents of these syringes were then flushed into the chamber with N_2.

After March 22, 1990, the NO and NO_2 were prepared for injection using a high vacuum rack. Known pressures of NO, measured with MKS Baratron capacitance manometers, were expanded into pyrex bulbs with known volumes, which were then filled with nitrogen (for NO) or oxygen (for NO_2). The contents of the bulbs were then flushed into the chamber with nitrogen. The NO was purified by passing it through cooled molecular sieve traps. This procedure was also used in a few earlier EC experiments, as indicated on the comments and spreadsheet entries for the affected runs. However, this procedure is not applicable for most EC nor any of the ITC runs.

Compounds which are liquids at room temperature were injected as follows: The desired amount of the liquid was injected, using a microsyringe, into a 5-liter Pyrex bulb equipped with stopcocks on each end and a port for the injection of the liquid. The port was then closed, and one end of the bulb was attached to the injection port of the chamber and the other to a nitrogen source. The stopcocks were then opened, and the vaporized contents of the bulb were flushed into the chamber for approximately 20 minutes.

Solid compounds were injected either by using vacuum techniques (similar to that discussed below for formaldehyde) or by placing the compound in glass filled tubes and flushing with N_2 for an amount of time sufficient to introduce the desired amount. If the vacuum method is used, the amount injected can be determined by the pressure of the vapor (measured by an MKS Baratron gauge) in a calibrated volume. If the tube flushing method is used, the amount injected, or appropriate amount of flushing time, can be determined by measuring the weight change in the tube.

Formaldehyde prepared by heating paraformaldehyde in an evacuated vacuum line with a 5-liter bulb attached until the pressure in the bulb corresponded to the desired amount of formaldehyde. The bulb was then closed and detached from the vacuum line, and its contents were flushed into the chamber with N_2 through the injection port. The formaldehyde was prepared on the same day as the start of the run. Separate tests where this technique was employed to inject the formaldehyde into the SAPRC EC (whose volume is constant and is accurately known) indicated that this technique is a reproducible and reliable method for injecting known amounts of formaldehyde into environmental chambers, provided that the dispersion tube was not used.

The components of the "urban surrogate" used in all the multi-day surrogate-NO_x-air runs conducted for the ARB-86 (Carter et al., 1986a) program (ITC865 through ITC891) were injected using a third technique. Dilute mixtures of these compounds prepared in two separate cylinders which were purchased for this purpose from Scott Environmental Technology, Inc. The first cylinder (Serial no. AAL5874) contained the surrogate components which are gaseous at room temperature, and consisted of 105 ppm ethene, 77.3 ppm propene, 149 ppm isobutene, and 165 ppm n-butane in N_2. The second cylinder contained the vapors of the surrogate components which are liquid at room temperature, and consisted of 164 ppm n-pentane, 77.2 ppm isoctane, 74.9 ppm toluene, and 64.3 ppm m-xylene, also in N_2. For each surrogate run, the desired pressures of each cylinder were introduced into evacuated 5-liter bulbs using a vacuum rack (with the pressure being measured using an MKS Baratron capacitance manometer), and then the contents of these bulbs were flushed into the chamber through the injection port.

3.2.8 Sampling Methods

Following the pure air fill, the continuous monitoring instruments for O_3 and oxides of nitrogen (see Section 4) were attached, and began to withdraw air from the chamber. Generally data were taken for at least a half an hour before the beginning of the irradiation. Usually the data was recorded in 15 minute intervals, though for some runs the data were recorded more frequently. The data recorded were usually 30 second averages centered around the time of the measurement given in the data base.

Sampling for formaldehyde, GC, GC-MS analysis using Tenax trapping was done prior to the irradiation (reported in the data sets as the T = 0 value) and, generally, at hourly intervals. Sampling times were usually 20 min for formaldehyde and 15 min for Tenax trapping. Sampling rates were measured with calibrated rotometers and reflected in the total sampling rates given in the data sheets for each run. For formaldehyde, concentrations and volumes of gas samples are reported at the midpoint of the sampling time (except at T= 0, as noted above), while volumes and concentrations derived from Tenax trapping are reported for the beginning of the sampling time.

Samples for each type of gas chromatographic analysis were generally taken before reactant injections, after injections and before irradiation, immediately before the start of the photolysis and at regular intervals thereafter. GC samples were withdrawn from the chamber either using 100 ml gas-tight, all-glass syringes or by collecting the 100 ml sample from the chamber onto Tenax-GC solid adsorbent cartridges. In the former case, the syringes were flushed at least three times with the sample gas before the sample for analysis was taken. A syringe was attached to the sample port of the chamber to withdraw a sample. In the case of indoor chambers, the sample port was a ca. 18 in x 0.25 in. Pyrex tube with a Becton-Dickinson stainless steel lever-lok stopcock manifold. The outdoor chamber had an ~18-in. x 0.25-in. FEP Teflon tube with a similar stopcock attached. Depending on the particular GC system used and the concentration range of the compound(s) being monitored, the contents of the syringe were either flushed through a 2 ml or 3 ml stainless steel loop (maintained at room temperature) and subsequently injected onto the column by turning a gas sample valve, or condensed in a trap cooled with liquid argon and then injected onto the column by simultaneously turning the gas sample valve and heating the loop with boiling water or ice water. In the analyses using the Tenax cartridge system, the sample was placed in series with the GC column, thermally desorbed at 220 C for 2 min. and cryofocused on the column.

4. ANALYTICAL METHODS AND DATA CORRECTIONS

4.1 Ozone

4.1.1 Measurement Methods

For most runs, ozone was monitored using one of several Dasibi Model 1003AH ozone analyzers. These work on the principle of UV absorption. The ozone concentration is obtained by measuring the relative intensity of transmitted UV radiation. The intensity is a function of the optics bench path length, the absorptivity of the ozone molecules, and the number of ozone molecules present. This quantitative relationship between these factors, i.e., Beer's law, is then used to calculate the ozone concentration. Calibration data for the applicable instruments, and the corrections made to the chamber data based on these, are discussed below.

The UV absorbance ozone monitors suffer from some positive interference (causing high O_3 readings) in the presence of sufficient amounts of some organic species which absorb in the same wavelength region. For the experiments in this data base, evidence for this problem was only found in runs containing injected cresols or naphthalenes. This is noted in the comments in the master run spreadsheet, where applicable.

Because of this interference, for many (though not all) runs containing initial cresols or naphthalenes, a Monitor Labs model 8410 ozone analyzer, which works on the principle of chemiluminescence from the reaction between ozone and ethylene, was used. Unfortunately, we were unable to locate calibration data for this instrument, so the accuracy of the data from this instrument is uncertain. In view of normal calibration practice in our laboratories at the time, it is unlikely that the instrument would be inaccurate by more than 10%. The calibration procedure was probably similar to that for the Dasibis, which is described below.

4.1.2 Calibration Methods

Primary Standards. Prior to Feb. 1979, the primary standards were used for the calibration of ozone monitors. The monitors being calibrated were sent to the California Air Resources Board laboratory at El Monte and calibrated with the known ozone concentration determined by the primary standard.

Transfer Standards. The transfer standards for calibrating ambient ozone monitors, which were approved by the U.S. Environmental Protection Agency on Feb. 8 1979, were used for all the experimental runs beginning in Feb. 1979. This new procedure is based on the use of ultraviolet (UV) photometry as a primary standard for ozone.

From Feb. 1979 to Dec. 30 1985, calibrations were carried out against a Dasibi Model 1003AH ozone monitor transfer standard which in turn was routinely calibrated by the California Air Resources Board. The ozone source was a Monitor Labs Calibrator Model 8500, with four different ozone concentrations, and the dilution gas was Medical Breathing Air. The analyzer being calibrated was first zeroed using Medical Air, then the calibrator was turned on to produce the highest concentration of ozone, ~.3 ppm. Both analyzers were allowed to equilibrate before the analyzers voltages were recorded. The ozone concentration was then reduced, and the output from both instruments was observed to verify that the response was linear, this being repeated at two lower ozone concentrations. If the response was not linear, then corrective action was taken. Finally, the analyzer being calibrated was again zeroed with Medical Air.

Starting in the beginning of 1986, an ozone generator and Teflon chamber were employed for the ozone calibration instead of Calibrator Model 8500. The purified dry air was used as the dilution gas. The ozone was made by inserting the ozone generator into the chamber and monitored by the transfer standard and the analyzer being calibrated. The ozone concentration was then increased gradually and the calibration factor for the analyzer was determined by least squares fit.

4.1.3 Calibration Data and Span Corrections

The summary of ozone calibrations is shown in Table 11 for the various ozone analyzers for which such data could be found. These data were used to assign calibration factors for each individual run. This was done either by averaging the ozone calibration data for the appropriate period of time, or by fitting the calibration data, as a function of time, to a line, and using that to estimate the calibration factor for the run, based on the time the run was carried out. The table indicates how these assignments were made. The columns in the table are as follows:

- Calibration date
- Calibration day number ("DayNo"). This is used to derive line fits, as a function of time, for calibrations which are assumed to change linearly with time. The "day number" is arbitrarily defined as the number of days after December 31, 1969. Each run also has a day number, calculated the same way. (The start date is used for multi-day runs.)
- Calibration span factor. (Factor the instrument reading is multiplied by to yield the "true" concentration.)
- Experimental standard deviation for the calibration span factor.
- Number of days since the first calibration in this set of calibrations. For estimation purposes, calibrations are grouped into "assignment sets" which are either averaged or fit to a line. The day of the first calibration in the assignment set was used as "time 0" in the linear regressions, when applicable.
- Set or assignment number for this group of calibrations ("Asn") (see below).

Table 11. Summary of ozone calibration factors and calibration factor assignments. (Based on calibration files as of 3/2/94)

Date	DayNo	Factor	Sdev	Days	Asn.	Cd	F(fit)	Unc.	Diff.	Runs	Avg/Intc	Sdev	Slope	Sdev
hInstrument 1070														
02/05/75	1862	1.108	0.0%	0	1	L	1.108	0%	0%		1.108	0%	-0.87E-01	0%
02/06/75	1863	1.021	0.7%	1	1		1.021	0%	0%					
02/06/75	1863	(undefined)												
08/05/75	2043	0.829	0.0%	0	2	A	0.826	0%	0%		0.826	0%		
09/05/75	2074	0.824	0.4%	31	2		0.826	0%	0%					
09/05/75	2074	(undefined)												
01/09/76	2200	1.001	0.0%	0	3	L	0.998	4%	0%	136	0.998	1%	-0.11E-05	404%
01/09/76	2200	0.815	0.0%	0	0	X								
09/22/76	2457	1.042	0.0%	257	3		0.998	4%	4%					
09/08/77	2808	0.981	0.0%	608	3		0.997	4%	-2%					
10/04/78	3199	0.930	0.0%	999	3		0.997	4%	-7%					
03/27/79	3373	1.015	0.0%	1173	3		0.997	4%	2%					
04/16/79	3393	0.971	0.0%	1193	3		0.997	4%	-3%					
11/28/79	3619	1.023	0.0%	1419	3		0.996	4%	3%					
09/23/80	3919	1.010	0.0%	1719	3		0.996	4%	1%					
06/14/93	8566	0.991	0.0%	6366	3		0.991	4%	0%					
12/08/93	8743	0.992	0.0%	6543	3		0.990	4%	0%					
Instrument 1140														
07/06/92	8223	1.035	0.8%	0	1	L	1.031	2%	0%	182	1.031	2%	0.42E-07	>999%
06/14/93	8566	1.014	0.0%	343	1		1.032	2%	-2%					
09/17/93	8661	1.047	0.0%	438	1		1.032	2%	1%					
12/08/93	8743	1.030	0.0%	520	1		1.032	2%	0%					
Instrument 1212														
02/05/75	1862	1.050	0.0%	0	1	L	1.050	0%	0%		1.050	0%	-0.56E-01	0%
02/06/75	1863	0.994	0.4%	1	1		0.994	0%	0%					
02/06/75	1863	(undefined)												
08/05/75	2043	0.807	0.0%	0	2		0.807		0%		0.807			
09/05/75	2074	0.854	0.0%	0	3		0.854		0%		0.854			
09/05/75	2074	(undefined)												
01/20/76	2211	1.040	0.0%	0	4	L	0.992	5%	5%	255	0.992	3%	0.39E-05	488%
09/08/77	2808	0.934	0.0%	597	4		0.995	5%	-7%					
10/04/78	3199	0.951	0.0%	988	4		0.996	5%	-5%					
03/27/79	3373	1.005	0.0%	1162	4		0.997	5%	1%					
04/16/79	3393	0.994	0.0%	1182	4		0.997	5%	0%					
11/28/79	3619	1.043	0.0%	1408	4		0.998	5%	4%					
09/23/80	3919	1.010	0.0%	1708	4		0.999	5%	1%					
10/03/83	5024	1.001	1.4%	2813	4		1.003	5%	0%					
09/21/89	7204	1.053	2.1%	0	5	L	1.073	5%	-2%		1.073	3%	0.16E-03	33%
09/25/89	7208	1.063	1.3%	4	5		1.073	5%	-1%					
02/26/90	7362	1.172	1.0%	158	5		1.098	5%	6%					
04/09/90	7404	1.064	0.9%	200	5		1.105	5%	-4%					
10/14/92	8323	1.250	0.1%	1119	5		1.253	5%	0%					
Instrument 1413														
01/09/76	2200	0.976	0.0%	0	1	L	0.979	1%	0%	25	0.979	1%	0.69E-05	75%
10/04/78	3199	0.992	0.0%	999	1		0.986	1%	1%					
07/17/81	4216	0.990	0.0%	2016	1		0.993	1%	0%					
Instrument 3378 (Minimum uncertainty of 5% used for run assignments)														
11/10/81	4332	1.003	1.0%	0	1	L	0.986	3%	2%	325	0.986	2%	0.18E-04	71%
05/11/82	4514	1.001	0.0%	182	1		0.989	3%	1%					
06/08/83	4907	0.964	0.1%	575	1		0.996	3%	-3%					
01/10/84	5123	0.982	0.0%	791	1		0.999	3%	-2%					

Table 11 (continued)

Date	DayNo	Factor	Sdev	Days	Asn.	Cd	F(fit)	Unc.	Diff.	Runs	Avg/Intc	Sdev	Slope	Sdev
07/30/84	5325	0.974	0.0%	993	1		1.003	3%	-3%					
02/25/85	5535	1.027	0.0%	1203	1		1.007	3%	2%					
12/30/85	5843	1.048	0.0%	1511	1		1.012	3%	3%					
12/01/88	6910	1.023	0.2%	2578	1		1.031	3%	-1%					
12/01/88	6910	1.023	0.2%	0	2	A	1.078	6%	-5%	190	1.078	6%		
09/21/89	7204	1.121	0.8%	294	2		1.078	6%	4%					
09/25/89	7208	1.019	1.1%	298	2		1.078	6%	-6%					
02/26/90	7362	1.105	6.4%	452	2		1.078	6%	2%					
04/09/90	7404	1.026	0.7%	494	2		1.078	6%	-5%					
11/14/90	7623	1.172	0.0%	713	2		1.078	6%	8%					
05/06/91	7796	1.139	0.4%	886	2		1.078	6%	5%					
05/17/91	7807	1.018	1.6%	897	2		1.078	6%	-6%					
05/17/91	7807	1.018	1.6%	0	3	L	1.017	0%	0%	348	1.017	0%	-0.24E-04	38%
05/21/91	7811	1.021	1.6%	4	3		1.017	0%	0%					
08/30/91	7912	1.009	1.8%	105	3		1.015	0%	-1%					
11/01/91	7975	1.016	1.7%	168	3		1.013	0%	0%					
01/10/92	8045	1.009	0.8%	238	3		1.012	0%	0%					
10/29/92	8338	1.006	0.9%	531	3		1.005	0%	0%					
Instrument 1790														
10/04/78	3199	0.932	0.0%	0	1	A	0.969	5%	-4%	4	0.969	5%		
11/28/79	3619	1.005	0.0%	420	1		0.969	5%	4%					

- Code giving assignment method or treatment of this calibration when making assignments. These are as follows: "L" = Data fit to a line for estimation purposes; "A" = Data averaged; "-" = previous calibration terminated; runs between this date and start of the next set are "uncalibrated"; "X" = Calibration rejected, i.e., not used in computing average or line fit for assignments.
- Calibration factor predicted by the average or linear regression for the date of this calibration ("F(fit)").
- Standard error of the estimate (for line fits) or standard deviation of the average as percent of predicted factor ("Unc.").
- Percent difference between experimental calibration factor and the regression estimate or average ("Diff.")
- Total number of SAPRC chamber experiments (of all types, not just the EC and ITC runs in this distribution) for which the ozone calibration factor for this instrument was estimated using this assignment set ("Runs").
- The intercept of the regression (i.e., regression value for the first calibration in the assignment set) if the line fit method was used, or the average if the average method was used ("Avg/Intc").
- Percent standard deviation of the intercept or the average.
- Slope if the line fit method was used, and its percent standard deviation.

The standard uncertainties of the linear regression estimates for the individual runs, or the standard deviations of the averages, give an indication of the minimum uncertainty in the ozone calibration factor due to scatter in the calibration data. In some cases the scatter is low, and uncertainties of less than 1% are derived using this method. However, based on the overall precision observed with these instruments, we consider it prudent to assume that the actual uncertainty is not less than 2%. The calibration data for Instrument 3378 was somewhat more scattered, and a minimum uncertainty of 5% was assumed for this instrument.

The ozone calibration factors for the runs using these instruments for the periods of time covered by these assignments were updated using the averages or regressions shown in Table 11. In addition, the uncertainty associated with these factors, which was either the uncertainty of the regression estimate or average, or the minimum uncertainty for the instrument (whichever was greater), was also included in the data files for the affected runs. This was used, along with the estimated zero uncertainty (discussed below), to determine the uncertainty of the ozone maximum for the run, as shown in the run spreadsheets.

If no uncertainty is given for the ozone maximum for a run, then calibration data are not available for the instrument used for the time period of the run. The modeler should use the data with caution when making conclusions about mechanism performance. The data may well be of high quality, but we cannot verify that.

There are no calibration data for the chemiluminescence ozone analyzer (instrument no. 8410), because we were unable to locate the records for this instrument. Therefore we could not make any span corrections or quantify the uncertainties in the calibrations. The run data files had no calibration corrections associated with data from this instrument. Our understanding is that calibrations were generally done (using a Dasibi) just prior to an experiment using the instrument. In any case, it us unlikely that the data would have to be corrected by more than ~10-15%, since if this discrepancy existed the instrument would probably have been adjusted or repaired, or a correction factor would have been entered into the data sets for the runs.

4.1.4 Zero Corrections and Uncertainties

Data from ozone analyzers can also be subject to zero errors, i.e., to give nonzero readings when the concentration is actually zero. The design of the UV instrument is such that it cannot give negative readings, which can be a potential source of bias. However, there is no significant indication of this sort of problem from the calibration data. On the other hand, there are indications of cases with positive zero errors in a number of runs. This would be the case if nonzero ozone readings were observed in the presence of NO at the beginning of the run before the lights are turned on. Because of their rapid reaction, O_3 and NO cannot coexist in the dark, and thus nonzero O_3 readings when excess NO is presence can only be due to zero error or interferences.

For all runs containing initial NO (which is the vast majority of the runs in the data base), ozone zero offsets were obtained by determining the O_3 reading in the presence of NO, and the data sets were corrected accordingly. The zero corrections (as well as the span factor) are stored with the data, so the modeler can derive the uncorrected data if desired. The zero corrections are also included on a run spreadsheet. Some runs had zero corrections as high as 15 ppb, but the vast majority of runs had no zero corrections or corrections of less than 1 ppb. The ITC had more cases where zero corrections were needed than the EC.

For the purpose of uncertainty estimates, all runs were assumed to have a zero uncertainty of 1 ppb or the zero correction, whichever was greater. Because of the small number of runs where zero corrections were needed, if no zero correction information is available (as would be the case for runs without added NO), the uncertainty was also assumed to be 1 ppb.

4.2 Oxides of Nitrogen

4.2.1 Measurement Methods

For all runs in the data base, oxides of nitrogen were monitored using instruments based on the chemiluminescence technique. In this method, NO is monitored directly based on light emitted from its reaction with ozone generated internally in the instrument, total monitored oxides of nitrogen ("NO_y") are monitored by converting them to NO using a catalyst, and "NO_2" is reported as the difference between the two. This is a satisfactory method for measuring NO at the concentration levels of these experiments, but its utility for measuring NO_2 is limited. This is because the catalyst converts other nitrogen-containing species such as PAN, organic nitrates, and nitric acid (Winer et al., 1974) to NO, so the "NO_2" data are useful only at the beginning of the run when NO and NO_2 are known to be the only NO_y species present in significant quantities, or when measurement data are available for all species converted to NO by the catalyst are present in significant quantities. Since nitric acid, which is known to be formed photochemically from NO_x, is not measured in any of our experiments, and the extent to which it reaches the converter is uncertain, we make no attempt to correct the "NO_2" data for these interferences, and consider the method only useful for determining initial NO_2 concentrations. For that reason, the names given to the NO_2 and NO_x measurements are "NO2-UNC" and "NOX-UNC", respectively. (Some earlier EC runs have NO2-CORR channels produced by PAN and organic nitrate measurements from NO2-UNC. These channels were not deleted, but their use for modeling is not recommended.)

The instruments used to measure NO and uncorrected NO_2 and NO_x in SAPRC chamber experiments to date were either Thermo Electron Corporation (Teco) model 14B, Teco Model 14B/E, or Columbia Scientific Industries Series 1600 analyzers. They all work basically by the same principle, though preliminary data from our laboratories indicate that the catalysts for the Columbia instruments do not appear to be as efficient in converting PAN to NO those for the Tecos. The work of Winer et al. (1974), who observed essentially 100% conversion for PAN and organic nitrates, was based on data using

Tecos. The various NO_x instruments used during the course of this program, and the time periods of their use, are listed in Table 6, above.

4.2.2 Calibration Methods

Prior to July 1990, Calibrations were performed bimonthly by diluting the output of a NBS or NIST cylinder containing ca. 100 ppm or ca. 50 ppm nitric oxide in nitrogen with Zero Air. The analyzer was first zeroed using zero air, then calibrated for NO by blending the calibration gas with Zero Air and measuring the flow of each gas with a bubble meter. The analyzer was allowed to equilibrate at each concentration for 30 minutes. The first concentration used was ca. 0.30 ppm. The analyzer's span controls were adjusted, if necessary, to match the NO output of the analyzer with the actual concentration. Two lower concentrations of NO were used to verify linearity of the analyzer. The converter efficiency was checked by setting a NO concentration of about 0.30 ppm, and then reacting this with a lesser concentration of ozone. If the converter was operating properly, the NO_2 reading equaled the difference in NO. The linearity of the converter was verified by using three different concentrations of ozone. After this procedure was completed, the analyzer was rezeroed with Zero Air. The accuracy and precision of this instruments in the absence of interfering nitrates was estimated to be better than 5 percent. Calibration factors for individual runs were determined based on the calibration result carried out before the runs.

Since July 1990 and onwards, the only difference for the NO-NO_2-NO_x calibration is that span calibrations were performed before each run instead of bimonthly. From the beginning of 1992, in order to record the drifts of zero and span for the analyzers being calibrated, zero and span adjustment was rarely performed for them, unless the difference of NO factor is more than 10 percent. Calibration factors for individual runs were assigned the factors measured on the same day. (This is not applicable to the EC and ITC runs in the present distribution, but is applicable for future distributions of SAPRC data.)

4.2.3 Calibration Data and NO Span Corrections

The raw data from the NO span calibrations and the NO_2 converter efficiency tests are given in computer data sets included with the distribution. Summaries of the results for the NO span calibrations for the various NO_x instruments are given in Table B-1, and Table B-2 gives the results of the NO_2 converter efficiency tests. (These tables are given in an Appendix because of their length.) The format of the data in these tables is the same as that for the O_3 calibration data in Table 11, which was discussed in detail in Section 3.1.3. As with the O_3 span data, NO span calibration factors or NO_2 converter are assigned for individual runs by averaging, or performing linear regressions on, calibration or converter efficiency data, carried out for the instrument around the time of the experiment.

Note, however, that before mid-1990 the general practice was to adjust the instrument during the calibration in an attempt to minimize the need for a span correction. Thus, calibrations carried out before and after such adjustments were not combined when computing the averages or linear regressions.

Because of this, the numbers of NO span calibration assignment sets are relatively large compared to ozone, where such adjustments were not made. In many cases, the assignment set consists of only two calibrations: the span factor measured after an adjustment, and the span factor measured before the adjustment in the next calibration. In those cases, the span factors for the runs between the two calibrations were derived from linear interpolations from the two measured factors, based on the day of the run relative to the times of the calibrations.

As with the O_3 calibrations, the standard uncertainties of the linear regression estimates for the individual runs, or the standard deviations of the averages, give an indication of the minimum uncertainty in the NO span correction factors due to scatter in the calibration data. In some cases the scatter is low, and uncertainties of less than 1% are derived using this method. However, based on the overall precision observed with these instruments, we consider it prudent to assume that the actual uncertainty is not less than 2%. In addition, if linear interpolation from only two points are used estimating the span correction factor for a run, the uncertainty of the span correction estimate is assumed to be the standard deviation of the average of the two points, or $1/\sqrt{2}$ times the difference between the two span factor measurements. This is to provide for the possibility (indeed, probability) that the sensitivity of the instrument did not change in a linear manner, as is assumed in the estimate.

Because the measurement of NO_y is made by converting NO_y to NO and then monitoring NO, the NO span corrections were also applied to "NOX-UNC" and "NO2-UNC".

4.2.4 NO_2 Converter Efficiency Checks.

Summaries of the results of the NO_2 converter efficiency checks are given in Table B-2. The NO_2 converter efficiencies for each run, and their associated uncertainties, were estimated in a manner analogous to the estimation of the span factors for O_3 and NO, as discussed above. As shown in the table, the converter efficiencies were 95% or better in most cases. However, there were exceptions, which are as follows:

- It was found that siloxanes, which were injected into the chamber around 3-4/91 (ETC-179 and subsequent runs), "poisoned" the NO_x converter. The converters were eventually replaced, but the exposure resulted in no valid NO_2 data for some runs, and low converter efficiencies for some others. This affects Teco #1510 and Columbia #1626 and runs ETC179 through ETC196.

- No applicable NO_x converter efficiency data could be found for Teco #1520 for runs EC349-EC416.

- A relatively low converter efficiency of 0.85 was measured for Teco #1530 on 2/4/81. This results in more uncertain NO_2 data than usual for runs EC462 - EC530.

- No applicable NO_x converter efficiency data could be found for Teco #1540 for runs OTC257-OTC270.

- The converter used in Columbia #1626 after 4/91 seems to have an efficiency around 95%. Although no correction to the NO_2 data was made in the data sets, a 5% upward correction may be appropriate. The uncertainty in the initial NO_2 values for affected runs are increased accordingly, though for most runs this was not the primary NO_x instrument.

- No applicable NO_x converter efficiency data could be found for Columbia #1625 for the period of runs EC862-EC903 and OTC145-OTC190.

The converter efficiencies estimated for the NO_2 data in the runs (and their uncertainties) were added to the data files for the runs (as auxiliary channel parameters — see Tables 9 and 10), but they were not used to correct the data. However, they were used when estimating the overall uncertainties in the initial NO_2 and NO_x concentrations in the runs. If there is no information available for converter efficiency, the initial NO_2 concentrations are assumed to have an additional 10% uncertainty. This is discussed further below.

4.2.5 Zero Corrections and Uncertainties

Data from NO-NO_x analyzers are also subject to zero errors. Although the instruments were zeroed electronically prior to each run and calibration, NO-NO_x zero checks were not routinely preformed during SAPRC chamber runs prior to 1990. (They were performed during the calibrations.) This affects all of the EC and ITC runs, and some of the ETC runs. However, methods are available for estimating these corrections based on measurements taken prior to and during most runs. Two methods are available in the case of NO and one in the case of "NO_2" and NO_y. These are as follows.

Estimation from Pre-Injection Measurements. In a typical run, measurements of the pure air used to fill the chamber are made prior to the NO and NO_2 injection. If it is assumed that the pure air is NO_x-free, this can serve as a basis for estimating zero corrections for both NO and NO_2. Because the time period between when the sampling from the NO_x instruments begins and the time when the NO and NO_2 are injected, and because these data are usually recorded only once every 5-15 minutes, there are often few or no NO and NO_2 measurements in the data set for this period. Therefore, the method used to make these estimates was to examine the strip charts for each run, and determine the difference between the "raw" (i.e., prior to any span correction) NO and NO_2 concentrations before and after the injection of these compounds. The difference between these values and the "raw" initial NO or NO_2 concentrations in the data set were then taken to be the zero corrections. (This somewhat roundabout method was used because the zero on the chart may not be exactly the same as the zero on the data system.) This highly labor-intensive procedure was used to make NO and NO_2 zero estimations for all potentially relevant indoor chamber runs prior to 1990. Most of this work was carried out by Jim Killus, with some assistance by one of the authors (Dongmin Luo).

Estimation of NO zeros from measurements in the presence of O_3. NO and O_3 cannot coexist at significant concentrations in the dark because of their rapid mutual reaction. In the presence of light they can coexist to some extent because the photolysis of NO_2 generates both NO and O_3, and a photostationary state is set up between this reaction, the reaction between NO and O_3, and (if other reactants are present) other processes which consume NO. However, if O_3 is sufficiently high, the photostationary state NO concentration would be sufficiently low that it can serve as an effective zero for the instrument. In addition, in most experiments both NO and NO_2 are consumed by the end of the run. Based on this, zero offset estimates were derived based on NO concentrations measured at the end of runs where significant ozone formation occurred and NO_x appeared to be mostly consumed.

Figure 7 shows distribution plots of NO and NO_2 zeros derived using the above two methods for the SAPRC EC and ITC runs. Also shown is the distribution of the differences between the NO zero corrections derived using the two methods. There is essentially no correlation between the NO zero corrections derived using the two methods, as can be seen by the fact that the width of the distribution plot of the difference is as wide as the distributions of the results from the separate methods, and also from plots of NO zeros derived by the two methods against each other (not shown). The estimates from the data at the end of the run are also more biased towards positive corrections than are those from the data at the beginning of the run.

Assignment of Zero Corrections for NO in EC Runs. Since the NO zero offsets derived from the strip charts at the beginning of the run have less bias in the distribution, and since it is possible that there is some NO still present or some NO interference at the end of some of the runs, we use the zero offsets derived from the strip charts at the beginning of the run to derive the NO zero corrections. However, the difference between the two methods is used to derive the uncertainty in the zero correction. If no information could be derived from the strip charts, no zero correction was used. In this case, the uncertainties in the zero corrections were assumed to be 12 ppb, based on the observed distributions of zero corrections for these runs.

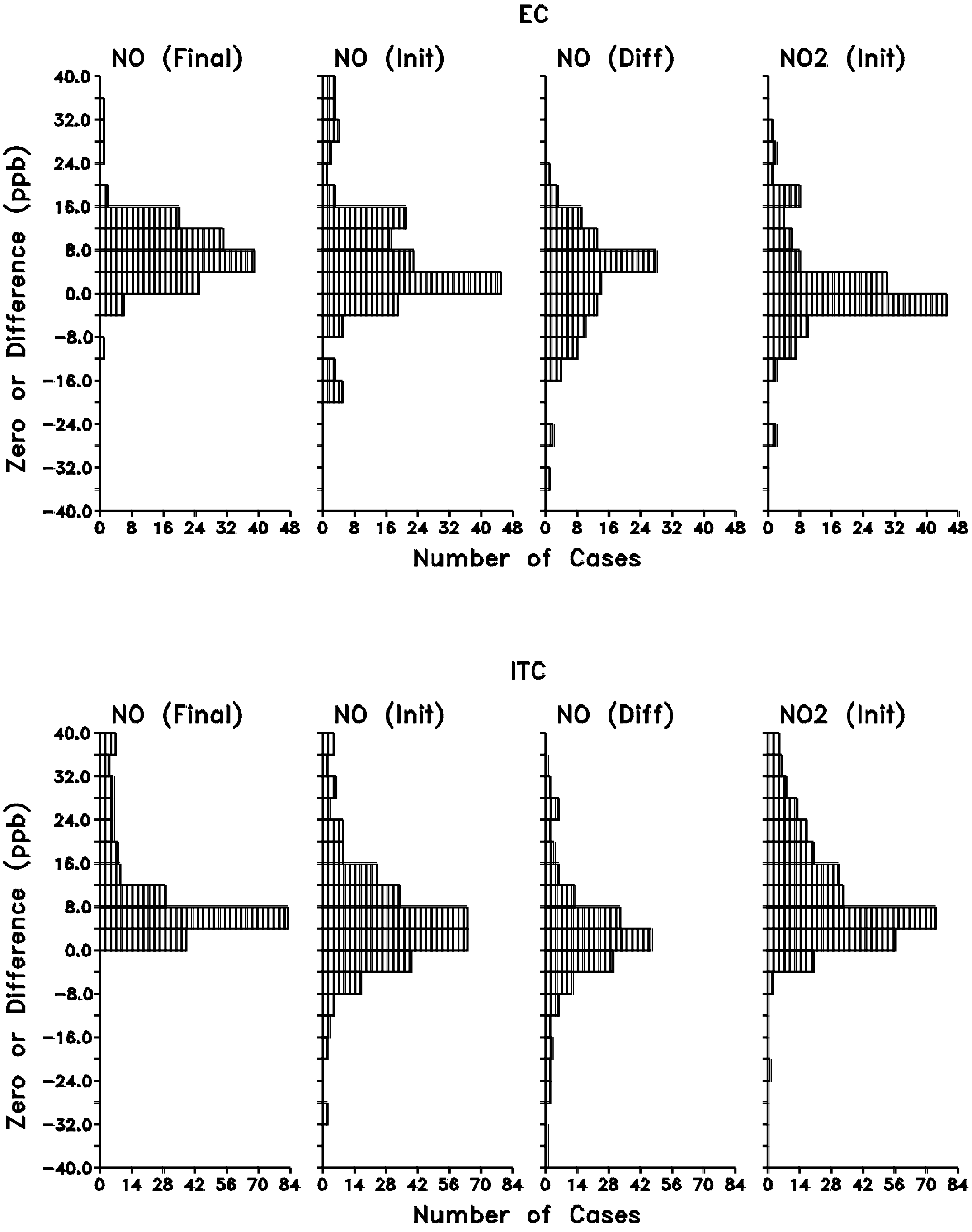


Figure 7. Distribution plots of zero corrections, or differences between zero corrections using different methods, for NO and NO_2 in the EC and ITC chamber runs. "(Init)" = corrections derived from data before the start of the run; "(Final)" = corrections derived from data at the end of the run; "(Diff)" = difference between the two correction methods.

Assignment of Zero Corrections for NO in ITC Runs. The NO zero corrections for ITC runs were derived in the same way as for EC runs, except that if the correction could not be derived from the strip chart data, an uncertainty of 10 ppb was assumed.

Assignment of Zero Corrections for NO_2 in EC Runs. The distribution of the NO_2 zero corrections derived from the strip chart data for the EC runs appears to be reasonably unbiased, and in general was lower than the zero corrections derived for NO. Lower zero errors are expected for NO_2 than NO for instruments which are functioning properly, since NO_2 is the difference between total NO_x (or NO_y) and NO. These corrections were applied to the data. However, the zero correction was assumed to be 100% uncertain, i.e., a zero correction uncertainty equal to the zero correction was used when deriving the uncertainty in the initial NO_2 concentrations. If the zero correction was less than 2 ppb, an uncertainty of 2 ppb was assumed. If the NO_2 zero correction could not be derived from the strip chart data, the data were not corrected, and a zero uncertainty of 15 ppb was assumed.

Assignment of Zero Corrections for NO_2 in ITC Runs. Figure 7 shows that there is a clear positive bias for the NO_2 zero corrections derived from the strip chart data for the ITC runs. Since similar instruments were used for both the ITC and EC, it is unlikely to be due to an instrument effect. A more likely cause would be carry-over of NO_2 from the previous run, or NO_x species offgasing from the walls. Thus, the "clean" air in the chamber at the start of the run contains some NO_2, which would result in a positive, and erroneous, "zero" correction if the NO_2 were assumed to be zero. Carry-over would not be expected to be a problem in the EC because it is evacuated completely, but the ITC cannot be completely evacuated. Instead, it is emptied to the extent possible, and then flushed for a period of time between runs. Carry-over of NO would be less of a problem, since in most runs sufficient ozone is formed by the end of the run to remove all remaining NO.

More direct evidence of NO_2 carry-over in the ITC can be seen from plots of the NO_2 "zero" correction derived from the strip chart data against the initial NO_x in the run on the previous day. Plots for the various instruments are shown in Figure 8, where it can be seen that a definite correlation exists. Three instruments were used in a sufficiently large number of runs to derive a relationship, and for two of these (#1510 and #1627) the slopes, which indicate the fraction of the NO_x from the previous run carried over to the next, were essentially the same. The slope is smaller (though possibly still significant) for #1626, which was used for runs ITC729-ITC791. Perhaps somewhat more thorough flushing procedures were used at that time, relative to the others.

In view of this evidence for NO_2 in the chamber initially, the NO_2 measurements at the beginning of the run could not be used as an indicator of the NO_2 zero corrections. However, the intercepts of the plots in Figure 8 give an indication of the probable average of the true zero corrections for the various

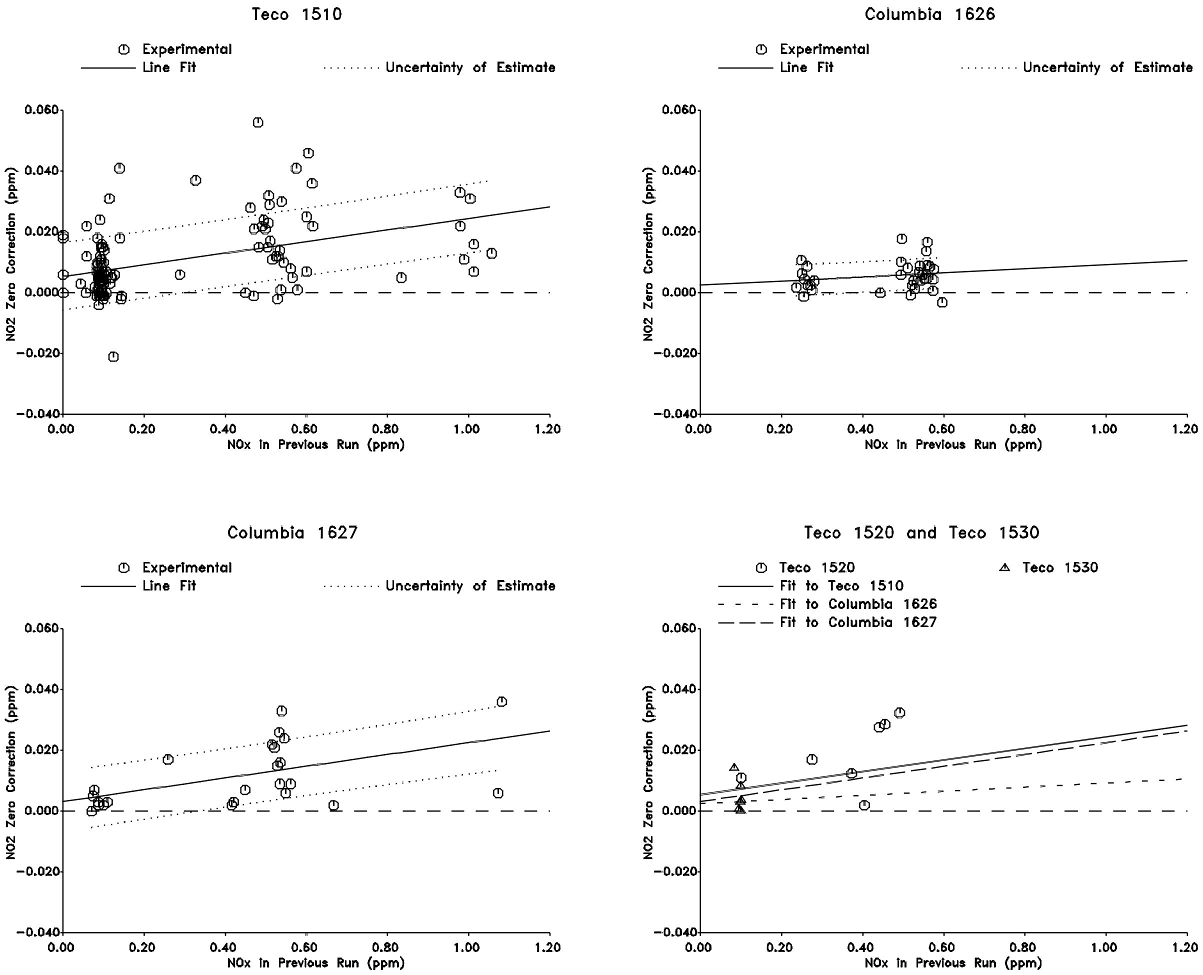


Figure 8. Plots of NO_2 zero corrections from ITC runs derived from initial NO_2 data against total NO_x concentrations in the previous ITC run.

instruments. In addition, the uncertainties of the predictions of the linear regressions of the "zero" derived from the initial measurements give an indication of the likely degree of scatter in the true zeros. In view of this, the following assignments were used:

Instrument	NO_2 Zero	Uncertainty	Notes
Teco #1510	5.4 ppb	11.0 ppb	
Teco #1520	5.4 ppb	11.0 ppb	Assumed to be same as #1510
Teco #1530	5.4 ppb	11.0 ppb	Assumed to be same as #1510
Col'a #1626	2.5 ppb	5.5 ppb	
Col'a #1627	3.2 ppb	9.5 ppb	

These global assignments were made for all ITC runs using the above instruments. The actual "zero" correction derived from the strip charts of the initial NO_2 data for the individual runs are given with the data sets (and in the ITC spreadsheet) but were not used to correct the data.

The Columbia #1627 instrument when used for runs ITC925-ITC997, exhibited significant zero drift for the NO and NO_x channels. Because of this, zero assignments were much more uncertain than usual. An uncertainty of ~50 ppb was assumed for NO measured with this instrument for these runs. Low NO_x runs in this series are probably not modelable. Data from this instrument should not be used for modeling if the run has data from some other NO_x instrument.

4.3 Organic Species by Gas Chromatography

4.3.1 Measurement Methods

Organic reactants and products were monitored using a number of different GC systems, each suitable for a particular set of compounds. These instruments are listed in Table 6. The columns, flow rates, temperature programs, history of significant changes, and other details concerning the instruments are summarized in Table 12, and are discussed below for each instrument. Note that as with other instruments, each GC instrument is identified with a unique 4-character code number and also a 8-character label. Different code numbers and labels are used for each GC instrument with a particular type of column, and are changed when the type of column in the instrument is changed. Table 12 indicates when column changes necessitated changing the instrument identification number and label. If a column was removed from an instrument and then replaced, there may be more than one entry in Table 12 for the same instrument number.

Although peroxyacetyl nitrate (PAN) was also monitored by GC, somewhat different procedures and considerations are involved. For that reason, the PAN analyses are discussed separately in Section 4.4, below.

Instrument 2290 "DMS-2". This instrument was one of the "DMS" GC systems and was used to monitor C2-C5 alkanes and alkenes. It consisted of the electrometer and flame ionization detector (FID) from a Varian 1400 GC with 36 feet by 0.125 inch stainless steel (SS) column packed with 10% 2,4-dimethylsulfolane on acid-washed 60/80 mesh Firebrick. At the end of this column, before the detector, was a 2’ x 1/8" SS "soaker" column packed with 10% Carbowax 600 on Firebrick. The carrier nitrogen flow through these two columns was set up at 26 ml min^{-1}, the hydrogen flow was set up at 27 ml min^{-1} and the oxygen flow was 300 ml min^{-1}. The columns were maintained at 0 C and the detector was heated to 115 C. The 100-ml gas samples were trapped on a 10" x 1/8" SS column packed with 10% 2,4-dimethylsulfolane on Firebrick, 60/80 mesh, immersed in liquid argon. The sample was then introduced to the column by simultaneously thawing the trap in the ice water and turning the gas sampling valve. In some experiments where these compounds were monitored at higher concentrations, sampling

Table 12. Summary of conditions for the gas chromatographic instruments used in the chamber runs.

Date	Description	Conditions
	Instrument 2290 (Varian 1400#8; DMS-2; FID; trap & loop)	
04/10/79	36’ x 1/8"ss 10% 2,5-dimethylsulfolane on c-22 Firebrick, 0 C, with "soaker" column 2’ x 1/8" SS 10% Carbowax 600 on C-22 Firebrick (30-60 mesh); 0 C ; FID	N2=26 ml/min H2=27 ml/min O2=300ml/min
09/25/81	Put new 36’x1/8" SS 10% 2,4-DMS on C-22 Firebrick & new 2’x1/8" SS 10% Carbowax 600 on C-22 Firebrick	N2=35 ml/min H2=35 ml/min O2=250ml/min
01/11/82	New "soaker" packing (with 10% C-600 on C-22 Firebrick 100/120 mesh)	N2=40 ml/min H2=40 ml/min O2=250ml/min
	Some changes made during 04/20/89 to 11/10/89 but no runs carried out	
04/20/89	30’ 23% SP-1700 on Chromosorb P 80/100mesh	
04/27/89	Changed carrier gas to Helium	
05/04/89	Switched to Nitrogen carrier gas	
	Instrument #2291 (Varian 1400#8; 30m GS-Q; FID; trap)	
11/10/89	Installed 30m x 0.53mm megabore gas-solid porous polymer GSQ column integrator used	He=3 ml/min (as carrier); N2=30 ml/min (as makeup); H2=58.1ml/min O2=210ml/min
01/16/90	Intergrator not integrate consistently; Detect.T 200 C used mv response insteady Column T 70 C	
04/06/90	Problems with GC (cut 12" from both ends of column; cleaned detector area; collector rod was broken)	
11/22/90	Problems; detector assembly removed, cleaned and etc.	
12/04/91	Inst.#2290 moved to burning tower (atmospheric chemistry trailer)	The same gas flow set
03/17/93	20sm was removed from both of ends of the column (was problems with chromatogr.)	
05/17/93	GSQ column was removed from	

Table 12 (continued)

Date	Description	Conditions
	Inst.#2290 & placed into GC Inst.#2800.	
	Instrument 2200 (Varian 1400 #1, DMS-1)	
06/27/72	34.5’ x 1/8’ SS 10% DMS (dimethyl sulfolane)+18" 10% Carbowax E-600 on C-22 Fi+rebrick	H2=50 ml/min N2=50 ml/min O2=330ml/min
05/13/75	Replambed DMS completely (cut 10" & etc.)	
07/02/75	New loop installed	
01/18/77	Replaced soaker material (10% C-600 on C-22 42/60mesh Firebrick; Shortered soaker column (2")	
11/06/77	Repacking trap (DMS/Firebrick)	
12/08/77	Put new PN trap	
06/17/80	Problems with injection valve	
08/25/81	SS loop was broken	
06/29/82	GC moved from Fawc.rm.121 to Champ.station #1	
08/10/82	Put "new" soaker into column	
11/15/82	Shut power off; Moved back to Champ.station	
11/17/82	Power on	
10/17/83	GC moved from Champ.station up to rm.121 Fawc.; O2=330ml/min	
03/08/85	GC moved to Champ.station	
04/09/86	Repacking soaker (w/ 10% Carbowax 600 on Firebrick 30/60mesh; N2=45ml/min	
03/06/89	Repacking 2’ soaker; N2 flow back to 50ml/min	
01/05/89	Used new ID Inst.	
04/03/89	Removed 34.5’ and soaker column and put in DMS-2 column from GC VA 1400#8	
	Instrument 2290 (Varian 1400#8; DMS-2; FID; trap & loop)	
04/10/79	36’ x 1/8"ss 10% 2,5-dimethylsulfolane on c-22 Firebrick, 0 C, with "soaker" column 2’ x 1/8" SS 10%	N2=26 ml/min H2=27 ml/min O2=300ml/min

Table 12 (continued)

Date	Description	Conditions
	Carbowax 600 on C-22 Firebrick (30-60 mesh); 0 C ; FID	
09/25/81	Put new 36’x1/8" SS 10% 2,4-DMS on C-22 Firebrick & new 2’x1/8" SS 10% Carbowax 600 on C-22 Firebrick	N2=35 ml/min H2=35 ml/min O2=250ml/min
01/11/82	New "soaker" packing (with 10% C-600 on C-22 Firebrick 100/120 mesh)	N2=40 ml/min H2=40 ml/min O2=250ml/min
	Some changes made during 04/20/89 to 11/10/89 but no runs carried out	
04/20/89	30’ 23% SP-1700 on Chromosorb P 80/100mesh	
04/27/89	Changed carrier gas to Helium	
05/04/89	Switched to Nitrogen carrier gas	
	Instrument #2291 (Varian 1400#8; 30m GS-Q; FID; trap)	
11/10/89	Installed 30m x 0.53mm megabore gas-solid porous polymer GSQ column integrator used	He=3 ml/min (as carrier); N2=30 ml/min
01/16/90	Intergrator not intergrate consistently; Detect.T 200 C used mv response insteady Column T 70 C	(as makeup); H2=58.1ml/min O2=210ml/min
04/06/90	Problems with GC (cut 12" from both ends of column; cleaned detector area; collector rod was broken)	
11/22/90	Problems; detector assembly removed, cleaned and etc.	
12/04/91	Inst.#2290 moved to burning tower (atmospheric chemistry trailer)	The same gas flow set
03/17/93	20sm was removed from both of ends of the column (was problems with chromatogr.)	
05/17/93	GSQ column was removed from Inst.#2290 & placed into GC Inst.#2800.	
	Instrument #2920 (Varian 1400 #3;10’C600;FID;LOOP & TRAP)	
11/04/75	10’ x 1/8" SS 10% Carbowax 600	H2=35 ml/min
11/04/75	10’ x 1/8" SS 10% Carbowax 600 on C-22 Firebrick(100-120 mesh);	H2=35 ml/min N2=50.5ml/min

Table 12 (continued)

Date	Description	Conditions
	70 C; FID	O2=250 ml/min
06/14/76	Installed 10" glass bead trap	
	instead 11" trap	
05/17/77	H2 flow changed	H2=45ml/min
10/26/77	Started analyze aromatics	
08/07/81	Column T was varying between 78 & 80	
	(Variation of Ret.times)	
	Instrument #2922 (Varian 1400 #3;10’c-600;FID;LOOP & TRAP)	
07/13/82	Installed 5’x1/8" 5% C-600 on C-22Firebrick	H2=45 ml/min
	(from 1400#2)	N2=50 ml/min
		O2=250ml/min
		Oven T 75 C
		Detect.T 200 C
	Instrument #2920 (Varian 1400 #3;10’C600;FID;LOOP & TRAP)	
07/29/82	10’10% C-600 column back	Gas flows set
		Detect.T 185 C
06/10/83	Started analyze terpenes	
04/19/89	Column temperature changed	Oven T 100 C
12/11/91	Column temprerature back to 75 C	
07/11/91	Started to use area response	
08/05/91	486 Lab computer on line	
12/04/91	C-600 gc moved to burning tower	N2: 48psi
		H2; 14psi
		O2: 30psi
	Instrument #2925 (Varian 1400#4; 10’C-600; FID; TRAP)	
08/27/82	10’ x1/8" SS 10%C-600 column	N2=50 ml/min
	installed	H2=45 ml/min
11/02/82	GC turned off	O2=250ml/min
12/18/82	Turned GC on	
06/03/83	Restart GC	
06/15/83	Put "old"(from Roger) 10’ 10%	
	Carbowax E-600 on 100/120mesh C-27 Firebrick	
06/20/83	New 10’ x1/8" SS 10% C-600 on 100/110	
	mesh C-22 Firebrick installed	
	No runs on data base carried out between 10/22/84 and 03/11/85	

Table 12 (continued)

Date	Description	Conditions
10/22/84	Moved GC from Champ.station to rm.121 Fawc.; Removed 10’10%C-600 column and put 6’ x 1/8" SS Porapak QS, that was used for methanol analysis	
03/11/85	GC was moved to the Champ.station	
03/13/85	Removed PQS column & installed 10’x1/8" SS 10% C-600 that was originally installed 830603	
06/10/85	Probably some problems; heated up detector, balanced GC	
	Instrument #2930 (Varian 1400#2; 10’C-600; FID; LOOP & TRAP)	
01/19/67	10’x10% C-600 column;FID	H2=35 ml/min
01/27/76	New 10’ 10% C-600 on C-22(100/120 mesh)	N2=50.5ml/min
03/24/76	Section of DMS column installed; H2=30ml/min; N2=30ml/min;O2=300ml/min	O2=250 ml/min
03/29/76	Changed column to 5’Porapak	
09/26/78	Moved Inst.1400#2 from rm.121 to rm.103 Fawc.	
10/06/78	20’x1/8"SS 5%C-600 on C-22(100/115 mesh) installed; back to original flow set; column T 95 C	
11/05/78	3’ 10%C-600 column installed; column T 90 C; O2 cahnged to 200ml/min	
11/14/78	5’5% C-600 column installed (from Inst.1400#1 to Inst.1400#2)	
01/09/79	O2 flow changed to 300 ml/min; Detector T 170	
01/28/81	10’x1/8"SS 5%C-600 on C-22 (100/110 mesh) installed	
07/31/81	5’5%C-600 SS column on C-22 (100/115 mesh)installed	
08/13/81	New 5’5%C-600 column installed	
11/04/81	New flow set; H2=45ml.min;N2=50ml/min; O2=280ml/min;detector T reset to 160 C	
01/06/82	Some changes:installed new burner tip & etc	
03/18/82	Problems;removed & cleaned collector, detector & flame jet	
07/14/82	1&1/2"of the 5’5%c-600 column were cut off	
07/30/82	New Valco gas sampling valve installed	
08/12/82	Put another glass bead trap	
10/20/82	Problems: cleaned detector, burner tip & etc.	

Table 12 (continued)

Date	Description	Conditions
	Instrument 1403 (Varian 1400#2; 3-PART; FID; LOOP & TRAP)	
11/20/74	Took out Carbowax E-600 column & put in 3P column	H2=25 ml/min N2=25 ml/min
12/17/75	Problems. Found N2 flow was 56ml/min instead 40ml/min	O2=300ml/min
09/24/76	Column T lowered from 65 C to 60 C	
10/11/76	A new Bentone 34/DMP section prepared (for 3P column)	
11/09/76	Took out 3-PART column & installed 5’ Porapak Q	
11/10/76	Reinstalled 3-PART column	
11/15/76	5’ Porapak Q installed again	
02/22/77	3-PART back in place	
03/04/77	Column T now 55 C	
05/04/77	1400’s #2 & #3 Inst. switched, i.e. 3-PART column into GC 1400#3	
05/12/77	Switched columns back, so 3-PART is in GC 1400#2	
10/27/77	Removed 3-PART column & placed orig. 3-PART column (from rm.103) The same temperature & gas flow set	
05/18/78	3-PART removed & returned to rm.103	
09/26/78	Inst.1400#2 moved from rm.121 to rm.103; 3-PART column is in bad shape	
	Instrument 2100 (Varian 1400#6; PN; FID; LOOP & TRAP)	
06/13/74	5’ x 1/8" SS Porapak N (80/100 mesh); FID	H2=60 ml/min N2=80 ml/min O2=400ml/min Column T 60C 2ml SS Loop;or 10ml Trap
11/03/75	PN column removed & put into VA 1200	
01/12/76	PN column back in VA 1400	
10/29/86	GC turned off	
12/16/86	Restarting PN column	
10/04/89	Just Loop analysis	
01/02/91	Started to use for Ethene @ a test compound Ethane	
01/29/91	New 6’ x 1/8" SS Porapak N	

Table 12 (continued)

Date	Description	Conditions
	installed	
08/05/91	New 486 Lab.computer on line Area response	
12/04/91	Moved to burning tower area (Trailer).	
	Instrument 2190 (RM-103; 5’ POROPAK-N GC; FID)	
	The log book for this instrument could not be located, so no information is available concerning operation conditions or calibration data. It is probably essentially a duplicate of Instrument 2100.	
	Instrument 2195 (Varian 1400; PN-3; FID; LOOP & TRAP)	
07/29/82	6’ x 1/8" ss Porapak N; FID	H2=60 ml/min N2=80 ml/min
07/30/82	New detector	O2=400ml/min Detector T 120C Column T 60 C
02/26/90	GC moved to room 103 Fawc.	
	Instrument 2120 (Varian 1400#1; PQS-1; FID; TRAP)	
	6’ x 1/8" CC Porapak QS (100/120mesh); FID 10" x 1/8" SS trap packed with glass beads	H2=40 ml/min N2=50 ml/min O2=300ml/min Detector T 200C Column T 110 C
09/10/85	Trap packed w/ 10% 2,4-dimethyl-sulfolane on Firebrick (60/80mesh) Before this tube was packed with glass beads 80 mesh	
	Instrument 1402 (Varian 1400#1; PN; FID; LOOP)	
01/10/91	6’ x 1/8" Porapak N 80/100mesh column installed Oven T 60 C	N2=40 ml/min H2=40 ml/min O2=240ml/min
05/09/91	Oven T increased (140 C for 2 hours) to attempt to clean the column since last calib. was significantly different	Oven T 120 C Detector T 200C

Table 12 (continued)

Date	Description	Conditions
	Instrument 1400 (Varian 1400#7; C-20M; FID; LOOP)	
02/01/78	20’ x 1/8" SS 5%total DC703/C20M on 100/120 AW, DMCS Chromosorb G; FID	N2=50 ml/min (as carrier) H2=45 ml/min O2=375ml/min
02/07/78	2"x1/8" trap (from DMS Inst.) packed w/ 10%DMS on 40/60 Firebrick	
03/15/78	New 10"x1/8" SS tubing packed w/ 4%OV-101 on 80/100 Chrom.G AW/DMCS	
04/14/78	Removed DC-703/C-20 column and installed 5’Porapak N column	
05/03/78	Removed PN column,setting up w/ 10’x1/8" SS 3.5%TCEP on 80/100 Phenylisocyanate/Poracil C	
05/04/78	9’ 1/8" SS 5%TCEP on 100/120 Chrom.W AW/HMDS installed	
06/02/78	10’x1/8" SS 5%b-b’-Oxydipropanitrite on 100/120 Chrom.W	
09/06/79	Reinstalled 20’x1/8" SS 5% total DC703/C20M; using OU-101 trap	Column T 60 C Detector T 170C
	Instrument 1400 (Varian 1400#7; C-20M; FID; LOOP)	
04/25/80	Reinstalled 20’ DC703/C20M; 3 ml SS Loop	O2=250ml/min
01/06/81	Problems;cleaning of detector & etc.	
01/19/82	Noise;put new burner tip	
03/26/82	O2 setting changed to 270ml/min	
04/07/82	New setting for O2 flow rate:336ml/min; column T 60 C;Detector T 180 C	
05/19/87	Problems; changed electrometers	
01/10/90	Replaced column w/ new one same type 2.5%Carbowax 20M+2.5%DC703 on 100/120 AW DMCS	
10/31/90	Instrument moved;since all the gas connections were changed ; O2=300ml/min;	
12/05/90	Inst.was disconnected.Then gases reconnecte detector completely cleaned & etc.	
10/05/92	GC moved to 103rm.Fawcett.	

Table 12 (continued)

Date	Description	Conditions
	Instrument 2701 (Varian 1400#5; C-20M; FID; TENAX)	
01/30/84	Removed Super Pak II column & put 6’ x 1/4" 4% Carbowax 20m/0.8% KOH on Super Pak II; Changed T programm	H2=30ml/min N2=30ml/min
	Instrument 2702 (Varian 1400#5; P-C-II; FID; TENAX)	
02/07/84	Changed column back to Super Pak II; Detector T 200 C	
	Instrument 2701 (Varian 1400#5; C-20M; FID; TENAX)	
03/26/84	4% Carbowax 20m + 0.8% KOH on Super Pak II put back (4" were lost)	
	Instrument 2702 (Varian 1400#5; P-C-II; FID; TENAX)	
04/02/84	Lost 40% of packing material of column; 4% Carbowax 20m/0.8% KOH on Super Pak II was removed and replaced with Super Pak II; New T program	
	Instrument 2701 (Varian 1400#5; C-20M; FID; TENAX)	
05/08/84	Replaced Super Pak II column with 4% Carbowax 20m/0.8% KOH on Super Pak II column (new packed)	
	Instrument 2702 (Varian 1400#5;P-C-II;FID;TENAX)	
06/04/84	Put Super Pak II column back; changed T programm	
	Instrument 2701 (Varian 1400#5; C-20M; FID; TENAX)	
11/06/84	Super Pak II column was broken; removed and replaced with Super Pak with 4% C 20m + 0.8%KOH; new T program	
	Instrument 2703 (Varian 1400#5; P-C-II; FID; TENAX)	
12/15/84	Changed column to Super Pak 20m; T programm for naphtalene	

Table 12 (continued)

Date	Description	Conditions
	Instrument 2650 (Varian 3700; se-54; FID; LOOP)	
09/02/80	No record identifying the column used could be found. 3-step Temp program starting at -90C.	H2=30 ml/min O2=300ml/min He=1.8ml/min (as carrier) He=30 ml/min (as makeup)
01/22/81	Installed 11.3 ml glass loop; changed T programm	
	Instrument 2750 (HP 5170A#2; SE=52C-2 ;FID; LOOP)	
06/05/80	fused silica Capillary column 30m SE-52-2	
01/14/81	Converted from gas phase injection to liquid phase injection Tinit=-50C @16C/min to 20C; 4C/min to 200C	
01/21/81	Detector T changed to 300 C	
02/04/81	Conversion to gas phase injection Glass loop installed; H2=30ml/min; N2=30ml/min; O2=230ml/min; He(as carrier)	
07/01/81	N2(as carrier)=1.15ml/min	
04/19/82	Column was broken (just to the top) & was lowered 5mm more; Detector T 250 C; Oven T 200 C	
08/03/82	Capillary column was broken (threaded to capillary column through a short lenght of Teflon tubing); N2(carrier)=1.41ml/min; N2(makeup)=30ml/min; H2=60ml/min; Med.air=200ml/min;	

Table 12 (continued)

Date	Description	Conditions
	Instrument 2850 (HP5711A#3; SC; FID; LOOP)	
11/13/81	30m x 0.322mm fused silica capillary column (by J&W; had a film thickness of 1 m composed of the bonded liquid phase DB-5C);FID	N2=0.6ml/min (as carrier); N2=30 ml/min (as makeup); H2=30 ml/mi O2=230ml/min
11/17/81	Removed trap and replaced loop	Tinit=50C,
12/15/81	Replaced 3" x 1/8" tubing (copper) (which protected capillary column through the oven wall) with a similar piece of Teflon tubing	8C/min to 200C
01/20/82	Replaced with 10.2ml glass loop instead 9.00ml glass loop	
03/05/82	GC was shut down	
08/09/82	GS moved to to Champ.station#1 & restart again; the same gas flow set;	
12/15/82	Column was broken	
06/06/83	Column was repaired & installed again	
11/15/83	Inst.#2850 moved to rm.121 Fawc.	
11/19/84	N2 flow 25ml/min	
03/11/85	GC moved to Champ.station again; N2(carrier)=1ml/min; N2(aux)=30ml/min	
06/24/85	The same gas flow set; Detector T 250 C; Column T 200 C	
07/01/85	Problems with H2 flow; Capillary column installed 1cm up into the burner jet’s tail	
12/03/85	GC moved to rm.121 Fawc.	
12/04/85	Changed gas flow N2(makeup)=45ml/min; Detector T 200 C (instead 250 C)	
05/13/86	Problems; some changes (fan,new cable & etc.); N2(carrier)=1.1ml/min; N2(aux)=30ml/min	

Table 12 (continued)

Date	Description	Conditions
	Instrument 2500 (HP 5880; DB-5; FID; TENAX)	
12/15/90	15m DB-5 (5% phenyl-methylsilicon) Megabore column; FID	N2=10 ml/min (as carrier);
03/10/91	Octamethylcyclotetrasiloxane and Decamethylcyclopentasiloxane also calibrated with prepared MeOH solution	N2=30 ml/min (as aux); H2=30 ml/min O2=150ml/min Detector T 250 C
	Instrument #2600 (HP5890#1; 15m DB-5; FID; LOOP & TRAP)	
08/13/91	15m x 0.53mm DB-5 Megabore column; FID; Detector T=300 C; 1/8" SS tubing trap w/0.066mm glass beads used;also loop	H2=30 ml/min O2=150ml/min He=10 ml/min (as carrier) N2=20 ml/min
	Instrument #2603 (HP5890#1; 30m DB-5; FID; LOOP)	
08/10/93	30 m DB-5 column installed	(as makeup) Tinit=-15 C; @30 C/min to 125C Tinit=-30 C; @35 C/min to 10C @20 C/min to 110C @70 C/min to 200C Latest:Tinit=-65C
	Instrument #2601 (HP5890#1; DB-5; FID; TENAX)	
11/19/92	30m x 0.53mm DB-5 Megabore column installed for Tenax system	Tinit=-30 C; @35 C/min to 10 C; @15 C/min to 200 C
8/10/93	15m Tenax column installed	
	Instrument 2800 (HP5890; 15M DB-5; FID; LOOP & TRAP)	
09/04/92	15m x 0.53mm DB-5 Megabore Column	H2=31.5ml/min O2=145ml/min He=10 ml/min (carrier) N2=20 ml/min (makeup) Detector T 300C Tinit=-50 C;

Table 12 (continued)

Date	Description	Conditions
	Instrument 2801 (HP5890; 30M DB-5; FID; LOOP & TRAP)	
11/10/92	30m x 0.53mm DB-5 Megabore Column installed	@20 C/min to 150 C & @70 C/min to 200 C
04/02/93	1/8" SS tubing loop 50sm long installed	Tinit=-65 C; @15 C/min to 35 C & @30 C/min to 175 C & @70 C/min to 200 C
	Instrument 2802 (HP5890; 30M GS-Q; FID; LOOP)	
05/17/93	30m x 0.53mm GSQ column (from old VA 1400)installed	Tinit=-55 C; @70 C/min to 35 C @15 C/min to 200 C
	Instrument 2700 (HP5890; DB-5; ECD; LOOP)	
08/15/91	15m x 0.53mm DB-5; ECD maintained at 250 C	He=9ml/min (as carrier); 5%methane/argon (as makeup) =94ml/min
12/04/91	Inst.#2700 moved to Burning tower area (trailer)	
04/04/92	Column was broken (removed 1’ length)	
09/03/92	A bulkhead fitting installed	
12/04/92	Some changes(different fittings; T; longer loop & etc.)	
01/13/93	T programm was changed	
01/28/93	New 1/8" Teflon tubing was placed from the CCL4/Tracer injector to bag itself	
02/01/93	Some not major changes to find optimum analysis for CCL4 & Tracer	
	Instrument 2710 (HP 5890#3; HP-1; ECD; LOOP)	
08/15/91	5m x 0.53mm megabore HP-1 column; ECD maintained at 50 C	He=10ml/min (carrier) 5%methyl/argon =60ml/min (makeup)
12/04/91	Inst.#2710 moved to Burning tower area	
12/04/92	Some not major changes	
01/13/93	T programm was changed	

was carried out by flushing a 2 ml loop with the sample from the chamber,with the contents of the loop then being injected into the column.

Instrument 2291 "GSQ". Beginning on November 11, 1989, the "DMS-2" column was replaced with a new 30 m x 0.53 mm megabore gas-solid porous polymer GSQ column and the detector temperature was maintained at 200C. It was designed to monitor n-butane, trans-2-butene, dimethyl ether, ethane, isobutene, isoprene, propane, propene and (for some runs) the mini surrogate component ethene. The helium carrier flow was set at 3 ml min^{-1}, the hydrogen at 58.1 ml min^{-1}, and the oxygen at 210 ml min^{-1}. In most cases, a 100 ml sample was trapped onto a SS loop immersed in liquid argon as described above, or the sample was collected in 3 ml SS loop and injected as described previously. Generally, the initial column temperature was 75 C and held for 1 minute, then a temperature ramp of 20 C min^{-1} was applied up to a final temperature of 120 C. In cases when both ethane and ethene were analyzed simultaneously the column was maintained isothermally at 50 C. The mv response was occasionally used to quantitate the amount of compound present, whereas, in most cases, an integrator was used to quantify the peak area. Beginning on January 22 1992 the peak area was measured with an Hewlett-Packard analog-to-digital converter and HP Chemstation software.

Instrument 2200 "DMS-1". This instrument was another separate "DMS" system and was also used to analyze C2-C5 alkanes and alkenes. It consisted of Varian 1400 GC with FID and a 36’ x 1/8" SS column packed with 10% 2,4-dimethylsulfolane on acid washed 100/120 mesh Firebrick. At the end of this column was a 21 x 1/8" "soaker" column packed with 10% Carbowax 600 on C-22 Firebrick (30/60 mesh). The carrier nitrogen flow through these two columns was set at 50 ml min^{-1}, as was the hydrogen flow. The oxygen flow was 300 ml min^{-1}. The columns were maintained at 0 C and the detector was heated to 115 C. The 100 ml gas samples were trapped as described above. The mv response was measured from the strip chart recording and used to quantitate the amount of compound present.

Instrument 2920 "10’C-600". This instrument consisted of a Varian 1400 GC with a flame ionization detector (FID) and a 10 feet by 0.125 inch stainless steel (SS) column, packed with 10% Carbowax 600 on C-22 Firebrick (30-60 mesh). For most runs starting from 1975, analysis of aromatic hydrocarbons, aliphatic aldehydes and ketones, organic nitrates and then later isoprene (1983-1989) were performed using this GC system. From 1991 this instrument was used to monitor n-C6 and m-xylene, acetaldehyde, acetone, ethylbenzene, isopropanol, octane, o-xylene, toluene, 1,2,3-trimethylbenzene, 1,3,5-trimethylbenzene and 1,2,4-trimethyl- benzene. The flow through this column was set at 50 ml min^{-1}, and, as was the case for most of the Varian GC’s, the carrier gas was nitrogen. The hydrogen flow was kept at 45 ml min^{-1}, and the oxygen was set at 250 ml min^{-1}. The detector was heated to 200 C, and the column was maintained at 75 C. The 100 ml samples that were drawn from the chamber were trapped by pushing the gas sample through a 10" x 1/8" SS tube, packed with glass beads (80 mesh) and immersed in liquid argon. The sample was carried onto the column by then immersing the trap in boiling water and simultaneously actuating the gas sampling valve which was heated to 125 C to prevent adsorption of compounds. The mv response was measured from the strip chart recording and used to quantitate the amount of compound present. Starting on August 12 1991 the peak area was measured with an Hewlett-Packard (HP) analog-to-digital converter and HP Chemstation software. This yielded a significantly improved quantification for all compounds, especially n-hexane.

Instrument 2922 "5’C-600B". This consists of the same instrument as the "2920" except that a shorter C-600 column was used. This was used to monitor some organic nitrates in EC runs which are not included in the data base.

Instrument 2925 "10’C600C". This was another "10’C-600" GC and was used for the same types of compounds: oxygenates, organic nitrates and aromatic hydrocarbons as #2920. It was used from 1982 to 1985. It consisted of a Varian 1400 GC with FID and 10’ x 1/8" SS column, packed with 10% Carbowax 600 on C-22 Firebrick (100/110 mesh). The flows for all gases were set as was the case for Instrument 2920. The detector was kept at 200 C, and the column was maintained at 75 C. The same trap technique was employed. The mv response was measured from strip chart recording and used to quantitate the amount of compound present.

Instrument 2930 "5’ C-600". This was used to monitor toluene, benzaldehyde, m-xylene, m-tolualdehyde and some other aromatic reactants and products during 1978 to 1984. It consisted of Varian 1400 GC with FID and a 5’x 1/8" stainless steel (SS) column packed with 5% Carbowax 600 on C-22 Firebrick (100/115 mesh). The nitrogen carrier flow was set at 50.5 ml min^{-1}, the hydrogen flow at 35 ml min^{-1}, and the oxygen flow at 250 ml min^{-1}. Sampling was done as for the 10’ 10% C-600 (2920), except that the traps in which the sample was concentrated were heated with boiling water instead of an ice bath, and the GC injection valves were heated to 95-100 C. The mv response was used to quantitate the amount of compound present.

Instrument 1403 "3-PART". This was used for some of the earlier EC runs to monitor aromatic hydrocarbons and/or oxygenates. It was a Varian 1400 GC with a flame ionization detector (FID) and a 3-part column consisting of three 1/8" stainless steel (SS) tubes in series, packed as follows: 5% 1,2,3,-tris(2-cyanoethoxy)-propane on HDMS Gas Chrom W (100/120 mesh) (10’); 5% Bentone 34 + 5% dinonyl phthalate on HDMS Gas Chrom W (100/120 mesh) (5’); and 10% Carbowax 600 on C-22 firebrick (30/60 mesh) or HDMS Gas Chrom W (100/120 mesh). The columns were held at 65 C; the carrier nitrogen flow through these three columns was set at 25 ml min^{-1}, as was the hydrogen flow, and the oxygen flow was 300 ml min^{-1}.

In general, this system did not separate the oxygenates as well as did the C-600 system, so use of the C-600 system for oxygenate analysis was preferred. However, the 3-part system gave better separation for ethylene oxide so it was used to monitor that compound. The mv response was measured from strip chart recording and used to quantitate the amount of compound present.

Instrument 1405 "SP-1000". (Not listed in Table 12.) This instrument consisted of Varian 1400 GC with a FID and a 6’ x 2mm I.D. glass column packed with 0.1% SP-1000 on Carbopak C, was used to monitor benzaldehyde, cresols and nitrotoluenes in 1976-1978. The nitrogen carrier flow was held at 20 ml min^{-1}, the hydrogen at 30 ml min^{-1}, and the oxygen at 200 ml min^{-1}. Samples for analysis on the SP-1000 column were collected by drawing a known volume of sample (generally ~ 10 liters) through a 60-80 mesh Tenax-filled, 3" x 4 mm I.D. tube at ambient temperatures. The Tenax tube was placed in series with the SP-1000 column and heated to 250 C, while the column was held at 150 C. The carrier gas then drove the compounds of interest off the Tenax tube and onto the column. Following the desorption process, which took 20 minutes, the column was temperature-programmed from 150 C to 250 C at 20 C min^{-1}. The procedure employed using this system was more difficult then any of the other GC analyses.

The same instrument was used for several runs to monitor cresols, nitrotoluenes and hydroxynitrotoluenes using a 10’ x 1/8" glass column packed with 60/80 mesh Tenax GC (Alltech). The sampling procedure employed was similar to that used for the SP-1000 system (since the same instrument was used). The Tenax traps were heated to 250 C and its contents were desorbed onto the 100 C column for 5 min. The column was then temperature-programmed from 100 C to 250 C at 20 C min^{-1}. The mv response measured from the strip chart recording or cm^2 response measured from integrator were used to quantitate the amount of compound present.

This instrument was only used in runs EC264 - EC346. As discussed by Pitts et al. (1979), significant problems were observed in the analyses methods with this instrument. As shown in the tabulations of calibration data in Appendix B, extreme irreproducability was observed in the calibration results with minor changes in the procedure. Because of this, we did not change the recommended calibration factors, but instead rely on those which were assigned at the time by the researchers who were familiar with the many problems involved. Contaminant peaks were also a significant problem. We recommend that modelers use the data from this instrument with extreme caution. At best, the data should be considered to be uncertain by at least ± 50%.

Instrument 2100 "PN-1". This consisted of Varian 1400 GC with a flame-ionization detector and a 5 feet by 0.125-inch stainless steel column packed with Porapak N, 80/100 mesh, and was used to monitor methane, ethane, ethene and acetylene. The nitrogen carrier flow was set at 80 ml min^{-1}, the hydrogen at 60 ml min^{-1} and the oxygen at 400 ml min^{-1}. The column was maintained at 60 C, while the detector was heated to 180 C. When a sample was to be analyzed for methane, 100 ml of sample was pushed through a 3 ml SS loop. The sample in the loop was then transferred onto the column by actuating the gas sample valve. Sampling for ethene, ethane and acetylene was accomplished by trapping the sample in 11’ x 1/8" SS column packed with 10% Carbowax 400 on Firebrick, 30/60 mesh, immersed in liquid argon. The sample was thawed by immersing the trap in ice water while turning the valve so that the sample was transferred to the column.

From January 1991, a new 6’ x 1/8" SS Porapak N column was installed into this instrument and used to analyze ethene and ethane. The nitrogen carrier flow was set at 80 ml min^{-1}, the hydrogen at 60 ml min^{-1}, and the oxygen at 400 ml min^{-1}. The column was kept at 60 C, while the detector was heated to 200 C. In these case, when a sample was to be analyzed, 100 ml of gas was pushed through a 2 ml SS loop and injected onto the column by actuating the gas sampling valve. The mv response was measured from the strip chart recording and used to quantitate the amount of compound present. Starting on August 12 1991 the peak area was measured with an Hewlett-Packard analog-to-digital converter and HP Chemstation software.

Instrument 2190 "PN-2". This instrument was very similar to the "PN-1" discussed above, and monitored the same compounds. It was used in the EC runs through EC565. Unfortunately, the log book for this instrument, containing all the calibration data and information about the conditions, could not be located. Therefore, the calibration data for it could not be re-evaluated. The accuracy and precision is probably similar to the PN-1 instrument.

Instrument 2195 "PN-3". This is similar to the ’PN-1’ GC and was also used to analyze methane, ethane, ethene and acetylene. It consisted of a Varian 1400 GC with a FID detector maintained at 120 C and a 6’ x 1/8" SS column packed with Porapak N, 80/100 mesh. The gas flows were the same as these set for Instrument 2100. The column was kept at 60 C. The same loop and trap methods were employed. The mv response was measured from strip chart recording and used to quantitate the amount of compound present.

Instrument 2120 "PQS-1". This consisted of a Varian 1400 GC with a flame ionization detector and a 6’ x 1/8" stainless steel (SS) column packed with Porapak QS 100/120 mesh (Inst.#2120) and was used to monitor methanol. The nitrogen carrier flow was set at 50 ml min^{-1}, the hydrogen flow at 40 ml min^{-1}, and the oxygen flow at 300 ml min^{-1}. The detector was heated to 200 C, and the column was maintained at 110 C. 100 ml samples drawn from the chamber were trapped by pushing the gas sample through a 10" x 1/8" SS tube immersed in liquid argon. For the indoor chamber runs and the outdoor chamber runs up to August 1985, the tube was packed with glass beads (80 mesh). For runs after August 14, 1985, the tube was packed with 10% 2,4-dimethylsulfolane on Firebrick (60/80 mesh). The sample was thawed by immersing the trap in boiling water and simultaneously turning the valve so that the sample was transferred to the column. The mv response was measured from the strip chart recording and used to quantitate the amount of compound present.

Instrument 1402 "PN-1400A". This instrument employed a 6' x 1/8" SS Porapak N column primarily to monitor ethene. The same loop technique, as used for "PN" GC, was performed. The mv response was used to quantitate the amount of compound present.

Instrument 1400 "C-20M". This consisted of a Varian 1400 GC with a flame ionization detector (FID) and a 20 feet by 0.125 inch stainless steel (SS) column packed with 2.5% Carbowax 20 M + 2.5% DC703 on acid washed dichlorodimethylsilane treated Chromosorb G, 100/120 mesh. It was used to monitor n-C_5~n-C_{10} alkanes, cyclohexane, methylcyclohexane, isoprene, MTBE, furan, thiophene, and a number of alkenes. The nitrogen carrier flow was set at 50 ml min^{-1}, the hydrogen flow at 45 ml min^{-1}, and the oxygen at 330 ml min^{-1}. The column was maintained at 60 C, while the detector was heated to 180 C. Analyses were performed by flushing the 3 ml SS loop with the contents of an 100 ml syringe. The sample in the loop was transferred onto the column by actuating the six-port gas sampling valve. Later, in 1991 this GC system was employed to analyze two test compounds, MTBE and hexamethyldisiloxane. The oxygen flow was reset at 300 ml min^{-1}, and the detector was kept at 200 C. The mv response was measured from the strip chart recording and used to quantitate the amount of compound present.

Instrument 2701 "SP C-20M". For the experiments in the data base, this instrument was used primarily to monitor Pyrrole. The column used was a 6 foot by 0.25 inch Pyrex column packed with 4% Carbowax 20M + 0.8% KOH on Superpak II. The temperature program consisted of keeping the column at 100 C for 2 minutes after injection and then heating the column at 10 C min^{-1} to 160 C. In most cases, the mv response was used to quantitate the amount of compound present, and, an integrator was occasionally used to quantify the peak area.

Instrument 2702 "SP C-II". This consisted of a Varian 1400 GC with a FID heated to 225 C and a 6 foot by 0.25 inch Pyrex column packed with Super Pak II. This instrument was used to monitor naphthalene, 2-methylnaphthalene, 2,3-dimethylnaphthalene, tetralin and n-tetradecane. Directly attached to the column, through the 245 C heated injector was a 5" x 1/4" Pyrex tube packed with Tenax GC (60/80-mesh) through which the nitrogen carrier gas flowed at 30 ml min^{-1}. The hydrogen flow rate was at 30 ml min^{-1}, and the oxygen flow was 260 ml min^{-1}. For analysis using this system, sampling via a syringe was not employed. Instead, the sample was obtained by attaching the Tenax packed tube to a "T"-joint in the continuous sampling instruments line, and drawing 100 ml of sample gas through the Tenax tube with a 100 ml gas tight syringe. Then the Tenax tube was reattached to the GC, and the carrier flow was restarted. Immediately thereafter, a heated desorber was attached to the Tenax tube. The desorber consisted of two burner blocks electrically heated to 255 C and cut-out to surround the 0.25 inch Tenax tube. The temperature program was started 2 minutes after the carrier flow was started. Two different temperature programs and two columns were used. The temperature program employed in this analysis consisted of keeping the column at 80 C for 2 minutes and then heating the column to 140 C at 8 C/min.

After an analysis was completed, and before another was begun, the column was cooled to the starting temperature, the carrier flow was stopped, the desorber was removed, and the Tenax tube was removed from the GC and capped.

Instrument 2650 "VAR3700". This consisted of a Varian 3700 GC with FID, interfaced to a Varian CDS III data system. It was used to monitor C5-C15 alkanes and aromatic hydrocarbons such as benzene, toluene, xylenes, and etc. From 1980 to 1984, a few different columns were employed, i.e., 10'SS 5% Carbowax 600, 10'SS 10% Carbowax 600 on C-22 Firebrick and 5'SS 10% C-600. Information concerning which column was used could not be located. The helium carrier flow was set at 1.8 ml min^{-1}, the nitrogen make-up at 30 ml/min, the hydrogen was at 30 ml/min, and the oxygen was at 210 ml/min. When a sample was to be analyzed, 100 ml of gas was pushed through a 2 ml SS loop and injected onto the column by activating the gas sampling valve. An integrator was used to quantify the peak area.

Instrument 2750 "SE-52C-2". This was a Hewlett-Packard 5710A gas chromatograph with a FID and employed a 30 m SE-52 coated fused silica capillary column. This system was capable of monitoring most C5-C13 alkanes, and was also used to monitor aromatics (benzene, toluene, xylenes, ethylbenzene, isopropylbenzene, etc.) and biogenic organic compounds (α-,β-pinene, d-limonene, 3-carene, p-cumene). The helium carrier flow was set at 1.5 ml min^{-1}, the hydrogen flow at 30 ml min^{-1}, as was the nitrogen (make up gas) flow, and the oxygen flow at 230 ml min^{-1}. The detector was heated to 200 C. The 100 ml sample was flushed through an 10 ml silylated Pyrex loop, and the contents of this loop were then transferred over a 12 minutes time span to the head of column which held at -90 C. The GC oven temperature then rose to -50 C over a 1.5 minute time period and was temperature programmed from -50 C to 200 C at rate 8 C min^{-1}. An integrator was used to quantify the peak area.

Instrument 2850 "DB-5C-1". This was a Hewlett-Packard 5711A gas chromatograph with FID and a 30 m x 0.322 mm fused silica capillary column. It was used to monitor C5 and higher alkanes and alkenes, aromatic hydrocarbons and some oxygenates and alkyl nitrates. Fused silica capillary column, manufactured by J&W Scientific, Inc., had a film thickness of 1 µm composed of the bonded liquid phase DB-5. The nitrogen carrier flow was set at 0.6 ml min^{-1} and the makeup gas, also nitrogen, was set to 30 ml min^{-1}. The hydrogen and oxygen flows were maintained at 30 ml min^{-1} and 230 ml min^{-1}, respectively. Before a sample was taken, the column oven was cooled to -90 C. Sampling was accomplished by flushing 100 ml of sample through a dichlorodimethylsilane treated 10.2 ml glass loop. The GC gas-sampling valve, which was maintained at 145 C, was then actuated, and the sample was transferred onto the head of the column (at -90 C) over a period of 12 minutes. The column was then heated from -90 to -50 C over a 1.3 minute duration. The temperature program was then started with the column being heated from -50 to 200 C at a rate of 8 C min^{-1}. An integrator was used to quantify the peak area.

Instrument 2500 "DB-5 TNX". This was a modified Hewlett Packard 5880A GC with Tenax cartridge sampling system, was used to monitor the compounds ethoxyethanol, carbitol, octamethylcyclotetrasiloxane. This GC was fitted with a 15 m DB-5 (5% phenyl-methylsilicone) megabore column and samples detected with an FID maintained at 200 C. The column would be kept at -10 C while the sample desorbed from Tenax cartridge (ca.2 min.), then a temperature ramp of 8 C min^{-1} would be applied up to a final oven temperature of 200 C. The nitrogen carrier flow was set at 10 ml min^{-1}, the hydrogen flow at 30 ml min^{-1}, and the oxygen flow at 150 ml min^{-1}. Peak areas were measured and used to quantitate the amount of compound present.

Instrument 2600 "HP1 DB5S". This is a Hewlett Packard 5890 Series II GC with a FID detector maintained at 300 C and a 15 m x 0.53 mm megabore DB-5 column. It was used to supplement (from October 8 1991) and then later (from January 22 1992) replace the "10'C-600" GC described above. As such, the compounds analyzed were identical to those detected on "10'C-600" GC with the exceptions that only methanol was analyzed on the HP GC, and that t-2-butene was analyzed on the HP GC, as well as on the "GSQ" GC. The helium carrier flow was set at 10 ml min^{-1}, the helium makeup gas at 20 ml min^{-1}, the hydrogen at 30 ml min^{-1}, and the oxygen at 150 ml min^{-1}. A 100 ml sample was taken and injected into the trap while immersed in liquid argon as described above. Initially the column was maintained at sub-zero temperatures (usually -15 C) while the sample flowed onto the column during desorption (trap immersed in boiling water). After a temperature ramp was applied (15 C min^{-1}) up to 125 C. From March 1992 loop analyses were used. For latest experiments, the initial temperature was -65 C and held for 2.5 minutes, then a temperature ramp (3 steps temperature program) was applied up to a final temperature of 200 C. The HP chemstation software allowed for quantification by peak area.

Instrument 2603 "HP1 DB5L". This consisted of the same instrument as the "2600", except that a 30 m x 0.53 mm DB-5 column, previously used for Tenax system, was installed for loop analysis. The procedures employed were similar.

Instrument 2601 "HP1 DB5T". This consisted of the second column and detector in the HP 5890 GC as instrument 2600. It column used was 30 m x 0.53 mm megabore DB-5. It was used to monitor hexamethyldisiloxane, octamethylcyclotetrasiloxane, pentamethyldisiloxanol and biogenic organic compounds, using the Tenax cartridge sampling system. When a sample was to be analyzed, 100 ml of gas was collected onto the Tenax-GC porous polymer, 60/80 mesh. These Tenax-GC samples were then thermally desorbed at 200 C onto the head of the DB-5 column held at -30 C for four minutes and then temperature programmed at 35 C min^{-1} to 200C. Peak area was measured and used to quantitate the amount of compound present.

Instrument 2800 "HP2 DB5S". This was a second Hewlett-Packard 5890 series II GC with a FID detector maintained at 300°C and a 15m x 0.53mm megabore DB-5 column. The compounds analyzed were identical to those detected on Instrument 2600. A 100 ml sample was taken and injected into the trap while immersed in liquid argon as described above. Initially the column was maintained at sub-zero temperatures (-50C) while the sample flowed onto the column during desorption (trap immersed in boiling water). The helium carrier flow was set at 10 ml min^{-1}, the hydrogen at 31.5 ml min^{-1}, and the oxygen at 145 ml min^{-1}. A temperature ramp was applied (2 steps temperature program) up to 200C and the HP chemstation software was used.

Instrument 2801 "HP2 DB5L". This consisted of the same instrument as the "HP2 DB5S", except that a 30 m x 0.53 mm megabore DB-5 column was used to give better separation. The procedures employed were similar.

Instrument 2802 "HP2 GSQ". This consisted of the same instrument as the two above, except that a 30m x 0.53mm 'GSQ' column from Varian 1400 (instrument 2290) was placed into this instrument and loop analysis was employed to analyze the lighter hydrocarbons: ethene, propene, n-butane, trans-2-butene. The procedures employed were similar to the above two.

ECD Instruments. The instruments listed above all used FID detection. The following instruments used ECD detection. Note that special considerations involved in the analysis of PAN are discussed separately in Section 4.4.

Instrument 2000 ECD-1. (Not listed in Table 12.) Instrument 2000 was used to monitor peroxyacetyl nitrate (PAN) and also different alkyl nitrates. It consisted of an Aerograph gas chromatograph with tritium foil electron capture detector (ECD) and a 12 inch x 0.125 inch FEP Teflon column containing 5% Carbowax 400 on Chromosorb G (80/100 mesh) operating at room temperature with a nitrogen carrier flow of 75 ml min^{-1}. The detector was equipped with a standing current control, and since the response was directly influenced by the standing current, it was maintained to within ±2 percent of a constant value during all experiments and calibrations. Analyses were carried out by flushing a ~2 ml loop with the sample, and injecting the contents of the loop onto the column. The mv response was used to quantitate the amount of compound present.

The analysis of PAN using this instrument, and its calibration history, is discussed in Section 4.4. The calibration data for organic nitrates using this instrument were not evaluated.

Instrument 4000 ECD-3. (Not Listed in Table 12.) This was another Aerograph gas chromatograph with electron capture detectors (ECD) and was used to monitor PAN and alkyl nitrates. The detector was equipped with a standing current control as described for Instrument 2000. In order to obtain PAN data during the nighttime for the indoor experiments, this instrument was set up with an automated sampling system at 15 minute intervals. Later, this automated GC was also used for the outdoor chamber experiments and other field projects. It had a 24 inch by 0.125 inch FEP column, packed with 5% Carbowax 400 on Chromosorb with 100/120 mesh operating at room temperature with a nitrogen carrier flow of 36 ml min^{-1}. The same loop technique was used. The mv response was used to quantitate the amount of compound present.

The analysis of PAN using this instrument, and its calibration history, is discussed in Section 4.4. The calibration data for organic nitrates using this instrument were not evaluated,

Instrument 2710 HP-ECD2. This was a Hewlett-Packard 5890 Series II GC outfitted with an ECD maintained at 50 C and a 5m x 0.53mm megabore HP-1 column was used to analyze for PAN (from September 3 1991 to November 26 1991). The helium carrier flow was set at 10ml min^{-1} while the 5% methane/argon makeup gas was set at 60 ml min^{-1}. A ca. 2 ml Teflon loop maintained at 25C was used to contain the sample prior to injection. Initially the column was maintained at sub-zero temperatures while the sample flowed onto the column, after which a temperature ramp was applied (15C min^{-1}). The HP chemstation software allowed for quantification by peak area.

Significant problems were encountered in obtaining acceptable data from this instrument. Satisfactory and reproducible PAN calibrations were never obtained. Data from this instrument should not be used for modeling.

Instrument 2700 HP-ECD1. The HP 5890 GC used to monitor PAN had a second detector and second column, whose combination was defined as instrument 2700. It was used primarily to monitor 2-chloromethyl-3-chloropropene and carbon tetrachloride. This ECD detector was maintained at 250 C and the column was a 15 m x 0.53 mm DB-5. The helium carrier flow was set at 9 ml min^{-1} while the 5% methane/argon makeup gas was set at 94 ml min^{-1}. The sampling valve was maintained at 120 C, with the sampling loop at a somewhat lower temperature. The column had a similar temperature program as used for instrument 2710, except that the temperature was ramped up to 150 C. The HP chemstation software was used.

This instrument was sometimes operated at a lower temperature to monitor PAN, but as with the 2710 the results have thus far been unacceptable and any PAN data from this instrument should not be used for model evaluation. The 2-chloromethyl-3-chloropropene and carbon tetrachloride data were of good quality for runs ETC339 up to the approximate time of ETC450, but for some reason the reproducability of the data from this instrument deteriorated significantly after that date.

4.3.2 Calibration Procedures

Calibrations of all GC's were performed at intervals of two months or less and, except for the calibrations of PAN or those using Tenax sampling, were carried out in the same general manner. First, all gas flows were measured to verify that no changes had occurred which would indicate that previous measurements were erroneous. After measuring these flow rates, a calibration mixture was made up in a flask, carboy or chamber (e.g., ETC) using different methods depending on the compound being calibrated. In 1991, a calibration bag (~3,000 l) was constructed and designed to perform calibrations. The calibration mixture, composed of known quantities of various compounds, was then injected into the appropriate GC and the elution time and height or area of each peak was recorded. The heights of the peaks were determined by multiplying the height on the strip chart by the attenuation and the response in millivolts or strip chart units was obtained. Prior to 1992, the peak areas were usually determined by multiplying the peak height by the width at half-height and multiplying by the attenuation. Beginning in March 1992, the peak areas were obtained with HP ChemStation software.

The calibration procedures for the various types of GC instruments used for runs carried out prior to 1979 are discussed by Pitts et al. (1979). These procedures, which were generally followed for many of the instruments used in subsequent runs, are briefly summarized below. The modifications employed after ~1991 are discussed in somewhat more detail. The calibration procedures for PAN are discussed in Section 4.4.

Gaseous Compounds. For gaseous compounds, two ca. 2000 ml flasks (exact volumes determined by measuring with water) were flushed with nitrogen for 20 minutes and then 2 ml of each pure gas was injected into the first flask with a 5 ml syringe. This flask was allowed to mix for 20 minutes, and then 2 ml from this flask was transferred into the second flask. The contents of this second flask were allowed to mix for an additional 20 minutes. This resulted in a concentration of ca. 1 ppm of the gas in the second flask. 100 ml of gas was then removed from the second flask and placed into the loop for quantification. Trap calibrations were accomplished by diluting a 5 ml sample from the second flask with nitrogen in a 100 ml syringe, and passing the contents of the syringe throughout the trap. For a flask containing 1 ppm of the compound, this method was equivalent to sampling 100 ml of gas containing 50 ppb of the compound.

For most calibrations after 1992, a chamber (e.g., ETC) or calibration bag was employed for the calibration. This bag was flushed with purified day air for at least a few hours to remove the contents. Since the exact bag volume is not known, ethene (in most cases), or hexane and cyclohexane (for last two years), were also injected, and by the independently determined calibration value for its detection, a volume for the bag could be determined. The samples were injected into the appropriate GC's in the manner described previously. The concentration of each component was calculated by knowing the amount of gas injected, and the calculated bag volume. Generally speaking, the chamber bag was used whenever possible to perform calibrations before the calibration bag was constructed.

When a chamber or Teflon calibration bag was employed for calibration, the gas compound being calibrated was made using a vacuum rack system. The appropriate pressure of this gas compound, measured using a MKS Baratron Gauge, was expanded into an evacuated bulb whose volume was determined by measuring with water, and was then diluted with nitrogen. The bulb was then closed and detached from the vacuum line and its content was flushed into the bag with nitrogen through the injection port for a couple minutes.

In April of 1993, in order to more closely follow the daily variations in the calibrations for each instrument, a LPO tank was filled with ethene, propene, n-butane, trans-2-butene, n-octane, toluene and m-xylene in approximate concentrations as would be in the chamber experiments being carried out at that time. An appropriate pressure of each compound, both gas and liquid, was introduced into a bulb which was then expanded into an evacuated LPO tank using vacuum rack system. The LPO tank was then diluted by pressurization with nitrogen. The concentration of each component was determined by knowing the amount of each compound used, the volume and the pressure of the LPO tank. The LPO tank was used each day after an experiment was done.

Liquid Compounds. Calibration of relatively volatile compounds that were liquids at room temperature and pressure was carried out using a ~50 l all-glass carboy, which was first cleaned by being heated from the inside with a heat gun, then cooled and finally flushed with nitrogen for one hour. The carboy was then dosed with 1 microliter of each pure liquid to be calibrated using a 10 microliter syringe. These were allowed to mix for one hour prior to any samples being taken. Trap and loop calibrations were both accomplished in a similar fashion. A sample was taken from the carboy using a 100 ml syringe and then 1 ml of this was transferred to 5 ml syringe which in turn was transferred to another 100 ml syringe, which was then diluted with 99 ml of nitrogen. This resulted in a 100 fold dilution of the sample from the carboy. The samples were injected in the manner described previously. The exact concentration of each compound in carboy was calculated by knowing the amount of liquid injected, its density and the volume of carboy.

Compounds which possess a relatively lower vapor pressure were calibrated by using one of the environmental chambers. The chamber was flushed using the same procedure as for a run, and then an appropriate amount of each sample was injected using the standard procedure for the compound, except with somewhat longer flushing times. If a chamber other than the EC was used, the chamber volume was determined by injecting a known amount of a compound which can be monitored with a method with a well-established calibration. The concentration of each component was calculated by knowing the amount of liquid injected, its density, and the calculated bag volume.

Calibrations were more difficult for liquids, such as acetaldehyde, which had high volatility at room temperature. After around 1991-1992 the procedure was to use the vacuum rack as described above for calibration of gas phase species. Before that time, calibrations for such species tended to be uncertain. The problems with the early acetaldehyde calibrations are discussed by Pitts et al. (1979).

During 1980-1982, a stock calibration solution, which included the various alkanes and aromatic compounds, was made for the calibration purposes. This was accomplished by syringing the desired compounds into a weighed vial. Concentrations were obtained by weighed vial on an Ainsworth Type 10 balance after the addition of each compound. In general, each stock solution was made up of six compounds. Then calibration was carried out using 46.75 l all glass carboy. One microliter of each solution was added.

Solid Compounds. Various calibration methods were used for compounds which are solids at room temperature. In some cases the vacuum rack was used, with known pressures of the vapor from the solids being introduced into bulbs of known volume and then flushed into the chamber. If Tenax cartridge sampling is used, calibrations were performed by preparing solutions of the compound of known concentrations in solvents such as methanol, and introducing known volumes of this solution directly onto the Tenax cartridge, which was then desorbed onto the column using the standard procedures. This was the usual procedure for calibrating the "SP-1000" (1405) GC used in the EC aromatics runs.

4.3.3 Calibration Data and Assignments

Calibration data for most, though not all, of the GC instruments described above were summarized and are given in Table B-3 in Appendix B. The format for the data in these tables is similar to that for the O_3 and NO_x calibration data in Tables 11, B-1 and B-2, as described in detail in Section 4.1.3. The only difference is that there is a separate column giving the retention time (R.T), if available. (If R.T. is given as zero, it means that information was not recorded.) As with the O_3 and NO_x calibrations, assignments of factors for individual runs were made either by averaging or fitting the calibration factors to linear regressions during the appropriate time period. Table 13 gives a summary of the species and instruments for which calibration data and assignments could be made. Included in the table are the species calibrated, the type of analysis or sampling method, the number of calibrations, the number of calibration assignments (i.e. the number of averages or linear regressions used for estimating factors for individual runs), the number of runs for which the calibrations for this species and analysis type was applicable, and the average, maximum, and minimum uncertainties in the various assignment sets due to irreproducability of the data. No uncertainty information is given if there are an insufficient number of calibrations available to obtain information concerning precision. The runs include all SAPRC chamber runs to date of potential utility for mechanism evaluation, including EC, ITC, ETC, DTC, XTC, and OTC runs. (Note that data from OTC runs are not included in the present release of the data base, though the GC data applicable to those runs are discussed here).

Table 13. Summary of GC calibration data applicable to runs in the data base.

Instrument	Species	Type	Number of:			Uncertainties (%)			Minimum
			Cals	Asns	Runs	Avg.	Max.	Min.	Unc.
2290 DMS-2	N-C4	Loop/mv	3	1	1	7	7	7	5
	N-C4	Trap/mv	4	1	54	2	2	2	
	2-ME-C3	Trap/mv	3	1	45	2	2	2	
	PROPANE	Trap/mv	3	1	46	1	1	1	
	PROPENE	Trap/mv	5	1	57	1	1	1	
	T-2-BUTE	Trap/mv	2	1	1	5	5	5	
2291 GSQ	N-C4	Loop/mv	2	1	6	13	13	13	5
	N-C4	Loop/area	2	1	4	14	14	14	
	N-C4	Trap/mv	2	1	4	14	14	14	
	N-C4	Trap/area	8	2	8	8	10	5	
	ISOBUTEN	Trap/mv	2	1	4				
	ISOBUTEN	Trap/area	8	2	8	8	11	7	
	2-ME-C3	Trap/area	4	1	4	7	7	7	
	ETHANE	Trap/area	2	1	3	5	5	5	
	ETHENE	Trap/area	2	1	8	8	8	8	
	PROPANE	Trap2/area	3	1	3	5	5	5	
	PROPENE	Trap/mv	1	1	1				
	PROPENE	Trap/area	2	1	7	33	33	33	
	ISOPRENE	Trap/area	2	1	3	20	20	20	
	ME-O-ME	Trap/area	1	1	4				
	T-2-BUTE	Trap/area	1	1	2				
2200 DMS-1	1-BUTENE	Loop#1	6	1	7	8	8	8	5
	1-BUTENE	Loop#2	7	3	2				
	N-C4	Loop#1	9	1	8	7	7	7	
	N-C4	Loop#2	16	5	22	3	4	1	
	N-C5	Loop#1	3	1	1	8	8	8	
	PROPENE	Loop#1	10	1	12	11	11	11	
	PROPENE	Loop#2	16	7	22	4	4	2	
	T-2-BUTE	Loop#1	6	1	7	8	8	8	
	1-BUTENE	Trap#1	8	2	7	7	8	7	
	1-BUTENE	Trap#2	20	6	92	5	6	3	
	13-BUTDE	Trap#2	12	5	4				
	ACETYLEN	Trap#2	23	7	525	4	6	1	
	N-C4	Trap#1	10	2	8	2	2	2	
	N-C4	Trap#2	35	8	616	9	16	2	
	2-ME-C3	Trap#2	28	8	528	11	33	9	
	2-ME-C4	Trap#2	10	5	26	26	26	26	
	ISOBUTEN	Trap#2	25	6	334	7	8	2	
	N-C5	Trap#1	4	1	1	19	19	19	

Table 13 (continued)

			Number of:			Uncertainties (%)			Minimum
Instrument	Species	Type	Cals	Asns	Runs	Avg.	Max.	Min.	Unc.
	N-C5	Trap#2	18	5	130	10	10	7	
	PROPANE	Trap#2	27	8	578	7	9	5	
	PROPENE	Trap#1	11	3	17	2	4	1	
	PROPENE	Trap#2	35	8	661	7	7		
	T-2-BUTE	Trap#1	9	2	7	6	6	6	
	T-2-BUTE	Trap#2	23	6	114	5	5	5	
2920 10’C-600	BUTYRALD	Trap/mv	13	5	58	7	8	2	10
	ACROLEIN	Trap/area	1	1	9				
	ACETONE	Trap/mv	26	5	575	15	15	7	
	ACETONE	Trap/area	6	2	3	24	24	24	
	2-C4ONO2	Trap/mv	16	3	47	11	12	9	
	2-C3ONO2	Trap/mv	2	1	7	9	9	9	
	135-TMB	Trap/mv	8	3	8	7	7	7	
	135-TMB	Trap/area	3	1	2	5	5	5	
	C2ONO2	Trap/mv	6	2	12	2	2	2	
	3-C5-KET	Trap/mv	5	2	20				
	2-C5ONO2	Trap/mv	18	4	33	4	7	3	
	3-C5ONO2	Trap/mv	18	4	33	2	5	2	
	M-XYLENE	Trap/area	14	1	70	6	7	6	
	M-XYLENE	Trap/mv	37	5	309	8	24	1	
	MEK	Trap/mv	22	6	329	11	20	2	
	MVK	Loop/area	1	1	4				
	MVK	Trap/area	5	2	14				
	N-C8	Trap/mv	3	1	4	2	2	2	
	N-C8	Trap/area	1	1	2				
	PROPALD	Trap/mv	22	4	115	11	33	1	
	STYRENE	Trap/mv	1	1	4				
	TOLUENE	Loop/mv	9	3	1	9	9	9	
	TOLUENE	Trap/mv	27	3	89	8	13	5	
	VALERALD	Trap/mv	2	1	28	14	14	14	
	BENZENE	Loop/mv	4	2	6				
	BENZENE	Trap/mv	13	3	35	2	7	1	
	BENZENE	Trap/area	2	1	2				
	METHACRO	Loop/area	1	1	3				
	METHACRO	Trap/area	6	2	14	6	6	6	
	ACETALD	Trap/mv	41	5	577	11	29	1	
	ACETALD	Trap/area	4	1	7	16	16	16	
	ACETALD	Trap/area	1	1	2				
	N-C6	Trap/area	4	1	1	2	2	2	
	N-C6	Trap/area	14	2	70	2	4	2	
	N-C6	Trap/mv	23	2	162	12	12	12	

Table 13 (continued)

			Number of:			Uncertainties (%)			Minimum
Instrument	Species	Type	Cals	Asns	Runs	Avg.	Max.	Min.	Unc.
	I-C3-OH	Trap/mv	3	1	4	23	23	23	
	124-TMB	Trap/area	1	1	2				
	123-TMB	Trap/area	1	1	2				
	C2-BENZ	Trap/mv	2	1	3	15	15	15	
	O-XYLENE	Loop/mv	2	1	4	1	1	1	
	O-XYLENE	Trap/mv	11	4	3	9	9	9	
	O-XYLENE	Trap/area	2	1	2				
	ISOPRENE	Trap/area	2	1	4	1	1	1	
	224TM-C5	Trap/area	1	1	2				
2925 10’C600C	ACETONE	Trap/mv	11	3	119	5	5	5	5
	MEK	Trap/mv	11	3	117	8	8	8	
	TOLUENE	Trap/mv	12	3	91	7	7	7	
	M-XYLENE	Trap/mv	11	3	74	3	3	3	
	ACETALD	Trap/mv	8	3	74				
	3-C5-KET	Trap/mv	11	3	79	10	10	10	
	3-C5ONO2	Trap/mv	1	1	13				
	3-C5ONO2	Trap/mv	10	3	38	26	26	26	
	2-C5ONO2	Trap/mv	1	1	1				
	2-C5ONO2	Trap/mv	10	3	20	15	15	15	
2930 5’C-600	3-C6ONO2	Trap/mv	4	2	5	7	7	7	
	2-C6ONO2	Trap/mv	4	2	5	7	7	7	
	M-TOLALD	Trap/mv	4	1	1	8	8	8	
	ACETALD	Trap/mv	5	2	21	8	8	8	
	ACETONE	Trap/mv	4	2	23	3	3	3	
	PROPALD	Trap/mv	3	1	22	3	3	3	
	BENZALD	Trap/mv	15	5	18	12	31	11	
	BENZALD	Loop/mv	2	1	5	11	11	11	
	TOLUENE	Trap/mv	7	3	10	15	15	15	
	M-XYLENE	Trap/mv	4	1	8	4	4	4	
	3-C7ONO2	Trap/mv	4	2	5				
	3-C8ONO2	Trap/mv	4	2	1				
1403 3-part	PROPALD	Trap#1(mv)	8	2	2	13	13	13	10
	MEK	Trap#1(mv)	9	2	23	10	10	10	
	3-C5-KET	Trap#1(mv)	2	1	1	7	7	7	
	BUTYRALD	Trap#1(mv)	4	1	33	34	34	34	
	ACETONE	Trap#1(mv)	3	1	1	7	7	7	
	2-C4ONO2	Trap#1(mv)	10	3	9	2	2	2	
	2-C5ONO2	Trap#1(mv)	9	3	1	8	8	8	
	3-C5ONO2	Trap#1(mv)	9	3	1	8	8	8	

Table 13 (continued)

			Number of:			Uncertainties (%)			Minimum Unc.
Instrument	Species	Type	Cals	Asns	Runs	Avg.	Max.	Min.	
	N-C9	Trap#1(mv)	1	1	1				
	N-C9	Loop#1(mv)	4	2	1				
	ACETALD	Trap#2(mv)	12	2	8	21	21	21	
	ACETONE	Trap#2(mv)	8	2	8	18	18	18	
	M-XYLENE	Trap#2(mv)	14	4	2				
	O-XYLENE	Trap#2(mv)	10	3	2				
1405 SP-1000	O-CRESOL	Tenax/mv	25	8	10	40	93	33	
	O-CRESOL	Tenax/mv	1	1	7				
	M-CRESOL	Tenax/mv	16	5	3	45	75	30	
	P-CRESOL	Tenax/mv	16	5	3	41	74	24	
	O-NO2TOL	Tenax/mv	23	8	3	70	74	67	
	M-NO2TOL	Tenax/mv	21	6	8	38	71	33	
	M-NO2TOL	Tenax/mv	1	1	7				
	P-NO2TOL	Tenax/mv	23	8	3	79	84	70	
	BENZALD	Tenax/mv	6	3	1				
	BENZALD	Tenax/mv	1	1	18				
	BENZALD	Tenax/mv	1	1	1				
	M-XYLENE	Tenax/mv	3	1	8	11	11	11	
	M-TOLALD	Tenax/mv	2	1	4	53	53	53	
2100 PN-1	ETHANE	Loop#1	21	1	39	5	5	5	5
	ETHANE	Loop#2	19	3	24	9	13	6	
	ETHANE	Loop/area	1	1	1				
	ETHANE	Trap#1	19	1	120	8	10	6	
	ETHANE	Trap#2	14	3	468	15	21	15	
	ACETYLEN	Loop#1	24	2	70	16	17	15	
	ACETYLEN	Loop#2	15	1	7	12	12	11	
	ACETYLEN	Trap#1	34	2	617	19	24	6	
	ETHENE	Loop#1	22	1	55	5	6	4	
	ETHENE	Loop#2	50	4	145	12	33	6	
	ETHENE	Loop/area	53	3	263	6	8	5	
	ETHENE	Trap#1	20	1	136	8	10	6	
	ETHENE	Trap#2	14	1	464	19	20	18	
	METHANE	Loop#1	23	2	119	5	6	5	
	METHANE	Loop#2	16	2	473	6	12	5	
2195 PN-3	ETHANE	Trap#1	10	4	87	14	18	12	5
	ACETYLEN	Trap#1	11	3	88	19	26	14	
	ETHENE	Trap#1	10	3	114	9	9	9	
	METHANE	Loop#1	10	2	79	8	11	7	

Table 13 (continued)

			Number of:			Uncertainties (%)			Minimum
Instrument	Species	Type	Cals	Asns	Runs	Avg.	Max.	Min.	Unc.
2120 PQS-1	MEOH	Trap/area	2	1	7	20	20	20	5
1400 C-20M	CYCC6	Loop/mv	5	2	1				
	ISOPRENE	Loop/mv	6	1	11	8	10	7	5
	N-C6	Loop/mv	11	3	4	3	3	3	
	N-C4	Loop/mv	5	1	1	5	5	5	
	N-C5	Loop/mv	10	3	12	3	3	3	
	N-C7	Loop/mv	8	2	21	3	3	3	
	N-C8	Loop/mv	9	2	15	4	4	4	
	SI2OME6	Loop/mv	2	1	2	2	2	2	
	FURAN	Loop/mv	4	2	5	8	8	8	
	224TM-C5	Loop/mv	3	1	4				
	MTBE	Loop/mv	4	2	7	7	7	7	
	ME-CYCC6	Loop/mv	3	2	4				
	1-HEXENE	Loop/mv	1	1	4				
1402 PN-1400	ETHENE	Loop#1	32	3	43	20	27	3	5
2701 SP C-20M	PYRROLE	Tenax/mv	4	1	5	7	7	7	5
2702 SP C-II	23-DMN	Tenax/ar	2	2	14				
	ME-NAPH	Tenax/ar	2	1	10	12	12	12	10
	NAPHTHAL	Tenax/ar	2	2	15				
	TETRALIN	Tenax/ar	2	1	10				
2650 VAR 3700	N-C9	Loop2/area	8	2	3				
	N-C10	Loop/area	4	1	2	3	3	3	5
	N-C10	Loop2/area	8	2	3				
	N-C11	Loop/area	4	1	2	1	1	1	
	N-C11	Loop2/area	8	2	3				
	N-C12	Loop/area	4	1	2	8	8	8	
	N-C12	Loop2/area	6	2	3				
	N-C13	Loop/area	4	1	2	6	6	6	
	N-C13	Loop2/area	6	2	3				
	N-C14	Loop2/area	6	2	2				
2750 HP3710A	BENZENE	Loop/area	3	1	12	5	5	5	5
	BENZENE	Loop2/area	3	2	7				
	C2-BENZ	Loop/area	3	1	14	2	2	2	
	N-C3-BEN	Loop/area	3	1	14	1	1	1	
	N-C5	Loop/area	1	1	6				
	N-C6	Loop/area	3	1	14	12	12	12	

Table 13 (continued)

Instrument	Species	Type	Number of: Cals	Asns	Runs	Uncertainties (%) Avg.	Max.	Min.	Minimum Unc.
	N-C6	Loop2/area	1	1	7				
	N-C7	Loop/area	3	1	14	4	4	4	
	N-C7	Loop2/area	1	1	7				
	N-C8	Loop/area	3	1	14	3	3	3	
	N-C8	Loop2/area	1	1	7				
	N-C9	Loop/area	3	1	15	4	4	4	
	N-C9	Loop2/area	1	1	7				
	N-C10	Loop/area	3	1	15	6	6	6	
	N-C10	Loop2/area	1	1	7				
	N-C11	Loop/area	3	1	15	10	11	10	
	N-C11	Loop2/area	1	1	7				
	N-C12	Loop/area	3	1	11	4	4	4	
	N-C12	Loop2/area	1	1	7				
	N-C13	Loop/area	3	2	14	1	1	1	
	N-C13	Loop2/area	1	1	7				
	N-C14	Loop/area	3	2	1				
	N-C14	Loop2/area	1	1	6				
	224TM-C5	Loop/area	1	1	6				
	I-C3-BEN	Loop/area	3	1	14	1	1	1	
	I-C3-BEN	Loop2/area	1	1	7				
	ME-CYCC6	Loop/area	3	1	14	5	5	5	
	ME-CYCC6	Loop2/area	1	1	7				
	124-TMB	Loop/area	4	1	14	1	1	1	
	124-TMB	Loop2/area	1	1	7				
	TOLUENE	Loop/area	3	1	10	4	4	4	
	TOLUENE	Loop2/area	2	1	8				
	TOLUENE	Loop3/ar	1	1	6				
	M-XYLENE	Loop/area	3	1	14	1	1	1	
	M-XYLENE	Loop2/area	2	1	11				
	M-XYLENE	Loop3/ar	1	1	6				
	O-XYLENE	Loop/area	3	1	14	1	1	1	
	O-XYLENE	Loop2/area	1	1	7				
2850 HP3711A	N-C5	Loop/mv	9	3	6	37	37	37	5
	N-C5	Loop/area	7	3	31				
	N-C5	Loop2/area	9	1	61	15	16	14	
	TOLUENE	Loop/mv	9	3	6	16	16	16	
	TOLUENE	Loop/area	4	2	31				
	TOLUENE	Loop2/area	16	2	89	21	28	18	
	M-XYLENE	Loop/mv	9	3	6	14	14	14	
	M-XYLENE	Loop/area	7	3	31				
	M-XYLENE	Loop2/area	9	1	73	14	16	14	

Table 13 (continued)

Instrument	Species	Type	Number of: Cals	Asns	Runs	Uncertainties (%) Avg.	Max.	Min.	Minimum Unc.
	224TM-C5	Loop/mv	9	3	6	1	1	1	
	224TM-C5	Loop/area	7	3	31				
	224TM-C5	Loop2/area	9	1	68	9	11	9	
	N-C6	Loop/area	6	3	21	6	6	6	
	CYCC6	Loop/area	3	1	11	2	2	2	
	N-C7	Loop/area	6	2	21	6	17	3	
	ME-CYCC6	Loop/area	4	2	27	5	5	5	
	N-C8	Loop/area	6	3	26	4	13	3	
	ET-CYCC6	Loop/area	3	1	11	2	2	2	
	P-XYLENE	Loop/area	3	1	16	10	10	10	
	N-C9	Loop/area	4	3	10				
	I-C3-BEN	Loop/area	7	3	16	18	18	18	
	135-TMB	Loop/area	3	1	16	40	40	40	
	N-C10	Loop/area	3	3	13				
	N-C11	Loop/area	4	3	10				
	TETRALIN	Loop/area	4	1	16	27	27	27	
	N-C12	Loop/area	4	3	10				
	N-C13	Loop/area	4	3	10				
	N-C14	Loop/area	6	4	12				
	1-HEXENE	Loop/area	2	2	8				
	1-C9-OLE	Loop/area	2	2	11				
	O-XYLENE	Loop/area	2	1	6	5	5	5	
	124-TMB	Loop/area	3	2	8				
	BENZENE	Loop/area	3	2	9				
	2-ME-C4	Loop/area	3	2	3				
	C2-BENZ	Loop/area	3	1	6	3	3	3	
2500 DB-5 TNX	N-C6	Trap/area	6	1	19	3	4	3	5
	M-XYLENE	Trap/area	6	1	24	7	10	6	
	CARBITOL	Trap/area	2	1	3	2	2	2	
	ETO-ETOH	Trap/area	2	1	3	5	5	5	
	(SIOME)4	Trap/area	3	1	3	122	122	122	
	(SIOME)5	Trap/area	2	1	2	39	39	39	
2600 HP1 DB5	N-C6	Trap/area	9	1	46	2	3	2	5
	N-C6	Trap/mv	2	1	3	1	1	1	
	N-C6	Loop/mv	1	1	2				
	N-C6	Loop/area	22	2	50	5	5	3	
	M-XYLENE	Trap/area	9	1	46	6	6	5	
	M-XYLENE	Trap/mv	2	1	3	1	1	1	
	M-XYLENE	Loop/mv	1	1	2				
	M-XYLENE	Loop/area	41	3	144	6	11	3	

Table 13 (continued)

Instrument	Species	Type	Number of: Cals	Asns	Runs	Uncertainties (%) Avg.	Max.	Min.	Minimum Unc.
	123-TMB	Trap/area	1	1	2				
	MEOH	Trap/area	2	1	3				
	224TM-C5	Trap/area	1	1	2				
	T-2-BUTE	Trap/area	1	1	2				
	T-2-BUTE	Loop/area	24	2	93	5	6	5	
	N-C4	Trap/area	1	1	1				
	N-C4	Loop/area	23	2	131	4	6	3	
	C2-BENZ	Trap/area	2	1	3				
	ACETALD	Trap/area	2	1	3	12	12	12	
	ACETALD	Loop/area	8	2	7	7	7	7	
	N-C8	Loop/area	29	2	157	4	5	3	
	P-XYLENE	Loop/area	1	1	2				
	METHACRO	Loop/area	5	2	12	17	17	17	
	MVK	Loop/area	7	1	7	15	15	15	
	ACETONE	Loop/area	8	2	21	8	10	7	
	CYCC6	Loop/area	17	2	107	6	8	4	
	TOLUENE	Loo/area	31	2	97	4	5	3	
	ISOPRENE	Loop/area	6	2	10	5	5	5	
	ME-CYCC6	Loop/area	2	1	1				
	A-PINENE	Loop/area	5	2	4	10	10	10	
	B-PINENE	Loop/area	5	2	2	9	9	9	
	BENZENE	Loop/area	3	1	1	7	7	7	
	ISOBUTEN	Loop/area	3	2	5				
	BIACETYL	Loop/area	1	1	2				
2601 HP1 DB5T	N-C6	Tenax/ar	4	1	9	3	3	3	5
	M-XYLENE	Tenax/ar	9	1	9	16	16	16	
	A-PINENE	Tenax/ar	7	1	7	5	5	5	
	B-PINENE	Tenax/ar	6	1	7	4	6	3	
	SABINENE	Tenax/ar	5	1	4	9	9	9	
	3-CARENE	Tenax/ar	6	1	4	5	5	4	
	D-LIMONE	Tenax/ar	5	1	4	7	7	7	
	NOPINONE	Tenax/ar	10	3	17	10	12	10	
	SI2OMEOH	Tenax/ar	3	1	6	52	52	52	
	SI2OME6	Tenax/ar	2	1	2	4	4	4	
	(SIOME)4	Tenax/ar	2	1	3	6	6	6	
2603 HP1 DB5L	N-C6	Loop/area	8	1	1	2	2	2	5
	M-XYLENE	Loop/area	14	1	19	8	9	8	
	135-TMB	Loop/area	6	1	1	10	10	10	
	T-2-BUTE	Loop/area	5	1	13	4	4	4	
	N-C4	Loop/area	4	1	43	6	6	6	

Table 13 (continued)

Instrument	Species	Type	Number of: Cals	Asns	Runs	Uncertainties (%) Avg.	Max.	Min.	Minimum Unc.
	N-C8	Loop/area	10	1	44	3	3	3	
	PROPENE	Loop/area	6	1	5	4	4	4	
	METHACRO	Loop/area	3	1	3	4	4	4	
	MVK	Loop/area	3	1	2	19	19	19	
	ACETONE	Loop/area	5	1	5	5	5	5	
	TOLUENE	Loo/area	10	1	16	3	3	3	
	ISOPRENE	Loop/area	5	1	6	11	11	11	
	A-PINENE	Loop/area	4	1	3	9	9	9	
	B-PINENE	Loop/area	5	1	3	10	10	10	
	BIACETYL	Loop/area	2	1	1	37	37	37	
2800 HP2 DB5S	CYCC6	Trap/area	1	1	2				5
	M-XYLENE	Trap/area	1	1	2				
	N-C4	Trap/area	1	1	2				
	N-C8	Trap/area	1	1	2				
	TOLUENE	Trap/area	1	1	2				
	T-2-BUTE	Trap/area	1	1	2				
2801 HP2 DB5L	CYCC6	Trap/area	3	1	12	10	10	10	5
	ISOPRENE	Trap/area	1	1	2				
	ME-CYCC6	Trap/area	2	1	1				
	M-XYLENE	Trap/area	5	1	8	9	9	9	
	M-XYLENE	Loop/area	2	1	4	7	7	7	
	N-C4	Trap/area	4	1	8	7	7	7	
	N-C4	Loop/area	1	1	4				
	N-C8	Trap/area	4	1	8	10	10	10	
	N-C8	Loop/area	2	1	4	2	2	2	
	PROPENE	Trap/area	5	1	16	18	18	18	
	TOLUENE	Trap/area	4	1	8	8	8	8	
	TOLUENE	Loop/area	2	1	4	4	4	4	
	T-2-BUTE	Trap/area	4	1	9	8	8	8	
	T-2-BUTE	Loop/area	1	1	2				
2802 HP2 GSQ	ACETALD	Loop/area	9	1	25	6	6	6	5
	ACETONE	Loop/area	7	1	15	7	7	7	
	BIACETYL	Loop/area	6	1	1	6	6	6	
	ETHANE	Loop/area	2	1	4				
	ETHENE	Loop/area	10	2	51	4	4	4	
	ISOBUTEN	Loop/area	1	1	5				
	ISOPRENE	Loop/area	5	1	6	2	2	2	
	METHACRO	Loop/area	3	1	1	3	3	3	
	MVK	Loop/area	3	1	2	3	3	3	

Table 13 (continued)

Instrument	Species	Type	Number of: Cals	Asns	Runs	Uncertainties (%) Avg.	Max.	Min.	Minimum Unc.
	N-C4	Loop/area	6	1	57	6	6	6	
	PROPENE	Loop/area	11	2	63	2	2	2	
2710 HP ECD-B	CCL4	Loop/area	1	1	4				10
2700 HP ECD-A	CCL4	Loop/area	19	3	107	25	37	13	5
	CCL4	Loop/ar#	1	1	4				
	CL2IBUTE	Loop/area	22	3	107	22	37	15	
	CL2IBUTE	Loop/mv	2	1	1				
	BIACETYL	Loop/area	2	1	2				

For each GC instrument, a minimum uncertainty level was assigned based on the level of precision typically observed with the instrument. This was usually 5%, except for a few instruments where 10% was considered to be more appropriate. As discussed above, the calibration data from the "SP-1000" (1405) instrument were extremely irreproducable, so a minimum uncertainty of 25% was assigned for that instrument.

The calibration assignments were checked for reasonableness by examining plots of the calibration data and the calibration assignments against time. Input files and software used to create these plots are included with the computer data sets in this distribution. The plots also show the times of the runs affected by the calibrations relative to the times of the calibrations and the effective assignments.

The run data files were then updated to incorporate the revised calibration assignments. Codes were also saved with the data (as auxiliary channel parameters) for the affected channel to indicate that the factor was revised by this process. In most cases the original calibration factor was retained in the data file for information purposes, though it was not used to calibrate the data. The uncertainty estimate based on calibration precision (or the minimum uncertainty, if it was greater) was also saved in the data file (using the "U-FAC" code, as indicated on Table 10), so information is available which can be used for uncertainty analysis. If the compound was an initial reactant in the experiment, the calibration uncertainty was also used to derive an estimate the uncertainty of the initial reactant concentration, which is given in the cham-VOC spreadsheet in the cham-USE.XLS file.

It should be emphasized that this uncertainty reflects precision of the data only, and not necessarily its accuracy. However, in most cases there is no reason to believe that the accuracy will be significantly different from the precision.

The present system of identifying the instrument and including the calibration factor in the data sets for the chamber runs at SAPRC was not implemented until around the time of ~EC400. Although the log books were usually sufficient to identify the O_3, NO_x and most other instruments, the fact that more than one instrument could monitor the same species, combined with frequently unclear record keeping, made unambiguous identification of GC instruments and the GC factors used for the earlier EC runs difficult. Even if the record keeping were clearer, the task of determining the factors used to derive the present data would have been monumental. In many cases, the only data entered or even written on the strip charts were calculated data with the factors assumed appropriate at the time. Therefore, factors were not updated for GC data for runs prior to ~EC400.

However, based on examining the notation on the strip charts for the earlier runs, we were able to identify the probable instruments used in the earlier EC runs. Based on this, and the calibration data for the instrument we could determine the probable instrument and calibration and uncertainty assignments for many of the GC channels in these runs. Although we could not correct the data with the re-evaluated factors (because the old factors used could not readily be determined), we could use the calibration information to estimate the probable precision uncertainty of these data. This probable precision uncertainty was included in the data base.

Note that there was some ambiguity in these earlier EC runs as to which of the "PN" (PN-1, or PN-2) or "DMS" (DMS-1 or DMS-2) GCs were used, since these instruments were frequently used interchangeably. Since the log book for the PN-2 was lost, the precision information for the PN-1 was entered in the data sets for all early EC runs using either of the "PN" instruments. However, the precision of the data for the PN-2 would be expected to be similar, since the instruments are very similar. The DMS-1 was assumed to be used in all the earlier EC runs where a DMS column was employed, but the possibility of the DMS-2 being employed could not be ruled out. Again, the uncertainty estimates derived using the DMS-1 are probably not inappropriate for the DMS-2.

Not all GC data could be assigned calibration factors and precision uncertainty estimates. Although every attempt was made to compile all the relevant calibration data available, calibration data could not be found for some instruments, and data for others may be incomplete. In some cases, calibration assignments were not made because there were no calibration data sufficiently close to the time of the run to allow a reliable calibration estimate. If the factors for the runs are being estimated using linear regressions on the calibration data, assignments were not made if the run was carried out more than 30 days after the last relevant calibration. This limitation was applied to prevent assignments being based on extrapolated factors which may be significantly outside the range of the data used to derive them. A longer time limit was allowed when averaging was used to estimate the factors, in this case, the estimates could be used if the run was carried out less than 60 days since the last calibration in the set. Case by case judgement was used to determine when it may be appropriate to use a calibration assignment for a run carried out before the first calibration in the relevant set; such cases were infrequent because the usual practice at SAPRC was to calibrate for a species before using the species in a run. If calibration assignments could not be made for a species, the old assignments were retained. This can be indicated in the data set by the lack of information concerning uncertainty estimates or derivation codes for calibration factors (see Section 2.3).

In terms of ozone model evaluation, the most important use of the GC data is establishing the initial VOC reactant concentrations. The run spreadsheets give the initial concentrations for the added VOC reactants for the runs in the data base, and indicate which GC instrument was used, the calibration uncertainty estimates, and codes indicating the status of the calibration and uncertainty derivation. If information concerning the instrument or its calibration is not available, this is indicated in the table. In addition, the initial VOC reactant summary information in the run spreadsheets give the estimates of the uncertainties in the OH reactivity of the initial VOC species. If no uncertainty figure is given, it is because calibration information is not available for one of the reactants.

4.3.4 General Uncertainty Considerations

The uncertainty assignments discussed above are referred to as the "minimum uncertainty" because they reflect precisions of the calibrations and not possible systematic errors. In assessing uncertainty in general, one must consider the nature of the compound, its ease of handling, and its behavior in GC analysis systems. In general, lower molecular weight ($nC \leq \sim 8$) hydrocarbons are the easiest to handle and the best behaved in GC analysis systems, and thus have the lowest uncertainty. If no uncertainty data are available for such a compound, it is probably still not unreasonable to assume the uncertainty is less than ~10%. The analysis of hydrocarbons becomes more uncertain as the molecular weight, and volatility decreases. However, as long as the same procedures are used during sampling as employed during calibration, one would expect these uncertainties to be reflected in the systematic errors during calibration.

The analysis of acetaldehyde using the "C-600" systems as employed for most of the EC and ITC runs was particularly prone to uncertainty. This is because of the broad and varying peak shapes on the C-600 column (combined with the lack of use of an integrator at the time), and the difficulty of handling liquid acetaldehyde. We believe that systematic errors are a definite possibility in the acetaldehyde analysis for most of the EC and ITC runs. This is indicated by the results of the many replicate propene - NO_x runs carried out in at SAPRC. Figure 9 shows plots of the acetaldehyde yield relative to the initial propene concentrations in the propene - NO_x runs carried out at SAPRC which are, or will be, included

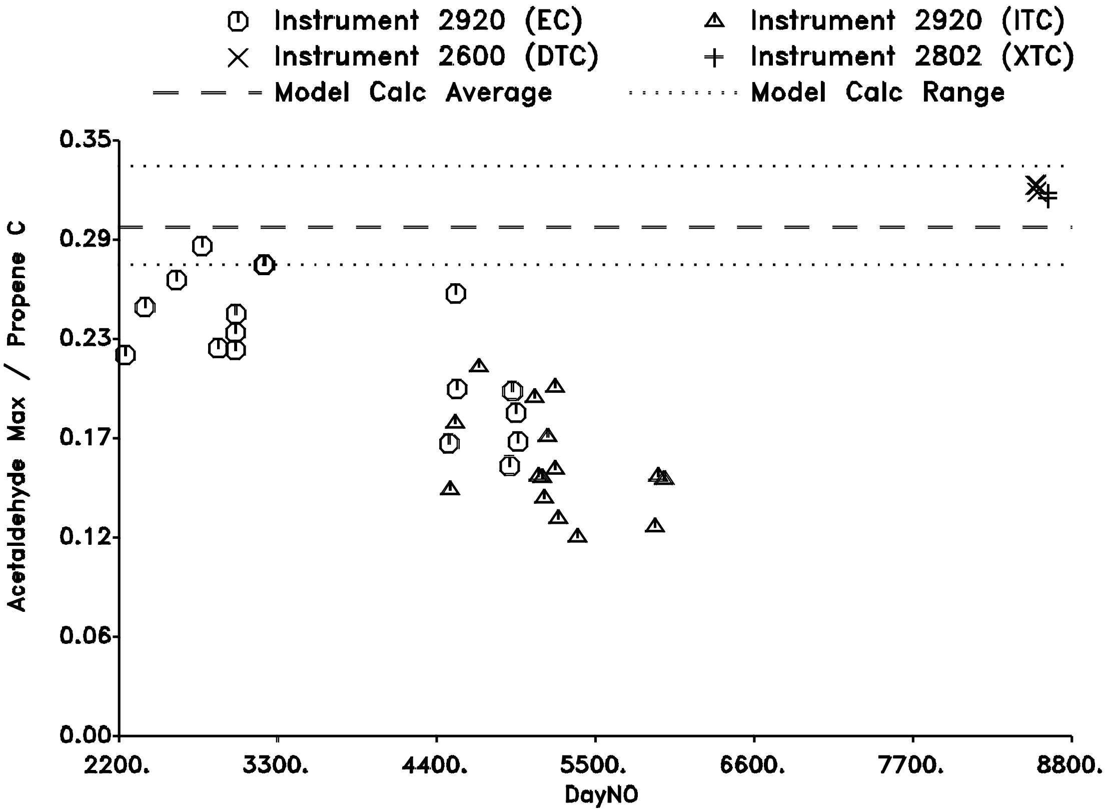


Figure 9. Plot of ratios of acetaldehyde carbons to propene carbons in the propene - NO_x runs against the date of the run. Range of results of model simulations of this ratio for these runs is also shown.

in the data base. It can be seen that the acetaldehyde yield monitored with the C-600 (instrument 2920), relative to initial propene, tended to decrease with time and was consistently lower than the relative yield obtained in more recent DTC and XTC runs using the HP5890 GCs.

Since the propene runs shown in Figure 9 were not exact duplicates, some of the differences in relative yields may be due to differences in the conditions of the experiment. To show the probable extent to which this may be a factor, the range of the relative yields predicted by model simulations of the runs is also shown. The range reflects calculations employing both the SAPRC-90 mechanism (Carter, 1990), which tends to overpredict rates of O_3 formation in the most recent runs, and an updated version of this mechanism (Carter, unpublished results; Carter, 1994), which tends to underpredict rates of O_3 formation in the earlier runs. It can be seen that the range of the relative acetaldehyde yields predicted by the model is much narrower than the range of the values measured with the C-600, and that the latter is consistently low, especially for the runs carried out between 1982 and 1986. On the other hand, the relative yields measured using the HP2890 systems (Instruments 2600 and 2802) are consistent with the range of model predictions, and are closer to the values measured prior to 1978 than the values measured in the 80's. Note that the yields of acetaldehyde in propene's reactions are considered reasonably well established, and model predictions of these yields in propene - NO_x runs are not particularly sensitive to how well the model performs in simulating other aspects of the runs.

The acetaldehyde measurements from the HP5890 GC's currently in use are much less uncertain for two reasons. Although the peaks are still wider than for hydrocarbons, the Chemstation data analysis software used with this system allows for integration of the peaks, which reduces uncertainties due to variabilities in this regard. Furthermore, acetaldehyde is now always prepared for calibrations using vacuum methods, which eliminates the uncertainties due to handling the highly volatile liquid. Models which can predict other features of the propene runs now can consistently predict the acetaldehyde yields using this method.

It is recommended that the aldehyde yields measured using the C-600 (instrument 2920) in the runs carried out in the 1980's not be used for model evaluation. The yields measured in the late 70's may be less unreliable, but might be biased low by up to ~30%. The yields in the propene runs could be used to "calibrate" this instrument for acetaldehyde if the modeler is willing to assume that the predictions in the propene runs are reliable. If this approach is used, the uncertainty is probably ±30%, not counting the uncertainty in the propene model.

A unique aspect of the EC data base is the measurements of the concentration-time profiles for the aromatic products, such as benzaldehyde and cresols, during 1978 (EC264-346). Unfortunately, as discussed above, analysis methods for those compounds had not been perfected and the GC system used to collect those data were subject to large variabilities in the calibration data. This variability was in part because the system was frequently changed in an attempt to improve the analysis. The factors in the data base were not changed because the researchers at the time probably had the best feel for the appropriate factors to use for any given experiment. The modeler should treat these data with caution, and probably consider them to be useful for qualitative purposes only.

4.4 Peroxyacetyl Nitrate (PAN) by ECD Gas Chromatography

As discussed above, peroxyacetyl nitrate (PAN) was monitored by gas chromatography with electron capture detection. The instruments used were the ECD-1 (2000), ECD-3 (4000), and the HP5890 with ECD (2700 or 2710). The PAN instrument is identified in the data sets for all the chamber runs and is also indicated in the spreadsheets where the maximum PAN is summarized. These instruments, their calibration histories, and uncertainties in the PAN data obtained from them, are discussed separately below.

4.4.1 Instrument 2000 (ECD-1)

Instrument Description and Sampling Method. Instrument 2000 consisted of an Aerograph gas chromatograph with tritium foil electron capture detector (ECD) and a 12 inch x 0.125 inch FEP Teflon column containing 5% Carbowax 400 on Chromosorb G (80/100 mesh) operating at room temperature with a nitrogen carrier flow of 75 ml min^{-1}. The detector was equipped with a standing current control, and since the response was directly influenced by the standing current, it was maintained to within ±2 percent of a constant value during all experiments and calibrations. Analyses were carried out by flushing a ~2 ml loop with the sample, and injecting the contents of the loop onto the column. The standing current was normally adjusted to 75% at attenuation 64. The mv response was used to quantitate the amount of compound present. The PAN retention time was typically 80 seconds. This instrument was linear to approximately 80 ppb and usable to perhaps 300 ppb. Calibrations were generally made up to approximately 100 ppb.

This instrument was normally used in Fawcett laboratory for EC and ITC runs, except when it was used for the outdoor chamber (OTC) experiments in 1983. After a gap of a number of years, it was then used for some of the earlier ETC runs.

Because of the nonlinear response of this instrument, a common practice during runs when high PAN yields were observed was to dilute the sample using glass syringes prior to injecting it into the instrument for analysis. The observed diluted concentration, which was in (or close to) the linear region, was then multiplied by the appropriate dilution factor before being entered in the data sheet for the run.

Calibration Methods. Methods for calibrating PAN are discussed by Pitts et al. (1979). The PAN was synthesized using the method of Stephens et al. (1965), and was purified by preparative gas chromatography and kept in a stainless steel tank at up to 100 psig. The PAN concentration was measured immediately prior to calibration by IR in a 10 cm cell using the 8.65 µ band ($\varepsilon = 13.9 \times 10^{-4}$ ppm^{-1} [Stephens et al, 1973]). Usually it was also measured again after the calibration, since it tended to decompose during the time of the calibration at room temperature. Concentrations were in the range of 200-2000 ppm. Most calibrations were based on a double dilution of PAN from the tank where the flows were measured with rotometers and the dilution ratio verified by inputing a hydrocarbon which could be accurately quantified by GC-FID before and after dilution. In some calibrations, standards were prepared by syringe injection of known amounts of PAN into a glass jar, and in others the EC was dosed with PAN, which was measured by long path in-situ IR while analyzing samples. The agreement of these the methods were generally within 20%.

Calibration History, Assignments, and Precision. Table 14 shows when the calibrations were carried out during the time period of the runs in the data base, and gives the calibration factors in the linear range. The full calibration data set for this instrument during the relevant period is shown in

Table 14. Calibration history of the ECD-1 PAN monitoring instrument (Instrument 2000).

Date	Cal ID Number	Range (ppb)	Linear Range Factor (ppb/mv)	Comments
6/30/71	9	0-275	3.44	
4/29/72		0-90	4.44	
6/24/72		20-200		Noted as "approx 1" in logbook
6/28/72		20-210	3.88	
11/11/72	10	40-140	3.19	
1/27/73		15-55	2.69	
5/5/73		10-115	3.31	
4/5/74	11	0-250	3.13	
12/11/74	12	0-100	4.19	
1/16/75				No notation in logbook
8/15/75		0-35	3.06	
2/25/76		0-19	2.63	
8/19/76		0-30	3.56	Logbook started recording factors as mv/ppb
4/6/77		5-178	4.00	
11/30/77		8-147	4.19	
2/2/78		0-67	4.63	
2/3/78		0-31	3.69	
8/26/78		8-101	4.13	
11/2/78		8-79	3.44	
6/9/79		6-44	3.13	
8/28/79				Moved to OTC facility. Used for OTC198 - 202.
9/1/79				One point calibration check
9/25/79				Moved from OTC facility station to 121 Fawcett
10/2/79		22-57	4.56	Two point calibration check
1/30/80		0-27	4.31	
2/27/80		13-46	3.31	
10/31/80		61-117	4.81	
11/6/80		15-89	4.19	
11/13/80		45	4.81	Data from ECD-3 included in log book.
2/2/82		0-43	1.44	This looks low - **Not counted in average**
2/8/85		15-62	3.69	Relocated and used for ETC010 - 038
Average			**3.78**	
Std Dev.			**0.64**	

Figure 10, which plots the calibration factor (ppb/mv) against ppb. Figure 10 also shows plots of the calibration factors in the linear region against when the calibration was carried out, and compares differences and uncertainties in the different methods of deriving general calibration factors as discussed below. The top plot in Figure 10 show that the calibration factor is clearly nonlinear, though it is probably not a bad approximation to assume it is linear for concentrations less than ~100 ppb (or ~25 mv).

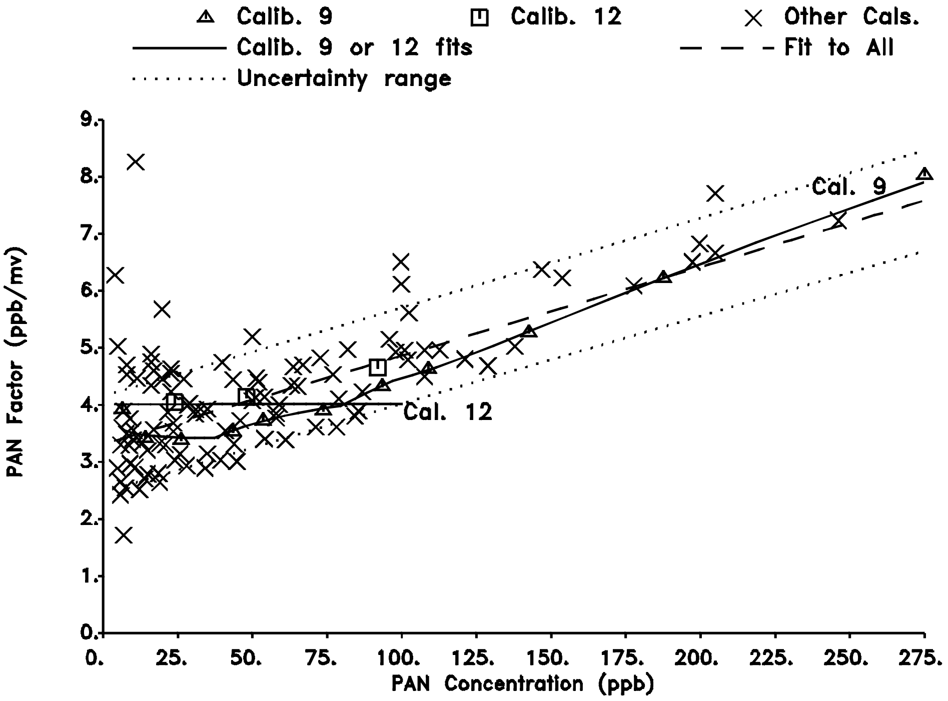
The data in Table 14 and Figure 10 suggest that the response of the ECD-1 is not changing systematically with time. The scatter in the data could reflect short-term fluctuations in instrument conditions, but could also reflect uncertainties in the calibration itself, which would be expected to be non-negligible because of the instability of PAN. These fluctuations, or the uncertainties in the calibration method, result in an approximately 17% uncertainty in the calibration in the linear region. The scatter of the calibration data in the nonlinear region (see top plot in Figure 10) is consistent with this level of precision

Because of the consistency of the calibration results throughout the time period the ECD-1 instrument was used, the recommended approach is to derive a single calibration curve to apply to all the ECD-1 data. As shown in Figure 10, a linear function of the PAN concentration can predict the factor to within the scatter of the data throughout the concentration region. The uncertainty of the estimation of the factor using this linear fit ranges from ±25% to ±15% depending on the concentration, as shown on the right-bottom plot in Figure 10.

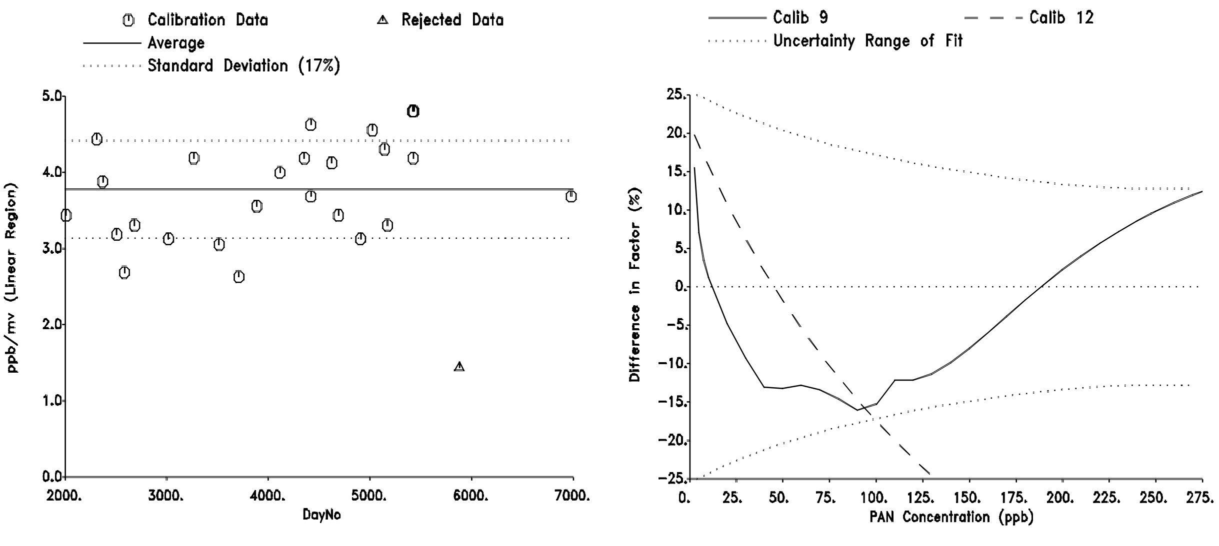
Unfortunately, the data processing of the PAN data for most of these runs was such that only processed data are in the data base, and the only reliable way to re-calibrate all the PAN data from this instrument would be to go back to the strip charts for all the runs and re-entering all the data. This would be a major effort which we decided was not worthwhile because, as discussed below, the result would probably not change the PAN values by more than their uncertainty levels.

The ECD-1 instrument was used for essentially all of the EC runs and for a majority of the ITC runs. After a gap of nearly three years, it was then used in a few early ETC runs. These data were processed using three different calibration assignments, as follows:

(1) Calibration #9 consisted of a nonlinear curve-fit to the calibration data taken in July of 1975. It was used for the earlier EC runs through EC355. It was also used in the early ITC runs, but not those in the present data base. The Calibration 9 fit consisted of using different linear fits in various mv ranges, and a quadratic fit in the highest mv range. This fit, and the data used to derive it, are shown in the top plot in Figure 10. The bottom-right plot shows the percent difference between this calibration



Calibration Factors vs PAN Concentration



Factor vs Time

Differences and Uncertainty

Figure 10. PAN calibrations on Instrument 2000 (ECD-1). (1) Plot of ppb/mv response against ppb showing various fits to the data; (2) Plot of calibration factors in linear region vs time; and (3) and of differences between fits used for the chamber runs relative to the fit to all the data.

and our fit to the entire calibration data set. It can be seen that this calibration agrees with our recommended factors to within the uncertainty of the derivation.

(2) Calibration #12 consisted of a nearly linear fit to the calibration data taken in December, 1978. It was used for EC-356 through EC407. It was nominally a polynomial fit, but the nonlinear term was so small that it was effectively negligible. As shown in Figure 10, this calibration agrees with the recommended factors when concentrations are in the linear range. As indicated above, samples were generally diluted to the linear range when calibration #12 was used. On spot checking some runs, we found cases where the technician erroneously applied the dilution factor to the mv prior to applying the calibration curve, which is inappropriate for nonlinear calibrations. Fortunately, the very small magnitude of the nonlinear term was such that the errors introduced by this mistake were negligible, so no corrections were made.

(3) After EC489 and ITC397 the PAN concentration was determined by the chromatographer using a calibration chart in the lab and entered into the data sheets directly in ppb. Documentation for the origin of calibration used in this chart is not known, but presumably it is based on the data base of all the calibrations carried out to that time. For that reason, we would expect the factors to be reasonably close to those presently recommended.

(4) The instrument was used briefly for the OTC runs conducted in June-September 1983. A one-point calibration check was performed at 9 ppb. PAN concentrations were entered directly to data sheets, using a factor of 3.5 ppb/mv. The origin of that factor is not known. This agrees with the recommended factor for the linear region within its uncertainty.

(5) A gap of nearly three years existed in the logbook prior to the instrument’s use in the ETC runs. It was calibrated on 2/9/89 just prior to ETC010 using a double dilution system. For ETC010 to ETC038 this calibration curve was used and the data were tabulated manually in hard copy in ppb. As shown in Table 14, this factor is very close to the recommended factor for the linear region based on the entire data set.

Based on the above considerations, the ECD-1 PAN data in the data sets were not corrected. The overall uncertainty in the data should be considered to be ±20%. This is the same as the uncertainty estimate given for this instrument by Pitts et al. (1979).

4.4.2 Instrument 4000 (ECD-3)

This was another Aerograph gas chromatograph with electron capture detectors (ECD). The detector was equipped with a standing current control as described for Instrument 2000. In order to obtain PAN data during the nighttime for the indoor experiments, this instrument was set up with an automated sampling system at 15 minute intervals. It had a 24 inch by 0.125 inch FEP column, packed with 5% Carbowax 400 on Chromosorb with 100/120 mesh operating at room temperature with a nitrogen carrier flow of 36 ml min^{-1}. Like the ECD-1, analyses were carried out by flushing a ~2 ml loop with the sample, and injecting the contents of the loop onto the column. However, in this case, an automated sampling system was used.

This instrument was used primarily for OTC runs, but was also used for some of the multi-day ITC runs (ITC874 - ITC893) because its automated sampling allowed data to be taken at night.

A summary of the calibration and usage history for this instrument is given in Table 15, and Figure 11 shows plots of selected calibration results. Like the ECD-1, the response is nonlinear, but the factors are fit reasonably well by a linear function of the concentration (see top plots in Figure 11). However, unlike the ECD-1, the response of this instrument varied significantly with time, so no single calibration curve is appropriate. The largest change occurred when the foil in the ECD detector was replaced in January, 1984, but significant drift in sensitivity occurred throughout the period of the runs of interest. The factor typically tended to decrease with time, except for the significant increases which occurred when the instrument was moved from the OTC lab to the EPA van in August, 1983, and when the instrument was moved back to the outdoor chamber facility from the mutagen lab. No reason could be found in the log book for the increases in the factors at those times.

Table 15 and the bottom plot in Figure 11 show when the ITC and OTC runs were carried out, relative to the times of the calibrations. The runs can be classified into five groups, as discussed below. In this discussion, the calibrations are identified by their "Cal ID" number, which are given as negative numbers to distinguish them from the calibration numbers for the ECD-1.

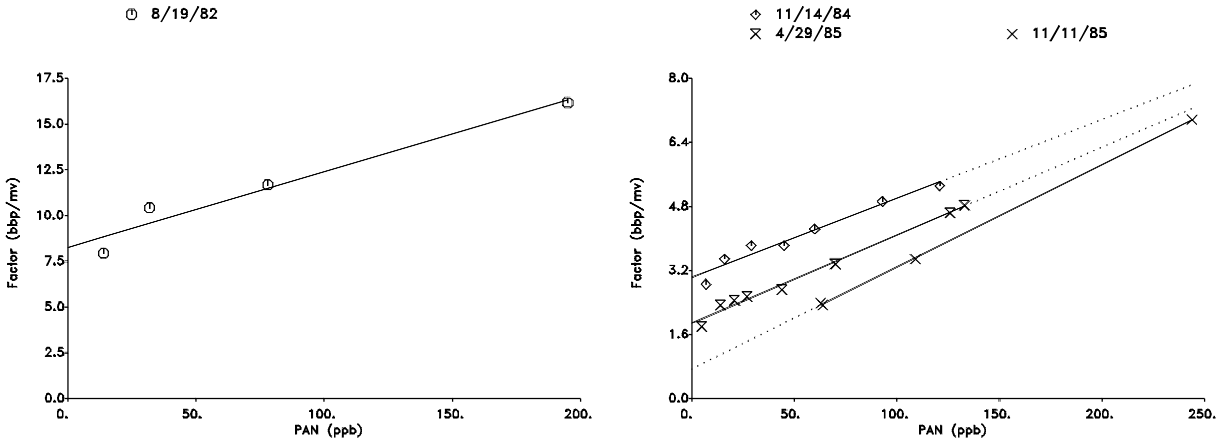
(1) The <u>1982 OTC runs</u> were carried out following calibration -1. The data sets for these runs have only the calculated PAN concentrations — as is the case for all the OTC and ITC runs where this instrument was used. It is reasonable to expect that this calibration -1 was used for all these runs, but this is poorly documented, and has been checked for only one run. A downward correction of up to 40% may be appropriate for the latter runs in this series, since lower factors were obtained in the next two calibrations. These data have not yet been corrected, since the 1982 OTC runs are not expected to be included in the data base.

(2) The <u>1983 OTC runs</u> where this instrument was used were carried out following calibration -3. As with the other OTC runs, only calculated PAN data are in the data base. It is reasonable to expect that calibration -3 was used for these runs, as was found to be the case in a spot check on one run. However, the next calibration, made shortly after the last run in this series, but after the instrument was moved, gave significantly higher factors. Since the instrument was moved, it is unclear whether a

Table 15. Calibration and useage history of the ECD-3 PAN analyzer (Instrument 4000).

Date	Range (ppb)	Factor [a] (units/ppb)	SC [b]	Comments
7/28/82				Set up in OTC facility and used for 1982 OTC runs.
8/1/82	0-200	0.65 ± 0.12	39	Nonlinear>40ppb. SC=39% [b]
2/8/83				Set up in Mobile laboratory for freeway study
3/31/83	15	~0.4		
6/6/83				Set up at OTC facility and used for 1983 OTC runs.
6/10/83	0-44	1.5 ± 0.2		
8/29/83				Moved to EPA Van at Burning Tower
9/2/83	0-27	0.84 ± 0.12	35	
9/27/83				Moved back to OTC Facility and used for more 1983 OTC runs.
10/3/83	0-57	0.48		
1/13/84				Moved to Mutagen Lab in Fawcett. New foil installed. Used for ITC792 when ECD-1 was having problems.
1/24/84	0-27	4.5 ± 0.4	76	
6/22/84				Moved to OTC facility.
7/31/84	5-9	8.4	75	
8/1/84	10-13	8.3		Carboy calibration, not dilution system.
10/29/84				Moved to Indoor Chamber Lab
11/1/84	61-117			Non linear range
11/6/84				Bad Cal, oven repaired
11/14	0-121	1.7 ± 0.3		
3/11/85				Moved to OTC facility. Used for 1985 OTC runs.
4/29/85	0-126	2.5 ± 0.2		
11/11/85	0-244	4.3 ± 1.1	74	
6/91 - 10/91				Used for ETC runs, but no entries found in log book for this period.

[a] Response units are percent of scale at attenuation of 16.
[b] SC standing current in percent of full scale at attenuation of 64.



Calibration for 1982 OTC Runs

Calibrations for 1984/1985 Runs

Linear Range Factor vs Time

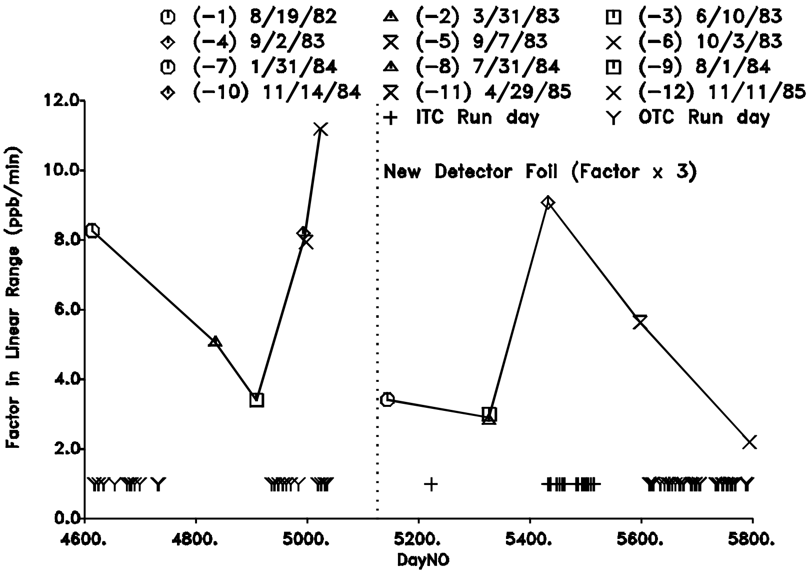


Figure 11. PAN Calibration data for ECD-3. (1) Plots of calibration factors vs concentration for the calibration applicable to the 1982 OTC runs. (2) Plots of calibration factors vs concentration for the calibrations applicable to the 1984/85 ITC runs and the 1985 OTC runs. (3) Plots of linear range calibration factors vs time, also showing times OTC and ITC runs using this instrument were carried out.

correction is appropriate. The data from these runs have not been corrected, so it is possible that the PAN values for the later runs are low by up to a factor of 2. These runs are not yet in the data base, but may be included in a later release. These data will be further evaluated at that time. (3) This instrument was used on a one-time basis in run ITC792 when the ECD-1 was failing. It is probable that the factor from the previous calibration (-7) was used. The subsequent calibration gave similar results, so this is probably not uncertain. The data were not changed.

(4) The 1984/1985 ITC runs were carried out following calibration -10, and a spot check of a number of runs indicated that this calibration was used for all these runs. However, the subsequent two calibrations gave factors which were significantly lower, and which suggest that the factor may be decreasing linearly with time during this period. If this is the case, the PAN data in the last run in the series should be reduced by up to 20%. However, the instrument was moved from the indoor chamber lab to the OTC facility before the next calibration, so the change may be due to the move rather than a continuous change in the instrument. The data were not corrected, but the run spreadsheets and run data files have entries indicating what the maximum PAN value would be if the ECD-3 PAN factor were assumed to decrease linearly with time between calibrations -10 and -11.

(5) The 1985 OTC runs were carried out between the times of calibrations -11 and -12. The PAN data for the earlier runs were input using factors from calibration -11, while the data from the latest runs were input using calibration -12. The run where the change occurred has not yet been determined. It is considered appropriate in this case to correct the data for these runs based on assuming the factor changes linearly with time. However, the necessary corrections to the PAN data for these runs, which are not included in the current release of the data base, have not yet been made.

The ECD-3 instrument was also used for runs ETC223-288, which were carried out in 1991. Unfortunately, we were unable to locate the log book for this instrument for this period. The data sets for these runs have a calibration factor of 10.2 ppb/mv, which is applied to all concentrations. This factor is significantly different from the previous factors, and the use of the same factor for all concentrations is probably inappropriate. Thus these data clearly need to be evaluated before they are used for mechanism evaluation. Because of the lack of documentation for the PAN calibrations for these runs, and the fact that PAN was not a high priority measurement when these runs were carried out, we recommend that the PAN data from these ETC runs not be used for mechanism evaluation. They are not included in the run spreadsheets, and the data channels are given "priority numbers" of 3, indicating that they are not reliable for modeling.

In general, based on the variability of the calibration data for this instrument, a minimum uncertainty of ~30% should be assumed for PAN data from this instrument. This minimum uncertainty is probably applicable for the ITC792 and the 1984/85 ITC runs, and should be applicable to the 1984

OTC runs once the data are corrected. The PAN data for the other runs discussed above are considerably more uncertain, and may not be suitable for modeling.

4.4.3 HP 5890 ECD Instruments (2700 and 2710)

This was a dual-column and dual-detector Hewlett-Packard 5890 Series II GC outfitted with two ECD detectors, and set up for loop sampling. It employed a 5m x 0.53mm megabore HP-1 and a 15m x 0.53mm megabore DB-5 column. It was used in an attempt to monitor PAN for a number of runs, starting with ETC268, but satisfactory results were never obtained. Although a considerable amount of effort was expended in an attempt to yield reliable calibration data and reproducible measurements, to date that effort has not been successful. Since none of the data from this instrument are considered reliable enough for modeling, it is not particularly useful to discuss its problems further here. No PAN data from this instrument are included in the run spreadsheets, and the PAN data on the runs are given "priority numbers" of 3 to indicate they are not reliable enough for modeling.

4.5 Formaldehyde by Chromotropic Acid

4.5.1 Method

This "wet chemical" method for monitoring formaldehyde is discussed by Pitts et al. (1979). Briefly, the sample is collected by passing air through a single impinger filled with distilled water at 1 lpm for typically 20 minutes. While two bubblers in series are recommended (the efficiency per impinger is approximately 80% according to Lodge [1989]), more than 90% recovery was obtained when this method was evaluated. No corrections were made in the data. This is reasonable since the recovery may be dependent on the concentrations measured. The flow is controlled by a needle valve and set with a rotometer; 0.1 ml of chromotropic acid reagent (0.10g of 4,5-dihydroxy-2,7-napthalenedisulfonic acid disodium salt in 10 ml of water) and 6ml of concentrated sulfuric acid are added to 4 ml of sample solution. The absorbance is measured at 580 nm for both the sample and a distilled water blank after allowing color to develop overnight. The method is calibrated by making standard solutions of sodium formaldehyde bisulfate by weighing. Alcohols, olefins, aromatics, and cyclohexanone may interfere if their concentrations are much higher than the formaldehyde.

4.5.1 Calibration History

The calibration record for the chromomotropic acid method is summarized in Table 16. Apparently only one calibration of the analytical method using sodium formaldehyde bisulfate was performed from September 1974 to June of 1976. Fifteen calibrations were performed between that date and September 1989. The mean response factor was 18.8 ug/Abs with a standard deviation of 2.3. Flow rates were occasionally checked and generally found to be within 2% of the nominal 1 lpm. Early on there appeared to be problems with how long to let the color develop and which spectrometer to use.

Table 16. Calibration record for formaldehyde monitoring using the Chromatropic Acid method.

Date	Range	Method	Factor		Comments
			ug/a	Sdev.	
9/19/74	A=.05-1.0	SFB	20.1		
5/17/76					New Bubbler Used
5/28/76					Compared new & old bubblers, A 2.5&4xlarger with new
6/17/76					Cary 14 & Spec 20 compared, Cary reads much higher
6/23/76	A=.01-.02	SFB	58.0		Reasonably linear to 5ug/sample, then response drops May have error in logbook with respect to calibration calcs
8/18/76					"Questionable bubbler", "New bubbler maybe"
1/25/77					Bubblers identified by letter-number
6/2/77					Prep for CH2O-EC study/bubbler comparison
6/13/77	A= .12-.28		17.1-20.1		Calibration with sodium formaldehyde bisulfate (SFB) "Spec 20, old and new Cary 14s"
7/1/77					Change from bubbler 3 to 4d/flow calibration
9/15/77	A=.10-.22	SFB			SFB Cal with Beckman 35 (not Spec 20 as previous)
9/20/77	A=.67-.54	SFB	18.7		Bubbler G-7/ Calibration/conc calcs
10/9/77	A=.02-.06	SFB			Cal looks bad
10/13/77	A=.004-.26	SFB	14.3	4.3	"1st good cal in bk 4, orig calc of ug was as a salt"
10/24/77	A=.08-.16	SFB	19.7	1.6	
10/28/77					"Bubbler B-4 used routinely, G7 occasionally"
11/2/77		SFB	14.7	3.1	Three point cal
11/16/77					Started using Spec 20 instead of Beckman 35
11/28/77					Beckman 35 used again (new cells were needed)
11/28/77	.009-.241	SFB	22.1	2.8	
12/12/77	019-.257	SFB	17.1	2.6	Known as Cal #2: y=20.2-.178
12/21/77					Comparison with FTIR values
12/28/77	.015-.245	SFB	19.9	1.2	Known as cal #3: y=20.65-.036
1/16/78					Comparison with FTIR values
3/16/78					Sumary of Cals # 2 and 3 and factors to use
12/27/78	.02-.23	SFB	20.4	1.4	Known as cal#4: y=43.49-.00464
1/17/79					Logbook no longer has references to bubbler B-4
4/25/79	.74->1	SFB	20.1		"Only one good pt, A’s are too high; known as cal#5"
5/2/79	.33-.74	SFB	21.1	0.5	Combined with cal #3: y=42.28x-.00377
4/23/84	.016-.238	SFB	18.6	1.8	Also called cal #4:y=39.58-0.0
4/16/87		DOAS			3 pt comparison in EC: DOAS=0.84x + 5; r=0.9996
4/20/87		DOAS?			CH2O inj into EC; varied N2 content/RH; no DOAS data shown
4/7/89	.032-.252	SFB	18.8	1.5	
9/28/89	.023-.263	SFB	19.4	1.2	
10/12/89					EC/UNC/FTIR comparison
Average Factor			18.8		
Standard Deviation			2.3		

4.5.2 Uncertainty

Lodge (1989) reported that three labs analyzing formaldehyde samples agreed within ± 5%. Collocated samples in September 1974 also showed this level of reproducability. The 12%variability of the response factor noted above is probably a good indication of the overall precision of the method. Several comparisons with spectroscopic methods showed generally good agreement (within 10%). Additional errors up to ten percent negative may be due to trapping efficiency, while the flow accuracy is estimated at 3%. One other source of error may be due to simply removing a 4ml aliquot from the bubbler rather than bringing the amount remaining in the bubbler up to a constant amount. All calculations were based on 10 ml solution in the bubbler at the end of sampling. Under typical conditions, if there were no carry over of liquid, this will result in readings which are too high by 2% for 50% RH to 4% for dry runs. Apparently this was not considered sufficiently significant to correct for given the other potential errors.

Based on these considerations, the minimum overall uncertainty of the measurement is estimated as between -25 to +15%. Runs prior to EC216 may have additional errors toward lower concentrations due to difficulties with residue buildup in absorption cells and bubbler problems. Runs prior to EC247 (11/14/77) may also have additional uncertainty due to the use of a single beam spectrometer; a double beam instrument was used after this date.

This minimum uncertainty estimate is applicable for "best case" conditions, when the impinger was functioning properly, when the cell was free of residue, and when proper procedures were employed. An examination of extent to which this has occurred in practice can be obtained by examining the data base of the repeated propene - NO_x runs, in a manner analogous to the discussion of the acetaldehyde data (Figure 9), above. Figure 12 shows formaldehyde yields, relative to the initial propene, in the propene - NO_x runs carried out to date in the indoor chambers which are, or will be, in the data base. This includes data from the "Dasgupta" instrument, discussed in the next section, as well as from this chromotropic acid ("C.A.") method. The range of results of model calculations of this ratio, using both the SAPRC90 (Carter, 1990) and an updated (Carter, 1994) mechanism are also shown. As with the acetaldehyde yields, the relative formaldehyde yield in the propene system is not considered to be particularly uncertain, and model predictions of this yield are not particularly sensitive to other mechanism uncertainties.

It can be seen from Figure 12 that in practice the performance of this analysis method was significantly worse than indicated by the uncertainty analysis discussed above. If the model predictions, which have a much narrower range than the scatter of the data, are considered to be reliable, the instrument can be seen to give appropriate measurements from time to time, but that it frequently has cases where anomalously low values are obtained. The Dasgupta method (discussed below) seems to have a bias in the opposite direction. It is interesting to note that the range of model predictions agrees both with the low range of the data using the Dasgupta method and the high range of the data using chromotropic acid, giving perhaps some degree of confidence in the model. In any case, because of the scatter in the data from the chromotropic acid method, and its frequent apparently anomalously low values, we recommend that data from this method be used only for determination of lower limit yields. The recommended uncertainty range for these data is +600% to -30%.

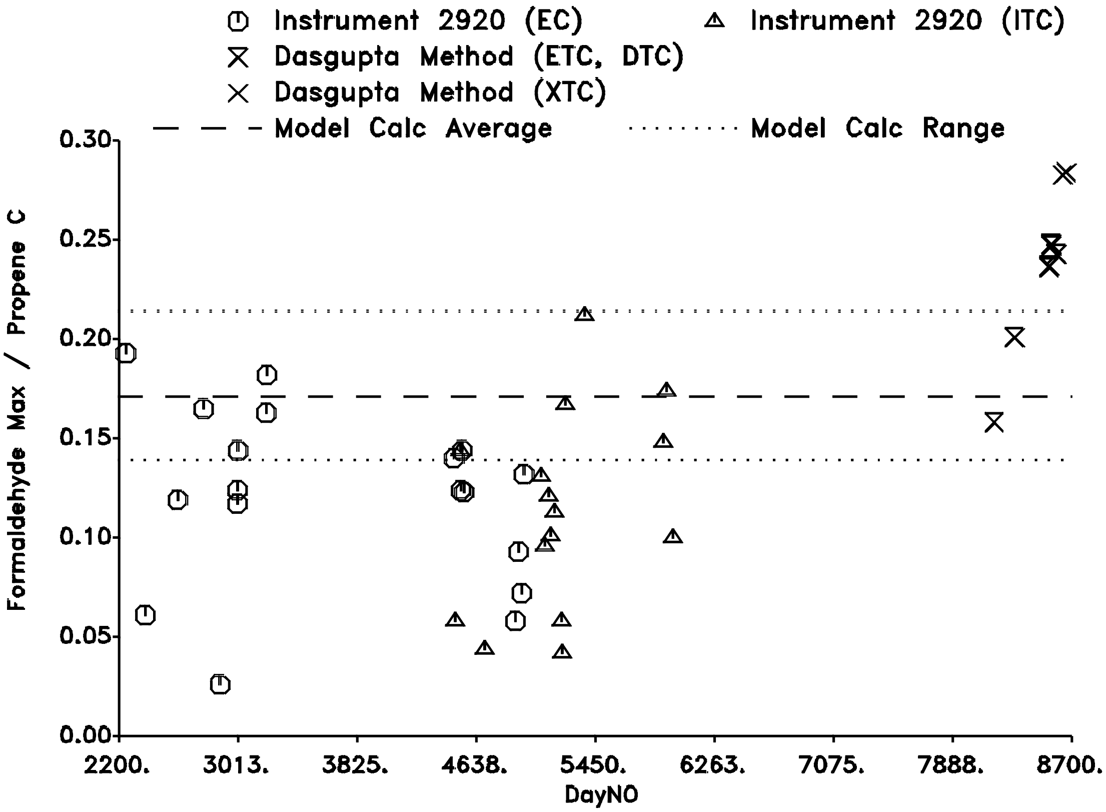


Figure 12. Plot of ratios of formaldehyde to propene carbons in the propene - NO_x runs against the date of the run. Range of results of model simulations of this ratio for these runs is also shown.

4.6 Formaldehyde by Diffusion Scrubber (Dasgupta Method)

4.6.1 Method

The method used follows that of Dasgupta et al. (1988, 1990). A diffusion scrubber is used to collect sample in water flowing through the tube at 40 ul/min by means of a peristaltic pump. The scrubber effluent is mixed with Nash reagent, also flowing at 40 ul/min. The mixture is maintained at 95 C for 25 seconds and the product (3,5-diacetyl-1,4-dihydolutidine) is quantified using a flourimeterby exciting at 406nm and measuring the resulting fluorescence at 500nm. This automated analyzer performs a zero and span check before and after every measurement interval.

Except as indicated, the system was designed to duplicate the diffusion scrubber formaldehyde analysis system employed in the UNC outdoor chamber, as described by Jeffries et al. (1990) The formaldehyde scrubber is 40 cm. in length and differs from the Dasgupta unit only in the end treatment of microporous tube connections and support. The system uses a 1/4 inch stainless-steel Ultra-Torr tee to form the inlet-outlet connections. Teflon tubing (1/4 inch o.d.) connects the two tees with the hydrophobic membrane tubing stretched inside the 1/4 inch tubing. Sample air is drawn through the annular space into and out of the side arm of the tees. HPLC grade water is pumped through the scrubber by a Gilson Minipuls peristaltic pump. After the scrubber, a micro-bore stainless steel tee brings the reagent and water together before passing through 80 cm of 0.508 mm i.d. stainless steel tubing maintained at 95 degrees C in a heated bed. The detector is a Fluoromonitor III model 1311 fluorometer, with a 30 micro-liter volume flow cell. The source was a 406 nm lamp with a 400 nm primary filter and a 500 nm emission filter. Liquid waste is collected directly from the flow cell outlet, without any added restriction.

An in-house formaldehyde permeation-tube-based formaldehyde generator was constructed to allow calibration checks as desired. The permeation tube (VICI Metronics) is maintained at 70° C. Mass flow controllers (Tylan model FC280) are used for the permeation tube flush air, dilution air and sample air flow. Digital outputs of these three flow rates are constantly monitored. Permeation tube oven temperature and heated bed temperature can also be monitored constantly. The formaldehyde calibrator and measurement system are mounted together on a small laboratory cart. The choice of zero air, calibration or sample measurement cycle can be manually selected or remotely controlled by timers or the data acquisition system.

4.6.2 Calibration History

The instrument was built in the summer of 1991 and refined until March 1992. A permeation tube with a certified rate of 472 ng/min @ 70C was used for generating span gas. The system was then compared with an FTIR using the SAPRC evacuable chamber which was dosed with formaldehyde. Using the FTIR values as the calibration standard, the permeation rate was calculated to yield a formaldehyde concentration in the calibration gas stream of 0.157 ppm for one comparison and 0.140 ppm for a second comparison three weeks later. The permeation rate was then determined by weighing the tube six times over 17 months. The results, given formaldehyde concentrations in the calibration gas stream, are summarized in Table 17, in a format similar to the calibration tables discussed previously. The results of the first determination and the last two appear to be anomalous, but the other data points are in good agreement with the FTIR determinations and indicate the rate drops slightly with time (slope of -0.046 ppb/day). If the anomalous points are neglected, the calibration precision is better than 5%. If the anomalous points are real, the calibration uncertainty would be 25% at the beginning time period, reducing to ~15% at the later dates. However, the mv response of the detector with the calibration standard, corrected for the -0.046 ppb/day slope, are reasonably consistent if these anomalous calibration points are neglected.

Table 17. Summary of calibration results for the Dasgupta formaldehyde analysis method (instrument 3001). Results are given as the computed concentration of formaldehyde in the calibration gas stream.

Date	DayNo	Standard (ppm)	Days	Asn.	Cd	Std.fit (ppm)	Unc.	Diff.	Runs	Avg/Intc (ppm)	Sdev	Slope (ppm/day)	Sdev
03/02/92	8097		0	1	L	0.152	2%		338	0.152	2%	-4.65E-05	13%
03/13/92	8108	0.115	11	0	X								
05/22/92	8178	0.150	81	1		0.148	2%	1%					
08/27/92	8275	0.140	178	1		0.143	3%	-2%					
09/30/92	8309	0.140	212	1		0.142	3%	-1%					
02/12/93	8444	0.140	347	1		0.136	3%	3%					
10/05/93	8679	0.123	582	1		0.125	3%	-1%					
10/25/93	8699	0.124	602	1		0.124	3%	0%					
12/07/93	8742	0.103	645	0	X								
01/21/94	8787	0.102	690	0	X								

4.6.3 Uncertainty

Since calibrations are performed before and after each measurement interval, the uncertainty is a combination of the accuracy of the calibration and the variability of the zero and span measurements. In order to calculate variability, data from twelve run days were analyzed (a total of 82 data points). The difference from each zero or span measurement interval was divided by two to represent the drift between the zero or span and the measurement interval (since each measurement was bracketed by a zero and aspan). The standard deviation of the zero was 3ppb and the span was 4ppb (out of a span concentration of 130ppb). Thus the overall uncertainty is approximately +/- 3ppb and +/- 7%.

The relative formaldehyde yields in the repeated propene runs give another indication of how well this instrument is performing in practice. This is shown in Figure 12, above, where it is compared with the data from the chromotropic acid method. Note that none of the propene runs were carried out around the time of the anomalous final two calibrations. The results suggest there may be a positive bias or drift in this measurement which is not being accounted for by the calibration data. Based primarily on the data in Figure 12, we tentatively estimate the formaldehyde measured using this instrument to have uncertainties of approximately +10% to -50%. This instrument is still being evaluated, and thus data from it must still be considered to be preliminary.

4.7 Carbon Monoxide

4.7.1 Beckman 6800 GC.

Method. CO was monitored in the earlier EC runs using a Beckman 6800 automated gas chromatograph. CO is separated from hydrocarbons by gas chromatography, methanated, and detected by flame ionization. The instrument looks at the "window" where the CO is detected and measures and records the height of the resulting peak.

Calibration History. Calibrations were performed prior to each run by introducing a standard directly from a tank of known concentration (concentration was determined by the tank vendor). While it would have been useful to introduce zero air to determine background response, this was rarely, if ever done. The calibration response factor to span gas was calculated and applied for each run. In early runs CO was injected prior to irradiation such that the total was approximately 2ppm. Thus the concentration change could be calculated from the amount injected and the known chamber volume.

The calibration is dependent on the accuracy of the CO concentration determined by the vendor. During the period of reported CO data for the EC, two calibration cylinders were used. The earliest data reflect the vendor's assay of first cylinder (#A-12088, 2.84 ppm on 2/15/74). A comparison with a more newly purchased cylinder (10.2 ppm) was done on Jan 13, 1976 between runs EC116 and EC121. As a result of this comparison and assuming the concentration of the newer cylinder was valid, the CO concentration of the original cylinder should be 2.21 ppm.

A review of the calibration folder shows data for the above-mentioned intercomparison in addition to data from a chamber injections. Based on the evacuable chamber volume of 5775 liters and the amount of CO injected, cyl#12088 concentration is approximately 2.5 ppm. On Dec 22, 1976 another new cylinder was received (# L-1880, 9.87ppm CO) and compared with #A-12088. Assuming the latest cylinder's concentration is correct, the old cylinder's concentration is now 1.81 ppm. A similar comparison on February 16, 1977 showed the older cylinder to be approximately 1.65 ppm and on March 10, 1978 it gave the concentration to be 1.45 ppm. A decay rate of 1.3 % percent per month was calculated. This was found to be linear based on four data points since cylinder A-12088 was new.

Uncertainty. The uncertainty depends on whether the analyzer was operated in the manual or automatic mode. After February 7, 1978, the instrument was operated manually (in this mode only a few measurements were generally made during the course of a run). The manual mode has the advantage that baseline drifts are better compensated for, and one does not depend on the chromatogram hitting the previously determined windows for zeroing and peak picking. The measurement-to-measurement precision is generally within a few per cent based on reported injections of calibration gas (the instrument was normally left on calibration gas for many determinations during a run). Since the instrument is calibrated daily, the best indication of the overall measurement precision would be the day-to-day variation of its response to calibration gas. The standard deviation of the response was calculated for four typical periods of instrument operation:

Runs	Relative Standard Deviation
EC077-EC106	5.5%
EC143-EC178	3.9%
EC241-EC257	6.8%
EC281-EC293	2.2% (manual mode)

The most significant uncertainty is the accuracy as determined by the calibration span gas concentration. Assuming that the aluminum cylinders are correct to their certified ±2 % and based on the limited number of intercomparisons (4 in two years) with the calibration cylinder used for this instrument, the estimated overall accuracy is approximately 5%. The later cylinders (ones used for comparison) were passivated aluminum whereas #A12088 was treated steel (an older technique); the belief was that the CO in the aluminum cylinders would be more stable.

Thus the overall uncertainty in the automatic mode (prior to EC 266) is about ±10%, and in the manual mode it may be slightly better, approximately ±7%. However, additional uncertainties may be introduced because of possible gradual losses of span gas concentration over time. Spot checks of the data indicate that attempts were made to correct for this, but they were not consistent. These checks suggest an additional uncertainty of at least ~10%, making the overall uncertainty of much of the data on the order of ~15%.

4.7.2 Dasibi Model 3003.

A Dasibi model 3003 CO analyzer was used to check CO in many of the ETC, DTC, and XTC runs. It is based on infrared gas filter correlation. This approach uses a single IR beam which passes through a spinning wheel containing two optical cells; one of which is filled with CO, the other with nitrogen. The CO-filled cells removes all radiation absorbed by that species while the NO-filled one passes all the radiation. The beam of light then passes through a sample cell (multi-pass optics are used to increase the path length) and to a detector. The difference in intensity between the two beams is a measure of the CO concentration in the cell. Potential interferents would need to absorb the radiation in the same spectral region as CO otherwise the two signals would cancel each other out. The manufacturer's stated lower detection limit is 100 ppb with a zero drift of less than 200 ppb per day. Calibrations are performed using compressed gas standards of known concentration.

This instrument was calibrated against span gas every time it was used to measure CO in a chamber run. The instrument was adjusted to read the assumed concentration in the calibration tank, and then was attached to the chamber prior to the irradiation to take a single reading. It was not run continuously.

The quality of the calibration tanks now used are such that the uncertainty can reasonably be expected to be on the order of ±5% or less. Since the instrument is used immediately after calibration, and no dilution uncertainties are involved, this can probably reasonably be considered to be the overall uncertainty.

4.7.3 CO Data Availability.

Although CO is undoubtedly present in measurable levels in all experiments, the availability and quantity of CO data varies greatly among the runs in the data base. The earlier EC runs (EC095-EC307 and EC338-EC407) have the most complete CO data, where CO concentrations are given as a function of time throughout the runs. The run spreadsheets give the initial CO concentrations for these runs. No CO data are available for some of the earlier EC runs, for all of the EC runs after EC407, for most of the ITC runs, and for all of the ETC runs prior to ETC047. After ETC047, and for most ETC and XTC runs, CO measurements were made prior to the irradiation and included in the comments section of the data files. The run spreadsheets include these initial CO concentrations. If no initial CO concentrations are given in the spreadsheets, then no CO data are available.

5. LIGHT CHARACTERIZATION

Light characterization for environmental chamber runs requires information about both the intensity and the spectrum of the light, and how they change with time. In the case of indoor chamber runs, the intensity and the spectrum are usually assumed to be constant during an experiment; the problem is assigning some measure of light intensity and a spectrum of relative intensities as a function of wavelength for each run. In the SAPRC indoor chambers, the absolute light intensities are determined by conducting NO_2 actinometry experiments to measure the NO_2 photolysis rate (referred to as "k_1"), and relative spectra, $J(\lambda)$, are measured using spectrometers. The photolysis rate for any reaction, k_i, can then be calculated using the expression:

$$k_i = k_1 \text{ x } \int J(\lambda)\sigma_i(\lambda)\phi_i(\lambda)d\lambda \ / \int J(\lambda)\sigma_{NO2}(\lambda)\phi_{NO2}(\lambda)d\lambda$$

where λ is the wavelength, $J(\lambda)$ is the relative spectral distribution, σ_i and ϕ_i are the absorption cross sections and quantum yields for the reaction, and σ_{NO2} and ϕ_{NO2} are the absorption cross sections and quantum yields for the photolysis of NO_2. The quantities of σ_i, ϕ_i, σ_{NO2} and ϕ_{NO2} are part of the photochemical mechanism and thus are beyond the scope of this document. The determination of k_1 and the $J(\lambda)$'s, which are characteristics of the chamber experiment, are discussed in the following sections.

Separate considerations are involved in characterizing light intensity and spectra for modeling outdoor chamber runs. Since no outdoor chamber runs are included in the present release of the data base, a discussion of this is beyond the scope of this document.

5.1 Evacuable Chamber

The light source for the SAPRC evacuable chamber consists of a 25 KW "solar simulator" which was discussed previously in Section 3.1.1. The intensity and spectral output of this light source depend on a number of factors, including the amount of power supplied to the lamp (which can be manually adjusted), the age and condition of the lamps, the conditions of the optics in the simulator housing, and the type and condition of the spectral filter used. All of these factors varied with time throughout the almost 9 years of EC runs in the present data base. Table 18 gives a log of the changes made to the EC light source which are relevant to this discussion. For the purpose of light characterization, the runs are classified into various "groups" which are indicated in the table. Reference will be made to these groups in the discussion below.

Table 18. Summary of log book entries regarding light characteristics in the SAPRC EC and results of NO_2 actinometry experiments.

Grp	Run	Date	Power	UVrad	Instrument [b]			Initial			Final			O2	-- k1 [d] --		Note
			(KW)	[a]	ID	Span	C.Eff	NO	NO2	NOX	NO	NO2	NOX	[c]	(old)	(new)	
1	093	09/25/75	12.0	0.300	A	1.00	1.00	0.06	2.93	2.95	1.11	1.86	2.93	[30]	0.300	0.273	
1	109	10/17/75	12.7	0.332	A	1.03	1.00	0.03	1.87	1.88	0.78	1.10	1.87	[30]	0.351	0.320	
1	111A	11/19/75	13.3	0.331	A	1.13	1.00	0.15	1.17	1.30	0.60	0.70	1.27	[30]	0.346	0.316	
	111B	11/19/75	13.3	0.333	A	1.13	1.00	0.60	0.70	1.27	0.78	0.49	1.25	[30]	0.262	0.238	[e]
1	112A	11/21/75	13.0	0.323	A	1.13	1.00	0.03	2.00	2.01	0.85	1.14	1.99	[30]	0.374	0.334	
	112B	11/21/75	13.0	0.325	A	1.13	1.00	0.85	1.14	1.99	1.27	0.70	1.97	[30]	0.359	0.336	[e]
	112C	11/21/75	12.8	0.321	A	1.13	1.00	1.27	0.70	1.97	1.50	0.45	1.95	[30]	0.370	0.357	[e]
	112D	11/21/75	12.9	0.322	A	1.13	1.00	1.50	0.45	1.95	1.62	0.33	1.93	[30]	0.298	0.297	[e]
	112E	11/21/75	12.8	0.321	A	1.13	1.00	1.62	0.33	1.93	1.69	0.25	1.92	[30]	0.305	0.307	[e]
		01/16/76	Trichloric filter in solar simulator														
		01/14/76	1/4" Pyrex panes replaced														
		02/18/76	New solar simulator lamp. Lamp position tuned after this.														
	119A	02/25/76	11.6	0.299	A	1.01	1.00	0.12	2.12	2.20	0.83	1.42	2.19	[30]	0.264	0.250	[f]
	119B	02/25/76	11.7	0.304	A	1.01	1.00	0.83	1.42	2.20	1.23	1.01	2.19	[30]	0.241	0.224	[f]
2	120	02/25/76	13.1	0.403	A	1.01	1.00	0.03	1.64	1.66	1.00	0.68	1.67	[30]	0.302	0.288	
2	126	03/08/76	12.9	0.392	A	1.01	1.00	0.08	2.07	2.10	1.16	1.00	2.08	[30]	0.246	0.233	
2	127	03/08/76	13.4	0.408	A	1.01	1.00	0.05	1.73	1.75	0.99	0.79	1.77	[30]	0.267	0.252	
	128	03/09/76	15.5	0.435	A	1.01	1.00	0.03	1.76	1.78	1.00	0.79	1.78	[30]	0.272	0.257	[f]
2	129	03/09/76	15.5		A	1.01	1.00	0.03	1.59	1.61	0.97	0.60	1.55	[30]	0.338	0.313	
2	132	03/15/76	15.4	0.505	A	1.01	1.00	0.03	1.65	1.67	0.98	0.67	1.64	[30]	0.310	0.289	
2	136	03/19/76	15.8	0.515	A	1.01	1.00	0.03	1.55	1.57	1.04	0.57	1.58	[30]	0.348	0.336	
	140	03/30/76	15.6	0.488	A	1.01	1.00	0.04	1.56	1.58	1.06	0.53	1.57	[30]	0.379	0.361	[g]
2	148	04/14/76	16.6	0.511	A	1.02	1.00	0.02	1.29	1.29	0.83	0.48	1.29	[30]	0.347	0.332	
	154	04/27/76	17.4	0.485	A	1.02	1.00	0.05	1.31	1.34	0.96	0.42	1.34	[30]	0.404	0.392	[g]
2	159	05/07/76	18.1	0.503	A	1.03	1.00	0.03	1.57	1.59	1.02	0.58	1.58	[30]	0.346	0.330	
2	167	05/26/76	19.8	0.518	A	1.04	1.00	0.07	1.35	1.40	0.94	0.49	1.40	[30]	0.355	0.342	
2	170	06/08/76	21.2	0.524	A	1.05	1.00	0.01	2.05	2.11	1.48	0.65	2.13	[30]	0.408	0.394	
		06/23/76	New lamp														
	173	06/23/76	11.5	0.264	A	1.01	1.00	0.04	1.69	1.74	0.82	0.93	1.74	[30]	0.200	0.191	
		06/25/76	New 1/4" Pyrex between solar simulator and EC														
3	175	06/25/76	12.7	0.352	A	1.01	1.00	0.05	2.13	2.18	1.35	0.83	2.18	[30]	0.325	0.307	
3	184	07/30/76	16.0	0.359	A	1.06	1.00	0.06	1.30	1.33	0.97	0.42	1.34	[30]	0.400	0.391	
3	187	08/04/76	16.6	0.359	A	1.07	1.00	0.07	2.11	2.12	1.50	0.74	2.16	[30]	0.370	0.355	
		08/18/76	Recoated flat and secondary														
	189	08/26/76	13.9	0.344	A	1.10	1.00	0.05	1.42	1.44	1.00	0.49	1.45	[30]	0.375	0.360	
4	215	02/11/77	17.1	0.355	A	1.19	1.00	0.02	1.33	1.35	0.98	0.39	1.35	[30]	0.436	0.423	
5	223	06/23/77	18.2	0.327	A	0.99	1.00	0.08	1.65	1.73	1.22	0.51	1.73	[30]	0.422	0.404	
	224	06/23/77	15.0	0.240	A	0.99	1.00	0.06	1.71	1.76	1.00	0.78	1.77	[30]	0.266	0.254	[h]
5	225	06/24/77	17.2	0.293	A	0.99	1.00	0.03	1.82	1.84	1.20	0.64	1.85	[30]	0.362	0.343	
5	229	08/05/77	17.9	0.255	A	0.98	1.00	0.08	1.70	1.77	1.12	0.65	1.77	[30]	0.332	0.314	
		10/23/77	Trichroic filter removed														
6	235	10/26/77	17.8	0.220	A	0.96	1.00	0.04	1.77	1.80	1.05	0.76	1.81	[30]	0.288	0.273	
6	244	11/08/77	19.6	0.233	A	0.96	1.00	0.05	1.67	1.72	1.06	0.67	1.72	[30]	0.316	0.301	
		12/13/77	New lamp. New optics														
7	261	12/28/77	13.4	0.313	A	0.95	1.00	0.07	1.58	1.65	1.18	0.48	1.65	[30]	0.414	0.409	
7	262	01/18/78	12.0	0.262	A	0.94	1.00	0.14	1.62	1.76	1.18	0.58	1.76	[30]	0.360	0.344	
	267	03/15/78	11.8	0.253	A	1.00	1.00	0.03	1.72	1.74	1.07	0.70	1.76		0.309	-----	[i]

Table 18 (continued)

Grp	Run	Date	SS	UVrad	Instrument [b]			Initial			Final			O2	-- k1 [d] --		Note
			(KW)	[a]	ID	Span	C.Eff	NO	NO2	NOX	NO	NO2	NOX	[c]	(old)	(new)	
7	274	03/28/78	12.1	0.262	A	1.01	1.00	0.05	1.85	1.89	1.28	0.64	1.91	[30]	0.373	0.357	
7	283	04/24/78	12.8	0.264	A	1.03	1.00	0.10	2.16	2.22	1.53	0.71	2.23	[30]	0.395	0.372	
		06/06/78	FT-IR Mirrors installed in EC														
8	295	07/10/78	14.3	0.256	A	1.09	1.00	0.05	1.75	1.80	1.30	0.53	1.82	[30]	0.425	0.408	
8	303	07/24/78	14.9	0.259	A	1.10	1.00	0.10	2.31	2.40	1.69	0.70	2.39	[30]	0.430	0.405	
8	313	10/09/78	16.1	0.256	A	1.07	1.00	0.04	1.78	1.82	1.34	0.48	1.82	[30]	0.472	0.451	
	321	10/20/78	18.3	0.248	A	1.09	1.00	0.04	1.83	1.87	1.17	0.71	1.88	760	0.328	0.524	[j]
	322	10/20/78	18.9	0.262	A	1.09	1.00	0.07	1.85	1.92	1.51	0.41	1.91	140	0.568	0.615	[k]
8	323	10/20/78	12.2	0.145	A	1.09	1.00	0.03	1.83	1.86	1.16	0.72	1.88	28	0.323	0.307	
		10/27/78	New Lamp														
9	324	10/31/78	15.0	0.180	A	1.11	1.00	0.05	1.39	1.42	0.98	0.45	1.42	27	0.396	0.377	
9	325	10/31/78	12.8	0.145	A	1.11	1.00	0.03	1.46	1.47	0.92	0.58	1.48	26	0.321	0.305	
9	326	10/31/78	18.2	0.230	A	1.11	1.00	0.06	1.45	1.50	1.18	0.35	1.51	23	0.522	0.502	
9	332	11/09/78	14.8	0.176	A	1.12	1.00	0.04	1.64	1.65	1.15	0.53	1.67	27	0.398	0.378	
9	333	11/09/78	15.1	0.183	A	1.12	1.00	0.03	1.52	1.54	1.07	0.52	1.60	30	0.375	0.363	
9	341	11/27/78	15.2	0.165	A	1.15	1.00	0.05	1.50	1.54	1.05	0.50	1.54	28	0.389	0.370	
9	342	11/27/78	15.1	0.163	A	1.15	1.00	0.05	1.49	1.53	1.05	0.50	1.54	26	0.387	0.369	
9	347	12/11/78	15.1	0.162	A	1.17	1.00	0.05	1.49	1.53	1.05	0.50	1.54	32	0.389	0.372	
			Following runs not documented by Pitts et al (1979).														
		01/12/79	15.0	0.152	A	1.22	1.00	0.05	1.53	1.58	0.79	0.80	1.58	960	0.373		[k]
10	348	01/12/79	15.1	0.154	A	1.22	1.00	0.03	1.57	1.59	1.05	0.54	1.59	10	0.373	0.346	
10	358	02/05/79	15.2	0.148	B	0.99	1.00	0.02	1.98	1.99	1.33	0.67	1.99	27	0.383	0.362	
	358	02/05/79	15.2	0.148	A	1.03	1.00	0.01	1.89	1.89	1.26	0.64	1.91	[30]	0.357		
10	359	02/05/79	16.2	0.162	B	0.99	1.00	0.02	1.97	1.99	1.35	0.64	1.98	23	0.389	0.371	
10	359	02/05/79			A	1.03	1.00	0.02	1.89	1.90	1.28	0.63	1.90	[30]	0.367		
10	364	02/15/79	16.2	0.154	A	1.02	1.00	0.02	1.79	1.81	1.22	0.60	1.81	25	0.384	0.364	
10	377	03/12/79	16.3	0.146	A	1.00	1.00	0.02	1.94	1.95	1.33	0.63	1.97	31	0.393	0.375	
10	378	03/12/79	16.3	0.147	A	1.00	1.00	0.02	1.93	1.94	1.33	0.62	1.95	29	0.399	0.380	
10	388	05/02/79	16.4	0.141	A	1.20	1.00	0.04	1.45	1.48	1.02	0.47	1.48	40	0.401	0.386	
		05/10/79	1/4" Pyrex removed. 1/16" Pyrex installed.														
10uv	395A	05/15/79	16.0	0.149	B	1.00	1.00	0.01	1.70	-	1.23	0.49	-	69	0.446	0.448	
10uv	395B	05/15/79	16.0	0.149	A	1.06	1.00	0.02	1.97	-	1.40	0.57	-	69	0.442	0.436	[l]
10uv	396A	05/16/79	16.1	0.144	B	1.00	1.00	0.01	1.80	-	1.26	0.54	-	35	0.428	0.410	
10uv	396B	05/16/79	16.1	0.144	A	1.06	1.00	0.01	2.00	-	1.40	0.61	-	35	0.420	0.401	[l]
		05/31/79	1/16" Pyrex removed. 1/4" Pyrex installed														
10b	408A	06/28/79	16.3	0.120	B	1.00	1.00	0.02	1.88	1.88	1.22	0.69	1.89	28	0.349	0.331	
10b	408B	06/28/79	16.3		A	1.06	1.00	0.02	2.05	2.08	1.32	0.73	2.06	[30]	0.358	0.336	
	427	01/18/80	15.9	0.126	B	1.06	1.00	0.09	2.43	2.52	1.87	0.62	2.46	44	0.550	0.479	[g]
11a	432	07/03/80	16.4	0.124	C	1.00	1.00	0.03	1.16	1.18	0.90	0.37	1.26	50	0.456	0.420	
11a	456	10/24/80	18.1	0.120	C	0.82	1.00	0.03	1.98	2.01	1.42	0.59	2.00	50	0.467	0.424	
11a	466	11/13/80	19.4	0.122	C	0.81	1.00	0.01	2.02	2.05	1.46	0.58	2.05	32	0.487	0.432	
11r	467	11/14/80	11.1	0.061	C	0.81	1.00	0.02	2.05	2.07	1.04	1.01	2.06	29	0.248	0.221	
		11/14/80	Solar simulator Secondary mirror defocused to fill primary														
	468	11/17/80	11.1	0.049	C	0.81	1.00	0.02	2.05	2.07	1.01	1.04	2.06	30	0.236	0.211	
	470	11/19/80	19.2	0.107	C	0.81	1.00	0.01	1.90	1.93	1.40	0.53	1.94	42	0.495	0.449	

Table 18 (continued)

Grp	Run	Date	SS	UVrad	Instrument [b]			Initial			Final			O2	-- k1 [d] --		Note
			(KW)	[a]	ID	Span	C.Eff	NO	NO2	NOX	NO	NO2	NOX	[c]	(old)	(new)	
		01/29/81	Recoated Flat installed. (Solar simulator focus presumed to be back to normal)														
		02/02/81	14.4	0.078	C	0.81	1.00	0.01	2.83	2.85	1.28	1.63	2.92	720	0.188	0.264	[k]
12	487	02/03/81	14.2	0.073	C	0.81	1.00	0.06	2.80	2.90	1.79	1.23	3.03	20	0.294	0.276	
12	494	02/17/81	19.8	0.083	C	0.97	0.85	0.03	1.57	1.60	1.04	0.60	1.64	27	0.351	0.314	
12	495	02/19/81	21.4	0.124	C	0.97	0.85	0.04	1.28	1.30	1.07	0.39	1.43	[30]	0.465	0.413	
12	504	03/11/81	19.4	0.103	C	0.98	0.85	0.07	1.68	1.72	1.25	0.60	1.80	[30]	0.390	0.346	
12	512	03/25/81	23.5	0.116	C	1.00	0.85	0.02	1.62	1.64	1.25	0.48	1.73	73	0.465	0.433	
12	513	03/26/81	16.9	0.080	C	1.00	0.85	0.05	1.63	1.67	1.07	0.69	1.74	33	0.310	0.280	
12	523	04/17/81	19.1	0.080	C	1.01	0.85	0.05	1.57	1.59	1.09	0.64	1.70	52	0.330	0.302	
12	528	04/24/81	20.4	0.080	C	1.02	0.85	0.02	1.55	-	1.10	0.59	-	48	0.355	0.324	
12	533	05/01/81	20.8	0.080	C	1.02	0.85	0.03	1.33	1.33	0.95	0.49	-	36	0.368	0.333	
		06/08/81	Different 1/4" Pyrex in place														
13	537	06/08/81	16.0	0.088	C	1.13	1.00	0.04	1.49	1.50	1.04	0.49	1.50	21	0.423	0.372	
13	571	08/20/81	16.1	0.077	C	1.03	1.00	0.08	0.74	0.80	0.53	0.29	0.80	23	0.351	0.317	
		08/20/81	Original 1/4" Pyrex in place														
14	572	08/20/81	19.1	0.097	C	1.03	1.00	0.02	1.04	1.08	0.77	0.28	1.05	[30]	0.522	0.467	
14	576	09/08/81	17.5	0.081	C	1.07	1.00	0.02	1.86	1.90	1.34	0.54	1.91	19	0.475	0.414	
14	583	09/17/81	18.6	0.082	C	0.98	1.03	0.02	1.05	1.08	0.77	0.31	1.05	42	0.473	0.440	
14	589	10/01/81	15.6	0.060	C	0.99	1.00	0.03	1.75	1.78	1.10	0.68	1.78	18	0.346	0.307	
14	593	10/09/81	20.2	0.080	C	1.02	1.00	0.02	1.92	1.94	1.34	0.61	1.95	[30]	0.436	0.386	
14	604	11/06/81	17.7	0.060	C	1.11	1.00	0.11	1.29	1.41	0.89	0.51	1.42	78	0.345	0.329	
14	609	11/13/81	18.3	0.060	C	1.00	1.00	0.09	2.01	2.11	1.34	0.75	2.10	45	0.368	0.329	
14	617	12/02/81	19.6	0.060	C	0.88	1.00	0.06	1.97	2.00	1.31	0.71	2.00	60	0.382	0.350	
		12/06/81	Differential UV (DUV) optics installed. DUV optics blocks part of light beam. Radiometer re-positioned.														
		12/09/81	Different 1/4" Pyrex in place														
15d	620	12/09/81	16.2	0.132	C	0.83	1.00	0.02	1.58	1.61	0.86	0.74	1.61	54	0.269	0.253	
		12/11/81	DUV optics removed. Radiometer restored to original position. Original 1/4" Pyrex installed.														
		01/07/82	DUV optics replaced.														
16d	625	01/08/82	20.5	0.031	C	1.17	1.00	0.05	1.44	1.50	0.93	0.58	1.51	43	0.334	0.306	
		01/22/82	1/8" Plexiglas filter installed.														
		01/25/82	1/8" Plexiglas filter Removed.														
		02/05/82	DUV Optics removed. Original 1/4" Pyrex in place.														
17	642	02/09/82	21.2	0.031	C	1.01	1.00	0.03	1.64	1.68	1.02	0.63	1.67	83	0.348	0.329	
17	653	02/25/82	21.5	0.030	C	0.99	1.00	0.07	1.38	1.46	0.93	0.52	1.46	76	0.359	0.344	
		03/02/82	Last run with measured spectral distribution with normal UV intensity.														
		03/10/82	Differential UV optics installed.														
		03/31/82	Differential UV optics removed.														
		03/31/82	New solar simulator Lamp and fresh optics.														
	658	03/31/82	12.8	0.039	C	0.95	1.00	0.07	1.81	1.89	1.16	0.72	1.89	40	0.338	0.306	
18	659	04/01/82	15.3	0.050	C	0.95	1.00	0.02	1.92	1.95	1.29	0.64	1.94	46	0.416	0.375	
		04/06/82	Plexiglas filter installed														
		04/07/82	Plexiglas filter removed Spectral distributions taken after this time have abnormally low UV intensity.														
19	667	04/20/82	15.6	0.048	C	0.91	1.00	0.06	1.82	1.88	1.27	0.58	1.87	[30]	0.437	0.384	
19	679	05/19/82	16.9	0.051	C	1.02	1.00	0.07	1.55	1.63	1.13	0.47	1.60	[30]	0.465	0.407	
19	688	06/10/82	18.0	0.048	C	1.07	1.00	0.03	1.57	1.61	1.08	0.52	1.61	[30]	0.413	0.369	

Table 18 (continued)

Grp	Run	Date	SS	UVrad	Instrument [b]			Initial			Final			O2	-- k1 [d] --		Note
			(KW)	[a]	ID	Span	C.Eff	NO	NO2	NOX	NO	NO2	NOX	[c]	(old)	(new)	
	727	08/11/82	10.1	0.0202	C	1.03	1.00	0.05	1.55	1.61	0.55	1.04	1.60	[30]	0.134	0.120	
	742	10/01/82	6.1	0.0074	C	1.11	1.00	0.02	2.03	2.05	0.46	1.57	2.04	69	0.084	0.075	
	755	10/25/82	10.4	0.0177	C	1.11	1.00	0.07	1.97	2.04	0.72	1.27	2.01	80	0.148	0.131	
	766	11/22/82	10.9	0.0177	C	0.96	1.00	0.01	1.89	1.92	0.76	1.13	1.91	100	0.174	0.165	
	770	11/30/82	15.4	0.0277	C	0.92	1.00	0.05	2.20	2.27	1.15	1.05	2.22	88	0.261	0.238	
20	865	06/09/83	16.2	0.0246	D	1.04	0.97	0.04	1.49	1.53	0.74	0.82	1.54	140	0.207	0.217	
20	866	06/09/83	20.7	0.0362	D	1.04	0.97	0.04	1.50	1.54	0.89	0.65	1.53	[30]	0.302	0.272	
		06/10/83	New solar simulator lamp														
21	867	06/23/83	13.8	0.0423	D	1.04	0.97	0.07	1.52	1.59	1.03	0.58	1.60	28	0.361	0.324	
		06/29/83	DUV Optics installed.														
21d	871	06/29/83	14.4	0.0410	D	1.04	0.97	0.05	1.52	1.57	0.98	0.60	1.58	32	0.340	0.309	
21d	878	07/11/83	14.0	0.0368	D	1.04	0.97	0.04	1.51	1.54	0.92	0.65	1.57	[30]	0.301	0.277	
		07/18/83	DUV Optics Removed.														
21	882	07/18/83	13.9	0.0345	D	1.04	0.97	0.05	1.55	1.58	0.95	0.63	1.56	[30]	0.329	0.292	
		07/22/83	DUV Optics installed.														
21d	889	07/27/83	14.3	0.0327	D	1.04	0.97	0.04	1.60	1.64	0.95	0.71	1.65	30	0.293	0.267	
21d	891	07/28/83	14.5	0.0322	D	1.04	0.97	0.04	1.64	1.67	0.95	0.75	1.69	50	0.254	0.261	
21d	893	07/29/83	14.5	0.0322	D	1.04	0.97	0.04	1.64	1.68	0.95	0.74	1.68	40	0.283	0.259	
		08/01/83	DUV Optics Removed.														
21	897	08/02/83	14.4	0.0328	D	1.04	0.97	0.03	1.56	1.58	0.96	0.65	1.59	30	0.319	0.289	
21	904	09/26/83	14.8	0.0290	D	1.01	0.97	0.04	1.67	1.72	0.96	0.78	1.74	26	0.272	0.250	
		10/06/83	Solar simulator Optics recoated														
	905	10/07/83	15.0	0.0216	D	1.01	0.97	0.20	1.09	1.29	0.76	0.53	1.29	22	0.264	0.234	
	906	10/10/83	18.5	0.0332	D	1.00	0.97	0.27	1.54	1.82	1.08	0.73	1.82	57	0.275	0.252	
	907	10/10/83	19.1	0.0342	D	1.00	0.97	0.27	1.45	1.72	1.07	0.62	1.71	38	0.321	0.282	
	908	10/10/83	18.1	0.0355	D	1.00	0.97	0.04	1.63	1.67	0.98	0.70	1.69	26	0.304	0.275	
		10/12/83	New 1/4" Pyrex in place														
	909	10/13/83	18.5	0.0425	D	1.00	0.97	0.03	1.68	1.68	1.06	0.63	1.66	50	0.352	0.327	
		10/14/83	1/8" Pyrex in place														
	910	10/14/83	18.3	0.0397	D	1.00	0.97	0.03	1.62	1.65	1.01	0.66	1.82	150	0.328	0.339	
		10/17/83	1/4" Pyrex back in place (original or new?)														
	919	11/02/83	19.1	0.0355	D	1.00	0.97	0.06	1.76	1.81	1.11	0.72	1.82	200	0.325	0.344	
	932	11/22/83	21.5	0.0380	D	0.99	0.97	0.02	1.11	1.13	0.72	0.42	1.13	400	0.360	0.535	
	937	02/10/84	11.0	0.0132	D	1.00	0.97	0.06	1.68	1.74	0.60	1.13	1.73	200	0.133	0.138	

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[a] UV radiometer output given in unitless quantities because unit not kept in calibration during the period covered by this document.

[b] Following codes used for instrument: "ID" = Identifies NO_x instrument used. A = Teco 14B/1 (#1510); B = Teco 14B/E (#1520); C = Teco 14B/3 (#1530); D = Columbia (#1625). "Span" = NO Span correction factor. "f(NO2)" = Measured NO_2 convertor efficiency.

[c] Measured O_2 in ppm. "[30]" = no O_2 data. 30 ppm assumed.

[d] NO_2 photolysis rate in min-1. "(old)" = previously reported value. "(new)" = recalculated.

[e] Multiple 1-minute irradiations of the same mixture in the chamber. Only the first irradiation is used for assigning k_1's for the runs.

[f] Lamp position being adjusted. Position different than used normally in following runs.

[g] Run rejected because k_1 is abnormally high for this group.

[h] Problems were noted in the log book with the radiometer filter, and the k_1 result is low for this set. Run rejected.

[i] The N_2 was in the chamber overnight. High O_2 suspected.

[j] Possible room air contamination.

[k] Not used in assigning k_1's for runs because of high measured O_2.

[l] O_2 assumed to be constant in this two-part run.

5.1.1 Summary of Light Intensity Information

Information relevant to light intensity for the EC runs in this data base comes in three forms. The primary information concerning absolute light intensity for these experiments comes from the NO_2 actinometry experiments which are conducted at regular intervals when chamber runs are being carried out. These consist of 1-2 minute irradiations of NO_2 in N_2. The results of these can be used to obtain an NO_2 photolysis rate (called "k_1" in the subsequent discussion), from which, given a relative spectral distribution and the NO_2 absorption cross sections and quantum yields, the spectral irradiance in the chamber can be calculated. These experiments, and their results, are discussed in more detail below.

However, the actinometry experiments measure the NO_2 photolysis rate only during that experiment, not during chamber runs which are of interest to modeling. (In the discussion below, the term "chamber run" will refer to all experiments in the EC where the light is used for other than actinometry experiments.) In addition to depending on the conditions of the lamps and optics, which degrade slowly with time and are periodically replaced or refurbished, the light intensity in a given experiment will depend on the power level of the solar simulator, which can be varied at will by the operator, and which will also vary slightly during a run. Because the power level of the solar simulator is the main factor controlling the light intensity on an hour-to-hour basis, it is recorded during every actinometry experiment and as a function of time during the chamber runs. These data, called "SSpower" in the tabulations, are in the computer data sets for the chamber runs through Group 10, and are recorded in the EC log books for most subsequent runs. As discussed below, for many groups of runs these data provide a useful means for estimating k_1 levels for the chamber runs from the k_1 levels measured during the actinometry experiments.

To provide information concerning the run-to-run variability of light intensity, an EG&G UV Radiometer (Model 550-1) is located at the end of the chamber opposite the solar simulator (outside the quartz window), facing the light beam. The output of this radiometer is recorded once during each actinometry experiment and as a function of time during each chamber run. These data, called "UVrad" in the tabulations, are in the computer data sets for the runs through Group 10, and is available in the EC log books for most subsequent runs. However, as noted by Pitts et al. (1979) this radiometer was not kept in calibration, and its response changed gradually with time. Therefore, these data do not provide any absolute measure of light intensity, nor can general relationships between k_1 and radiometer output be expected to apply. (For this reason, the "UVrad" data in the tabulations are given as unitless quantities.) However, since it is reasonable to expect the radiometer response to be essentially constant during the limited time period of a given run group, these data also provide a useful means to use actinometry results to estimate k_1 levels in the chamber runs.

In the following section, the NO_2 actinometry experiments and their analyses are discussed, and their results are tabulated. Then the correlations between SSpower and k_1 and UVrad and k_1 observed during the various groups are examined, and the results are used to derive recommended k_1 values for the individual chamber runs.

5.1.2 NO_2 Actinometry Experiments

The NO_2 actinometry experiments carried out in the EC consisted of photolysis of approximately 2 ppm of NO_2 in 1 atm N_2 for one or two minutes, and monitoring the change in NO, NO_2 and NO_x. In later experiments, O_2 was monitored as well. In the past, the NO_2 photolysis rate (k_1) was then calculated using the equation given by Holmes et al. (1973), with (for later experiments) parameters updated as described by Pitts et al. (1979), but it will be recalculated for this work as discussed below. Table 18 gives the data obtained during these experiments which are used to calculate k_1 values and a summary of the results, along with comments from the log books relevant to the light intensity or actinometry measurements. The experimental methods and analyses of the results are discussed in the following sections.

Experimental Methods and Measurement Results. The experimental procedure for most of the EC actinometry experiments was discussed by Pitts et al. (1979). The chamber was evacuated overnight prior to the experiment (as was the case for most EC runs), and was then injected with N_2 from tanks or (in a few later experiments) evaporated N_2 from liquid nitrogen dewars. The chemiluminescence NO - NO_x instrument being used for the EC runs at that time was attached to the chamber, and two or three NO, NO_2 and NO_x measurements were recorded in the log book after the readings had stabilized. Generally strip charts were not used -- the readings were taken directly from the meters or the computer data system. Meanwhile, the solar simulator light was turned on and was warming up with the light shuttered so it did not enter the chamber. Once stable NO, NO_2 and NO_x readings are made and noted, the light was unshuttered and entered the chamber for one (up to Feb 25, 1976) or two (for all later runs) minutes, and the radiometer readings and solar simulator power was recorded. The light was then shuttered and the NO, NO_2 and NO_x readings were then tabulated. Table 18 gives the initial and final NO, NO_2 and NO_x readings made during these experiments, and the duration of the irradiation. The averages of the radiometer and SSpower readings for these experiments are also given in Table 18.

In a few early experiments, the light was unshuttered again several more times for one-minute periods, and the further changes to NO and NO_2 were recorded. These cases are noted in Tables 18 with an "A" or "B" appended after the run number.

The NO - NO_x monitors used during these experiments were generally the same as employed during the associated experimental run, and the calibration methods used for them are described elsewhere. Table 18 gives the raw data from the instruments, and the span and NO_2 converter corrections which were applied. Note that the span corrections are based on calibrations using ~0.5 ppm (usually) of NO in dry air, and the NO_2 converter checks were generally based on measurements of ~0.2 - 0.3 ppm of NO_2. No zero error corrections are applied to these data. The instruments were electronically zeroed prior to the experiments, but no checks were routinely made to assure that non-zero readings will be obtained from NO_x-free N_2.

One concern with these data comes from the fact that the NO - NO_x monitors used in these experiments only directly measure NO; data for NO_2 is obtained by converting NO_2 to NO using a catalyst (converter), and measuring the change in monitored NO which results. If the converter were not completely efficient in converting NO_2 to NO, then low NO_2 readings would be obtained. As indicated above, this converter efficiency is checked from time to time, and except for the group 12 experiments, where these checks indicate that the NO_2 data should be corrected by a factor of ~1.1-1.2 because the converter was only 85-90% efficient, these checks indicate good (100 ±3%) converter efficiency. However, the concentrations of NO_2 involved in the converter checks are an order of magnitude lower than used in these experiments, and the checks are done in dry air, not N_2.

The possibility that the NO_2 converter may not be completely efficient under the conditions of the actinometry experiments can be checked by examining the change in $[NO_x]$ and $[NO]+[NO_2]$ resulting from the conversion of NO_2 to NO during the irradiations. If the converter were not completely efficient, the measured $[NO_x]$ (or $[NO]+[NO_2]$) would increase as a result of the irradiation, since at the beginning of the run the NO_x is essentially all NO_2, while at the end much of it is NO, whose data would not be affected by this problem. The NO_x data, tabulated in Table 18, indicate no such increase. Furthermore, if it is assumed that the total $[NO]+[NO_2]$ should stay constant during an experiment, then the NO_2 converter efficiency, $f(NO_2)$, can be estimated as follows:

$$[NO]_0+[NO_2]_0 \dashrightarrow [NO]_f+[NO_2]_f$$

$$[NO]_0+([NO_2]'_0/f(NO_2)) = [NO]_f+([NO_2]'_f/f(NO_2))$$

or

$$f(NO_2) = \frac{[NO_2]'_0-[NO_2]'_f}{[NO]_f-[NO]_0}$$

where $[NO]_0$, $[NO]_f$, $[NO_2]'_0$, $[NO_2]'_f$ are the initial and final measured NO and NO_2, respectively, and $[NO_2]_0$ and $[NO_2]_f$ are the true initial and final NO_2 concentrations, which differ from the measured values by a factor of $f(NO_2)$. These values are tabulated in Table 18. If the data from group 12, where the converter is known to have problems, are excluded, the average converter efficiency is 1.00 ± 0.03. Clearly, this is not a significant area of concern with these data.

A second problem which is not so easy to check is the possibility of zero errors in the NO and NO_2 measurements. As indicated above, the instrument is electronically zeroed, but usually no information is available for its readings when NO_x-free N_2 is sampled. As discussed elsewhere, zero offset errors of up to 60 ppb can sometimes occur, though errors greater than ~35 ppb are rare. Tests suggest that much of this may be due to a humidity interference in the NO_x measurements, which would not be applicable to these experiments, which all use dry N_2. Zero drift should not be a problem, since relatively little time elapses between the electronic zeroing of the instrument and the taking of the data which are used. As shown below, the k_1 result is much more sensitive to offset errors in NO_2 than in NO. Based on the changes in offset errors in the NO_2 measurements in the experimental runs (discussed elsewhere), a reasonable error estimate would be ± 30 ppb.

In 1979 and following years O_2 was also monitored in the chamber during the NO_2 actinometry experiments. The instrument used was a Delta F Corp. trace O_2 analyzer (Model FA31110S). It was not calibrated at our laboratories, so the accuracy of its measurements is uncertain. Because of this, we do not use data from actinometry experiments with high O_2 concentrations, even though the present data analysis method (discussed below) can take the effect of O_2 into account.

The results of the O_2 measurements, when available, are given in Table 18. Except for a few experiments with anomalously high O_2, which generally can be attributed to known potential problems such as leaks of errors in experimental procedures, the measured O_2 was typically in the range of 20-40 ppm. (O_2 measured in the N_2 tanks was typically 20 ppm or less.) Based on this, we assume for runs with no O_2 measured that approximately 30 ppm of O_2 is present, unless there is some reason to suspect higher O_2 levels, such as N_2 being left in the chamber overnight prior to the experiment. Table 18 includes some actinometry runs with no O_2 data for which high O_2 is suspected, but computed k_1 values for these runs are not reported. Sensitivities of computed k_1 values to O_2 are also discussed below.

Temperature and pressure were not measured during these experiments. For the purpose of data analysis, we assume the temperature is 303 K, which is the average temperature for most experiments in the EC. However, the temperature for the actinometry experiments may be lower because the irradiation time is so short. The atmospheric pressure in Riverside is typically 740 mm Hg, or 0.97 atm.

Data Analysis. The amount of NO_2 converted to NO during these experiments is used to derive the NO_2 photolysis rate, or k_1. However, the calculation of k_1 from these results is complicated by the fact that NO_2 photolysis is not the only reaction which affects the rate of conversion of NO_2 to NO in this system. If O_2 is absent, the main reactions are:

$$NO_2 + h\nu \longrightarrow NO_2 + O \qquad (1)$$

$$O + NO_2 \longrightarrow NO + O_2 \qquad (2)$$

$$O + NO_2 + M \longrightarrow NO_3 + M \qquad (3)$$

$$O + NO + M \longrightarrow NO_2 + M \qquad (4)$$

$$NO_3 + NO \longrightarrow NO_2 + NO_2 \qquad (5)$$

$$NO_3 + NO_2 + M \longrightarrow N_2O_5 + M \qquad (6)$$

$$N_2O_5 + M \longrightarrow NO_3 + NO_2 + M \qquad (7)$$

Based on this mechanism, and making steady state assumptions for NO_3 and N_2O_5, Holmes et al. (1973) derived an equation to compute k_1 given the initial [NO] and [NO_2], the final [NO_2], and rate constants for reactions (2-4). This equation was used to derive the k_1 values associated with the EC runs in the data base up to the present time. The k_1 values tabulated by Pitts et al. (1979) used the equation derived from the k_2, k_3, and k_4 values used by Holmes et al. (1973), while k_1 values calculated for more recent runs used the Holmes et al. (1973) equation with updated rate constants, which give ~10% higher k_1 values (Pitts et al. 1979). Thus, up to now the available data base has been inconsistent in the data analysis method.

The above simple mechanism, and the k_1 equation based on it, ignore the effects of the (typically 30 ppm) O_2 present in the experiment, the photolysis of NO_3, and other reactions which may be occurring. The mechanism in the presence of O_2 is more complex, and not amenable to a simple steady-state analysis such as that of Holmes et al. (1973). To address this problem, we decided to abandon the approximate data analysis approach of Holmes et al. (1973) and use a full kinetic model to find the k_1 value which fits the results of the experiment. The k_1 for a given experiment was computed by conducting model simulations of the experiment, given the initial measured [NO] and [NO_2] and measured or assumed [O_2], and finding the k_1 value which gave the closest least squares fit to the final measured [NO] and [NO_2]. A nonlinear optimization program was used to determine the best fit.

The chemical model to compute the k_1 values is that of Carter (1990), with the addition of reaction (4). The rate constant used for Reaction (4) is that given in the NASA (1992) recommendation. A list of the reactions and rate constants used in the mechanism are given in Table 19. The photolysis rates were computed using the spectral distribution appropriate for experiments conducted around the end of 1978. Chamber effects were ignored except for dilution due to sampling. The standard dilution rate of 1% per hour was assumed, which is totally negligible in these 1-2 minute irradiations. Atmospheric pressure was assumed to be 740 torr (0.97 atm.), which is usual for Riverside. Humidity was assumed to be negligible, so reactions involving water (forming OH and HO_2) are not included in the model. (Assuming water is present does not significantly affect the result, even at 50% RH.)

The performance of this mechanism in simulating the conversion of NO_2 to NO when photolyzed in N_2 can be evaluated in part by simulating the results of run EC-112, where five consecutive one-minute irradiations, interdispersed with 7-15 minutes of darkness, were carried out. The results of modeling this run, using a k_1 value fit to the data from the first one-minute irradiation only, is shown in Figure 13. It can be seen that good fits are obtained to the amounts of NO converted to NO_2 during each of the one minute irradiations. The model tends to slightly overpredict NO and NO_x after the first irradiation. However, this may be due to measurement error since essentially perfect fits can be obtained if the initial NO_2 and NO are adjusted downwards by 2% to agree better with the total NO_x measured during most of the experiments (dashed lines). This adjustment causes a 0.3% change in the computed k_1.

Possible errors in computed k_1's resulting from the use of the same spectral distribution when computing k_1's for all experiments and from ignoring chamber wall effects were examined in several sensitivity calculations. Exactly the same k_1 is obtained if the optimization are repeated using the low UV spectral distributions for the experiments in the EC-900's, or even using the spectral distribution of blacklights, where NO_3 photolysis is essentially zero. This is not surprising, since NO_2 photolysis is probably the only light-dependent process of significance in this system. (The fact that the results are the same even if blacklight spectra are used indicates that the NO_3 photolysis rate is not important in affecting the results.) The use of the standard EC chamber wall model of Carter and Lurmann (1991) had no significant effect on simulations of run EC-112. The simulations all assumed that water is absent, but simulations using water as high as 50% RH yielded essentially the same results. (The additional reactions assumed if water is present, involving formation of OH and HO_2 radicals, are given by Carter [1990].)

The more likely sources of errors in the computed k_1's are measurement errors in NO, NO_2 or O_2, or incorrect assumptions concerning O_2 levels in experiments where it was not measured. Possible errors in the measurements of NO and NO_2 were discussed in the previous section, and the O_2 readings should be considered to be uncertain since that quality assurance procedures were not routinely employed with that system. The effects of such errors were examined in several sensitivity tests, whose results are summarized in Table 20. The data in the table was generated by using a model calculation (with chamber effects included) of an NO_2 actinometry experiment, and then calculating optimum k_1 values which fit these data, modified as indicated on the table, using the same procedure as used to generate the k_1's in Table 18. The level of agreement between the "optimized" k_1's and the k_1 used to compute the "experiment" indicate the extent to which errors in the input data affect the accuracy of the predicted k_1.

Table 19. Reactions and rate constants used to compute the NO_2 photolysis rate from the results of the NO_2 actinometry experiments.

Rxn. Label	Kinetic Parameters [a]				Reactions
	k(303)	A	Ea	B	
1	k_1 varied				NO_2 + HV = NO + O
2	1.40E+04	9.54E+03	-0.24	-1.00	O + NO_2 = NO + O_2
3	2.20E+03	(Falloff Kinetics)			O + NO_2 = NO_3
	k0 =	3.23E-03	0.00	-4.00	
	kINF =	3.23E+04	0.00	-1.00	
		F= 0.60			
4	2.33E+03	(Falloff Kinetics)			O + NO = NO_2
	k0 =	3.23E-03	0.00	-3.50	
	kINF =	4.40E+04	0.00	-1.00	
		F= 0.60			
5	4.05E+04	2.49E+04	-0.30	-1.00	NO + NO_3 = NO_2 + NO_2
6	1.81E+03	(Falloff Kinetics)			NO_2 + NO_3 = N_2O_5
	k0 =	7.90E-02	0.00	-6.30	
	kINF =	2.20E+03	0.00	-1.50	
		F= 0.60			
7	Keq x k6				N_2O_5 = NO_2 + NO_3
Keq=	3.30E-03	3.72E+13	22.26	1.00	
8	6.32E-01	3.67E+01	2.44	-1.00	NO_2 + NO_3 = NO + NO_2 + O_2
9	k1 x 1.505	[b]			NO_3 + HV = NO + O_2
10	k1 x 1.410E+01	[b]			NO_3 + HV = NO_2 + O
O_2 Reactions					
11	2.06E-05	2.16E-05	0.00	-4.30	O + O_2 + M = O_3 + M
12	2.86E+01	2.94E+03	2.78	-1.00	O_3 + NO = NO_2 + O_2
13	5.31E-02	2.06E+02	4.97	-1.00	O_3 + NO_2 = O_2 + NO_3
14	6.64E-10	1.19E-10	-1.05	-2.00	NO + NO + O_2 = NO_2 + NO_2
15	k1 x 3.856E-02	[b]			O_3 + HV = O + O_2
16	k1 x 1.653E-03	[b]			O_3 + HV = O*1D2 + O_2
17	4.23E+04	2.82E+04	-0.25	-1.00	O*1D2 + M = O + M
18	assumed negligible [c]				O*1D2 + H_2O = 2 OH

[a] Except as indicated otherwise, rate or equilibrium constants for reactions in this table are given by the expression k (or Keq) = A x $e^{Ea/RT}$ x $(T/300)^B$, where k and A are in ppm, minute units, T is the temperature in degrees K, and R is 0.0019872 kcal deg^{-1} $mole^{-1}$. If the notation "Falloff Kinetics" is used, then the rate constant is computed using the standard falloff expression (e.g., see NASA (1992), where k0 and kINF are the low and high pressure rate constants, respectively.

[b] Photolysis rates relative to NO_2 are calculated using the spectral distribution of EC-340 and the absorption cross sections and quantum yields given by Carter (1990).

[c] Actinometry experiments carried out using dry N_2.

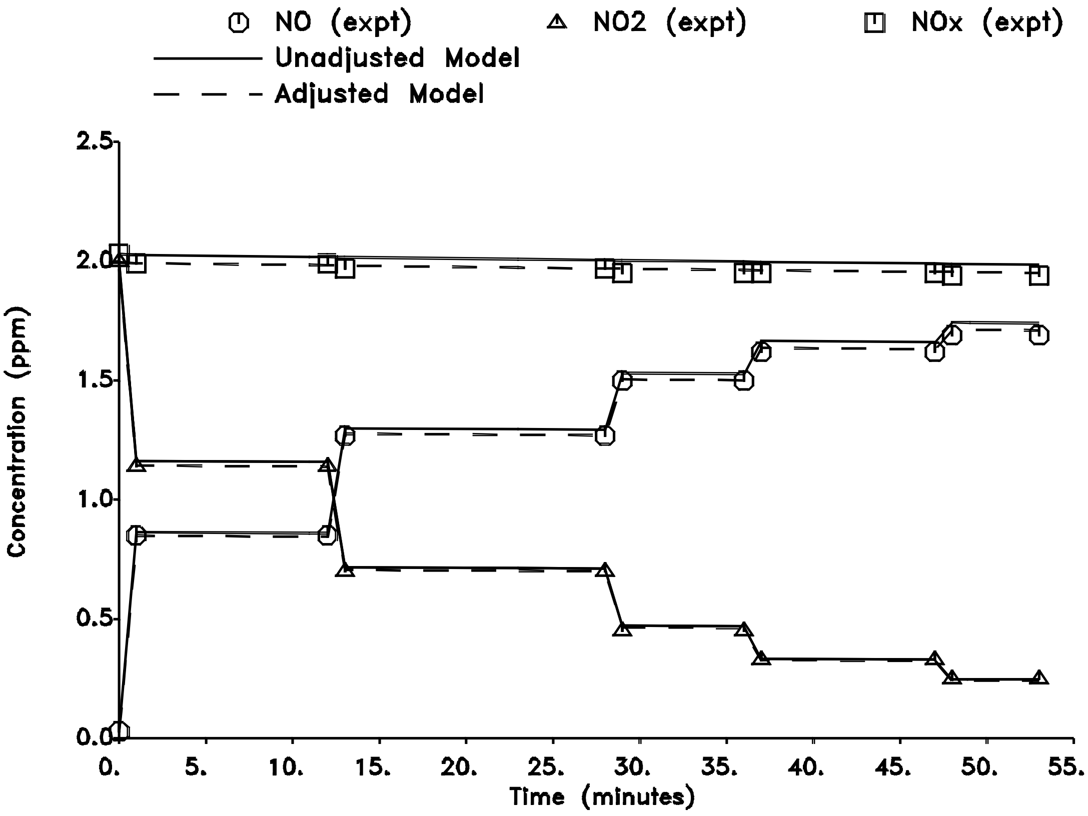


Figure 13. Experimental and calculated NO, NO_2, and NO_x data for the NO_2 actinometry experiment EC112.

It can be seen that an error in O_2 by ± 30 ppm causes approximately a 3% error in the k_1. Since except for a few experiments the O_2 varied by less than this amount, the lack of O_2 data for the earlier runs is not considered to be a major source of error in most cases. Obviously if the run has more than 100 ppm O_2 and the standard 30 ppm is assumed, the k_1 derived in the data could be in error by 7% or more. Runs without O_2 data where problems are suspected are therefore rejected. It is concluded the effect of O_2 is not a major problem affecting our confidence in this data base, provided that the presence of the ~30 ppm of O_2 is not neglected in the data analysis.

Sources of error regarding the NO_x measurements include span errors, affecting both NO and NO_2 by an equal factor, zero offset errors which would affect one or both by a constant amount, and NO_2 converter problems which would affect the NO_2 data only. Table 20 shows that the k_1 values are not sensitive to span errors or zero offset errors affecting only NO. (Zero errors affecting NO are more likely than those affecting NO_2 because NO_2 measurements are actually differences between NO_x and

Table 20. Results of sensitivity calculations on computations of k_1 from calculated 2-minute NO_2 actinometry experiments. Calculations use k_1 = 0.333 min-1, initial NO_2 = 2 ppm initial NO = 33 ppb, and varying amounts of O_2. Calculated using standard EC wall model of Carter and Lurmann (1991) and spectral distribution appropriate for run EC-112.

O_2 [a]		Measurement Error [b]		Derived k_1	
Actual	Assumed	NO	NO_2	(min-1)	(error)
Effect of O_2 error.					
0	30	0	0	0.343	+3%
30	30	0	0	0.333	[c] 0%
60	30	0	0	0.324	-3%
120	30	0	0	0.307	-8%
240	30	0	0	0.279	-16%
Effect of systematic NO-NO_x span error.					
30	30	-5%	-5%	0.334	0%
30	30	+5%	+5%	0.333	0%
Effect of reduced NO_2 converter efficiency					
30	30	0	-5%	0.341	2%
Effect of NO and/or NO_2 zero offset errors.					
30	30	+33 ppb	0	0.334	0%
30	30	-32 ppb	0	0.332	0%
30	30	0	+33 ppb	0.322	-3%
30	30	0	-33 ppb	0.345	+4%
30	30	+33 ppb	+33 ppb	0.324	-3%
30	30	-32 ppb	-33 ppb	0.343	+3%

[a] "actual" = value used in simulation of the actinometry experiment. "assumed" = value used when computing the optimum k_1 which fit the data.
[b] "measurement error" = "assumed" value - "actual" value.
[c] This result shows the effect of ignoring the chamber wall effects in the optimization for k_1.

NO.) The k_1 is affected by NO_2 converter efficiency errors, though the sensitivity is less than linear. As discussed above, the results indicate that for most runs converter efficiency errors are minor, or at most 5% -- corresponding to 2% or lower errors in k_1. The k_1 result can also be non-negligible if there is an NO_2 offset error much greater than 30 ppb. Such a large offset error is anomalous, and would show up in the routine calibrations of the instruments, and probably as discrepancies between initial and final [NO_x] or between [NO_x] and [NO]+[NO_2] data taken during the actinometry experiments. The span uncertainty in NO_2 is probably the major experimental factor affecting the uncertainty in these k_1 measurements.

The new k_1 values shown in Table 18 are lower, by 4% on the average, than the k_1 values which have previously been used. This must primarily be due to updates in the mechanism, since including O_2 in the analysis causes derived k_1 values to increase relative to values derived assuming O_2 is absent. It should be recognized that the k_1 values derived in this work are model dependent, and should be re-derived if significant changes are made to the mechanism listed in Table 19. This is particularly true if rate constants for reactions (2), (3), or (5) undergo significant change. Table 18 contains the input data from which updated k_1's can be calculated, should that be appropriate. However, the rate constants for these and most of the other reactions in Table 19 are reasonably well established, and changes large enough to significantly affect the computed k_1 values are not anticipated.

5.1.3 Estimation of k_1 for the Chamber Runs

Several different approaches can be used to assign k_1 values to the individual chamber runs based on the results of the actinometry experiments, and their appropriateness and relative merits vary among the run groups. The most obvious approach is to use correlations between the radiometer readings and the k_1 measurements, since the radiometer data are the most direct measure of light intensity which is available for essentially all runs. As indicated above, such correlations cannot be made on a global basis, since the radiometer response changed slowly with time. In addition, for some groups of runs, the experimental procedure was to adjust the solar simulator power to yield a given radiometer value, so the radiometer value did not vary. Nevertheless, in many such cases the k_1 varied despite holding the radiometer readings constant. In these cases correlations between k_1 and the radiometer output are useless, but correlations with the solar simulator power can be of utility. If there are insufficient data to obtain correlations between k_1 and radiometer output or solar simulator power for a run group, or if the correlations are poor or questionable, the remaining approach is to assume that the k_1 is constant for a particular run series, or, if it is found to vary, to assume it varies in a consistent or linear manner with time. This is only applicable for run groups where every effort was made to assure that the light intensity was consistent from experiment to experiment.

The EC run spreadsheet "EC-LITE" gives the averages of the radiometer and solar simulator power measurements taken during the chamber runs of potential interest to modeling. The standard deviations of these averages, which are also included in the spreadsheet, indicate that in almost all cases there is essentially negligible variation in light intensity or solar simulator power during a run. In some cases there is relatively little variation in average SSpower or UVrad within a run group, while in other cases there is run-to-run variability of these measures of light intensity, suggesting run-to-run variability in k_1 for these groups. In the cases where there is little variability, the results of the actinometry experiments in the group with similar SSpower and UVrad readings can be averaged to yield k_1 estimates for the runs. In cases where there is variability, correlations between SSpower and/or UVrad and k_1 must be derived, as discussed below.

One would expect SSpower and UVrad to be highly correlated, and in general this is indeed the case. However, the correlation is not perfect because of variations in the spectral distribution and, over longer periods of time, because the UV sensor is not routinely calibrated because it is used primarily to monitor relative changes. In addition, during some periods, the operating procedure is to hold the power constant and allow the UVrad to vary as the lamps age, while during other periods, the procedure is to adjust the power to achieve constant UVrad readings. Thus, if there are variations in light characteristics, one would expect that k_1 would correlate with UVrad during periods where the former procedure is employed, while the k_1 would correlate with SSpower when the latter procedure is employed.

Figures 14-18 show plots of k_1 vs solar simulator power or vs radiometer output for all the actinometry experiments which are associated with run groups of potential interest for modeling. Different symbols are used for experiments in different run groups. For those groups where the correlations appear to be sufficiently good to be potentially useful, least squares fit lines through the data are also shown. It can be seen that in some cases the k_1 data correlate better with one measure than another, though in many cases they correlate with both. In some cases, the data suggest that the same correlation(s) can be applied to several consecutive run groups, and that combining them for the purpose of k_1 estimates might be appropriate.

These correlations, and methods for estimating k_1's for individual experiments based on them, are discussed for each run group (or set of groups) below. The groups assigned to each individual model evaluation experiment is given in the "EC-LITE" spreadsheet in the column "k1 set".

<u>Group 1</u> (See Figure 14.) Both radiometer level and solar simulator power varied for chamber runs in this group. These two light measures appear to be about equally useful in predicting k_1 in the three experiments in this group. However, for consistency with the methods used for groups 2 and 3, discussed below, the recommendation is to use the values predicted using the least squares lines for SSpower.

<u>Group 2</u> (See Figure 14.) The chamber runs in this group also had a range of radiometer and solar simulator power levels. Two actinometry experiments in this group are rejected because they appear to be anomalously high compared to the other runs with similar UVrad or SSpower. (They were also rejected by Pitts et al. [1979].) Excluding these, the line for SSpower appears to be more successful in predicting k_1, particularly for those experiments conducted with the higher radiometer power. The recommendation is to use the least squares fit line for SSpower only.

<u>Group 3</u> (See Figure 14.) The chamber runs and actinometry experiments in this group all had essentially the same radiometer value, so only the correlation with the solar simulator power can be used.

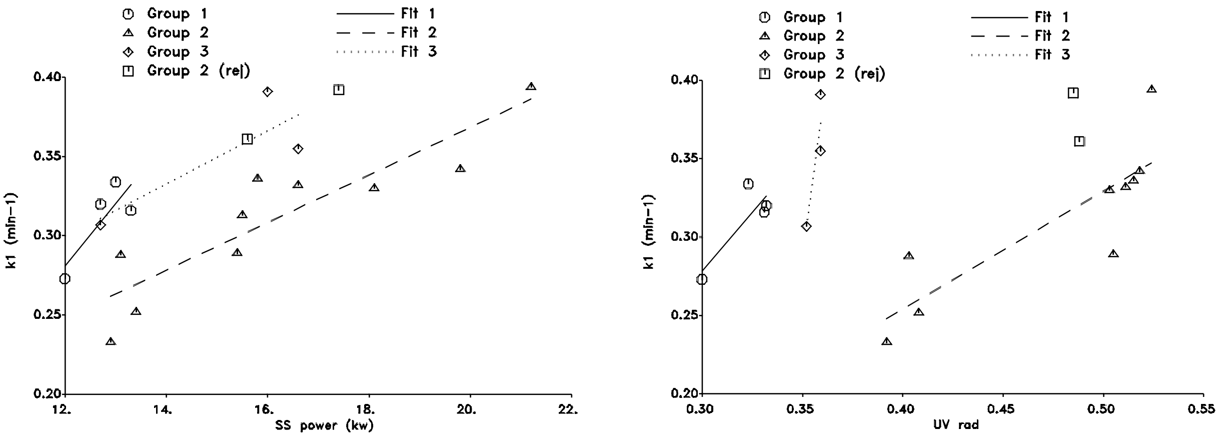


Figure 14. Plots of k_1 vs solar simulator power and UV rad for EC run groups 1-3.

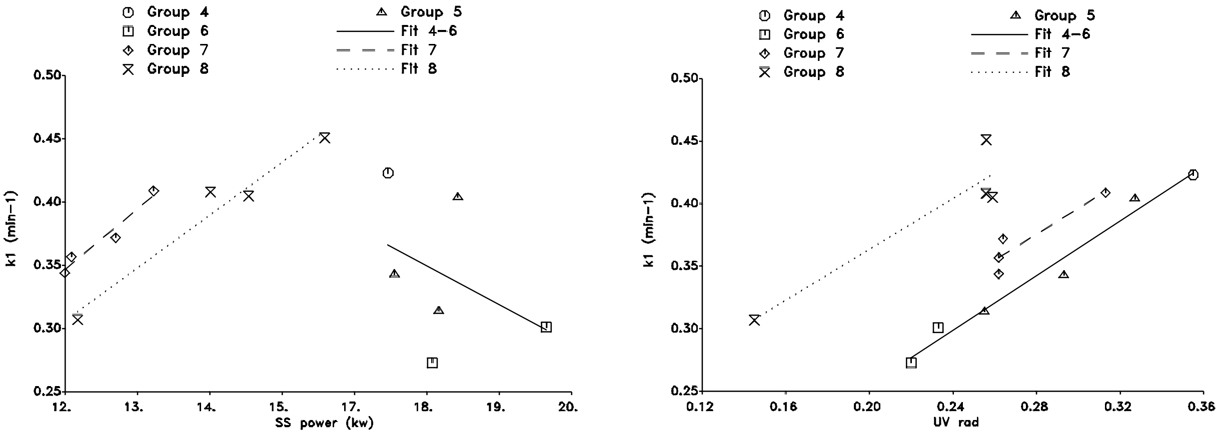


Figure 15. Plots of k_1 vs solar simulator power and UV rad for EC run groups 4-8.

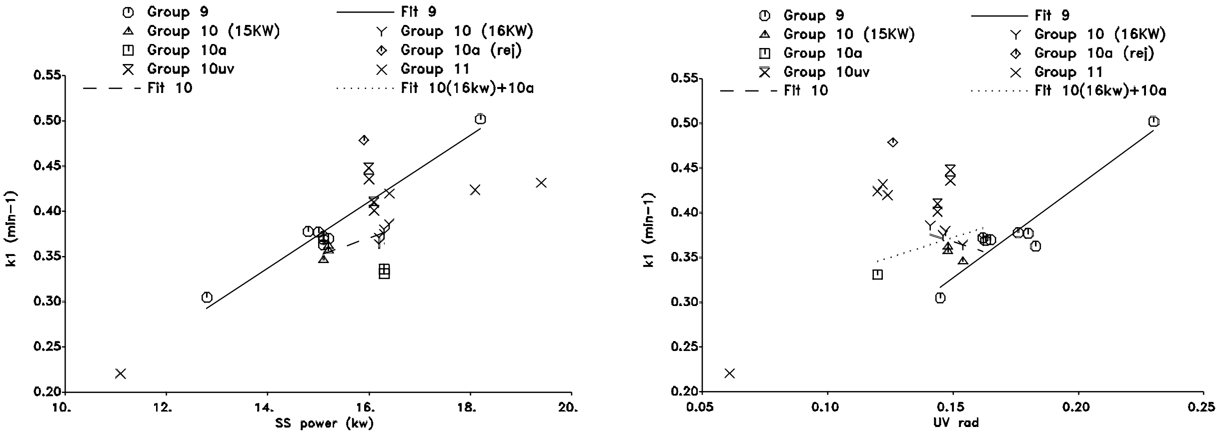


Figure 16. Plots of k_1 vs solar simulator power and UV rad for EC run groups 9-11.

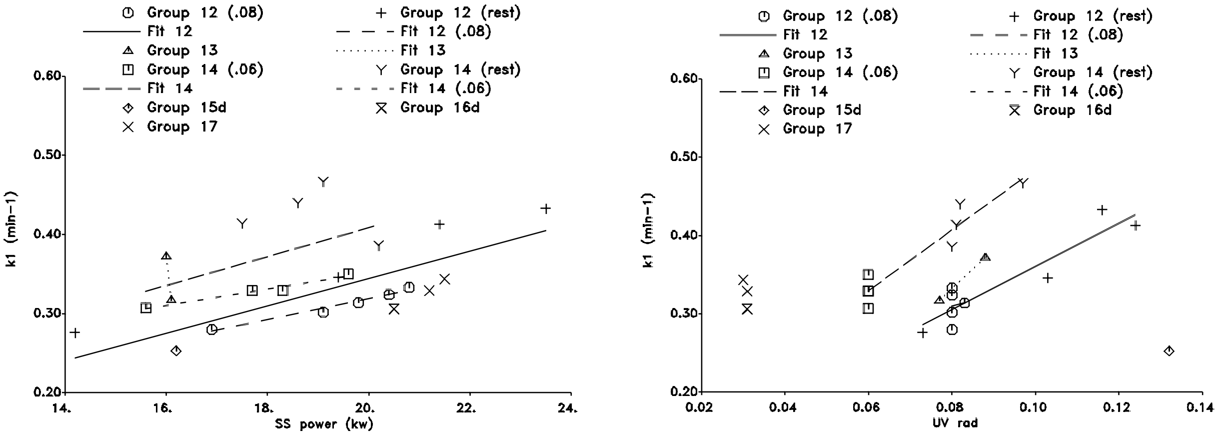


Figure 17. Plots of k_1 vs solar simulator power and UV rad for EC run groups 12-17.

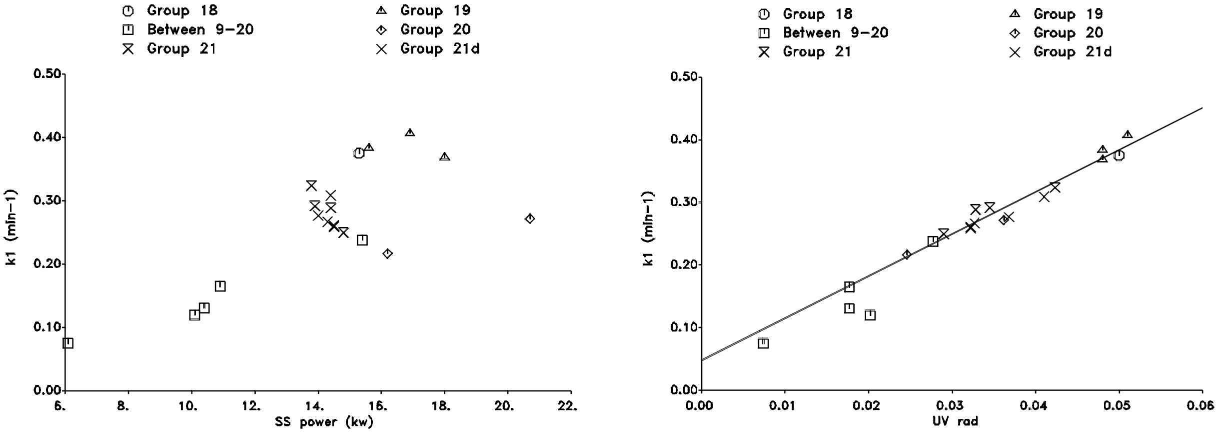


Figure 18. Plots of k_1 vs solar simulator power and UV rad for EC run groups 18-21.

Note that the slope of the least squares fit line is the same as found for the much larger number of points for Group 2.

Groups 4 - 6 (See Figure 15.) Groups 4 and 5 are separated by four months but by no known change to the light source, and Group 6 differs from Group 5 in that the trichroic filter was removed. The solar simulator power in these groups was not varied significantly, so it is not useful in predicting k_1. However, k_1 has a reasonably good linear relationship with UVrad, with the experiments in all three groups falling on the same line. (The fact that the trichroic filter apparently does not affect this correlation is not surprising, since the UV radiometer is not sensitive to the IR wavelengths which that filter removes.)

The recommendation is to use the line for UVrad derived from the actinometry experiments in all three groups.

Group 7 (See Figure 15.) The experimental runs in this group have essentially the same radiometer readings, but the solar simulator power required to achieve these readings increased with time. The actinometry experiments in this group (which had a wider range of radiometer readings than the chamber runs) indicate that k_1 increases with the solar simulator power in a linear manner, so the recommendation is to estimate k_1 runs using the least squares fit line for SSpower.

Group 8. (See Figure 15.) This group is analogous to Group 7 since all chamber runs in this group had essentially the same average radiometer reading, but the solar simulator power increased with time, and the actinometry experiments indicate a good correlation between k_1 and solar simulator power over a wider range of light intensities. Therefore, solar simulator power is also used to estimate the k_1's for runs in this group.

Group 9. (See Figure 16.) Unlike the previous two groups, the chamber runs in Group 9 all had essentially the same solar simulator power, and the average radiometer levels decreased continuously with time. Therefore, although it appears that the k_1's in this group are linearly predicted by both SSpower and UVrad, the least squares fit line for UVrad is the recommended means to estimate k_1's for the runs.

Group 10. (See Figure 16.) The solar simulator power was apparently adjusted to yield a constant radiometer reading of ~0.15 for the chamber runs in the first half of this group, while for the runs in the second half it was held constant at ~16.3 KW, and the radiometer readings steadily declined. There does not appear to be a positive correlation between UVrad and k_1, so the apparent relationship between SS power and k_1 is used to estimate k_1 levels for these runs.

Group 10uv (See Figure 16.) These experiments employed a different Pyrex filter than the runs in Groups 10 and 10a. All experiments in this group had essentially the same radiometer readings and SS power levels, so the recommendation is simply to use the average of the k_1 measurements for the chamber runs with the same power and radiometer levels.

Group 10a. (See Figure 16.) This group should have the same light conditions as Group 10, but its one actinometry experiment has a lower UVrad level and a lower k_1. The chamber runs in this group have essentially the same SS power, but average UVrad varied slightly. To determine the dependence of k_1 on UVrad for estimating k_1's for the chamber runs in this group, we use the results of the one Group 10a actinometry experiment combined with the results of the Group 10 actinometry experiments which have the same SS power level (runs 369-388).

Group 11 (See Figure 16.) Except for parts of runs EC-457 and EC-458, where the SS power was deliberately reduced, all chamber runs in this group had average UVrad of 0.12. The three actinometry experiments in this group at this UVrad level had essentially the same result, despite a rather wide variation in solar simulator power. Therefore, for all runs except for the parts of EC-457 and 458 where the power was reduced, we use the average of the k_1's from the experiments with the 0.12 radiometer reading. These are designated as in "Group 11a" for the purpose of assigning k_1 values. The k_1 for the reduced power portions of EC-457 and EC-458 ("Group 11r") are assigned the k_1 from actinometry run EC-467, which had the reduced power UVrad level.

Group 12. (See Figure 17.) Most or all of the runs in this group were carried out with UVrad = ~0.08, and the solar simulator power required to achieve this level increased with time. (The UVrad and SSpower data are not yet tabulated for all runs in this and subsequent groups.) The left plot in Figure 17 shows that k_1 is linearly related to the SSpower for the actinometry experiments with UVrad = ~0.08, but the results for most of the experiments at other radiometer levels do not fall as close to that line. For chamber runs where the average radiometer reading is between 0.07 and 0.09 ("Group 12a"), the recommendation is to use the line for SSpower derived from the data of the actinometry experiments where UVrad = ~0.08 only. For runs at other radiometer levels ("Group 12b"), the recommendation is to use the line for UVrad derived from all the actinometry experiments in this group.

Group 13. (See Figure 17.) The two actinometry experiments in this group had the same SSpower, but different UVrad levels. The dependence of the k_1 on UVrad for these two runs is consistent with the dependence observed for other groups of runs. Therefore, the recommendation is to use the line for UVrad defined by the two points in this group.

Group 14. (See Figure 17.) The chamber runs in the first half of the group had an average UVrad of ~0.08 or higher, while most or all of the runs in the second half had a UVrad of ~0.06. The k_1's measured in the actinometry experiments where UVrad was ~0.06 had a good linear fit to SSpower, but SSpower could not predict k_1 for the other actinometry runs. For the chamber runs where UVrad is in the range 0.057 to 0.063 ("Group 14b") the line for SSpower derived from the UVrad = ~0.06 actinometry experiments is recommended. For the other runs ("Group 14a"), the line for UVrad derived from all the actinometry runs in the group should be used.

Group 15d (See Figure 17.) Only one actinometry experiment and two chamber runs are in this group. They all have approximately the same UVrad, though the SSpower in the actinometry experiment is somewhat lower than in the chamber runs. It is assumed that the k_1 measured in the one experiment is appropriate for the two chamber runs.

Group 16d (See Figure 17.) Only one actinometry experiment is in this group, and the experimental runs in this group have similar light intensity. It is assumed that the k_1 measured in the one experiment is appropriate for this group.

Group 17 (See Figure 17.) The two actinometry experiments in this group have similar light SSpower, UVrad and k_1's. The average of the k_1's from these experiments is recommended for runs in this group with similar UV levels.

Groups 18 through 21 (See Figure 18.) As shown in the right plot in Figure 18, plots of k_1 vs UVrad for the actinometry experiments for all these groups fall on the same line. This is in contrast to most of the previous groups, where in general the relationship between UVrad and k_1 varied from group to group. There is no obvious explanation why this should be the case, except that the light in the EC for runs in Groups 19+ has significantly less intensity at lower wavelengths than for the previous groups. (The reason for this change in spectral distribution is unknown. It is discussed in the following section.) In any case, the recommendation is to use the line for UVrad derived from the actinometry experiments in these groups to estimate k_1's for all the chamber runs in these groups. (The points for the experiments for the actinometry experiments carried out during the time interval between Groups 19 and 20 were not used in computing the recommended line, though their results were reasonably consistent with this line.)

Group 21d. (See Figure 18.) These experiments have optics for UV spectroscopy in the chamber, which may block part of the light beam. Therefore, for these runs, a separate regression between k_1 and UVrad is used, based on actinometry experiments carried out under these conditions. Although one would expect the optics to reduce the k_1 without affecting the UVrad, Figure 18 shows that the effect is small.

Table 21 gives a summary of the recommended methods and parameters for deriving k_1 assignments for the various run groups. The k_1 values calculated using these assignments, and their estimated uncertainties, are included in the EC run spreadsheets, and in the data sets for each run. The estimated uncertainties are uncertainties in the assignments from the regressions or averages, except for those cases where the estimates are based on an insufficient number of actinometry runs for reliable uncertainty estimates. For those cases, a minimum uncertainty of ~4% is assumed. This is based on the typical uncertainties for run groups with sufficient data for statistical analyses.

The k_1 values assigned to the various runs are included in the EC run spreadsheet, along with their estimated uncertainty due to variations in the k_1 measurements. An indication of the variability of the measured k_1's and how they compare with the k_1's assigned to the experiments in the data base is shown in Figure 19, where the experimental k_1's and the k_1's assigned to the individual EC runs are

Table 21. Regressions results used to assign k_1 values to EC runs.

Group	Basis [a]	No. [b]	Intercept	Slope
1	SSpower	4	-0.190 ± 0.237	0.0393 ± 0.0186
2	SSpower	10	0.068 ± 0.042	0.0150 ± 0.0026
3	SSpower	3	0.098 ± 0.168	0.0167 ± 0.0111
4-6	UVrad	6	0.037 ± 0.024	1.09 ± 0.08
7	SSpower	4	-0.155 ± 0.088	0.0418 ± 0.0070
8	SSpower	4	-0.133 ± 0.075	0.0366 ± 0.0052
9	UVrad	8	0.017 ± 0.051	2.07 ± 0.29
10	SSpower	8	0.060 ± 0.073	0.0194 ± 0.0046
10a	UVrad	6	0.240 ± 0.076	0.88 ± 0.52
10uv	Avg k1	4	0.424 ± 0.021	
11a	Avg k1	3	0.425 ± 0.006	
11r	Avg k1	1	0.221	
12a	SSpower	5	0.054 ± 0.025	0.0132 ± 0.0013
12b	UVrad	9	0.086 ± 0.039	2.75 ± 0.42
13	UVrad	2	-0.068 ± 0.000	5.00 ± 0.00
14a	UVrad	8	0.097 ± 0.036	3.88 ± 0.49
14b	SSpower	4	0.145 ± 0.025	0.0103 ± 0.0014
15d	Avg k1	1	0.253	
16d	Avg k1	1	0.306	
17	Avg k1	2	0.337 ± 0.011	
18-21all	UVrad	15	0.048 ± 0.016	6.71 ± 0.42
18-21	UVrad	10	0.056 ± 0.019	6.60 ± 0.48
18-19	UVrad	10	0.056 ± 0.019	6.60 ± 0.48
20	UVrad	10	0.056 ± 0.019	6.60 ± 0.48
21	UVrad	10	0.056 ± 0.019	6.60 ± 0.48
21d	UVrad	5	0.095 ± 0.023	5.15 ± 0.66

[a] Method used to assign k_1 for runs: SSpower = regression of k_1 vs solar simulator power; UVrad = regression of k_1 against UV radiometer data; Avg k1 = Average of k_1 in the group.

[b] Number of k_1 experiments used in regression.

plotted against time. As expected, the k_1's assigned to the runs do not vary much within a particular group of runs, but are much more variable when considering the entire data set.

5.1.4 Spectral Distribution

The spectral distribution of the light in SAPRC EC runs could be affected by a number of factors. These include the age of the lamp, the quality of the optics, the transmission of the Pyrex filter and the quartz windows, and the lamp power. The spectral output (as well as the intensity) of the xenon arc lamps was observed to change as the lamp ages, and in general should change when lamps are replaced, as occurred from time to time. In addition, the Pyrex filter and perhaps the quartz windows might be

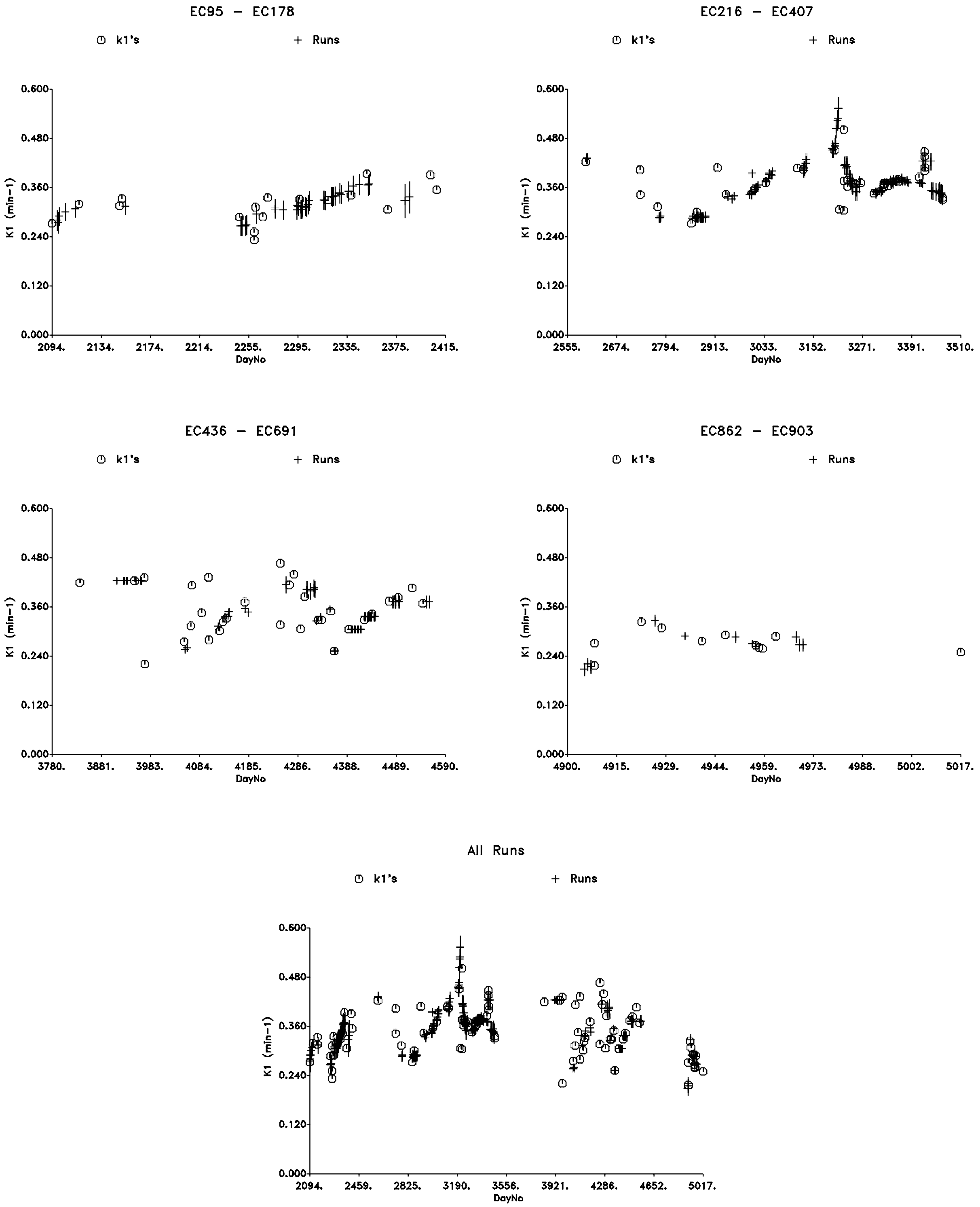


Figure 19. Plot of experimental k_1 data and k_1 values assigned to individual EC runs, against run day. Error bars show uncertainties in k_1 estimates for the runs.

expected to slowly solarize with time, which might change their transmission characteristics. The quality of the optics, which also varies with time (and which are periodically re-coated) is another potential source of variability of the light spectrum in the chamber. For this reason, it would not be appropriate to use a single spectral distribution to characterize all EC runs; spectral distributions appropriate for each run, or at least each run set, must be used.

For all EC runs being considered for modeling, spectral distribution measurements were made either using a McPherson spectrometer with a Hamamatsu photomultiplier or a SPEX spectrometer with a 1P28 photomultiplier. The McPherson was used for the earlier runs up to EC156, and the SPEX was used for all subsequent runs. Typically, one measurement was made during an experiment, with relative intensities at 10 nm intervals from 280 - 380 nm and 403, 430, and 500 nm being recorded and included in the computer data base. For some runs, strip chart recordings of the spectra are available in the run file (but not in computer-readable format), while for most others the relative intensity readings were taken directly from the instrument and tabulated for specific wavelengths, and no strip chart is available. The EC run spreadsheets include a list of the raw relative spectral data for all the runs being considered for modeling, along with notes indicating special conditions or problems. The absolute magnitudes of the light intensity readings are arbitrary, being normalized to give values of 1000 for 360 nm.

Before these relative spectral data can be used for calculating photolysis rates, the following problems need to be addressed: (1) the response of the photomultiplier used with the McPherson or the SPEX is not equal at all wavelengths, and correction factors for this response need to be applied; (2) the light passes out of the chamber through a quartz window before reaching the spectrometer; (3) the accuracy of the wavelengths reported by the SPEX needs to be verified; and (4) spectral data are needed for finer wavelength intervals than those given in the data base; and (5) data are not available for wavelengths above ~500 nm because the photomultiplier has low or no sensitivity at such wavelengths. These are discussed below.

Instrument Response Corrections. We were unable to locate any information concerning the calibration of the McPherson spectrometer system used for the earliest EC runs in the data base, except for the correction factors incorporated in the chamber data processing software. Thus, no re-evaluation of instrument response corrections was made for this instrument. Since the instrument was used for only a relatively short period, it is reasonable to assume that the appropriate correction factors should be the same for all these runs.

The spectra for most of the EC runs in the data base were taken using the SPEX. This system was calibrated against a standard light source in April of 1976 and in November of 1982. It has not been calibrated since then, but calibration information can be obtained from EC spectra taken simultaneously with this instrument and a LiCor model 1800 spectroradiometer made in October of 1989 when Dr. Ken

Sexton of the University of North Carolina (UNC) visited our laboratories. The wavelength-dependent correction factors from these various calibrations are shown in Figure 20 and are also summarized in Table 22. The 1989 "calibration" suggests a degradation of the sensitivity of the instrument at longer wavelengths relative to 1982. On the other hand, the sensitivity of the instrument to higher wavelengths appeared to be slightly greater in 1982 than it was in 1976. The data from the various calibrations are all reasonably consistent for wavelengths between ~320-400 nm. When comparing the SPEX with the LiCor in 1989, the light intensity is too low at wavelengths < 320 nm to provide meaningful calibration information, but the 1976 and 1982 calibrations are in reasonably good agreement in this region. Clearly, the greatest uncertainty in the calibration data is for wavelengths in the 400-500 nm region.

Since the two absolute calibrations are in good agreement in the 300-400 nm range, and the 1989 results are not inconsistent with them, the correction factors we use for these wavelengths are the averages of those from the 1976 and 1983 calibrations. These are also given in Table 22. For the 430 and 500 nm data, the factors for the individual runs are derived based on the day the run was carried out compared to the dates of the 1976 and 1982 calibrations. As shown in the run spreadsheets, a large majority of the EC runs in this data base was carried out between the times of the 1976 and the 1983 calibrations. For these runs (EC-143 through EC-691), the calibration factors for the individual runs were derived by linear interpolation of the data from the two calibrations, based on the time of the run relative to the time of the calibration. The 1976 calibration was used for the few runs (EC-95 through EC-142) carried out before that calibration. The last run in the data base (EC-903) was carried out in August of 1983, which was approximately 9 months after the 1982 calibration, but over 6 years before the instrument was recalibrated in 1989. Based on this, we assume that the 1983 calibration is still applicable for runs up to EC-903. If linear interpolation based on date and the 1983 and 1989 calibrations had been used, the correction factor at 500 nm would be ~6% higher. However, the calibration using the LiCor had a greater degree of uncertainty, and if the instrument response changed in a non-linear manner, it was more likely to occur during the >6-year period after the last run rather than the ~9 month period before it.

Based on the level of agreement between the various calibrations, the uncertainty in the relative spectrum due to calibration uncertainties are estimated to be <~5% at 300 nm, essentially negligible for 320-380 nm, and increasing to ~10% at 500 nm for runs up to the time of the 1982 calibration. For runs after that, the 500 nm correction factor may be up to a factor of 1.6 low. This uncertainty would not affect most photolysis rates except for α-dicarbonyls (to a small extent), and (to a larger extent) NO_3 and the photolysis of O_3 to $O(^3P)$.

End Window Effect Correction. The SPEX is located at the far end of the chamber, and the light passes out of the chamber through a quartz window before reaching the instrument. To obtain an indication of the magnitude of this effect, a transmission spectrum of this end window was taken in early

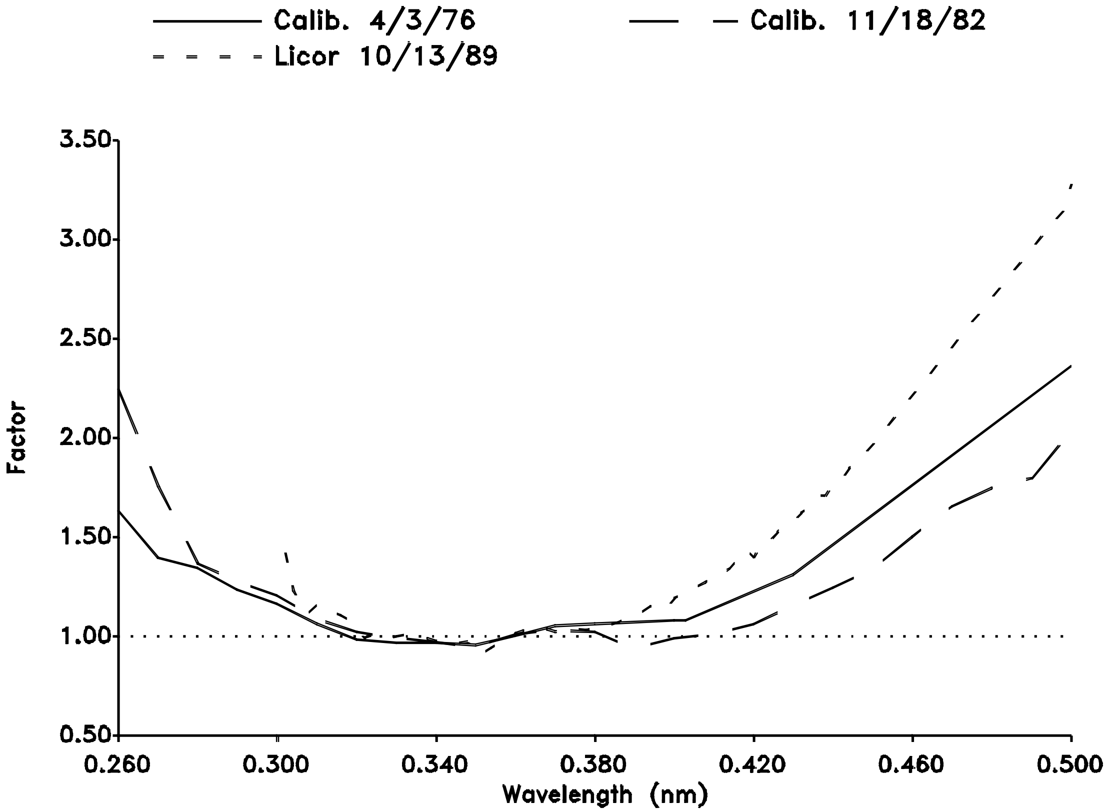


Figure 20. Plot of spectral response factors for the SPEX spectral radiometer.

1984, and the result is shown in Figure 21 for the wavelength region affecting the reported SPEX data. The data were corrected by increasing the relative spectrum at wavelengths less than 500 nm by the ratio of the transmission at 500 nm to the transmission at that wavelength. The maximum correction is ~7%.

Note that the spectrum shown in Figure 21 was taken at a much later date than the EC experiments in the data base, and the solarization of the quartz windows may be less for the earlier runs. In this case, the data may be over-corrected for this effect. But since the maximum correction is only ~7%, it is likely that any error introduced by assuming that the transmission is constant will be significant.

Wavelength Errors. The spectrometers may have been adjusted for correct wavelength settings when they were new, but to our knowledge the wavelength settings have not been adjusted since. Fortunately, the xenon arc light source in the solar simulator has several well-defined atomic lines of xenon, which can be used to obtain information concerning the wavelength accuracy of the instrument

Table 22. Correction factors used for instruments used to measure EC spectral distributions.

λ	McPherson		SPEX		End Window
(nm)		4/3/76	11/11/82	1989	Correction
280	0.670	1.405	1.444	1.424	1.077
290	0.726	1.291	1.347	1.319	1.068
300	0.767	1.217	1.272	1.244	1.059
310	0.815	1.111	1.149	1.130	1.053
320	0.859	1.030	1.078	1.054	1.046
330	0.907	1.012	1.050	1.031	1.041
340	0.944	1.012	1.024	1.018	1.036
350	1.000	1.000	1.000	1.000	1.032
360	1.056	1.049	1.067	1.109	1.028
370	1.130	1.101	1.088	1.119	1.023
380	1.185	1.111	1.078	1.139	1.020
403	1.333	1.136	1.051	1.338	1.013
430	1.630	1.370	1.218	1.726	1.008
500	3.704	2.469	2.155	3.581	1.000

for any runs where strip charts of the spectrum are available. Although strip charts were not taken for most runs, they were taken in late 1975 for the earliest runs in the data base (when the process of taking the spectrum was first initiated), in mid-1976 when the SPEX was first used, and again in early 1982 around the time of some experiments with variable spectral filters (EC661-2). The most intense line in the spectral region of interest is at 467.1225 nm. The wavelengths observed for this line for these runs are as follows:

Runs	Instrument	Date	Wavelength (nm)	Correction (nm)
EC101, EC103, EC106	McPherson	10/75	468.3 ± 0.3	-1.2
EC157, EC163	SPEX	5/76	468.0 ± 0.3	-0.9
EC661, EC662	SPEX	4/82	469.3 ± 0.2	-2.2

More recently, an EC spectrum taken in late 1989 indicate a correction of only -0.5 nm, while the positions of the Hg lines in a blacklight spectrum taken in late 1993 indicate the need for a much greater correction of -17 nm. However, these latter spectra probably do not reflect the condition of the instrument as it was routinely used when the EC runs were being carried out. The last EC run in the data base was carried out in 1984, after which time the SPEX was used only on an intermittent basis.

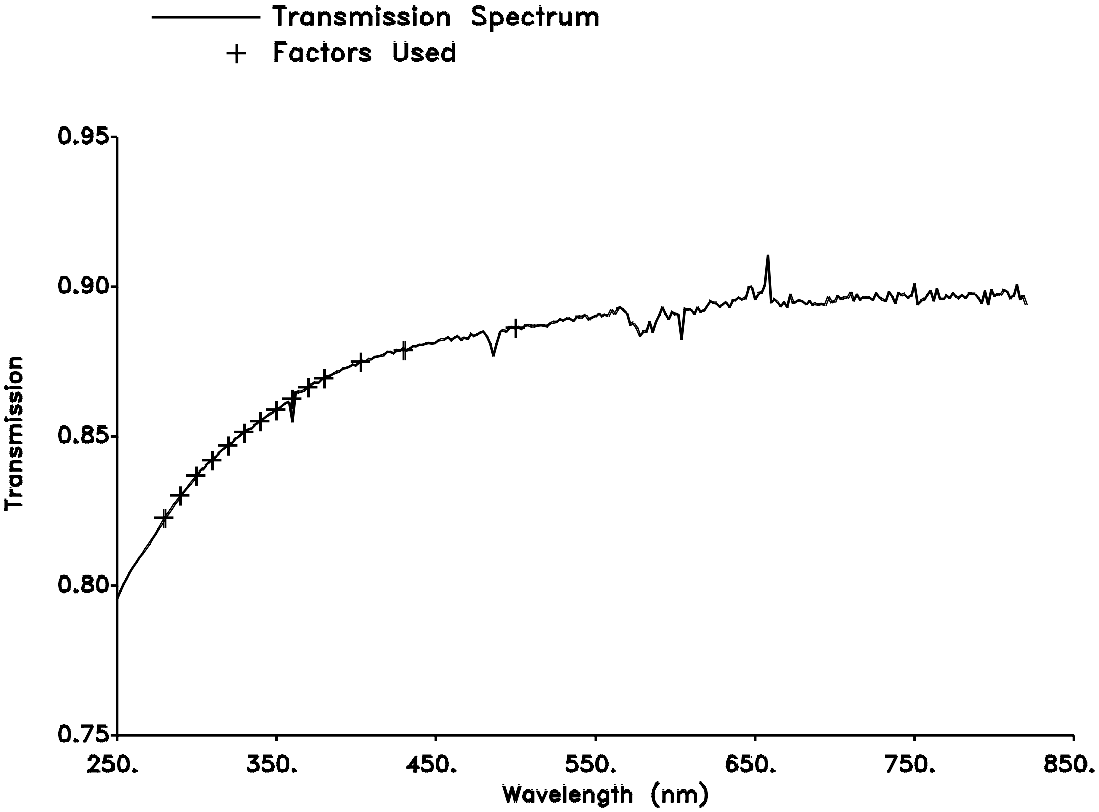


Figure 21. Plot of transmission spectrum for quartz end window in EC, and correction factors used for spectral measurements taken through it.

It is recommended that the data from the McPherson be corrected by subtracting 1.2 nm from the stated wavelength, and the data from the SPEX be corrected using the wavelength offset errors from the spectra taken in late 1975 and early 1982, and assuming that the offset error changes linearly with time between these two dates, and then is constant after 1982. An uncertainty of 3 nm would probably be appropriate for error sensitivity analyses. Note that these corrections have already been incorporated when producing the "ModSdist" data in the run data sets for the EC experiments. (The uncorrected data are also in the files if the modeler wishes to make different corrections.)

Full Light Source Spectra. The EC run data base has relative intensities of the light source for a specific set of wavelengths only, and thus does not give information concerning the full spectrum. Data are reported at 10 nm intervals for wavelengths between 280 and 380 nm, and then at 403, 430, and 500 nn. (403 nm is chosen because it is at a local minimum in the intensity of the spectrum.) Data above 500 nm are not available for the SPEX because the instrument lacks sufficient intensity at the longer wavelengths.

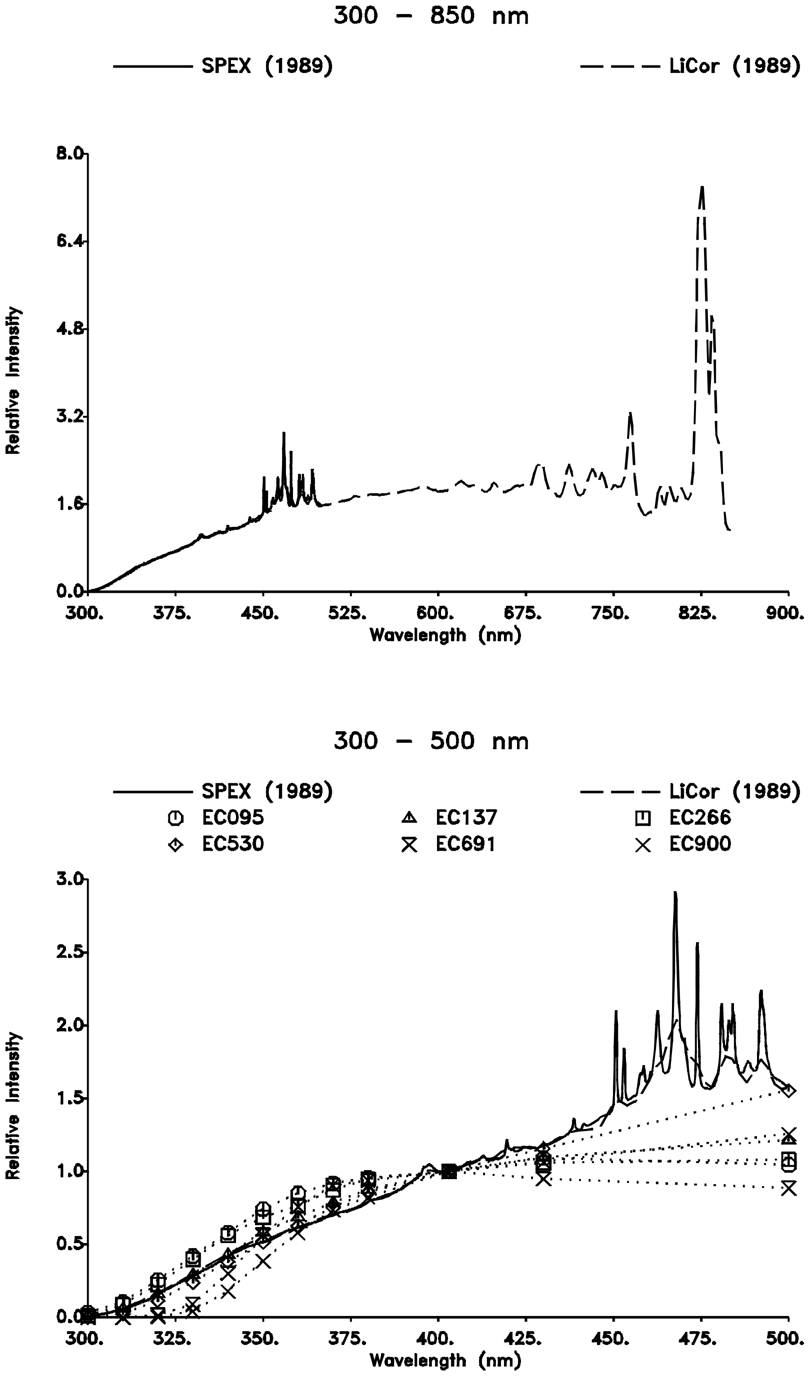
In 1989, the University of North Carolina (UNC) LiCor 1800 spectrometer was used to measure the spectrum for the solar simulator light source in the 300-850 nm range, and at the same time a spectrum was taken using the SPEX which was digitized. The two spectra are shown together for various wavelength intervals in Figure 22, along with spectra at the reported wavelengths for representative sets of runs. The 1989 SPEX spectrum was corrected for differences in instrument response so it agrees with the LiCor spectrum, while the spectra for the various runs were corrected as discussed above. It is recommended that a combined spectrum, using the SPEX data for wavelengths below 500 nm (because of the greater resolution of the instrument), and using the LiCor data for larger wavelengths, be used as the basis for deriving spectra for modeling purposes. The data for these spectra are included in the distributed data base.

Figure 22 shows that the EC light spectra varied significantly for the runs in the data base, and it would not be appropriate to use the 1989 spectra for all the runs. The recommended procedure to use when modeling specific runs is discussed later in this section.

<u>Run to Run Variation of Spectra</u>. An indication of how the measured spectral distribution in the EC runs varied with time is given in Figure 23, which shows a plot, against EC run number, of the relative spectral intensity for selected wavelengths. The intensities shown are normalized to 1000 at 380 nm. Also shown in the figure (under run "1000") is the relative spectrum measured in 1989 using the UNC LiCor spectrometer. Not shown in the figure are spectra which appear to be anomalous compared with other runs carried out around the same time, or runs with significantly different spectra because unusual spectral filters were used. The solid or dotted vertical lines show when lamps were changed and the dashed vertical lines show when the mirrors were re-coated.

It can be seen that the spectrum varied significantly with time, with the most notable feature being the general trend towards reduced intensity at the short wavelengths. A temporary increase in the relative intensity at short wavelengths occurs when the light is replaced, though the relative intensity for the new lamps generally were less than the previous new lamp. One lamp change (shown by the dotted vertical line in Figure 23) was unusual in that it caused no apparent change in the spectral distribution. Re-coating the mirrors did not appear to affect the spectral distribution to a measurable extent.

The most dramatic change in the spectral distribution occurred in March-April of 1983, when there was a sudden and dramatic drop in the relative intensities at short wavelengths. (This is evident in Figure 22 and on the 330 nm plot in Figure 23. At the time, we thought this was due to degradation


300 – 850 nm

300 – 500 nm

Figure 22. Spectra of the SAPRC solar simulator taken in 1989, and corrected and smoothed spectral distribution data for representative EC runs.

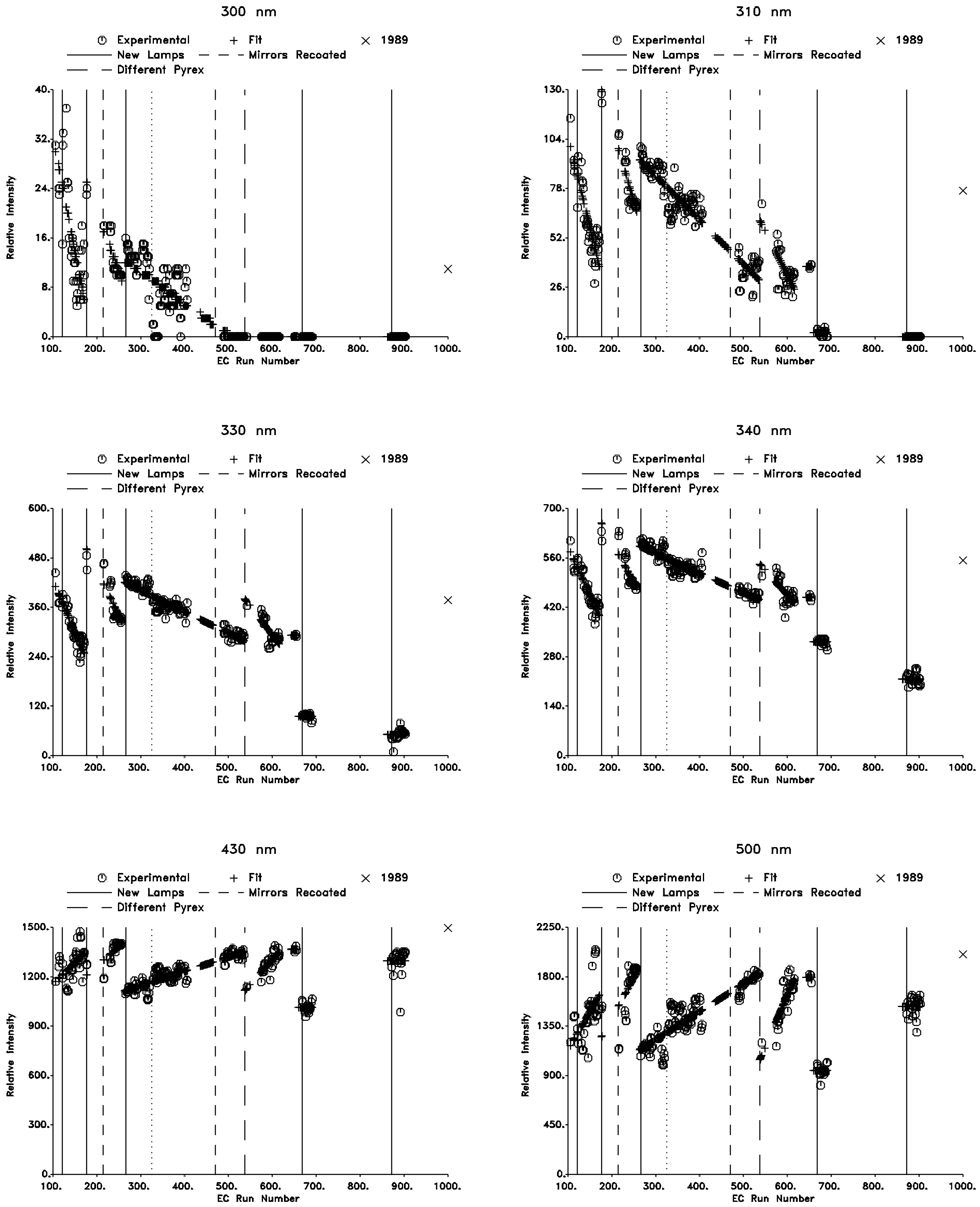


Figure 23. Plots of relative spectral intensities at various wavelengths against EC run number. Intensities are normalized to give 1000 at 380 nm.

of the solar simulator, but the spectrum taken in 1989 show the relative UV intensities in approximately the levels which were observed previously.

The most likely explanation for the sudden drop in relative intensity at short wavelengths is that a solarized or otherwise inappropriate filter was inadvertently put in place. The change occurred after we did several experiments with a Plexiglas filter, and perhaps the error occurred when the Plexiglas filter was removed. We think that it is unlikely that the change due to a malfunction of the SPEX or some other measurement error (such as a filter being between the SPEX and the chamber) for several reasons. The SPEX has not undergone repair, recalibration or significant maintenance since the 1983 spectra were taken. In addition, propene-NO_x-air runs were done prior to and after the change in spectraldistribution. The propene runs after the spectral distribution changed form less ozone than do similar runs after the change, and their results can be reasonably well fit by models using the 8/83 spectrum, but not using spectra taken earlier. Also, as discussed above, these runs seem to have a different type of correlation with UVrad data than do runs carried out previously.

We consider the spectra in these post 3/83 EC runs are roughly as well characterized as the other EC runs in the data base. This presents opportunity for the modeler to test mechanisms under more varied sets of lighting conditions than otherwise would be possible.

Recommended Spectral Distributions for Modeling. Figure 23 shows that there is some run-to-run scatter in relative spectral data which probably reflect measurement imprecision. This is particularly the case at the lowest wavelengths, where relatively small responses are being measured. For modeling purposes, especially for runs where spectral distribution data are missing or anomalous, we recommend using a smoothed set of spectra derived by fitting straight lines to the changes in relative intensities at the various wavelengths for the various sets of runs. For this purpose, the runs were grouped into sets as indicated by the solid vertical lines in Figure 23, and fits were made to the data for all the runs in that group, excluding those with apparently anomalous data, or with known special conditions such as using different filters. These were then used to obtain a set of "smoothed" spectra for the tabulated wavelengths for each run. These smoothed spectra are also shown in Figure 23, and are included in the data sets and spreadsheets for the EC runs (with the channel name "ModSdist").

The smoothed spectra only give the relative intensity at the wavelengths (300, 310, ... 430, 500 nm) for which spectral data were tabulated. We recommend combining these with the full spectrum taken using the SPEX and LiCor to obtain a synthesized spectrum which can be used for modeling. The 1989 SPEX data is recommended for wavelengths less than 500 nm because of its superior resolution, while the 1989 LiCor data can be used for wavelengths above 500 nm, where the SPEX does not provide information. The specific approach is up to the modeler. In our software, the method used is to use the ratios of the relative intensities in the run-specific and 1989 complete spectra to determine the correction factors for the 1989 spectrum at the given wavelengths applicable to the run, obtain the correction factors for intermediate wavelengths by linear interpolation, and then use these correction factors and the 1989 spectrum to derive a run-specific complete spectrum for modeling. (See SDADJ.FOR in the distributed program files for the specific algorithm used.)

Note that small wavelength offset errors are not taken into account in producing the smoothed spectral data which are in the spreadsheets. However, the correction was made in the "Sdist" and "ModSdist" channels in the run data sets.

5.2 Blacklight Chambers

The SAPRC ITC, ETC, and DTC are irradiated using diametrically opposed banks of Sylvania 40-W BL blacklamps backed by reflective material. The light intensity is measured by using a slightly modified version of the quartz tube technique of Zafonte et al. (1977) which is discussed below. The results of these measurements, and the k_1 values recommended for modeling, are then summarized separately for each chamber. Measurements of light spectra using the LiCor 1800 spectrometer indicate that the light source in all three of these chambers has essentially the same spectral distribution, which is as expected given that the same types of lights are employed. Therefore, we have derived a single spectrum that we recommend be used when modeling experiments from these chambers.

5.2.1 Quartz Tube Actinometry Method

As with the actinometry experiments used for the EC, the basic method involves irradiating ~2 ppm of NO_2 in N_2 for brief periods of time, and measuring the amount of NO which is formed. However, in this case, a plug flow rather than a static reactor is used. The reactor consists of a 100 cm segment of 25 mm (nominal) quartz tubing with 0.25 in. o.d. extensions at each end. Unless noted otherwise in the tabulations, in the ITC and ETC runs the tube was placed in the middle of the chamber enclosure, without the Teflon bag, with the long axis parallel to the light banks, and with a Teflon sleeve around the tube simulate to the effect of the Teflon reaction bag on the light intensity. In the DTC runs the tube was generally placed between the two reaction bags. The ends of the tube were covered with black tape so the volume exposed to the light is well defined. Unless noted otherwise, the volume exposed to the light was 295 ml, and the flow rate of the NO_2 in N_2 was 1 liter/minute. A tank of commercially-prepared ~2 ppm of NO was employed; the tanks were changed only infrequently, and these events are noted in the data tabulations. The NO, NO_2, and NO_x from the tube is monitored using either a Teco or a Columbia NO_x monitor both with the lights on and with the lights off. Span and zero checks on the NO_x instrument are usually performed around the same time.

Zafonte et al. (1977) recommends calculating the NO_2 photolysis rate (k_1) by using the expression:

$$k_1 = \frac{[NO]^{light} - [NO]^{dark}}{[NO_2]^{light} + \frac{1}{2}\left([NO]^{light} - [NO]^{dark}\right)} \times \frac{F}{V} \times \frac{1}{\Phi} \qquad (I)$$

where $[NO]^{light}$ and $[NO_2]^{light}$ are the NO and NO_2 concentrations from the tube with the lights on, $[NO]^{dark}$ is the NO concentration with the light off, F is the flow rate, V is the volume of the tube exposed to the light, and Φ is an "effective quantum yield" factor which takes into account the kinetics of the reactions involved in converting NO_2 to NO when it is photolyzed in N_2. As indicated above, for most of our experiments, F = 1 liter min^{-1}, and V = 0.295 liters. Φ was calculated by Zafonte et al. (1977), but the rate constants they used were somewhat out of date.

Equation (I) may be an appropriate data analysis method if an updated value of Φ were employed. One needs to conduct model simulations of the flow tube experiments to determine the appropriate value of Φ. Therefore, in this work we simulated all the NO_2 actinometry experiments, using a plug flow model with the inputs appropriate for each experiment, and the updated chemical mechanism given in Table 19, above. The simulations consisted of optimizing the k_1 input in the calculations for each experiment to minimize the difference between the observed and calculated NO and NO_2 when the tube was exposed to light. The results are given in the data tabulations for each chamber. These are the recommended values to use as the basis for deriving the NO_2 photolysis rates for the individual chambers, as discussed in the following sections.

Although Equation (I) was not employed in deriving the recommended NO_2 photolysis rates, it is far easier to use on a day-to-day basis than direct modeling of each experiment. To assess its utility, values of Φ were calculated from the model optimized k_1 for each experiment. The average for the ITC runs was 1.66 ± 0.02. Using this value in Equation (I) gave k_1's which agreed with the model optimized value to within 2.5% for all experiments. This is well within the uncertainty of the measurement.

Note that Equation (I) predicts that instrument span errors which affect measured NO and NO_x equally would not affect the calculated k_1. However, if the NO_x converter is not completely efficient, it would cause the derived k_1 values to be too high. An indication of NO_2 converter efficiency problems can be obtained by noting the change in NO_x measurements occurring between the initial (dark) and the final (light) measurements. The chemical transformations occurring in this system involve only interconversions of NO and NO_2, so if the converter were operating properly, the NO_x value would not change. Experiments where measured NO_x changed by more than 3% are noted in the data tabulations. Except for the DTC runs, where for some unknown reason the NO_x changes were always in the range of 3-7%, runs where the NO_x changed by more than 3% were not used to derive k_1 values recommended for modeling.

5.2.2 Light Intensity Data and Assignments

Table 23 gives the results of all the NO_2 actinometry experiments carried out using the quartz tube method which are relevant to the current data base, which include all those relevant to the blacklight chamber runs. This includes all data necessary to recompute k_1 using a different set of rate constants. Also given in the table are notes indicating any special conditions, and whether the results of this experiment were used for deriving k_1 values for the various experiments, as discussed below. The data in the "New k_1" column are the new values derived in this work. The data in the "Old k_1" column are the k_1 values which were originally derived for the experiments, which may have been used in previous modeling studies of these runs. Most of the new values are ~8-10% higher than the previous values.

ITC k_1 Data and Assignments. Figure 24 shows a plot of the k_1 values measured in the ITC against ITC run number. Since most of the experiments were carried out using 70% lights (i.e., 70%of the lights were on, and the rest were off), the few runs carried out at 100% or 50% lights were multiplied by the appropriate factor (0.7 or 1.4, respectively) to place them on a comparable basis.

It can be seen that there is a general decline in k_1 between the first run in the series and around the time of ITC600. This can be attributed to the conditioning of the lights, which were new when this series of runs started, but which have not been replaced since then. The jump in k_1 around the time of ITC700, and its subsequent apparent decline, is more difficult to explain, except for the fact that the tank of NO_2 in N_2 was changed at that time (as indicated by the dotted vertical line in the figure). Thus, this jump is probably an artifact of the measurement method, and is assumed not to reflect any real change in the light intensity in that chamber.

The ITC actinometry data were found to be reasonably well fit by the following expression, where "%Lts" is the percentages of lights which were used (usually 70), and RunID is the ITC run number.

$$k_1 = \frac{\%Lts}{70} \times 0.351 \times \left(1+e^{-0.0023\ (RunID-385.1)} \right) \qquad (II)$$

A plot of Equation (II) is shown in Figure 24 as the "curve fit" line. The parameters in Equation (II) were derived using a nonlinear least squares optimization program and the data from all actinometry runs except those where the tube was in a nonstandard position, and where the total NO_x measurements did not change by more than 3% when the lights were turned on. The average deviation from the fit was 4% for the experiments used to determine the parameters, and 5% for all experiments.

Equation (II) was then used to compute the k_1 for all the ITC experiments which we recommend be used for modeling. The recommended k_1 values are included in the data files for the runs, and in the "ITC-MISC" spreadsheet.

Table 23. Results of NO_2 actinometry experiments carried out in the blacklight chambers and the XTC.

Run		Date	%Lts	Dark		Light		Chg.	Tube		Inst	Conditions	k_1	
				NO	NO2	NO	NO2	NOx	Flow	Vol.	[a]		Old	New
ITC428	a	1/29/82	50	0.114	1.110	0.266	0.965		1.08	0.296	T		0.336	0.320
ITC428	b	1/29/82	70	0.114	1.110	0.327	0.910		1.08	0.296	T		0.478	0.463
ITC428	c	1/29/82	100	0.114	1.110	0.410	0.840		1.08	0.296	T		0.682	0.670
ITC433		2/5/82	100	0.112	1.100	0.402	0.831		1.13	0.296	T		0.624	0.690
ITC441		2/17/82	70	0.112	1.070	0.315	0.896		1.13	0.296	T		0.423	0.466
ITC447		2/25/82	70	0.101	1.040	0.289	0.858		1	0.296	T			0.405
ITC454		3/12/82	70	0.105	1.060	0.306	0.886		1	0.296	T		0.376	0.418
ITC458		3/18/82	70	0.105	1.060	0.304	0.877		1	0.296	T		0.378	0.418
ITC464		3/26/82	70	0.127	1.230	0.349	1.000		1	0.296	T		0.369	0.411
ITC470	a	4/2/82	70	0.120	1.110	0.326	0.903		1	0.296			0.380	0.421
ITC470	b	4/2/82	100	0.120	1.110	0.425	0.844	3%	1	0.296		[b]	0.565	0.639
ITC476		4/9/82	70	0.117	1.120	0.310	0.945		1	0.296			0.342	0.380
ITC481		4/20/82	70	0.122	1.110	0.315	0.930		1	0.296			0.334	0.386
ITC486		4/27/82	70	0.110	1.040	0.292	0.865		1	0.296			0.352	0.391
ITC491		5/3/82	70	0.108	1.010	0.274	0.843		1	0.296	T		0.331	0.367
ITC495		5/7/82	70	0.105	1.010	0.280	0.841		1	0.296	T		0.348	0.387
ITC505		5/21/82	70	0.103	0.979	0.261	0.821		1	0.296	T		0.324	0.360
ITC509	a	5/26/82	100	0.125	1.040	0.365	0.806		1	0.296	T		0.479	0.538
ITC509	b	5/26/82	70	0.125	1.050	0.297	0.877		1	0.296			0.330	0.367
ITC515		6/4/82	100	0.107	1.010	0.335	0.785		1	0.296	T		0.468	0.525
ITC516		8/11/82	100	0.105	0.995	0.326	0.778		1	0.296	T		0.460	0.515
ITC517	a	10/18/82	100	0.109	0.960	0.350	0.758	4%	1	0.296	T	[b,c,d]	0.507	0.570
ITC517	b	10/18/82	100	0.109	0.965	0.357	0.755	3%	1	0.296	T	[b,c,e]	0.521	0.587
ITC517	c	10/19/82	100	0.105	1.000	0.343	0.727	-3%	1	0.296	T	[b,c]		0.585
ITC528		11/4/82	70	0.127	1.150	0.298	0.958		1	0.296			0.302	0.335
ITC528		11/4/82	100	0.127	1.150	0.368	0.903		1	0.296			0.435	0.487
ITC528		11/4/82	100	0.127	1.150	0.371	0.907		1	0.296		[b,e]	0.439	0.490
ITC535		11/12/82	70	0.131	1.150	0.312	0.966		1	0.296	T		0.318	0.351
ITC543		11/22/82	70	0.127	1.120	0.320	0.944		1	0.296	T		0.342	0.381
ITC551		12/8/82	70	0.128	1.130	0.327	0.935		1	0.296	T		0.357	0.395
ITC558		12/16/82	70	0.129	1.100	0.300	0.920		1	0.296	T		0.000	0.349
ITC564		12/24/82	70	0.130	1.100	0.302	0.925		1	0.296	T		0.314	0.349
ITC576		1/28/83	70	0.127	0.922	0.292	0.950	17%	1	0.296	T	[b]	0.301	0.327
ITC583	a	2/4/83	70	0.120	0.879	0.259	0.710	-3%	1	0.296	T	[b]		0.368
ITC583	b	2/4/83	70	0.131	0.879	0.295	0.879	15%	1	0.296	T	[b]	0.315	0.350
ITC589		2/11/83	70	0.141	1.130	0.319	0.943		1	0.296	T		0.320	0.354
ITC594		2/18/83	70	0.143	1.400	0.303	0.996	-17%	1	0.296	T	[b]	0.274	0.304
ITC596		2/23/83	70	0.148	1.170	0.310	1.010		1	0.296	T	[b,f]	0.276	0.304
ITC601	a	3/1/83	70	0.140	1.120	0.297	0.971		1	0.296	T	[b,f]	0.275	0.306
ITC601	b	3/1/83	70	0.140	1.130	0.291	0.970		1	0.296	T	[b,f]	0.265	0.295
ITC604		3/4/83	70	0.137	1.080	0.300	0.922		1	0.296	T		0.300	0.333
ITC611		3/14/83	70	0.137	1.100	0.308	0.926		1	0.296	T		0.312	0.347
ITC615		3/17/83	70	0.135	1.100	0.305	0.919		1	0.296	T		0.313	0.348
ITC622		3/29/83	70	0.130	1.080	0.295	0.916		1	0.296	T		0.305	0.339
ITC629		4/8/83	70	0.134	1.270	0.287	0.939	-14%	1	0.296	T	[b]	0.276	0.308
ITC667		6/30/83	70	0.126	1.030	0.291	0.876		1	0.296	T		0.318	0.353
ITC675		8/9/83	70	0.135	1.110	0.294	0.952		1	0.296	T		0.286	0.316
ITC691		11/28/83	70	0.147	1.520	0.365	1.300		1	0.296	T		0.286	0.315
ITC696		12/1/83	70	0.148	1.410	0.343	1.160	-4%	1	0.296	T	[b]	0.286	0.317
ITC701		12/6/83	70	0.149	1.440	0.349	1.160	-5%	1	0.296	T	[b]	0.293	0.325
ITC705		12/9/83	70	0.151	1.330	0.337	1.110		1	0.296	T		0.285	0.316
ITC708		12/13/83	70	0.149	1.270	0.337	1.080		1	0.296	T		0.296	0.328
ITC708		12/13/83	70	0.037	2.150	0.372	1.810		1	0.296	T	[g]	0.312	0.341
ITC718		1/4/84	70	0.038	2.330	0.390	1.930		1	0.296	T		0.310	0.336
ITC727		1/4/84	70	0.029	2.070	0.387	1.730		1	0.296	C		0.346	0.378
ITC732		1/25/84	70	0.027	2.060	0.373	1.730		1	0.296	C		0.337	0.366
ITC738		2/6/84	70	0.028	2.020	0.364	1.720		1	0.296	C		0.328	0.358
ITC741		2/8/84	70	0.026	2.000	0.362	1.700		1	0.296	C		0.332	0.362
ITC746	a	2/14/84	70	0.030	2.020	0.368	1.710		1	0.296	C		0.332	0.362
ITC746	b	2/14/84	70	0.035	2.110	0.405	1.700		1	0.296	T		0.362	0.397
ITC753		2/24/84	70	0.028	2.200	0.394	1.900		1	0.296	C		0.324	0.354

Table 23 (continued)

Run		Date	%Lts	Dark		Light		Chg.	Tube		Inst	Conditions	k_1	
				NO	NO2	NO	NO2	NOx	Flow	Vol.	[a]		Old	New
ITC758		3/1/84	70	0.034	2.240	0.398	1.920		1	0.296	C		0.321	0.348
ITC764		3/9/84	70	0.030	2.220	0.390	1.900		1	0.296	C		0.320	0.348
ITC769		3/16/84	70	0.028	2.220	0.380	1.930		1	0.296	C		0.309	0.336
ITC773	a	3/21/84	70	0.030	2.220	0.387	1.900		1	0.296	C		0.316	0.345
ITC773	b	3/21/84	70	0.033	2.050	0.363	1.690		1	0.296	T		0.328	0.358
ITC777	a	3/26/84	70	0.029	2.250	0.382	1.930		1	0.296	C		0.310	0.337
ITC777	b	3/26/84	70	0.036	1.940	0.354	1.590		1	0.296	T		0.336	0.367
ITC783	a	4/6/84	70	0.032	2.140	0.380	1.860	3%	1	0.296	C	[b]	0.316	0.344
ITC783	b	4/6/84	70	0.036	2.020	0.352	1.660		1	0.296	T		0.321	0.350
ITC790	a	4/16/84	70	0.036	2.190	0.372	1.900		1	0.296	C		0.300	0.326
ITC790	b	4/16/84	70	0.042	2.020	0.358	1.690		1	0.296	T		0.358	0.344
ITC794	a	4/20/84	70	0.036	2.030	0.398	1.820	7%	1	0.296	C	[b]	0.351	0.365
ITC794	b	4/20/84	70	0.036	2.120	0.384	1.660	-5%	1	0.296	T	[b]	0.350	0.383
ITC804	a	5/3/84	70	0.041	2.220	0.406	1.910		1	0.296	C		0.322	0.351
ITC804	b	5/3/84	70	0.043	2.160	0.384	1.790		1	0.296	T		0.321	0.350
ITC809	a	5/10/84	70	0.043	2.240	0.423	1.930	3%	1	0.296	C	[b]	0.331	0.361
ITC809	b	5/10/84	70	0.037	2.110	0.398	1.720		1	0.296	T		0.351	0.384
ITC813		5/21/84	70	0.038	2.070	0.385	1.710		1	0.296	C		0.339	0.372
ITC830		6/8/84	70	0.043	2.140	0.403	1.780		1	0.296	T		0.339	0.371
ITC833		6/13/84	70	0.040	2.000	0.384	1.650		1	0.296	T		0.331	0.381
ITC862		9/24/84	70	0.050	2.140	0.397	1.850		1	0.296	T		0.317	0.346
ITC869		11/1/84	70	0.060	2.260	0.432	1.860		1	0.296	T		0.336	0.367
ITC876		11/20/84	70	0.070	2.630	0.497	2.200		1	0.296	T		0.327	0.357
ITC883		1/3/85	70	0.070	2.340	0.449	1.950		1	0.296	T		0.327	0.358
ITC890		1/25/85	70	0.072	2.330	0.430	1.970		1	0.296	T		0.316	0.336
ITC894		2/7/85	70	0.063	2.370	0.440	1.980		1	0.296	T		0.321	0.351
ITC923		3/10/86	70	0.028	1.850	0.343	1.570		1	0.296	T		0.337	0.368
ITC933		3/26/86	70	0.086	1.910	0.385	1.600		1	0.296	T		0.317	0.346
ITC950		4/25/86	70	0.101	1.890	0.395	1.570		1	0.296	T		0.316	0.347
ITC959		5/12/86	70	0.098	1.920	0.392	1.610		1	0.296	T		0.309	0.339
ITC971		6/23/86	70	0.212	1.780	0.517	1.490		1	0.296	C		0.378	0.382
ITC998		8/14/86	70	0.110	2.270	0.470	1.960		1	0.296	T		0.310	0.341
ITC1375		9/22/88	100	0.150	[h]	0.622	1.580	[h]	1	0.296	T		0.438	0.536
ITC1376		9/22/88	100	0.190	[h]	0.622	1.530	[h]	1	0.296	C		0.455	0.511
ITC1560		11/6/89	70	0.029	[h]	0.342	1.780	[h]	1	0.296	C		0.340	0.325
ITC1560		11/6/89	70	0.027	[h]	0.343	1.800	[h]	1	0.296	C	[b,i]	0.340	0.324
ITC1560		11/6/89	70	0.029	[h]	0.360	1.780	[h]	1	0.296	C	[b.j]	0.357	0.342
ETC043		10/24/89	100	0.031	2.110	0.465	1.660		1	0.295	C			0.474
ETC043		10/24/89	100	0.028	2.120	0.460	1.675		1	0.295	C			0.468
ETC043		11/3/89	100	0.033	2.120	0.495	1.650		1	0.350	C	[k]		0.425
ETC048		11/21/89	100	0.030	2.150	0.508	1.650		1	0.350	C	[k]		0.437
ETC048		11/21/89	100	0.026	2.150	0.435	1.700		1	0.295	C			0.440
ETC048		12/13/89	100	0.029	2.150	0.430	1.720		1	0.295	C			0.428
ETC066		1/29/90	100	0.021	2.120	0.381	1.730		1	0.295	C			0.387
ETC076		2/20/90	100	0.021	2.070	0.375	1.710		1	0.295	C			0.385
ETC084		3/9/90	100	0.014	2.030	0.360	1.670		1	0.295	C			0.385
ETC096		4/18/90	100	0.029	2.060	0.343	1.680		1	0.295	C			0.351
ETC105		5/10/90	100	0.021	2.100	0.353	1.730		1	0.295	C			0.359
ETC111		5/25/90	100	0.020	2.080	0.340	1.730		1	0.295	C			0.347
ETC121		6/25/90	100	0.020	2.080	0.320	1.740		1	0.295	C			0.326
ETC136		7/25/90	100	0.021	2.100	0.338	1.740		1	0.295	C			0.342
ETC140		8/1/90	100	0.023	2.060	0.330	1.710		1	0.295	C			0.338
ETC142		10/26/90	100	0.018	2.190	0.371	1.800		1	0.295	C			0.366
ETC146		11/6/90	100	0.024	2.200	0.378	1.820		1	0.295	C			0.364
ETC152		1/8/91	100	0.023	2.320	0.380	1.940		1	0.295	C			0.346
ETC162		2/11/91	100	0.024	2.190	0.357	1.830		1	0.295	C			0.342
ETC162		2/11/91	100	0.024	2.190	0.357	1.830		1	0.295	C			0.342
ETC206		5/9/91	100	0.035	2.260	0.389	1.890		1	0.295	C			0.351
ETC206		5/9/91	100	0.035	2.260	0.389	1.890		1	0.295	C			0.351
ETC322		12/2/91	100	0.010	2.200	0.304	1.857		1	0.295	T			0.302
ETC337		2/9/92	100	0.009	2.020	0.342	1.700		1	0.295	C			0.366
ETC340		2/21/92	100	0.015	2.010	0.339	1.690		1	0.295	C			0.359

Table 23 (continued)

Run	Date	%Lts	Dark		Light		Chg.	Tube		Inst	Conditions	k_1	
			NO	NO2	NO	NO2	NOx	Flow	Vol.	[a]		Old	New
ETC340	2/21/92	100	0.003	2.100	0.303	1.800		1	0.295	T			0.315
ETC341	2/24/92	100	0.010	2.050	0.326	1.730		1	0.295	C			0.343
ETC341	2/24/92	100	0.004	2.090	0.306	1.760		1	0.295	T			0.324
ETC359	3/25/92	100	0.014	1.990	0.350	1.660		1	0.295	C			0.377
ETC359	3/25/92	100	0.005	2.130	0.342	1.795		1	0.295	T			0.352
ETC369	4/22/92	100	0.030	2.050	0.426	1.642		1	0.295	C	[b]		0.441
ETC369	4/22/92	100	0.008	2.150	0.404	1.745		1	0.295	T			0.418
ETC394	6/24/92	100	0.007	2.110	0.345	1.770		1	0.295	C			0.357
ETC394	6/24/92	100	0.003	2.120	0.327	1.770		1	0.295	T			0.344
ETC448	10/16/92	100	0.012	2.000	0.328	1.680		1	0.295	C			0.353
ETC448	10/16/92	100	0.009	2.050	0.326	1.690		1	0.295	T			0.352
ETC461	11/13/92	100	0.012	2.000	0.323	1.690		1	0.295	C			0.346
ETC461	11/13/92	100	-0.010	2.240	0.324	1.900		1	0.295	T			0.331
ETC498	1/29/93	100	0.006	2.020	0.315	1.700		1	0.295	C			0.342
ETC511	4/21/93	50	0.008	2.100	0.063	2.050		1	0.295	C	[k]		0.054
ETC511	4/21/93	100	0.002	2.120	0.342	1.760		1	0.295	C	[b,c]		0.361
ETC512	4/26/93	50	0.100	2.100	0.330	1.870		1	0.295	C	[b,c,m]		0.238
ETC512	4/26/93	100	0.100	2.120	0.440	1.780		1	0.295	C	[b,c]		0.358
ETC513	4/26/93	50	0.100	2.050	0.330	1.900	4%	1	0.295	C	[b,c,m]		0.234
ETC513	4/26/93	100	0.100	2.050	0.460	1.760	3%	1	0.295	C	[b,c,m]		0.381
DTC001	12/9/92	100	0.020	2.060	0.880	1.215	3%	1	0.295	C	[b,c]		1.072
DTC001	12/9/92	50	0.020	2.060	0.485	1.575	5%	1	0.295	C	[b,c]		0.528
DTC001	12/9/92	100	0.020	2.055	0.810	1.270	5%	1	0.295	C	[b,c]		0.973
DTC001	12/10/92	50	0.020	2.075	0.450	1.625	6%	1	0.295	C	[b,c]		0.479
DTC001	12/10/92	50	0.020	2.075	0.500	1.590	5%	1	0.295	C	[b,c]		0.538
DTC001	1/4/93	50	0.045	2.000	0.380	1.645	6%	1	0.295	C			0.379
DTC004	1/28/93	50	0.020	2.035	0.395	1.660	5%	1	0.295	C			0.416
DTC004	1/28/93	50	0.020	2.040	0.375	1.680	6%	1	0.295	C	[n]		0.392
DTC004	1/28/93	50	0.015	2.040	0.355	1.705	5%	1	0.295	C	[p]		0.372
DTC004	1/28/93	50	0.015	2.035	0.355	1.705	5%	1	0.295	C	[q]		0.372
DTC005	1/29/93	50	0.020	2.050	0.385	1.680	5%	1	0.295	C			0.402
DTC005	1/29/93	50	0.020	2.045	0.365	1.695	5%	1	0.295	C	[n]		0.379
DTC005	1/29/93	50	0.015	2.040	0.335	1.715	6%	1	0.295	C	[r]		0.350
DTC016	3/17/93	50	0.015	1.765	0.295	1.495	5%	1.12	0.295	C			0.393
DTC016	3/17/93	50	0.010	1.760	0.285	1.460	7%	1.14	0.295	C			0.403
DTC017	3/18/93	50	0.010	1.730	0.290	1.490	3%	1.13	0.295	C			0.399
DTC017	3/18/93	50	0.015	1.760	0.285	1.490	5%	1.12	0.295	C			0.381
DTC018	3/22/93	50	0.020	1.755	0.335	1.460	4%	0.98	0.295	C			0.391
DTC018	3/22/93	50	0.010	1.750	0.305	1.440	6%	1.02	0.295	C			0.390
XTC077	8/9/93	100	0.120	2.150	0.440	1.820		1	0.295	C	[b,c]		0.331
XTC078	8/13/93	100	0.110	2.160	0.431	1.850		1	0.295	C	[b,c,n]		0.327
XTC078	8/13/93	100	0.110	2.160	0.425	1.850		1	0.295	C	[b,c]		0.322
XTC078	8/13/93	100	0.110	2.160	0.416	1.850		1	0.295	C	[b,c,r]		0.313
XTC078	8/13/93	100	0.110	2.160	0.426	1.850		1	0.295	C	[b,c,n]		0.323
XTC078	8/13/93	100	0.110	2.160	0.420	1.850		1	0.295	C	[b,c]		0.317
XTC078	8/13/93	100	0.110	2.160	0.413	1.850		1	0.295	C	[b,c,r]		0.310
XTC078	8/13/93	100	0.110	2.160	0.413	1.850		1	0.295	C	[b,c,r]		0.310
XTC079	8/19/93	100	0.135	2.060	0.380	1.830		1	0.295	C			0.257
XTC079	8/19/93	100	0.135	2.060	0.380	1.800		1	0.295	C			0.261
XTC079	8/19/93	50	0.122	2.060	0.253	1.920		1	0.295	C			0.135
XTC089	9/3/93	100	0.168	2.080	0.404	1.850		1	0.295	C			0.246
XTC100	10/1/93	100	0.175	2.140	0.419	1.900		1	0.295	C			0.247
XTC117	11/11/93	100	0.010	2.843	0.335	2.518		1.01	0.295	C	[b,s]		0.250
XTC119	11/15/93	100	0.061	2.792	0.406	2.447		1.01	0.295	C	[b,s]		0.272
XTC124	12/1/93	100	Steady state experiment								[t]		0.240

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[a] "T = Teco, C = Columbia

[b] Not used to compute parameters for k1 estimations for runs.

[c] Without reaction bag

[d] Lower Half

Table 23 (concluded)

[e] Upper Half
[f] Some lamps out
[g] New NO2 Bottle
[h] No data
[i] Perpindicular orientation
[j] Vertical orientation
[k] Outdoor chamber quartz tube used
[m] Lower light bank only
[n] Tube positioned near top of chamber enclosure
[p] Tube in vertical orientation
[q] Tube inside "A" side reaction bag
[r] Tube positioned near bottom of chamber enclosure
[s] Data not used because NO_2 convertor bad
[t] Stationary state actinometry used. See text.

ETC k_1 Data and Assignments. Figure 25 shows a plot of the k_1 values measured in the ETC chamber against run number. As with the ITC, a rapid decline in light intensity is observed with new lights, with the intensity stabilizing after the lights are aged. With the exception of one anomalous point, the data taken using the Columbia are reasonably well fit by the following function,

$$k_1 = 0.351 \times \left(1+e^{-0.0457\ (\mathrm{RunID}-17.32)} \right) \tag{III}$$

which is similar to that shown above for the ITC except that the ageing process appears to have been much more rapid in this chamber. Equation (III) was used to compute the k_1 for all the ETC experiments in the data base. The assigned k_1 values are included in the run data files and in the "ETC-K1" spreadsheet.

DTC k_1 Data and Assignments. The actinometry experiments conducted in the between the time it was new through DTC-18 indicate no significant decay in light intensity with time. This can be attributed to the fact that the lights were turned on and aged prior to use. The actinometry measurements were made in several different positions gave similar results, though the intensity near the floor was somewhat lower than average (See Table 23). The average of the actinometry measurements made when the reaction bags were in place, excluding both the highest and lowest values, was 0.388 ± 0.011 min^{-1}. In view of the fact that there is no indication of change in light intensity with time in this chamber, this average value was assigned to all DTC runs, and included in their run data sets. However, there were unfortunately no actinometry measurements in this chamber after DTC018, so the light intensity for the subsequent runs must be considered to be more uncertain. However, even if the high initial actinometry results are attributed to light decay rather than the lack of the reaction bag in the chamber, and the data are fit a functional form such as used in Equations (II) and (III), the predicted k_1 for the last experiment would be only ~1% lower than that for run DTC018.

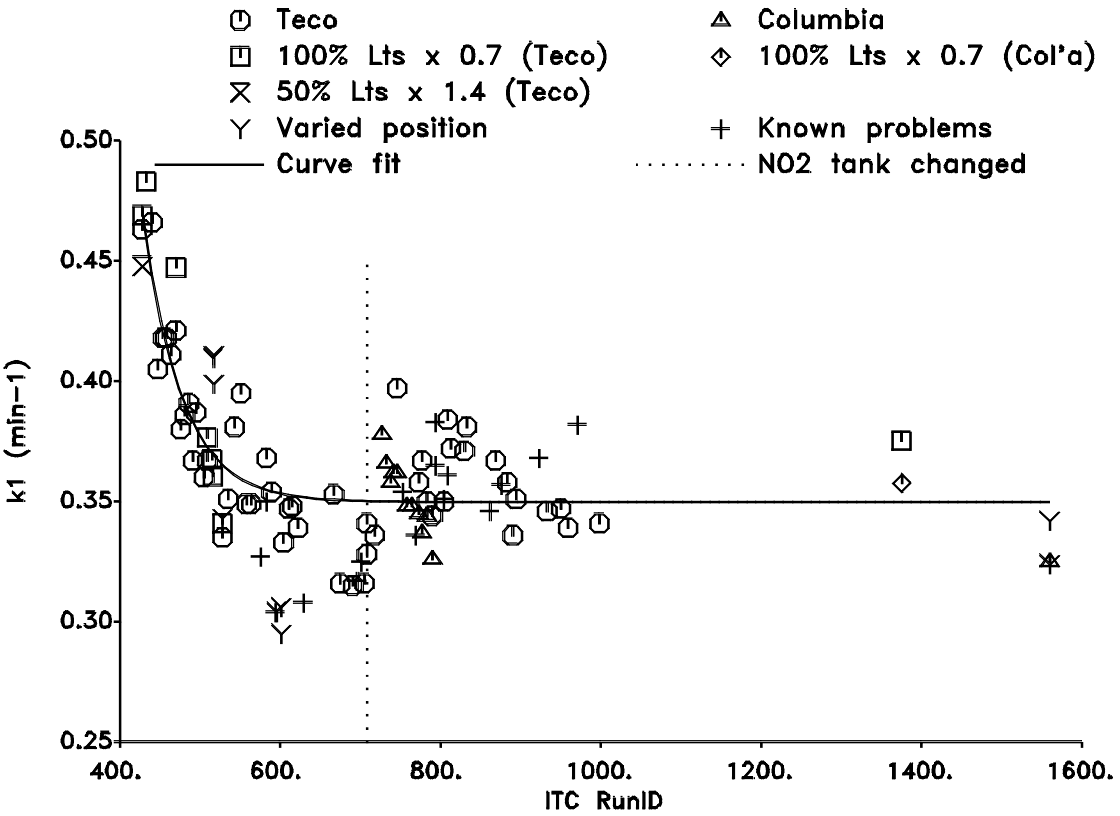

Figure 24. Plot of k_1 measurements in the ITC against run number.

5.2.3 Blacklight Spectral Distributions

Blacklight spectral distributions were taken using three different types of spectral radiometers and in several different chambers. Representative spectra are shown for various spectral regions in Figure 26. Spectra of a number of blacklight chambers were taken using the LiCor, and the differences between spectra taken in different chambers were found to be comparable to the differences between spectra taken at different times in the same chamber. Examples of this are shown in Figure 27, which gives plots of differences between spectra taken in the ITC and the ETC, compared to differences between averages of the spectra taken in each of the chambers. In view of this, we recommend using a single blacklight spectrum for all chambers using this type of light source.

The top right and the bottom plots compare spectra taken using the different types of spectroradiometers. All the different spectra are normalized to give the same NO_2 photolysis rate, and the relative intensities shown are given on a quantum (not power) basis. The radiometers used included

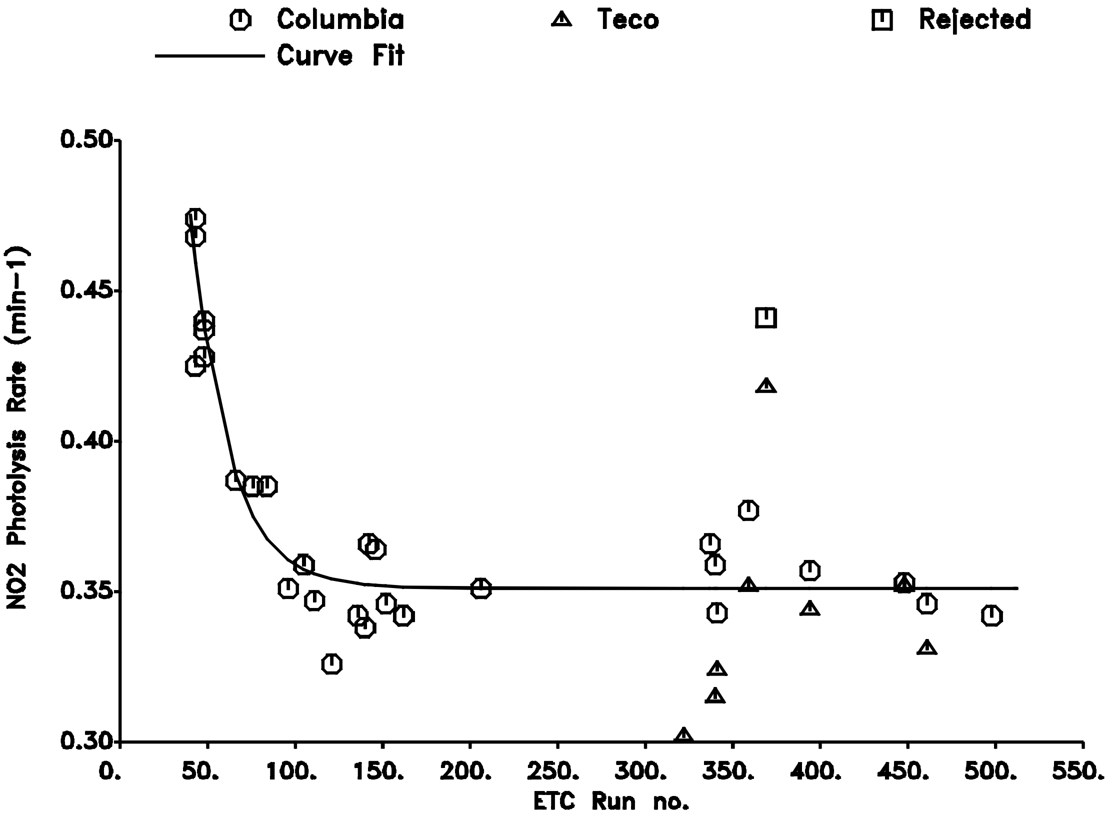

Figure 25. Plot of k_1 measurements in the ETC against run number.

SAPRC's LiCor 1800 portable radiometer, General Motors Research Laboratory's (GMRL) Optronics 752 spectroradiometer, and the SPEX spectroradiometer which was used in the EC.

The LiCor 1800 is portable and easy to use, and conveniently provides computer-readable spectra in the 300 - 850 nm range. This is why it was used to compare spectra from different chambers. However, it has relatively poor resolution compared to the other instruments, as is shown in the bottom right plot in Figure 26, which gives a close-up view of the 435.8 Hg line as measured by the different instruments. The sharper the spectral line the better the resolution of the instrument. (Note that despite the large differences in resolution, the area under the 435.8 nm line agree reasonably well for the three instruments.)

The Optronics spectrum was taken by Dr. Nelson Kelly of GMRL, using a lamp and fittings we sent him. The lamp was an aged lamp from one of our chambers, and the fittings were of the same type as used in the construction of the ETC and DTC. This spectrometer provides much better resolution than

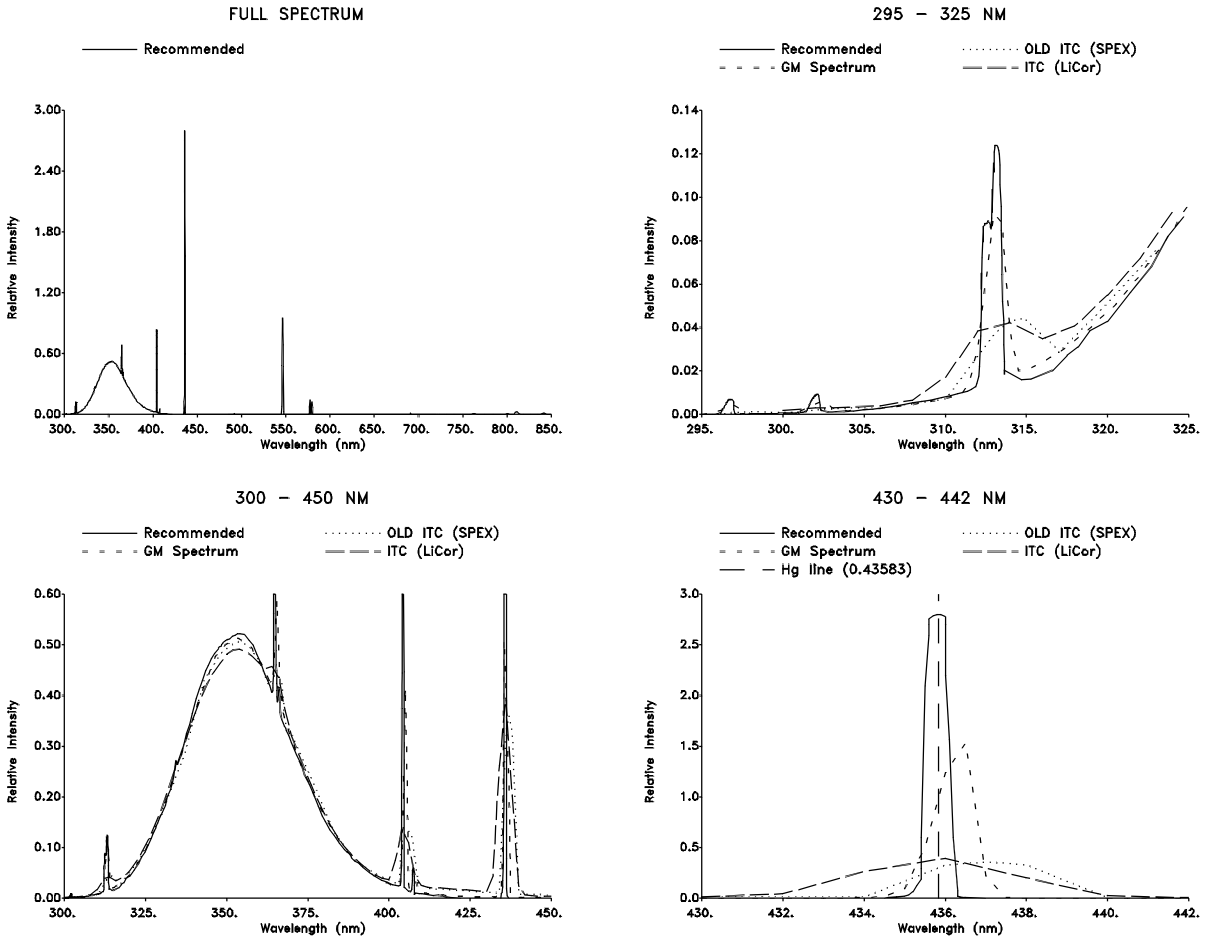

Figure 26. Blacklight spectra for selected spectral regions.

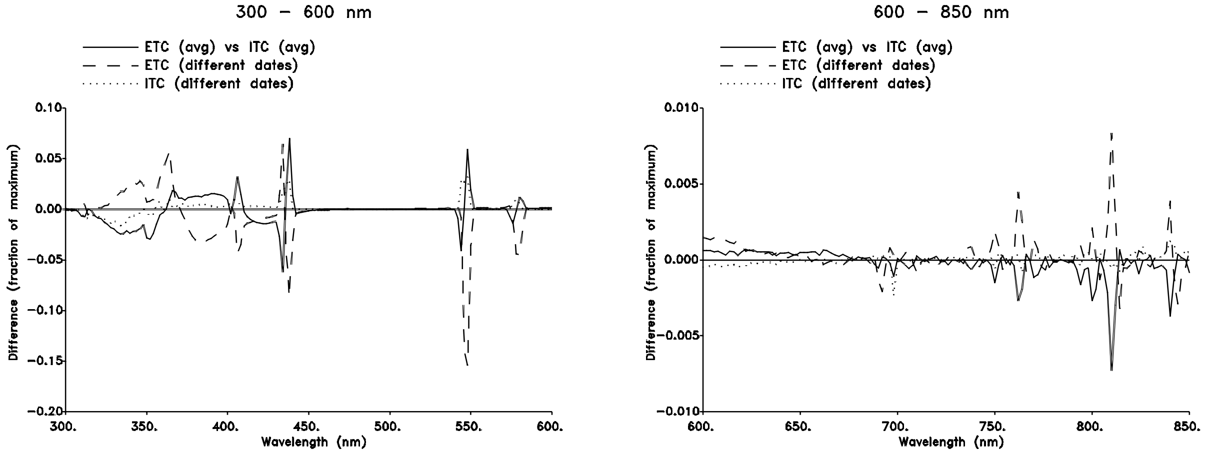

Figure 27. Differences between various blacklight spectra taken using the LiCor spectral radiometer.

the LiCor, and provides data in the 250 - 750 nm range (though the data above ~720 is not consistent with the LiCor and may not be reliable).

The SPEX spectrum was taken at a very slow scanning rate, and provided the best resolution of the instruments we tried. However, it has several problems which must be overcome before the data can be used. Unlike the LiCor and the Optronics, the SPEX does not provide data in computer-readable form. Therefore, the data were manually digitized from strip charts. Several parts of the spectrum had to be pieced together for the digitizing process. For maximum sensitivity in the critically important (but low intensity) UV region, the strip charts were taken at a higher gain than used for the rest of the spectrum. Different parts of the spectrum were fit together as a single spectrum by fitting overlapping regions, and using the known wavelengths of the conveniently-located Hg lines to calibrate the wavelengths and assure that the different regions were combined properly. The combined spectrum provided data from 288 to 437 nm.

Also shown in Figure 26 is the spectrum we have used previously in modeling ITC runs, which is labeled as "OLD ITC (SPEX)". This was also taken using the SPEX and digitized, though with the instrument running at a much faster scan rate. The higher scan rate caused a significant decrease in the resolution, making it comparable to the LiCor.

A recommended spectrum for modeling was synthesized by using the most appropriate instrument for each spectral region. The highest resolution spectrum is considered most appropriate for modeling, since too-low resolution spectrum may give inappropriate photolysis rates for species with highly banded spectra. Thus the new SPEX spectrum was used (without modifications) for the spectral regions where it provided useable data. It does not provide useful data above ~437 nm, so the Optronics (GM) spectrum was used for 437-720 nm. Above 720 nm the intensity of the GM spectrum seems to drop off relative to the LiCor, so the LiCor spectrum was used for 750-850 nm. (The GM and LiCor spectrometers agree well, at least in terms of areas under peaks, at wavelengths below 720 nm). The GM spectrum was also used for the 292.4 - 294 nm region, since the SPEX spectrum appeared to be noisy or poorly digitized there. However, the SPEX data was used for the 289.4 nm line (the shortest wavelength region where this light source has any intensity) because it was sharper than the line in the GM data, but had the same area. However, it had to be shifted 0.8 nm so its position agreed with that in the GM spectrum and the known position of that line. The recommended spectrum is shown by the solid curves in Figure 26, and is included in the distributed data base in the file ITCUSE.SDR. Note that since the spectra are used in a relative sense when deriving photolysis rates (see discussion at the beginning of this section), the absolute magnitude of the recommended spectrum is arbitrary.

5.3 Xenon Arc Teflon Chamber

5.3.1. XTC Light Intensity

The XTC chamber is irradiated using four 6.5 KW xenon arc lights which, for all the experiments discussed here, was run with a power setting of 4 KW. A lower than maximum setting was used to minimize the deterioration rate of the lamps and extent the lamp life. The light intensity and uniformity system was measured by NO_2 actinometry. Three sets of actinometry experiments were conducted: (1) quartz tube actinometry measurements at various positions in the XTC area before the reaction bag was installed; (2) several quartz tube actinometry and one NO, NO_2, O_3 steady state actinometry experiment inside the reaction bag at various times interdispersed with the experimental runs, and (3) an extensive series of quartz actinometry measurements at various positions in the chamber several months after the experiments were completed.

The results of the first two sets of actinometry experiments, which were carried out immediately prior to or during the experimental runs, are included in Table 23, above, and Figure 28 shows a plot of the actinometry results measured after reaction bag was installed against run number. The initial results gave an NO_2 photolysis rate of 0.32 min^{-1} in the center position, which was within the desired specifications of the system as discussed in Section II. The light intensity was ~20% lower when measured in the reaction bag, averaging 0.256 ± 0.012 min^{-1}. The measurement using the steady state method, which consists of simultaneously monitoring NO, NO_2, and O_3 and deriving k_1 using the photostationary state relationship (Carter et al., 1994a), agreed with the results of the quartz tube measurements to within the variability of the determination. The later actinometry experiments tended to indicate a slight decrease in light intensity with time, though one experiment, XTC119, had a light intensity which was slightly higher than the initially measured values.

A more precise indication of the relative changes in the light intensity was obtained from the Li-1800 spectral measurements made during the course of the experimental runs. Usually at least three such measurements were during each run. The spectroradiometer was in the same location during all the runs, so the measured spectral intensities give a good indication of the relative light intensities during the run. These spectral intensities can be converted to quantities proportional to NO_2 photolysis rates by integrating the products of these intensities with the NO_2 absorption cross sections and quantum yields. These NO_2 photolysis rates are then placed on an absolute basis using the results of the quartz tube or steady state actinometry experiments. This was done by fitting the Li-1800-calculated NO_2 photolysis rates to a linear function of the XTC run number to determine the relative change in photolysis rate with time, and by using a constant factor adjusted to minimize the difference between the Li-1800-calculated values and the results of the absolute actinometry determinations. The apparently anomalous run XTC119 was not used in determining this factor. The resulting adjusted Li-1800-calculated photolysis rates are shown on Figure 28, where it can be seen that they agree well with the trend indicated by the actinometry

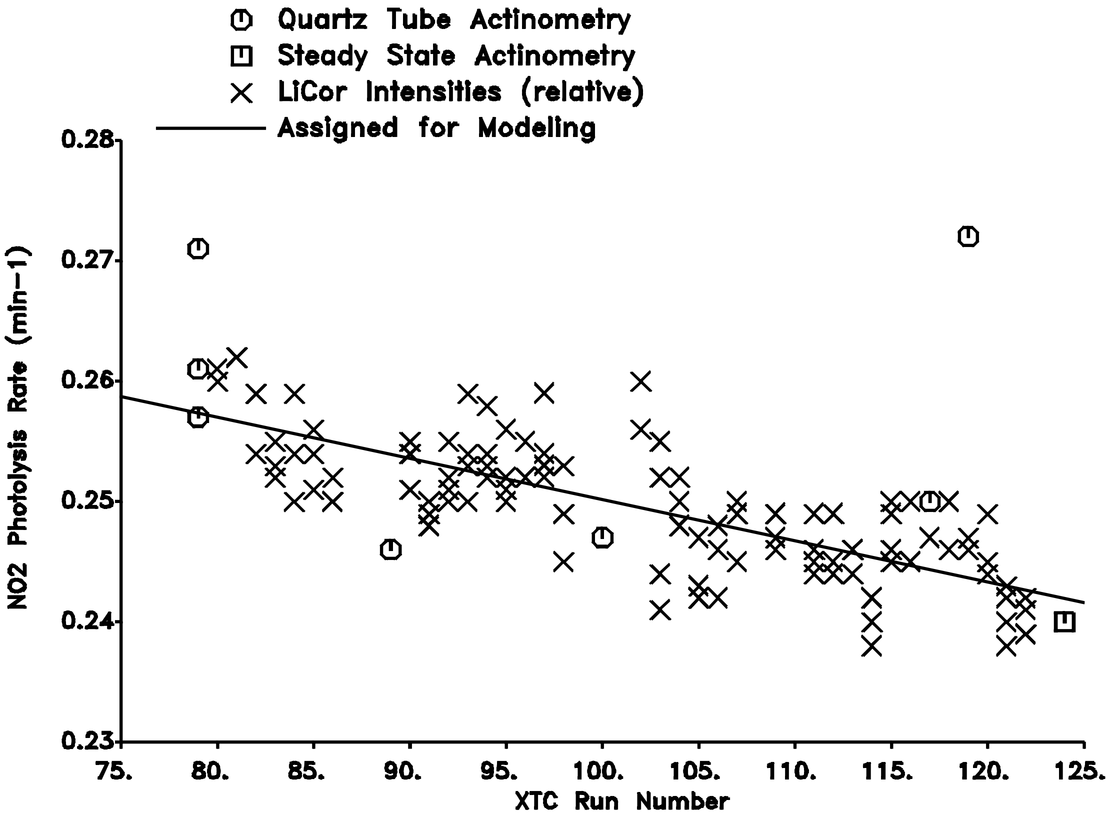

Figure 28. Plots of NO_2 photolysis rates in the XTC chamber against run number.

results, except for the apparently anomalous run XTC119, whose result was high by ~10%. These data indicate a ~6% decline in the NO_2 photolysis rate during the course of these experiments.

The NO_2 photolysis rate used for modeling the XTC runs was derived from the linear fit to the Li-1800-calculated photolysis rates, adjusted to agree with the actinometry results as indicated above. The line used for these assignments is also shown on Figure 28. This line was used to derive the k_1 assignments for the individual runs, which are included in the run data sets and are listed in the "XTC-MISC" spreadsheet. The details of the actinometry data and assignments are in the "XTC-K1" spreadsheet.

5.3.2. XTC Light Uniformity

The uniformity of the light intensity in the XTC was measured on two different occasions. When the chamber was first constructed, the NO_2 photolysis rate was measured with the quartz tube in central, upper, and lower position in the area where the reaction bag was to be located. The results, given in

Floor Level (22")

	-4%	-4%
	-3%	-1%
	6%	6%

(lights)

Mid Level (43")

(window)

-6%	-12%	-5%
0%	-1%	3%
8%	11%	10%

(lights)

Upper Level (65")

3%	2%	2%
7%	7%	7%
10%	12%	9%

(lights)

Figure 29. Summary of results of light uniformity measurements in the XTC. Values shown are the percentages by which the NO_2 photolysis rates in various locations differ from the average for all locations.

Table 23, indicate a ~2% higher intensity in the upper position and a ~3% lower intensity in the lower position. A more extensive series of relative light intensity measurements in the XTC chamber area was made several months after the last experiment for this program, after the reaction bag was removed. The results of these light uniformity measurements are given in Figure 29, which shows the NO_2 photolysis rates, relative to the average, in 24 locations in the chamber enclosure. The results show that the light uniformity is within ±12% of the average, with the highest intensities being in the center and upper level on the side closest to the lights, and the lowest intensities being immediately in front of the sampling window.

5.3.3 XTC Light Spectrum

Spectra of the XTC light source were taken using the SAPRC LiCor spectroradiometer at least three times during each experiment. There was no significant change in spectrum during an experiment, though the spectra did change somewhat during the course of the XTC experiments in this data set. Representative plots of XTC light spectra compared to the solar spectra are shown on Figure 30, where they are compared with solar spectra for zenith angles of 0° and 60°, respectively. The spectra shown are all normalized to give the same NO_2 photolysis rate. As discussed above, the intensity of the XTC lights were found to decline gradually with time during the course of the experiments for this program. Figure 31A, which shows a plot of the ratio of an XTC spectrum taken around the end of the program to one taken initially, shows that the extent of the decline was highly wavelength-dependent. The decrease in intensity can be seen to be minor for wavelengths above 400 nm, but becomes increasingly important for wavelengths lower than that. This is probably due to solarization of the pyrex filters, which were not changed during the course of the program. The manufacturer recommends changing the spectral filter periodically to maintain approximately constant UV intensity.

Unlike the NO_2 photolysis rate, whose decrease in intensity with time (shown on Figure 28) was approximately linear, the decline in intensity at the shortest wavelength was nonlinear, increasing more rapidly when the lights were new. This is shown on Figure 31B, which gives a plot of the absolute intensity at the shortest wavelength measured by the LiCor (300 nm) against XTC run number. Thus the spectrum, if not the overall intensity, tends to become more stable as the lamps age.

The LiCor spectra measured during the XTC runs are stored on the runs' data sets with the names "Sd-hhmm", where "hhmm" gives the clock time when the spectrum was taken. At present, we recommend that no corrections be applied to the XTC LiCor data when deriving spectral distributions for modeling, though in the future we will obtain higher resolution spectra whose use might be better for modeling than the relatively low resolution LiCor data (e.g., see Figures 22 and 26). In the meantime, the recommendation is to use the average of the spectral distributions measured during an experiment to derive the photolysis rates for modeling. This approach is used by the model simulation programs which are distributed with these data.

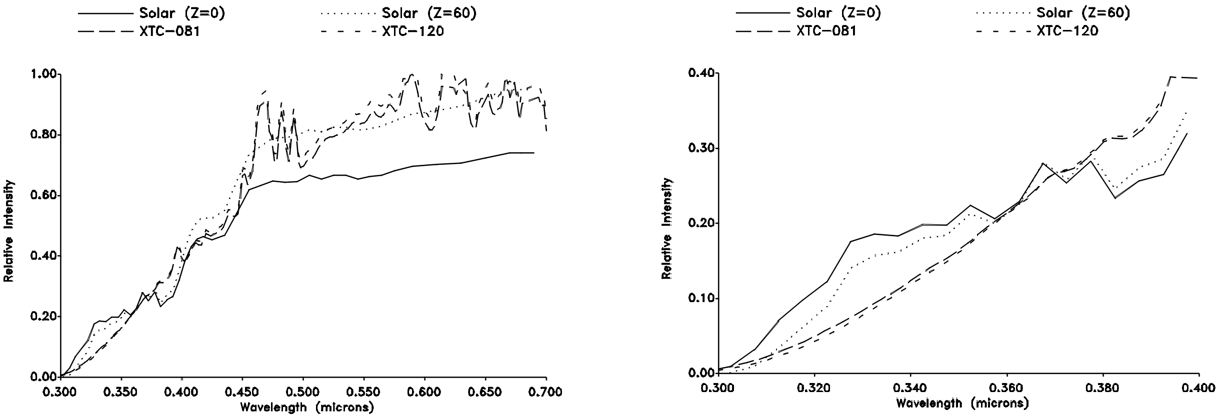

Figure 30. Representative XTC spectra compared with solar spectra for zenith angles of 0° and 60°. The spectra are all normalized to give the same NO_2 photolysis rate.

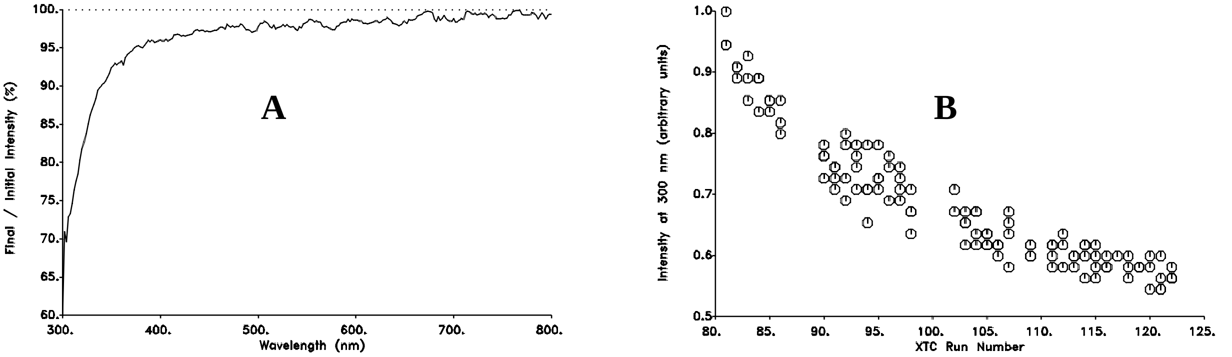

Figure 31. (A) Ratio of spectrum of run XTC120 relative to that of run XTC081 against wavelength, showing the decline of spectral intensity as a function of wavelength during the experiments for this program. (B) Plot of relative intensity at 300 nm against XTC run number.

6. CHARACTERIZATION OF OTHER CONDITIONS

Run conditions which must be characterized when modeling chamber experiments include initial reactant concentrations and reactant injections, light intensity and spectral distribution, temperature, humidity, dilution, chamber contamination effects, and heterogeneous reactions on chamber walls. The methods used to characterize reactants and light were discussed in previous sections. Information concerning the other types of characterization data are discussed in this section.

6.1 Temperature

6.1.1 General Method

Iron-Constantan thermocouples were used to monitor the temperature as a function of time in all the SAPRC chambers. In most of the EC, ITC and ETC runs, these were used in conjunction with a "Doric" temperature readout. This device converted the raw mv of the thermocouple to a voltage using an internal zero point. Two Dorics have been used. The first one had an internal switching box, the "newer" one (1980) used an external switching box. The first was used in all the earlier EC runs which do not have instrument identifications, and in the runs with temperature instrument numbers in the "18xx" series (see Table 6). In some runs, single channel devices were used, one for each chamber (Analogic). Most recently, the thermocouples were interfaced directly to the Kiethly data acquisition system using a 4-channel special board designed for use with thermocouple. These are identified with temperature instrument numbers in the "19xx" series.

6.1.2 Recommended Temperature Profiles for Modeling

The temperatures are recorded in the data sets with the same frequency as the data from the continuous monitoring instruments (e.g., O_3 and NO_x). This was usually once every 15 minutes, and sometimes as frequently as once every 5 minutes. It is probably not necessary to follow all the temperature fluctuations for model simulations, though the general trends in temperature should be represented. For modeling purposes, we derived recommended "smoothed" temperature profiles by fitting the temperature data to a series of line segments, whose end points were determined subjectively. For most indoor runs, two segments were used, one to represent the rapid temperature change (of a few degrees C) when the lights are turned on, and the other to represent the much more gradual temperature change during the run. Runs with poor temperature control, outdoor runs, or multi-day indoor runs where the lights were turned on and off, had many more temperature segments. These temperature segments are included in the data sets with the channel name "Tmodel", with the instrument ID the same as that for the temperature channel used to derive it.

If it was judged appropriate to make corrections to the temperature data, these corrections were made to the "Tmodel" channel, but not the original temperature channel. This was the case in all the EC runs and some of the XTC runs. In those cases, the data in the "Tmodel" channel will be offset from the detailed temperature data channel. The corrections made are discussed below for the specific chambers.

6.1.3 Calibrations

No logbooks were maintained for the temperature instruments. The calibration binder shows a calibration of an iron-constantan thermocouple (conducted 8/3/76) and a "digital thermocouple calibration" (unknown in date). The latter is probably the Doric and compares digital deg F with "true" degrees C. It is not clear how "true" temperatures were measured. The digital numbers are consistently 1.5 degrees C higher than "true". A search of EC logbooks for the periods of interests (EC books 6-13) shows only one calibration. This was done on 5/2/77 for the "newer" and "other" Dorics. The "other" Doric was probably the one reported in the data. The zero points were adjust approximately 2 degrees F lower for both. Both were then calibrated with an ambient air temperature water bath against a "large" thermometer. The "large" thermometer is most likely one that was traceable to the NBS (now NIST). The older Doric read the same as the NIST thermometer to the nearest tenth of a degree after the zero correction. Spot checking the raw and final data showed that no temperature correction was applied prior to the change of the zero point. It seems that the previous data should be corrected downward by 2° F. This is also consistent with the data in the calibration binder.

In view of this, the "Tmodel" temperature profiles recommended for modeling the EC runs carried out prior to 5/2/77 (i.e, run EC217 and those previous) were corrected downwards by 2° F (1.1° K). (The correction was not applied to the regular temperature channel.) This does not affect runs in the data base from the other chambers, which were carried out after this date.

The temperature probe used in the ETC runs, the three temperature probes used in the DTC and XTC runs (instruments 193x, 194x, and 195x) and the three temperature probes used in the 1992 OTC runs (instruments 190x, 191x, and 192x) were calibrated against a NIST thermometer in June 1993. This was accomplished by immersing both temperature probes into a water container. The temperature was then increased gradually by heating the water in the container using a heat gun and monitored by both instruments. Both instruments were allowed to equilibrate before any readings were recorded. Several readings were recorded at the same temperature level. The readings for the indicator being calibrated were obtained from the printout of the data system and the data for the NIST indicator were obtained from reading the thermometer directly. The data were fit by equations of the form: Corrected temperature (°C) = Slope x [Readout temperature (°C)] + intercept, where the slopes and intercepts were as follows:

Chamber	Instrument ID	Slope	Intercept	
ETC	1800		1.018	-0.41
DTC, XTC	193x	1.005	-0.39	
DTC, XTC	194x	1.005	-0.41	
DTC, XTC	195x	1.019	-0.72	
OTC (1992)	190x	1.007	-0.325	
OTC (1992)	191x	1.006	-0.337	
OTC (1992)	192x	1.010	-0.287	

(The instrument ID for the ETC runs will be established when these runs are added to the data base.) The ETC, DTC, XTC and applicable OTC temperature data have been corrected accordingly.

6.1.4 Evacuable Chamber

The temperature monitoring for the EC runs is discussed by Pitts et al. (1979). The thermocouple runs was located in a glass probe in dark space at the end of the chamber opposite the solar simulator. The Doric Model DS-350 temperature readout was stated to have an accuracy of ± 2° F. As discussed by Pitts et al. (1979) tests for radiative heating were carried out by closing the shutter of the solar simulator, and noting the immediate temperature change. These tests indicated radiative heating of 2° F. The Tmodel profiles have been reduced by this amount.

6.1.5 Blacklight Chambers

The temperature was monitored in essentially the same way for all the blacklight chamber experiments in the present data base. An unshielded thermocouple probe was located approximately twelve inches into the chamber, near the center of the chamber wall. Subsequent comparison of temperatures monitored with this method with simultaneous readings using an aspirated temperature probe (discussed below) indicate that there is a slight but non-negligible radiative heating of the unshielded thermocouple probe. Tests as a function of light intensity indicate that data taken using this method should be corrected by

$$T^{corr}\ (°C) \approx T^{unshielded\ probe} - k_1 \text{ x } 2$$

where k_1 is the NO_2 photolysis rate in min^{-1}. The typical k_1 in a blacklight chamber experiment is ~0.3 min^{-1}, which yields a correction of -0.6° C. This correction was applied to all blacklight chamber runs where this method was used.

6.1.6 Xenon Teflon Chamber

For the XTC runs after run XTC091, the temperature was monitored with the thermocouple inside an opaque 1/4" OD sample line inside the chamber, with air being drawn through at a rate of 2 l/min. This is referred to as the aspirated temperature probe. Provided that the flow rate past the sensor is sufficient, this method is considered to give the more accurate temperature reading. Tests showed that a flow rate of be at least 2 l/min was required for the measured temperature to be independent of the flow. Therefore, for runs after XTC091, the Tmodel values given in the run files were derived from the measured temperatures without correction.

Reliable temperature data are not available for XTC runs prior to XTC092. For these runs (as well as subsequent runs) the temperature was monitored using a thermocouple inside the chamber shielded by a piece of reflective aluminum. During that period temperature probes were also located in the formaldehyde and NO_x/O_3 sampling lines, but these data were not considered to be as reliable because the sensors were outside the chamber. (The last digit in the temperature instrument number in the data set indicates the location of the probe.) Although the temperature readings in the sample lines were higher than the temperature in the laboratory, they tended to decrease with time during the run, while the probes inside the chamber indicated that the temperature was increasing slightly.

A comparison of data from the aspirated and unaspirated probes indicated that the latter had to be corrected by -6.5°C. However, if this correction was made for the earlier runs where only the unaspirated probe was used, the average temperature in the experiments was found to be significantly lower than the subsequent experiments where the more reliable method was used. Since there was no reason to believe the temperature range was different in the earlier runs, we have decided to reject all temperature data for these runs. For modeling purposes, we recommend using the average temperature measured in the subsequent runs, which is 301.6±0.8°K. (The standard deviation refers to the average of the run averages, not the averages of all the measurements.) Therefore the run files for XTC081-XTC091 give Tmodel with a constant value of 301.6°K. (This neglects variations of temperature with time; if the modeler wishes to incorporate this, the recommended procedure would be to derive an average time profile from all the data.) Since the temperature was found to be relatively consistent from run to run in this chamber, the estimates for the temperatures in the earlier runs are unlikely to be in error by more than ~2°K.

6.1.7 Outdoor Teflon Chamber

Prior to run OTC-254 (June 1992), temperature was monitored using a Doric Model DS 350-T3 digital iron-constant thermocouple indicator. This thermocouple was installed in each manifold sample port so the air temperature was measured immediately as it flowed out of the chamber. This instrument was calibrated periodically using ice water as the source for 0°C and boiling water as the source for 100°C.

For the runs in 1992 (run OTC-254 to OTC 270), temperature was monitored using three unshielded thermocouple, each in a different location, and each interfaced to the Kiethly data acquisition system. One (defined as instrument 1909) was used to monitor ambient temperature, one (instrument 1913) was located in one of the reaction bags, and one (instrument 1925) was located in a "T" in one of the sample lines. The data for the first two may be designated in the data sets as being associated with a particular run side, though actually they should be associated equally with both sides. The "instrument 1925" data are recommended for use when modeling, though a correction may be appropriate because the "T" was not shielded from sunlight. However, no correction was made. For some of these runs, there is also data for the sample line probe for times when there was no flow rate in that line; the data for those times (designated as instrument 1928) should not be used.

For the runs in 1993 (OTC-272 through OTC-318), there was a temperature probe in a shielded "T" in the sample line for each bag side, located immediately adjacent to the bag. It is believed that a temperature correction is probably not necessary in this case. The ambient temperature probe was the same as in the 1992 runs.

6.2 Humidity

6.2.1 EC and ITC Runs

Except as noted differently in the run spreadsheets, most EC and ITC runs were carried out at approximately 50% RH. As discussed in Section 3.1.3, the SAPRC air purification system which serves these chambers allows for the humidity to be controlled by combining a dry air stream direct from the purifier with a "wet" stream from the purifier which was saturated in a spray tower with heated distilled water. For the EC runs prior to ~EC400, the humidity was monitored using a wet-bulb/dry-bulb thermometer in the air stream immediately before it entered into the chamber and was noted in the log book.

The average measured humidity for the EC runs which were intended to be 50% RH was 50 ± 4%, with the minimum and maximum being 39 and 63%, respectively. This indicates a highly consistent humidity of the output of the pure air system when it was set to achieve the desired 50% RH in the EC. Humidity was not consistently measured for the later EC runs in this data base. However, given the given the consistency of the output of the humidified pure air system when 50% RH in the EC was desired, we believe the humidity in runs that the logbook indicates as using humidified air can be assumed to be reasonably close to ±50%, with an uncertainty of no more than ± 10% RH.

A few EC runs were carried out with "dry" air, which consisted of the unhumidified output from the pure air system. Humidity measurements during such runs ranged from 4 - 7%, with the average being 6 ± 1% RH. No ITC runs in the data base had notation in the log books as having a "dry" fill, so all ITC runs were assumed to be 50% RH.

The run spreadsheets have the humidity information available for these runs, as well as the corresponding calculated H_2O concentration. The average H_2O concentration for the appropriate type of run (whether ~50% RH nominal or ~5% RH nominal) is recommended for modeling purposes for those runs where no humidity data are available.

The earlier EC runs also have humidity data from a "Brady Array" (Thunder Scientific) mounted in a bulkhead fitting. The calibration curve supplied by the manufacturer was used. As discussed by Pitts et al. (1979), variations were observed in the readings from this instrument during a run which cannot be accounted for by variations in temperature. The EC run spreadsheet has initial humidities measured by this instrument, and the run data sets have the values as a function of time. As can be seen in the EC run spreadsheet, the run-to-run variation in humidity measured by this instrument is significantly greater than the humidity as measured by the wet/dry bulb thermometers. In view of this, and the recommendation of Pitts et al. (1979), we recommend that the humidities used for modeling be based on the wet/dry bulb data as discussed above.

Humidity was measured on an intermittent basis in the ITC, with the results being somewhat more variable than with the EC. The average RH was 62 ± 10%. However, the results were less variable when expressed in terms of H_2O concentration, which averaged $1.85 \pm 0.17 \times 10^4$ ppm (after excluding ITC975 and ITC1005, which were unusually wet or dry, respectively). This H_2O concentration is recommended for modeling runs where no humidity data were available.

6.2.2 ETC, DTC, and XTC Runs

All of the ETC and XTC runs, and all but a few of the DTC runs were carried out with the unhumidified output of the AADCO air purification system. Humidity measurements were not made for most of these experiments. For the ETC runs prior to ETC323 the air purification system was the same as used in the EC runs, for which the measured RH averaged 6 ± 1% when unhumidified air was used. The ETC runs after ETC322 and all the DTC and XTC runs used unhumidified air directly from the AADCO air purification system. The few humidity measurements of the AADCO output indicated a humidity of ~5%, comparable to the unhumidified output of the system used with the EC and ITC. Based on this, we recommend using a default RH of 5% when modeling runs using these chambers, unless information is available to the contrary. The run spreadsheets give the recommended humidities for each run.

6.3 Dilution

6.3.1 Evacuable Chamber

Dilution of the chamber contents due to sampling is expected to be non-negligible in the EC because of its rigid structure. Before EC197, makeup air was supplied using laboratory air filtered with a canister containing purafil, charcoal, and drierite, and after than the makeup air was supplied using a Teflon bag which was filled at the same time the chamber was filled. For runs up to EC407, the sampling rates for the instruments were monitored periodically, and the total sampling rate for each run was entered into the run's data set. This information is also summarized in the EC run spreadsheet. Except for run EC231, where the chamber was accidently diluted with N_2 during the run, the average sampling rate for these EC runs was 1.75 ± 0.21 liters/minute. (The sampling rates for the individual runs for which this information is available are in the "EC-MISC" spreadsheet in the "Samp Rate" column.) For a measured chamber volume of 5774 liters (Pitts et al, 1979), this yields a dilution rate of 1.8 ± 0.2 %/hour. This is recommended for use when modeling the EC runs where sampling data are not available.

6.3.2 Teflon Bag Chambers

For the other chambers, the flexible design of the reaction bag, in principle at least, allows samples to be taken without the need for adding replacement air. Some dilution may occur from time to time due to leaks. For most modeling applications, the dilution in these chambers (with the possible exception of the DTC, discussed below) can probably be neglected. If more accurate representation of dilution is important, the recommended procedure when modeling these chamber runs is to estimate dilution rates based on rates of decay of slowly reacting species, after correcting for their reaction with OH radicals, as discussed by Carter et al. (1993a). If a run has two species, A, and B, which react only with OH radicals with known rate constants of k_A and k_B, where $k_A \neq k_B$, then the dilutions can be obtained from the slope of plots of the equation

$$\frac{k_A \ln\left(\frac{[A]_0}{[A]_t}\right) - k_B \ln\left(\frac{[B]_0}{[B]_t}\right)}{k_A - k_B} = D\ t \qquad \text{(IV)}$$

where $[A]_0$, $[B]_0$, $[A]_t$ and $[B_t$ are the measured concentrations of species A and B at the start of the experiment and at time t, respectively. This derivation requires runs where two suitable species, one fairly reactive and one fairly unreactive, are present together, and where at least the less reactive species is monitored with a reasonably high degree of precision.

Equation (IV) can only be used to derive dilution information if species A and B are monitored at the same time. For many runs, particularly in the DTC and XTC, the slowly and rapidly reacting VOCs were monitored at different times using different instruments, so Equation (IV) could not be used. In these cases, an alternative method can be employed, if it is assumed that the OH radical concentration is approximately constant. If this is assumed, then

$$D \approx \frac{k_A \mathrm{slope}(\ln\left(\frac{[A]_0}{[A]_t}\right) \text{ vs } t) - k_B \mathrm{slope}(\ln\left(\frac{[B]_0}{[B]_t}\right) \text{ vs } t)}{k_A - k_B} \qquad \text{(V)}$$

Although use of Equation (IV) is preferred because it is valid even if [OH] varies with time, Equation (V) can be used to estimate dilution in experiments where species are monitored at different times. This is referred to in the applicable spreadsheets as the "constant OH method".

The results of our analyses of dilution information for specific teflon chambers are summarized below.

<u>ITC</u>. Dilution is expected to be negligible in the ITC because of its relatively large volume and the fact that it is designed to allow one side to readily collapse as samples are withdrawn, or if leaks occur (see Figure 2 in Section 3.1.2). We have assumed dilution in this chamber in our previous mechanism evaluation studies using this chamber (Carter et al., 1986b, Carter and Lurmann, 1990, 1991), and spot checks of simulations of slowly reacting species tend to support this assumption. However, we have not carried out a detailed analysis of ITC runs using Equation (IV), and the modeler may wish to examine this if it is suspected that dilution may be an important factor in the application being considered.

<u>ETC</u>. The results of dilution analyses of the ETC runs using Equation (III) are given in the spreadsheet "ETC-MISC". In the case of runs ETC047 through ETC419, where most experiments contained n-hexane and m-xylene, the dilution rate was found to be 0.48 ± 0.25 %/hour (Carter et al., 1993a). This is a negligible dilution rate for most types of mechanism evaluation applications. In the absence of a more detailed evaluation by the modeler, we recommend using this average value when simulating ETC runs. This is given in the chamber characterization model input (.CHR) files distributed with these data. Dilution assignments are not included in the run files for the individual ETC runs.

<u>DTC</u>. The spreadsheet "DTC-DIL" gives the results of our analyses of dilution in the DTC experiments. Analyses were carried out using both Equation (IV) and (V), though use of results from the former is preferred where the data permit it. The "use" columns in the spreadsheet indicate the dilution values assigned for the individual experiments. The average dilution in all the DTC runs was 0.5±1.0 %/hour. The relatively high variability in the apparent dilution in this chamber can be attributed to leakage of the mixing system used to exchange reactants between the chamber sides (unpublished results from this laboratory).

Because of the variability in dilution in the DTC runs, dilution assignments were made for all DTC runs in the present data base. These are included in the individual files as "Model_Input (s): Dilution" comment records, where "s" is the side number. (The RCHADINP program used to create modeling input files read these comments to provide the run-specific dilutions; these override any dilution values given in the chamber characterization [.CHR] files.) For DTC runs without dilution information, the dilution rates were estimated based on data from the other DTC experiments in the same chamber side. These analyses, along with the estimated uncertainties of the DTC dilution assignments, are in the "DTC-DIL" spreadsheet.

<u>XTC</u>. The spreadsheet "XTC-DIL" gives results of our analysis of dilution in the XTC experiments. Analyses were carried out using both methods, and recommended dilutions are given for each experiments (in the "use" "value" column). For the few experiments with no dilution information, the average dilution, excluding the experiments with anomalously high values, are used. Uncertainty estimates are also given for the assigned dilutions. A few runs have high dilutions because of known

leaks in the chamber, so those high values should be used when modeling. The dilution estimates are included in the individual files as "Model_Input: Dilution" comment records.

6.4 Wall and Contaminant Effects Characterization Data

Modeling environmental chamber experiments also requires an appropriate representation of wall and contaminant effects. These include heterogeneous reactions on the walls, wall adsorption of reactants, contaminant offgasing, and contamination of injected NO_x with HONO. The development of methods to represent these effects is primarily the responsibility of the modeler, and a detailed discussion of this is beyond the scope of this document. However, to assist the user of these data, we summarize here the information and assumptions we have used when modeling experiments in this chamber in our recent report on the effect of chamber and light source on mechanism evaluation results (Carter et al., 1994a). We should emphasize, however, that we expect to re-evaluate these parameters again as part of our own mechanism evaluation process, and that the wall effects model and parameters given in this section are given primarily to provide the modeler with a starting point in this effort.

Table 24 shows the reactions and the parameterization approach in the wall effects when evaluating the RADM2 (Carter and Lurmann, 1990) and the SAPRC-90 (Carter and Lurmann, 1991) mechanisms, which was also employed in our recent chamber and light source effects study (Carter et al., 1994a). The parameters shown in the table must be specified when modeling a chamber run, and in general are chamber-dependent. The values of these parameters, which we used in our chamber and light source effects modeling study are given in Table 25. Except for the treatment of the continuous chamber radical source, which is discussed in more detail in the following section, the principles and assumptions behind this wall model and the derivations of these parameters for previously modeled runs are primarily as discussed in detail by Carter and Lurmann (1990). Since that paper is in the open literature, that discussion is not duplicated here. Major changes were made to the radical source assignments for the ITC and (to a lesser extent) the EC, and the radical source assignments for these and the other chambers are discussed below. Some updates to the other chamber and wall effects parameters were also made subsequent to those of Carter and Lurmann (1991), and assignments of values to these parameters had to be assigned for the new experiments not modeled by Carter and Lurmann (1991). Brief discussions of the basis for the estimates of those parameters are summarized in the rightmost column of Table 25.

Table 24. Reactions and parameters used to represent chamber wall processes and contaminant effects during the evaluation of the RADM2 and the SAPRC-90 mechanisms. See Carter and Lurmann (1990, 1992) for a detailed discussion.

Rate Constant or Parameter [a]	Process or Meaning of Parameter [b]
	Dark Wall Reactions
k(O3W)	O_3 = (loss of O_3)
k(N25I)	N_2O_5 = (wall NO_x)
k(N25S)	N_2O_5 + H_2O = (wall NO_x)
k(NAW)	HNO_3 = (wall NO_x)
k(NO2W)	NO_2 = #y_{HONO} HONO + #1-y_{HONO} (wall NO_x)
k(NONO2W)	NO + NO_2 + H2O = #2 HONO
	Represents Contaminant Offgasing effects
k(XSHC)	HO. = HO_2.
	Light Induced Wall Reactions
RS-I x k_1	HV = HO.
RS-S x k_1	NO_2 + HV = #.5 HONO + #.5 (wall NO_x)
E-NO2 x k_1	HV = NO_2 + #-1 (wall NO_x)
E-HOHO x k_1	HV = HONO + #-1 (wall NO_x)
	Parameters
y_{HONO}	HONO yield in NO_2 hydrolysis reaction
f_{HONO}	Fraction of initial NO_2 converted to initial HONO

[a] If a reaction is shown in the right column, the parameter, or the parameter multiplied by k_1, is the rate constant for the reaction. k_1 is the NO_2 photolysis rate.

[b] "#" used to indicate product coefficient.

Table 25. Recommended values for chamber wall and contaminant effects parameters to use as a starting point when modeling runs in this data base.

Parm.[a]	Cham.[b]	Set[b]	Value(s)	Discussion
k(O3W)	EC	all	$1.1\text{x}10^{-3}$ min^{-1}	Ozone decay rates in humidified air (the condition of most of the EC runs) in different EC experiments reported by Pitts et al. (1979) were 1.6, 2.7, 0.7, and 1.0 x 10^{-3} min^{-1}. The recommended value is the average of these, with the high value excluded.
	ITC	all	$1.5\text{x}10^{-4}$ min^{-1}	The results of the O_3 dark decay rate experiments in the ITC (in units of 10^{-4} min^{-1}) are: Bag 5: ITC624 = 2.0, ITC641 = 0.56±0.10; Bag 6: ITC697 = 1.9; Bag 7: ITC823 = 1.65±0.06. The recommended value is the average of these.
	ETC	1,2	$1.50\text{x}10^{-4}$ min^{-1}	ITC default used. Consistent with limited O_3 decay data in the first ETC reactor.
	ETC	3	$1.22\text{x}10^{-4}$ min^{-1}	Based on O_3 decay runs ETC410, ETC456 in this reaction bag.
	OTC	all	$1.67\text{x}10^{-4}$ min^{-1}	As used by Carter and Lurmann (1990, 1991) for previous SAPRC OTC runs.
	DTC, XTC	all all	$1.5\text{x}10^{-4}$ min^{-1}	Limited data available indicate that value used for ITC is not inappropriate.
k(N25I), k(N25S)	EC	all all	$4.65\text{x}10^{-3}$ min^{-1}, $2.22\text{x}10^{-6}\text{-}k_g$ ppm^{-1} min-1	Based on the N_2O_5 decay rate measurements in the EC reported by Tuazon et al. (1983). k_g is the rate constant for the gas-phase N_2O_5 reaction in the mechanism being evaluated.
	All TC	all	$2.8\ \text{x}10^{-3}$ min^{-1}, $1.5\text{x}10^{-6}\text{-}k_g$	Based on the N_2O_5 decay rate measurements in the ETC reported by Tuazon et al. (1983). Although we previously estimated there rate constants were lower in the larger Teflon bag chambers (Carter and Lurmann, 1990, 1991), we now consider it more reasonable to use the same rate constants for all such chambers.
k(NO2W), y_{HONO}	EC	all	$2.8\text{x}10^{-4}$ min^{-1} 0.5	Based on dark NO_2 decay and HONO formation measured in the EC by Pitts et al. (1984).
	all-TC	all	$1.6\text{x}10^{-4}$ min^{-1} 0.2	Based on dark NO_2 decay and HONO formation measured in the ETC by Pitts et al. (1984). Assumed to be the same in all Teflon bag chambers, (see discussion of N25I,N25S).
k(NONO2W)	all	all	0.0	Assumed to be zero based on the fact that Pitts et al. (1994) observe no effect of NO on dark HONO formation, and the fact that Carter et al. (1982) observe no effect of NO on the chamber radical source.
k(XSHC)	EC	0.0		This has been assumed to be negligible in previous model evaluations using EC runs (Carter and Lurmann, 1990, 1991). Can be estimated by modeling NO_x-air runs where CO is measured. (Not an important parameter affecting model predictions except for pure air or NO_x-air runs.)
	all-TC	250 min^{-1}		As given by Carter et al. (1994). Estimated by modeling several ITC pure air irradiations. Consistent with simulations of pure air runs in the ETC. (Not an important parameter affecting model predictions except for pure air or NO_x-air runs.)
RS-I, RS-S	EC	1	0.293 ppb $1.62\text{x}10^{-3}$	Based on re-evaluation of Carter et al. (1994a); see also Section 6.5.1. Standard assignment used in previous mechanism evaluations were adjusted downward by 25%.

Table 25 (continued)

Parm.[a]	Cham.[b]	Set[b]	Value(s)	Discussion
RS-I, RS-S (cont'd)	ITC	all	0.08 ppb 0	Based on re-evaluation of Carter et al. (1994a); see also Section 6.5.1. Derived by modeling n-butane - NO_x experiments. Significantly lower than previous assignments which were derived from tracer - NO_x - air experiments as discussed by Carter et al. (1982).
	DTC	2	0.08 ppb 0	Assumed to be the same as in the ITC, where 50% air was also used. Tracer - NO_x run DTC061 are fit by a much higher radical source, which is analogous to the situation with the ITC. See Carter et al. (1994a).
	ETC DTC XTC	all 1 all	3.70×10^{9} $e^{-18.99/RT}$ ppb, 0	Based on evaluation of Carter et al. (1995a); see also Section 6.5.2. R=0.0019872 kcal $°K^{-1}$ mol^{-1}, and T is the temperature in °K. Derived based on modeling n-butane - NO_x - air irradiations in the DTC, XTC, and OTC. Temperature dependence is necessary to fit the OTC experiments.
E-NO2	EC	all	0.5 ppb	Fits PAN yields in acetaldehyde-air run EC253. We recommend that this assignment be re-evaluated.
	ITC	all	0.15 ppb	Reasonably consistent with model simulations of acetaldehyde - air runs in the ITC and OTC (Carter and Lurmann, 1991). We recommend that this assignment be re-evaluated..
	ETC	1	0.11 ppb	Based on simulations of acetaldehyde - air run ETC019. Within the range of variability of values which fit modeling of pure air runs.
	ETC	2	0.03 ppb	Based on simulations of acetaldehyde - air run ETC319. Within the range of variability of values which fit modeling of pure air runs.
	ETC	3	0.04 ppb	Based on model simulations of acetaldehyde - air runs in this bag.
	DTC	all	0.03 ppb	Based on model simulations of pure air run DTC049. Consistent with ETC value.
	XTC	all	0.03 ppb	Assumed to be the same as used for ETC (bag1) and DTC runs.
f_{HONO}	EC	1	0.07	Based on simulations of 50% RH NO_x-air runs in the EC reported by Carter et al. (1982) and as used by Carter and Lurmann (1990, 1991). Based on analysis of tracer - NO_x runs in the EC. We recommend that this be re-evaluated. May be important in simulations of some runs.
	ITC	all	0	As used in the mechanism evaluations of Carter and Lurmann (1990, 1991). Based primarily on modeling tracer - NO_x experiments. Somewhat uncertain, since modeling subsequent ETC experiments using similar NO_x injection methods indicated significant initial HONO (Carter et al., 1993a).
	ETC	1	0.015	Based on model simulations of tracer-NO_x and experiments. Attributed to HONO contamination in the injected NO_x.
	ETC, DTC, XTC	2,3 all all	0	All these experiments employed NO_x injection procedures designed to remove HONO contamination. Model simulations of runs discussed by Carter et al. (1993a) indicated that this procedure successfully removes HONO.

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[a] See Table 24 for definition of parameters

[b] All-TC refers to all teflon chambers. "Set" refers to characterization set.

6.5 Chamber Radical Source Assignments

One of the most important chamber effects parameters which can effect mechanism evaluations is the chamber radical source. Because of the sensitivity of simulations of chamber runs to this parameter, an inappropriate radical source assignment is probably the most likely source of compensating errors when evaluating mechanisms using chamber data. As part of our recent study on the effects of chamber and light source on mechanism evaluation results, we re-assessed the previous EC and ITC radical source assignments of Carter and Lurmann (1991), and used an integrated approach to assign radical source parameters for all teflon chambers, which is applicable to the ETC, DTC, and XTC. Because the report of Carter et al. (1994a) may not be readily available in the open literature, we include below selected relevant discussions of the chamber radical source assignments given in that report.

As indicated on Table 24, the chamber-dependent radical sources are represented in the model by the following two parameterized "reactions":

$$\text{walls} \rightarrow \text{OH} \qquad \text{Rate} = \text{RS-I} \times k_1$$

$$\text{walls} + NO_2 \rightarrow \text{OH} + (NO_x \text{ on walls}) \qquad \text{Rate} = \text{RS-S} \times k_1 \times [NO_2]$$

where k_1 is the NO_2 photolysis rate and RS-I and RS-S are the NO_x-independent and NO_x-dependent radical source parameters. The values for these two parameters are adjusted for the particular chamber and chamber conditions as discussed below.

In our previous evaluations of the SAPRC-90 (Carter and Lurmann, 1991) and the RADM-2 (Carter and Lurmann 1990) mechanisms, the magnitudes RS-I and RS-S were derived using analyses of radical tracer - NO_x - air runs as described by Carter et al. (1982). These analyses involve computing the OH radical concentration from decay rates of trace levels of propene or isobutene in NO_x - air irradiations, and assuming that the major radical sink is the reaction of OH with NO_2, and thus equating the magnitude to the radical source to the rate of that reaction. These analyses indicated that the radical source in the EC tended to increase with temperature and humidity, but for the temperature and humidity range of most experiments, RS-I = 0.39 ppb and RS-S 2.16×10^{-3}. Experiments in the ITC indicated no discernable NO_2 dependence in that chamber, so RS-S = 0 was assumed when modeling all experiments in the ITC and other Teflon bag experiments. The value of RS-I indicated by the analyses of the tracer - NO_x runs was found to vary with the reaction bag employed, ranging from 0.15 to 0.6 ppb (Carter and Lurmann, 1990, 1991). Simulations of tracer-NO_x and n-butane-NO_x runs in the ETC were best fit using lower radical source parameter than those used for the ITC, as would be expected since dry air is used in the ETC while the ITC runs used humidified (~50% RH) air. In our previous model simulations of ETC runs (Carter et al., 1993a), a low RS-I value of only 0.02 ppb was used in the simulations of the experiments after ETC-90 (where the NO_2 injection procedure was modified to eliminate HONO contamination in the NO source). This was based on simulations of a single tracer - NO_x experiment, but is reasonably consistent with results of other ETC experiments which are sensitive to the radical source, as discussed below.

An alternative methods for deriving the radical source are to simulate rates of NO decay and O_3 formation observed in CO - NO_x - air or alkane - NO_x -air experiments. These compounds have insignificant radical sources in their mechanisms, so the reactions causing NO oxidation and ozone formation in these systems are initiated almost entirely by radicals formed from the chamber radical source. Thus model simulations of these runs are highly sensitive to this parameter. Although use of CO - NO_x runs might be preferable because of the simpler chemistry CO, there are relatively few such runs in the SAPRC chamber data base. Also, Jeffries (private communication) has observed some evidence that there may be anomalous chamber effects involving CO in the UNC outdoor chamber — though we see no evidence for such problems in the limited number of CO runs in SAPRC chambers. N-butane - NO_x runs provides a better alternative for the SAPRC data base because there is a much larger number of such runs, and because the atmospheric chemistry of n-butane, though not as simple as that of CO, is quite well characterized (Atkinson, 1990, and references therein).

For this study, we evaluated the existing radical source assignments for the EC and ITC for consistency with the butane and CO - NO_x experiments in those chambers. Based on the results of this evaluation, we concluded that the use of the tracer - NO_x -air experiments may be giving inappropriately high radical sources, especially in the ITC, and that use of n-butane - NO_x - air is a more reliable and consistent method for deriving the radical source. This is then used as the basis for deriving the radical sources for the other chambers modeled in this study. This evaluation of the previous radical source assignments, and the new radical source assignments used in this study, are discussed below.

6.5.1. Re-Evaluation of Previous Radical Source Assignments

ITC. Model simulations carried out by Carter et al. (1994a) shows that if the radical source assignments of Carter and Lurmann (1990, 1991) are employed, the model consistently overpredicts, by 50% to more than a factor of 2, the rate of d(O_3-NO) formation in the n-butane runs. This is a definite indication of the model using too high a chamber radical source, since n-butane runs are highly sensitive to this parameter and are not considered to have an uncertain mechanism (Carter and Lurmann, 1991, and references therein). Supporting evidence that the chamber radical source in the model is high comes from the simulations of the ITC ethene and propene runs. which indicate a consistent positive bias for almost all the runs when this radical source assignment is used (Carter et al., 1994a). Although the fits to the ethene and propene runs are definitive in this regard because they are less sensitive to chamber radical sources and also have mechanism uncertainties related to radical effects, it is perhaps significant that the bias is consistent and in the same direction as indicated by the modeling of the n-butane runs.

Figure 32 shows the results of the model simulations of the ITC butane and alkene runs where the ITC radical source was adjusted downward so the model better fit the butane runs[1]. (These are the same experiments which had the positive bias in the initial simulations discussed above.) The d(O_3-NO) formation rate in the four ITC butane runs are fit reasonably well using a RS-I value of 0.08 ppb, which is from 50% to over 80% lower than the values derived from the tracer - NO_x experiments. Figure 32 shows that in addition to the model giving much better fits to the highly sensitive n-butane runs, the bias in the simulations of the ethene and propene runs is significantly reduced or eliminated. It is also appears to us to be more reasonable to use a single value for the radical source parameter when modeling all ITC runs, rather than a set which varies by up to a factor of 4 depending on the reaction bag, as was the case previously. One would not expect such a large variation among reaction bags unless contamination effects were important, in which case variation within a single bag (or old vs new) would also be expected.

Additional evidence for problems or inconsistencies with the tracer - NO_x method for deriving the radial source for the ITC comes from the several tracer -NO_x runs where ~50 ppm or more of CO was added after two hours of irradiation. Model simulations discussed by Carter et al. (1994a) show that the lower radical source which fits the n-butane runs gives the better fit to the d(O_3-NO) data in the ITC CO runs, while the higher radial source indicated by the tracer data gives the better fit to the propene tracer consumption rate.

It is unclear why the tracer - NO_x runs tend to be fit by higher radical source values than the n-butane, CO, and other runs. Dilution is not the problem, since any small amount of dilution in this chamber is corrected for in the analysis of the tracer-NO_x runs by using data from a more slowly reacting compound, usually propane or n-butane (Carter et al, 1982). There may be some heterogeneous loss process for the trace levels of propene which are affecting the results, or some background or other effects are occurring in the ITC tracer - NO_x runs which are not accounted for by the model. In any case, the results of modeling the n-butane and CO runs tend to give consistent results, and tend to be supported by the results of modeling of the large numbers of propene and ethene runs. For this reason, we conclude that modeling rates of NO consumption and O_3 formation in n-butane runs is to be a less uncertain way to derive radical input rates for Teflon chambers than analyzing or modeling tracer decay rates in NO_x - air irradiations. For this reason, modeling n-butane runs is the primary method we now recommend for deriving radical input rates.

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[1] The format for displaying model performance on this figure is as follows: The top plots show, for each of the experiments modeled, the concentration-time plots of the hourly d(O_3-NO) values, with the solid lines being the experimental data and the dotted lines being the model calculation. The quantity "d(O_3-NO)" is defined as the change [O_3]-[NO] during the course of the experiment. The bottom plots show the normalized bias of the model calculation for each of the hourly d(O_3-NO) values. Note that the "x" axis of the plots is time, with the plots for each experiment given immediately adjacent to each other.

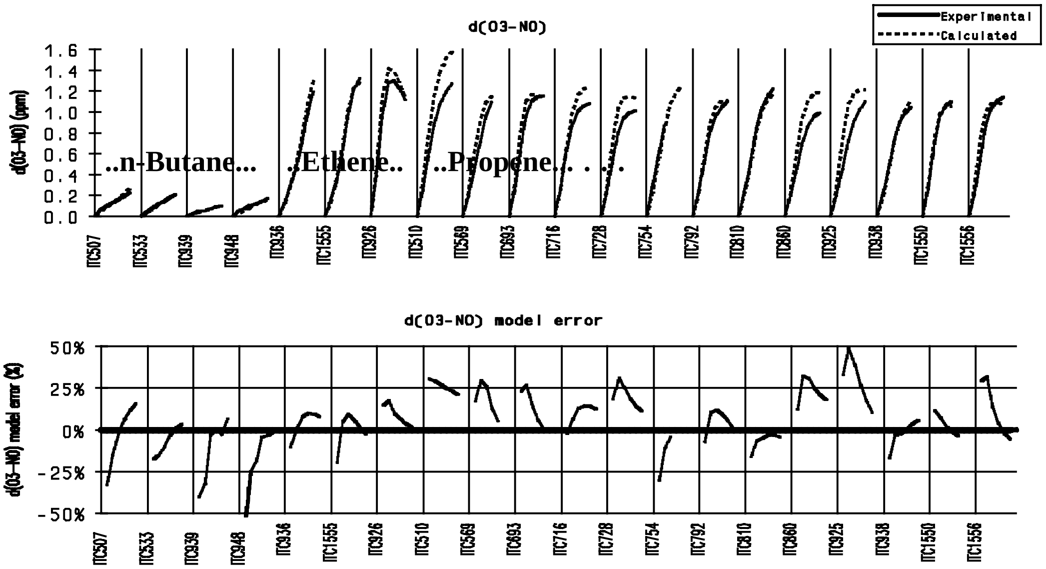

Figure 32. Results of model simulations of d(O_3-NO) of the n-butane - NO_x, ethene - NO_x and propene - NO_x experiments carried out in the SAPRC ITC, where the model used the radical source assignments adjusted to fit the n-butane runs.

EC. The plots on the left side of Figure 33 show the results of the Carter et al. (1994a) model simulations of the EC n-butane runs using the previous radical source assignments. It can be seen that, like the ITC, the model with the previous radical source assignments has a definite bias for to overpredict d(O_3-NO) in n-butane runs, though the bias is much less than is the case with the ITC. Reducing both RS-I and RS-S by 25% significantly reduces this bias, as is shown on the right hand plots, though the biases vary in the individual runs. The reduced parameter values were therefore what we currently recommend for mechanism evaluation. This relatively small change does not have a significant effect on the simulations of the alkene, aromatic, and surrogate runs discussed in the following section.

ETC. The radical source assignments used when modeling the ETC incremental experiments in the study[2] of (Carter et al., 1993) were based on model simulations of a single tracer - NO_x run. This tracer - NO_x run was fit by a relatively low RS-I of 0.2 ppb, which is a factor of 4 lower than that derived from modeling the n-butane - NO_x runs in the ITC. A lower radical source in the ETC runs is

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[2] In this discussion consider only those ETC runs carried out after the NO_x injection procedure was modified to eliminate apparent HONO contamination. Because of the apparent HONO contamination, the radical source assignments for the experiments carried out prior to that time are made separately, as indicated in Table 25. Because of the variability of initial HONO in these earlier experiments, they should be given lower priority in mechanism evaluation.

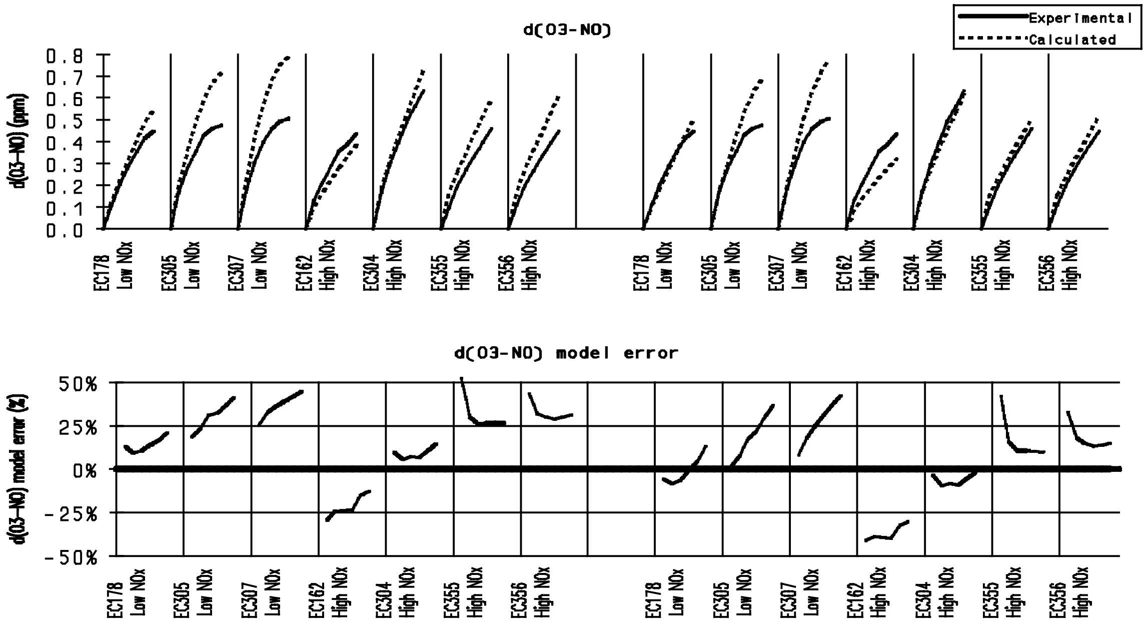

Figure 33. Results of model simulations of d(O_3-NO) in the EC n-butane - NO_x runs using the previous and the adjusted radical source assignments.

not unexpected because ETC runs were carried out dry, while all the ITC runs were humidified to 50% RH. Results of the tracer - NO_x experiments in the EC indicated that the radical source tends to increase with humidity (Carter et al, 1982). Results of model simulations of ETC n-butane experiments carried out after the NO_x injection procedure was changed indicate that, unlike the case with the ITC, the n-butane runs are fit using the tracer-derived radical source without a significant bias, indicating reasonable consistency between the tracer-NO_x and butane - NO_x data (Carter et al., 1994a). This suggests that humidity may be playing a role in the inconsistency observed with the ITC runs.

6.5.2. Radical Source Assignments for Dry Teflon Chamber Experiments

One should expect the factors affecting the chamber radical sources to be similar in the ETC, DTC, XTC, and OTC because they all have the same type of chamber surface and they are most or all experiments carried out in them used dry air. The variables which differ are the size of the chamber, the temperature (which may vary from run to run), and the light source. We would not expect the size of the chamber to be a major factor in the case of these chambers, because the DTC and ETC are comparable in volume, and although the OTC is larger, during most of the OTC experiments the reaction bag is partially deflated, and thus has comparable or even larger surface/volume than the ETC or DTC chambers. The UNC outdoor chamber, which is also constructed of FEP Teflon film, is much larger in volume than any of the SAPRC chambers, but the radical source in that chamber is comparable to or somewhat larger than that in the ITC (Carter and Lurmann, 1990, 1991). Thus the factors which need to be considered is the temperature and the light source. For reasons discussed above, we consider modeling n-butane - NO_x or CO - NO_x experiments the most reliable means for deriving the magnitude of the chamber radical source in Teflon bag experiments. Table 26 lists all the n-butane runs carried out in these chambers under conditions applicable to most of the runs in these chambers, and gives the value of the RS-I parameter which Carter et al. (1994a) found to give the best fits to the d(O_3-NO) data in each. It can be seen that the radical sources are much higher in the OTC than in the other chambers. This could be attributed to the different light source or the higher temperatures of the OTC runs (Carter et al., 1994a). However, there is no significant differences between radical sources in the DTC and the XTC runs, which have comparable temperatures but different light sources. As discussed by Carter et al. (1994a), the solar light spectrum applicable to the OTC is much more like that of the XTC than the DTC. This indicates that the nature of the light source is not an important factor affecting the chamber radical source, but that the temperature is clearly very important.

Temperature dependencies of rates of elementary reactions are generally given in terms of Arrhenius plots, where the log of the rate constant is plotted against 1/RT, where R is the gas constant. The slope then gives the activation energy of the reaction. Although the radical source is almost certainly not an elementary process, the Arrhenius relationship suggests a possible parameterization for the temperature dependence. Figure 34 shows an Arrhenius plot for the radical sources for the n-butane runs listed on Table 26. It can be seen that the Arrhenius parameterization works fairly well in predicting how the radical sources in the various chambers depend on temperature, though the radical sources in the ETC are somewhat lower than expected based on those in the DTC and XTC. The data for the DTC, XTC, and OTC are reasonably well fit by

$$\text{RS-I}^{\text{DTC, XTC, OTC}} = 3.70\text{x}10^{9}\ e^{-18.99/RT} \qquad \text{(VI)}$$

Where RS-I is in ppb, R=0.0019872 kcal $°K^{-1}$ mol^{-1}, and T is the temperature in °K. This suggests that whatever process(es) are responsible for the radical source in these chambers, the rate determining step has an activation energy of ~20 kcal/mole. However, this expression overestimates, by a factor of ~2, the radical sources in the two n-butane experiments in the ETC.

Based on the fits to the n-butane experiments, Equation (VI) is used for modeling the all the SAPRC Teflon chamber experiments where dry air was used. Figure 35 shows the performance of the model with this radical source assignment in simulating the n-butane runs in these chambers. As expected from Figure 34, the model gives acceptable fits to the runs in the DTC, XTC, and OTC, but somewhat overpredicts the rate of d(O_3-NO) formation in the ETC runs. Thus, although this radical source assignment appears to give a consistent chamber model for all these chambers which is consistent with the results of most of the n-butane experiments, it may cause overpredictions of d(O_3-NO) formation rates in simulations ETC experiments which are sensitive to this parameter. Although for consistency we used

Table 26. Summary of radical source values which best fit data in model simulations of ETC, DTC, XTC, and OTC n-butane experiments. (From Carter et al. 1994a)

Run	NOx (ppm)	n-Butane (ppm)	Avg T (K)	Best Fit RS-I (ppb)
ETC214	0.49	3.93	299.4	0.03
ETC318	0.52	4.22	298.3	0.02
DTC058A	0.24	3.68	300.9	0.07
DTC058B	0.24	3.78	300.9	0.06
XTC085	0.55	3.80	298.5	0.08
XTC098	0.57	4.06	302.5	0.07
OTC296A	0.53	4.47	310.3	0.16
OTC296B	0.52	4.98	310.3	0.12
OTC303A	0.54	3.85	313.4	0.25
OTC303B	0.52	3.78	313.4	0.20
OTC307A	0.46	3.66	318.6	0.35
OTC307B	0.48	3.70	318.6	0.30

Equation (VI) when modeling ETC runs in our chamber and light source effects study (Carter et al. 1994a), the mechanism evaluator may wish to re-assess these assignments.

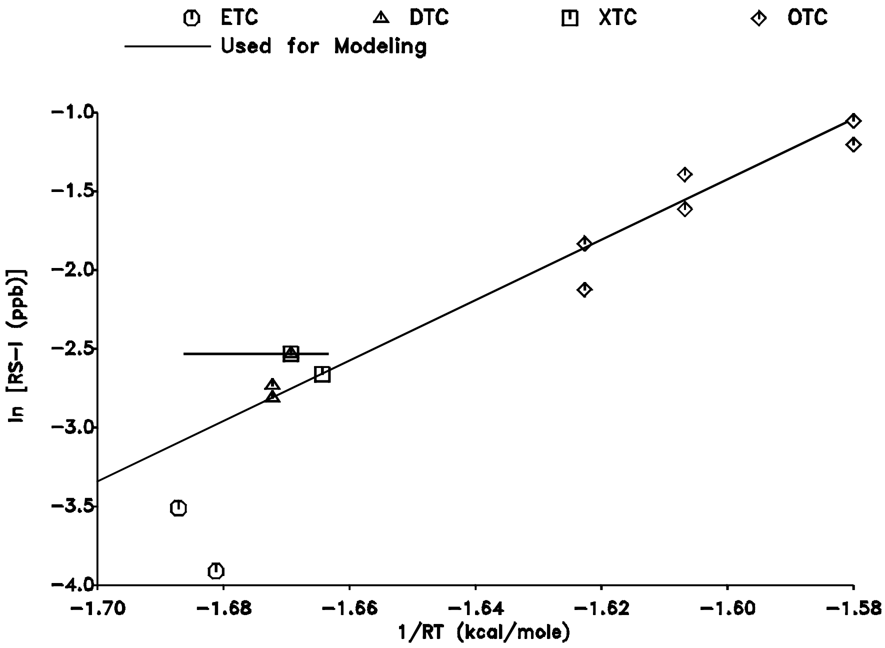

Figure 34. Arrhenius plot showing the temperature dependence of radical source input parameters which fit the ETC, DTC, XTC, and OTC n-butane runs.

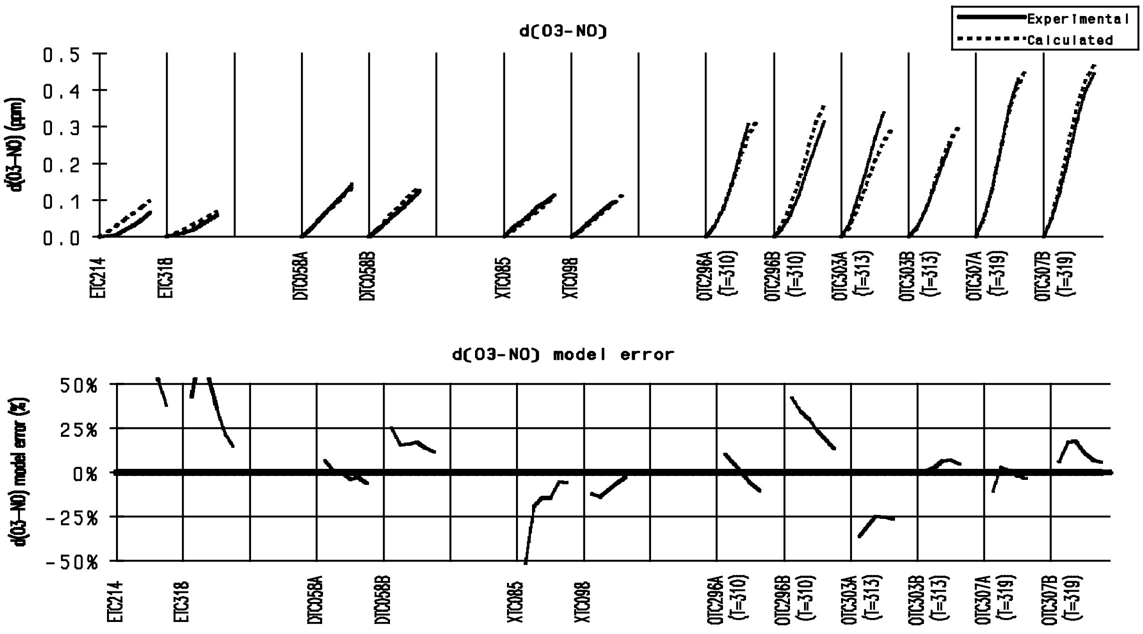

Figure 35. Results of model simulations of the ETC, DTC, XTC, and OTC n-butane - NO_x experiments using the radical source assignment given in Equation (VI).

7. DISCUSSION AND RECOMMENDATIONS

The data base described in this document provides important input for the evaluation of chemical mechanisms for use in urban and regional oxidant models. Although many of the chamber experiments in this distribution have been used in previous mechanism evaluations, a number of potentially significant corrections have been made to these data, and a number of other potentially important experiments which have not been modeled previously have been included in the data base. This includes most of the available characterization runs which are essential to the development of appropriate models for chamber effects. This document provides backing information for most of the important measurements, including the relevant calibration data and their associated uncertainties. This information has been used to derive estimates for uncertainty ranges for the important measurements. These uncertainty estimates, which have not been available previously in a consistent and documented manner, should be useful to the development of appropriate model performance criteria, and to the evaluation of the uncertainty ranges of model parameters which are adjusted to fit these data. Although some information of this type had been available in the various project reports prepared for the programs where these data were developed, with this document, and the associated spreadsheet files and other data sets, this information is now available in a comprehensive and consistent format which was developed with the specific needs of the modeler in mind.

However, it is essential that the modeler recognize the limitations of this data base. In the first place, the present distribution includes data only from SAPRC experiments carried out through the end of 1993, and does not include the extensive body of SAPRC outdoor chamber experiments (Carter et al., 1984a, 1986a, 1994a), nor the experiments we are currently carrying out for mechanism evaluation and VOC ozone reactivity assessment. We expect to include these in future distributions, to be prepared as a part of our ongoing environmental chamber programs. In addition, UCR does not have the only laboratory where environmental chamber experiments useful for mechanism evaluation have been carried out. A large data base of University of North Carolina (UNC) outdoor chamber experiments is now being prepared by the UNC researchers as part of the overall effort of preparing an environmental chamber data base for the EPA. The UNC researchers are also working with Dr. Graham Johnson and his group to develop a data base of the large number of CSIRO outdoor chamber experiments carried out in Australia (Jeffries, private communication, 1993). Environmental chamber experiments which are potential candidates for this data base have been or are being carried out at other laboratories (e.g., Kelly, 1994). As discussed by Jeffries et al. (1992), a comprehensive and complete mechanism evaluation requires the use of data not only from different environmental chambers, but also from different research groups. Therefore, although the data distributed with this document are extensive, and include a wide variety of experiments carried out in two quite different types of environmental chambers, they are not, by themselves, sufficient for a comprehensive mechanism evaluation.

It is important that users of environmental chamber data recognize the many problems which can be associated with chamber experiments which might affect the accuracy of the results or the modeler's ability to accurately characterize the conditions of the experiment. When preparing this data base, we attempted to identify and note all problems which might affect the use of the experiment (or particular measurements associated with it) for mechanism evaluations. Some runs were found to have sufficiently serious problems that they were either removed from the data base, or included but with the recommendation that they not be modeled. However, because of the large number of runs involved, combined with the number of things that can go wrong, we cannot guarantee that all problems have been detected and noted. Therefore, if the model simulation is in gross disagreement with the results of an experiment, the possibility that the problem exists with the data and not the model cannot be totally ruled out. The best means to verify whether a discrepancy represents a real problem with the model is to simulate similar experiments and see if similar discrepancies are observed. However, this may not always be possible, especially when testing mechanisms for compounds for which only a few runs are available. In this case, it is important that the modeler have some understanding of what types of problems might be expected to occur with the data or run conditions. One of the objectives in preparing this backing documentation is to help the modeler obtain this understanding.

It has been argued (Jeffries, unpublished writings) that model simulations of chamber experiments can provide a valuable means of quality control. Problems which may not be evident when examining the data alone can become evident when one sees unusually large inconsistencies between experimental data and model predictions. However, the use of modeling for data evaluation can be dangerous, for reasons which should be fairly obvious. Poor quality data which seem to agree with model predictions go unchallenged, while higher quality data which disagree with our expectations undergo careful scrutiny, with an effort being made to find excuses to reject the data or apply corrections which bring them more in line with model predictions. This may have occurred to some extent to the experiments in this data base which have been modeled previously, though for this work the input data were re-derived from the original chamber data sets, and the input files developed previously were not used. For the most part the present data base does not have the benefits of quality improvement which might result from modeling, but it also does not have the biases which might be introduced by this process.

Although the distribution includes all the files necessary to simulate the modelable experiments in the distribution, a considerable amount of work remains before these data can be used for this purpose. The chamber effects model implemented in the distributed files represents the state of the art about five years ago, and has not been re-evaluated based on new information. The chamber effects parameters in the distributed .CHR files are based on a number of assumptions, approximations, and simplifications which each modeler should evaluate in light of his or her own knowledge. The various factors which must be considered have been discussed in detail elsewhere (Carter et al., 1986; Gery et al., 1988; Jeffries et al., 1992; Carter et al., 1994a).

Finally, it should be pointed out that there are over 1000 modelable experiments in the present data base — and this is not counting the additional UCR experiments which will be included in future distributions. Although it is important that a variety of experiments be modeled in an evaluation, it is clearly not necessary to model all these experiments, many of which are very similar. In this work we have provided information needed to prioritize the runs in terms of data quality, but did not develop a prioritized or recommended list for model evaluation purposes. We feel that this should be the job of the model evaluator, since the prioritization of the experiments is highly dependent on the objective of the evaluation.

8. REFERENCES

Atkinson, R., W. P. L. Carter, and A. M. Winer (1983): "Evaluation of Hydrocarbon Reactivities for Use in Control Strategies," Final Report on California Air Resources Contract No. A0-105-32, May.

Atkinson, R. (1990): "Gas-Phase Tropospheric Chemistry of Organic Compounds: A Review," Atmos. Environ., 24A, 1-24.

Beauchene, J. H., P. J. Bekowies, J. M. McAfee, A. M. Winer, L. Zafonte and J. N. Pitts, Jr. (1973): "A Novel 20 KW Solar Simulator Designed for Air Pollution Research," Proc. Seventh Conf. on Space Simulation, Paper No., 66, NASA Special Publication 335, pp 811-825.

CARB (1994): Computer files implementing version 6.21 of the Urban Airshed Model (UAM) as provided by the Technical Support Division of the California Air Resources Board, Sacremento, CA.

Carter, W. P. L., R. Atkinson, A. M. Winer, and J. N. Pitts, Jr. (1982): "Experimental Investigation of Chamber-Dependent Radical Sources," Int. J. Chem. Kinet., 14, 1071.

Carter, W. P. L., P. S. Ripley, C. G. Smith, and J. N. Pitts, Jr. (1981): "Atmospheric Chemistry of Hydrocarbon Fuels: Vol I, Experiments, Results and Discussion," Final report to the U. S. Air Force, ESL-TR-81-53, November.

Carter, W. P. L., Dodd, M. C., Long, W. D. and Atkinson, R. (1984a): Outdoor Chamber Study to Test Multi-Day Effects. Volume I: Results and Discussion. Final report, EPA-600/3-84-115, November

Carter, W. P. L., Winer, A. M., Atkinson, R., Dodd, M. C. and Aschmann, S. A. (1984b): Atmospheric Photochemical Modeling of Turbine Engine Fuels. Phase I. Experimental studies. Volume I of II. Results and Discussion. Final Report to the U. S. Air Force, ESL-TR-84-32, September.

Carter, W. P. L., W. D. Long, L. N. Parker, and M. C. Dodd (1986a): "Effects of Methanol Fuel Substitution on Multi-Day Air Pollution Episodes," Final Report on California Air Resources Board Contract No. A3-125-32, April.

Carter, W. P. L., F. W. Lurmann, R. Atkinson, and A. C. Lloyd (1986b): "Development and Testing of a Surrogate Species Chemical Reaction Mechanism," EPA-600/3-86-031, August.

Carter, W. P. L. (1987): "An Experimental and Modeling Study of the Photochemical Reactivity of Heatset Printing Oils," Report #2 on U. S. EPA Cooperative Agreement No. CR810214-01

Carter, W. P. L., A. M. Winer, R. Atkinson, S. E. Heffron, M. P. Poe, and M. A. Goodman (1987): "Atmospheric Photochemical Modeling of Turbine Engine Fuels. Phase II. Computer Model Development," Report on USAF Contract no. F08635-83-0278, Engineering and Services Laboratory, Air Force Engineering and Services Center, Tyndall Air Force Base, Florida, August.

Carter, W. P. L. and R. Atkinson (1989): "A Computer Modeling Study of Incremental Hydrocarbon Reactivity", Environ. Sci. and Technol., 23, 864.

Carter, W. P. L. (1990): "A Detailed Mechanism for the Gas-Phase Atmospheric Reactions of Organic Compounds," Atm. Environ., 24A, 481-518.

Carter, W. P. L., and F. W. Lurmann (1990): "Evaluation of the RADM Gas-Phase Chemical Mechanism," Final Report, EPA-600/3-90-001.

Carter, W. P. L. and F. W. Lurmann (1991): "Evaluation of a Detailed Gas-Phase Atmospheric Reaction Mechanism using Environmental Chamber Data," Atm. Environ. 25A, 2771-2806.

Carter, W. P. L., J. A. Pierce, I. L. Malkina, and D. Luo (1992): "Investigation of the Ozone Formation Potential of Selected Volatile Silicone Compounds," Final Report to Dow Corning Corporation, Midland, MI, November.

Carter, W. P. L., J. A. Pierce, I. L. Malkina, D. Luo and W. D. Long (1993a): "Environmental Chamber Studies of Maximum Incremental Reactivities of Volatile Organic Compounds," Report to Coordinating Research Council, Project No. ME-9, California Air Resources Board Contract No. A032-0692; South Coast Air Quality Management District Contract No. C91323, United States Environmental Protection Agency Cooperative Agreement No. CR-814396-01-0, University Corporation for Atmospheric Research Contract No. 59166, and Dow Corning Corporation. April 1.

Carter, W. P. L., J. A. Pierce, I. L. Malkina, D. Luo, and W. D. Long (1993b): "Experimental Determination of the Reactivity of Isoprene with Respect to Ozone Formation," Draft final report for UCAR Contract No. 59166, Southern Oxidant Study, January 28.

Carter, W. P. L, D. Luo, I. L. Malkina, and J. A. Pierce (1993c): "An Experimental and Modeling Study of the Photochemical Ozone Reactivity of Acetone," Final Report to Chemical Manufacturers Association Contract No. KET-ACE-CRC-2.0. December 10.

Carter, W. P. L. (1994): "Development of Ozone Reactivity Scales for Volatile Organic Compounds, J. Air Waste Manage. Assoc., in press.

Carter, W. P. L., D. Luo, I. L. Malkina, and J. A. Pierce (1994a): "Environmental Chamber Studies of Atmospheric Reactivities of Volatile Organic Compounds. Effects of Varying Chamber and Light Source," Final report to National Renewable Energy Laboratory, Contract XZ-2-12075, Coordinating Research Council, Inc., Project M-9, California Air Resources Board, Contract A032-0692, and South Coast Air Quality Management District, Contract C91323.

Carter, W. P. L., D. Luo, I. L. Malkina, and J. A. Pierce (1994b): "Environmental Chamber Studies of Atmospheric Reactivities of Volatile Organic Compounds. Effects of Varying ROG Surrogate and NO_x," Final report to Coordinating Research Council, Inc., Project M-9, California Air Resources Board, Contract A032-0692, and South Coast Air Quality Management District, Contract C91323.

Darnall, K. R., R. Atkinson, A. M. Winer, and J. N. Pitts, Jr. (1981): JAPCA, 31, 262.

Doyle, G. J., P. J. Bekowies, A. M. Winer and J. N. Pitts, Jr. (197): "Charcol-Absorption Air Purification System for Chamber Studies Investigating Atmospheric Photochemistry," Environ. Sci. Technol., 11, 45.

Dasgupta, P. K, Dong, S. and Hwang, H. (1988): "Continuous Liquid Phase Fluorometry Coupled to a Diffusion Scrubber for the Determination of Atmospheric Formaldehyde, Hydrogen Peroxide, and Sulfur Dioxide," Atmos. Environ. 22, 949-963.

Dasgupta, P.K, Dong, S. and Hwang, H. (1990): Aerosol Science and Technology 12, 98-104

Gery, M. W., G. Z. Whitten, and J. P. Killus (1988): "Development and Testing of the CBM-IV For Urban and Regional Modeling,", EPA-600/ 3-88-012, January.

Jeffries, H. E., M. W. Gery and W. P. L. Carter (1992): "Protocol for Evaluating Oxidant Mechanisms for Urban and Regional Models," Report for U. S. Environmental Protection Agency Cooperative Agreement No. 815779, Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC.

Jeffries, H. E., K. G. Sexton, J. R. Arnold, Y. Bai, J. L. Li, and R. Crouse (1990): "A Chamber and Modeling Study to Assess the Photochemistry of Formaldehyde," Report on EPA Cooperative Agreement CR-813964, Atmospheric Research and Exposure Assessment Laboratory, EPA, Research Triangle Park, NC.

Holmes, J. R., R. J. O'Brien, J. H. Crabtree, T. A. Hecht, and J. H. Seinfeld (1973): "Measurement of Ultraviolet Radiation Intensity in Photochemical Smog Studies," Environ. Sci. Technol., 10, 787.

Kelly, N. A. (1994): General motors research laboratories, Warren MI, private communication.

Lodge (1989): "Methods of Air Sampling and Analysis, 3rd edition," Lewis Publishers Inc., Chelsea MI.

NASA (1992): "Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling, Evaluation Number 10," JPL Publication 92-10, August 15.

Pitts, J. N., Jr., K. Darnall, W. P. L. Carter, A. M. Winer, and R. Atkinson (1979): "Mechanisms of Photochemical Reactions in Urban Air," EPA-600/3-79-110, November.

Pitts, J. N., Jr., R. Atkinson, W. P. L. Carter, A. M. Winer, and E. C. Tuazon (1983): "Chemical Consequences of Air Quality Standard and of Control Implementation Programs," Final Report to the California ARB Contract No. A1-030-32, April.

Pitts, J. N., Jr., E. Sanhueza, R. Atkinson, W. P. L. Carter, A. M. Winer, G. W. Harris, and C. N. Plum (1984): "An Investigation of the Dark Formation of Nitrous Acid in Environmental Chambers," Int. J. Chem. Kinet., 16, 919-939.

Stephens, E. R., F. R. Burleson and E. A. Cardiff (1965): "The Production of Pure Peroxyacyl Nitrates," J. Air Pollut. Control Assoc., 15, 87.

Stephens, E. R., and M. A. Price (1973): "Analysis of an Important Air Pollutant: Peroxyacetyl Nitrate," J. Chem. Educ., 50, 351.

Winer, A. M., J. W. Peters, J. P. Smith and J. N. Pitts, Jr. (1974): "Response of Commercial Chemiluminescent NO-NO_2 Analyzers to Other Nitrogen-Containing Compounds," Environ. Sci. Technol., 8, 1118.

Tuazon, E. C., R. Atkinson, C. N. Plum, A. M. Winer, and J. N. Pitts, Jr. (1983): "The Reaction of Gas-Phase N_2O_5 with Water Vapor," Geophys. Res. Lett., 10, 953-956.

Zafonte, L., P. L. Rieger, and J. R. Holmes (1977): "Nitrogen Dioxide Photolysis in the Los Angeles Atmosphere," Environ. Sci. Technol. 11, 483-487.