

**QUALITY ASSURANCE PROJECT PLAN
FOR THE UCR EPA
ENVIRONMENTAL CHAMBER FACILITY**

DRAFT

**Revision 1
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Quality Assurance Project Plan
EPA Environmental Chamber Facility
University of California at Riverside, CE-CERT

Quality Assurance Project Plan Approval and Distribution

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Signatures indicate that this Quality Assurance Project Plan (QAPP) is approved and will be fully implemented in conducting the research project described in this document.

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1 PROJECT DESCRIPTION

1.1 Introduction

This Quality Assurance Project Plan (QAPP) describes the quality assurance elements of a research project to characterize and operate a next-generation environmental chamber facility, with particular emphasis on the quality assurance elements of the operation. The main purpose of this facility is to perform experiments to increase the level of understanding of the chemical processes involved in the formation of ground-level ozone (O₃) and particulate matter (PM) that result from emissions into the atmosphere. The results of these experiments will be used to evaluate and refine photochemical models used to predict the effects of emission controls on ambient air quality. An important goal of this project is to provide the necessary assurance that the ensuing recommended control strategies employed to achieve attainment for these pollutants will be efficient and cost effective.

The project is performed at the University of California at Riverside, College of Engineering-Center for Environmental Technology (CE-CERT), under cooperative agreement No. CR 827331-01-0 with the U.S. Environmental Protection Agency (EPA). The target date for the beginning of its operation is February 2002, and its operations under this project are scheduled for 2-3 years thereafter. Generally, this project will consist of research on environmental chamber design, facility development, and chamber characterization and evaluation. The remainder of the program will involve conducting experiments to evaluate photochemical models and to address issues of relevance to regulatory assessment and control strategy development.

This QAPP presents a project overview and detailed descriptions of the quality assurance (QA) elements necessary to demonstrate that the chamber measurements are of the quality needed to evaluate and refine the models. The data quality objectives for each of these measurements are specified herein. This QAPP also provides the framework for implementing project QA activities by addressing topics such as responsible individuals, test protocol designs, data integrity, documentation, preventive maintenance, and corrective actions.

1.2 Background

The high costs of O₃ and PM pollution and the regulations needed to abate them means that an ability to reliably predict the effects of emission controls on air quality has significant economic value. Because of the complexity of the chemical processes involved, data from environmental chambers are essential to assuring that photochemical and particulate models present predictions with sufficient accuracy. However, current environmental chamber technology is more than 20 years old and is not adequate for testing models under conditions representative of rural atmospheres or the expected cleaner urban atmospheres as attainment of air quality standards are met. The development and operation of the next-generation environmental chamber facility described herein is therefore crucial in providing the data needed for evaluating models under conditions relevant to today's control strategy problems. These data are needed within the following general areas:

1.2.1 Ozone Formation and Chemical Mechanism Evaluation

The following problems complicate the development of effective control strategies for reductions in O₃ concentrations:

- It is difficult to predict the changes in O₃ concentrations when NO_x and VOC emissions are reduced.
- Reducing NO_x emissions actually may cause O₃ concentrations to become higher in some urban areas, but NO_x reductions are also necessary to reduce secondary particulate matter.
- NO_x reductions are probably the only means by which significant O₃ improvement can be obtained in rural or downwind areas.
- VOC controls are often effective in reducing O₃ in urban areas, but may have little effect on O₃ in downwind areas where it is largely NO_x-limited.
- Some VOCs have little effect on O₃ even in urban areas, while other VOCs can have large effects, depending upon the environment where they are emitted.
- The relative effects of different VOCs on O₃ formation can depend on the environment where they are reacting, with the NO_x levels being an important factor, but not necessarily the only one.

A critical component for predictions of O₃ and other secondary pollutant formation is the chemical mechanism, i.e., the portion of the model used to predict the chemical reaction products. Because many of the chemical reactions are not sufficiently understood, the predictions of impacts on emissions on air quality contain a high degree of uncertainty. This uncertainty can be reduced by testing the model's prediction directly against the results of chamber experiments that simulate the range of conditions in the atmosphere. These experiments involve introducing known amounts of representative pollutants to a large enclosure, and measuring the changes in reactant concentrations and secondary pollutants formed when they are irradiated with artificial sunlight under controlled conditions for periods of a day or longer.

The database from existing chambers has a number of significant limitations and data gaps that could affect the accuracy of the mechanisms used in the models to predict control strategies (Dodge 2000). Uncertainties exist concerning characterization of chamber conditions, particularly how wall artifacts affect the gas-phase reactions (Carter and Lurmann, 1990, 1991), and inappropriate treatment of these effects could cause compensating errors in the gas-phase mechanism (Jeffries et al, 1992). Most chamber experiments lack measurement data for important intermediate and product species. This limits the level of detail to which the mechanisms can be evaluated and the types of air quality impact predictions that can be assessed. Furthermore, chamber background and wall effects, when combined with the limited analytical equipment currently available at environmental chamber facilities, the current environmental chamber database is not suitable for evaluating chemical mechanisms under the lower NO_x conditions. Relatively low NO_x conditions are also expected to become more typical in urban areas as attainment of the air quality standards is approached. The nature of the radical and NO_x cycles and the distribution of VOC oxidation products change as absolute levels of NO_x are reduced. Therefore, models developed to simulate urban source areas with high NO_x conditions may not satisfactorily simulate downwind or cleaner environments where NO_x concentrations are low.

VOCs tend to have low impacts on O₃ at high VOC/NO_x ratios. However, they can have other effects such as promoting formation of secondary PM or formation of toxic or persistent products. In addition, models predict that some VOCs cause reduced O₃ under low NO_x conditions, but the amount of reduction is highly

dependent on environmental conditions (e.g., see Carter and Atkinson, 1989; Carter, 1994). Further, it is possible that VOC regulations may be de-emphasized in low-NO_x areas, because they are believed to have low or possible negative effects on O₃. Thus it would be important their other air quality impacts be accurately assessed.

Another major deficiency in the current mechanism evaluation database is the lack of adequate information on the effects of temperature on VOC reactivity. Outdoor chambers yield data at varying temperatures, but because of lack of temperature control it is difficult to study temperature effects systematically and, probably more importantly, to obtain adequate characterization information concerning how temperature-dependent chamber artifacts may affect the results. The only indoor chamber used for mechanism evaluation where temperature can be varied in a controlled manner is the SAPRC evacuable chamber (EC) (Pitts et al, 1979; Carter et al, 1996), and only a limited number of variable temperature experiments have been carried out (Carter et al, 1979, 1984). That facility is not currently being used for mechanism evaluation experiments, and because of its relatively large wall effects is probably not suitable for low-NO_x experiments in any case (Carter et al, 1996). Other than that, there is currently no environmental chamber facility capable of generating well-characterized mechanism evaluation data under controlled conditions at differing temperatures. Nevertheless, the limited available data indicate that temperature effects can be important (e.g., Carter et al, 1979, 1984, see also Carter et al, 1993), and thus there is a need for a facility that can generate adequate mechanism evaluation data in this regard.

1.2.2 Evaluation of PM Impacts and Secondary Organic Aerosol Formation

Urban fine particulate matter is constituted of a complex mixture of both primary and secondary organic and inorganic compounds and comes from a wide variety of sources. While contributions of primary PM can be estimated directly from the knowledge of emission rates, contributions of secondary PM are more difficult to assess because they are formed by complex homogenous and heterogeneous processes. Secondary PM consists primarily of nitrate, sulfate, and secondary organic aerosol (SOA), and most of it forms as fine particulate matter of less than 1.0 μ aerodynamic diameter. Since smaller diameter particles have been shown to be more irritating to the human pulmonary system, these are of particular concern. The nitrate and sulfate are derived largely from gaseous emissions of NO_x and sulfur dioxide, while secondary organic aerosols are formed from the oxidations of VOCs, which form products with sufficiently low vapor pressures to partition into the aerosol phase.

The atmospheric chemical reaction pathways of VOC molecules sufficiently large to lead to SOA are complex, and resulting oxidation products are both numerous and difficult to quantify analytically. As a result, it is currently not possible to determine the aerosol formation potential of individual VOCs and their contribution to the secondary organic urban particulate burden strictly on the basis of atmospheric chemical reaction mechanisms. However, secondary organic aerosol yields have been measured in environmental chamber experiments over the past decade or so, primarily using the Caltech outdoors chamber (e.g., see Hoffmann et al., 1997; Forstner et al., 1997, and references therein). Initially it was believed that each VOC should possess a unique value of its aerosol yield, but Odum et al. (1996) found the chamber data are much better described by a two-parameter gas/aerosol absorptive partitioning model. Within that framework, semi-volatile products from the atmospheric oxidation of an ROG can partition into an absorbing organic aerosol phase at a concentration below their saturation concentration, analogous to the partitioning that occurs between the gas and aqueous phases of a water-soluble atmospheric constituent.

Although the outdoor chamber database provides important information on the effects of individual VOCs on SOA formation, the use of outdoor chambers has a number of limitations. Perhaps the most serious problem is the lack of temperature control and the variability of temperature during the experiment. Inability to control temperature also means that humidity cannot be controlled unless the experiment is carried out under dry conditions. Temperature is important because of its effect on vapor pressure, which affects the tendency of particles to partition into the aerosol phase. Humidity is important because it will affect the nature of the aerosol material, which in turn will affect the partitioning of the organic products onto that material. Because of the importance of controlling humidity, most outdoor chamber aerosol yield experiments are carried out dry. In addition, the chambers currently used for such studies have a non-rigid design, and aerosol lifetimes may be reduced by the constant stirring due to winds causing turbulent deposition. This makes interpretation of the aerosol dynamics more difficult. In addition, variable lighting conditions make the experiments more difficult to use for model evaluation. Finally, the current outdoor chamber systems are not well suited for carrying out experiments using the low concentrations of NO_x or other pollutants that are more characteristic of regional or near-attainment conditions.

1.2.3 Evaluation of Impacts of VOC Oxidation Products

Organic pollutants may have other adverse impacts on air quality besides contributing to O_3 and secondary PM formation. If the emitted VOC itself is toxic or has other adverse direct impacts, this can be assessed given knowledge of the VOC's atmospheric reaction rates and deposition velocities. A more difficult problem is assessing the impacts of the oxidation products of the VOCs. For example, VOCs may react to form toxic products, products that persist in the environment, or products (such as PAN or organic nitrates), which can serve as NO_x reservoirs whose subsequent reactions, may significantly enhance O_3 formation in downwind, NO_x -limited environments. An assessment of this requires knowledge of the identities and yields of the VOC's major reaction products. This is difficult because the products are not known or not quantified for many VOCs. In addition, the products formed when a VOC reacts in the atmosphere will change when NO_x levels become sufficiently low that radical-radical reactions begin to dominate in the photooxidation mechanisms.

Conducting laboratory studies of products formed from the photooxidations of VOCs is a sound approach for obtaining the data needed for assessing VOC impacts. However, conditions in laboratory experiments designed for product studies are usually not very similar to atmospheric conditions, particularly those with lower pollution levels. In principle, identifying and quantifying products in simulated atmospheric conditions in environmental chambers should provide information on the actual products formed under more realistic conditions, the subsequent lifetimes and fates of these products, and how they vary with conditions. Furthermore, obtaining product concentration-time profiles in conjunction with chamber experiments for mechanism evaluation permits a much more comprehensive evaluation of the details of the overall mechanism than otherwise would be possible. However, with the possible exception of the Europhore chamber in Europe (Becker, 1996), environmental chamber facilities currently in use for mechanism evaluation do not have the advanced analytical capabilities necessary for carrying out comprehensive product measurements in conjunction with environmental chamber experiments.

1.2.4 Evaluation of Model Representations of NO_y and Radical Budgets

The tropospheric production of O_3 and other oxidation processes are governed by the budgets of free radicals and the fate of nitrogen oxides (NRC, 1991; Seinfeld, 1989; Kleinman et al., 1997). There is a

growing awareness that models cannot be adequately evaluated by simply comparing observed versus simulated O_3 (Tesche et al., 1992; Reynolds et al., 1994). Furthermore, because models can have compensating errors in representations of radical budgets and NO_x removal processes, even comparing observed and simulated yields of oxidation products may not necessarily provide an adequate evaluation of how well the model represents these processes. For these reasons, advanced model evaluation requires process level diagnostics that characterize the budgets of HO_x and NO_x (Arnold et al., 1998). Furthermore, because the budget of HO_x also affects the production and removal of VOC, hazardous organic pollutants, and certain greenhouse gases, the use of process diagnostics to test the radical budget will increase confidence in chemical tracer models used to simulate certain hazardous air pollutants and greenhouse gases.

A number of process-level diagnostics have been used or proposed for use in model evaluations using ambient data (Kleinman, 1994; Jeffries and Tonnesen, 1994; Milford et al., 1994; Sillman, 1995, 1998; Arnold et al., 1998; Kleinman et al., 1997; Tonnesen and Dennis, 1998a,b). Process diagnostics have also been compared with ambient observations to evaluate grid models (Sillman et al., 1995, 1997; Imre et al., 1997). The ability to confirm the model representation of chemical processes in those studies is uncertain, however, for the following reasons:

- The complete set of measurements necessary to characterize HO_x and NO_x budgets has not been available in field studies because measurements are difficult to collect or are of uneven quality due to the difficulties of operating the instruments in field conditions.
- In ambient conditions the concentrations of important species are affected by transport, dispersion, and deposition, and by variability in temperature, humidity and actinic flux, thereby complicating the interpretation of the chemical processes.
- It is possible that important ambient processes may not be represented in the model simulations, but that compensating errors still enable the model to match observations.

Chamber experiments present an opportunity to obtain a more complete and rigorous evaluation of chemical processes. For any given chemical process, two types of process diagnostics can be defined: (1) local measures of instantaneous production and loss rates; and (2) air-parcel diagnostics that represent the cumulative production and loss in an air parcel over a period of time. In principle, a more rigorous test of certain portions of the radical cycle can be obtained because, for example, local radical initiation must be balanced by local radical termination, and the integral of both the local initiation and local termination rates should be approximately balanced by the cumulative production of termination products. However, for ambient conditions, transport and dilution prevent a direct comparison of local and air-parcel diagnostics. Chamber experiments could be especially useful for evaluating radical budgets because the confined volume makes it possible to balance local and air-parcel diagnostics.

Chamber experiments present potential problems due to the wall effects and deposition to or off gassing from walls. However, the project chamber has been designed to minimize these effects. In any case, in an appropriately designed and characterized chamber it should be easier to quantify these effects than in the ambient atmosphere. Thus, characterization of radical budgets in carefully controlled chamber presents an important opportunity to investigate the adequacy of current photochemical mechanisms for a wide range of precursor levels and environmental conditions.

For these reasons, it is desirable to investigate the usefulness of process diagnostics in an environmental chamber where the system inputs and chamber conditions can be carefully controlled. The use of a chamber also facilitates the operation and calibration of analytical instruments and provides a complete set of necessary measurements thereby reducing the possibility of compensating errors in unmeasured processes.

1.2.5 Evaluation of Ambient Monitoring Methods

Data from State and Local Air Monitoring Stations (SLAMS) are required for determination of compliance with National Ambient Air Quality Standards (NAAQS). These data are also used to determine air quality trends, to evaluate emissions inventories, and to evaluate airshed model performance. Further, they support observational analysis methods for assessing control strategies in situations where modeling is too uncertain to be useful. The data from SLAMS and other monitoring are only as good as the measurement methods and quality assurance procedures used to obtain them. The methods have been established for the routine monitoring of criteria pollutants such as O₃, CO, NO₂, and SO₂ through the EPA Reference and Equivalence Program. However, measuring many other critical species under field conditions, such as NO_x species other than NO, or speciated organic precursors and products, is extremely difficult and uncertain. Considerable research is being conducted in the development of advanced methods and instrumentation for monitoring these critical species with more accuracy. These methods are then tested in major field projects such as the Southern Oxidant Study (SOS) and Supersites Program.

One way these tests are performed is by means of intercomparison studies, where the same species are measured using differing methods in the same air mass. Such studies are useful, but have limitations. Because one does not know *a priori* what is actually in the air mass, it is necessary that at least one of the methods being compared be considered the reference. In addition, it must be assumed that the instruments being intercompared are not subject to the same types of interferences or biases. Therefore, agreement of different methods only indicates that it is possible that they are accurate, but does not provide definitive evidence that this is the case. Furthermore, it may not always be obvious which method is correct when they disagree, or it may be that the more “reliable” method may actually have an unanticipated problem.

An environmental chamber system provides viable alternative to the inherent limitations of field intercomparison studies for evaluating analytical methods. At a minimum the history of the air mass and the initial pollutants injected will be known, and in many cases the correct concentrations of the subject compounds will also be known or can be computed, or at least varied in a systematic way. However, most existing environmental chamber systems also have limitations. Some methods require long path lengths or require large sample volumes, which requires use of very large chambers. Most large outdoor chambers are not useful for simulating environments with the relatively low pollutant levels characteristic of much of the ambient atmosphere. The large chamber system described in this project allows for generating and controlling known low pollutant conditions as well as control over temperature and light intensity. This provides a very useful means to perform method evaluations and intercomparisons.

1.3 Project Scope and Work Objectives

The objectives developed for this project are a result of continuing interaction with a number of organizations and disciplines affected by or interfacing with the planned work. These organizations include the California Air Resources Board (ARB), the Reactivity Research Working Group (RRWG), a division of

NARSTO, and the U.S. EPA. An Advisory Committee consisting of members of each of these organizations is being formed. In addition, the project objectives have been formulated and refined through the use of workshops and requested peer reviews of the project Draft Research Plan and Progress Report (Carter, 2002). These mechanisms ensure rigorous peer review and participation by the appropriate disciplines and organizations.

The objectives of this project are to develop and operate a next-generation environmental chamber facility needed for evaluating gas-phase and gas-to-particle atmospheric reaction mechanisms, for determining secondary aerosol yields, and for measuring VOC reaction products and radical and NO_x indicator species under more realistic and varied environmental conditions than previously has been possible. During the initial part of this project the objectives will consist of research on chamber design, facility development, and chamber characterization and evaluation. The objectives during the remainder of the program will include conducting the experiments needed for model evaluation and to address issues of relevance to regulatory assessment and control strategy development. These would include, but not necessarily be limited to, the following:

- Determining whether current predictions of effects of VOC and NO_x changes on ozone and secondary aerosol formation are applicable to lower pollutant concentrations.
- Assessing differences among VOCs in terms of effects on ozone, secondary aerosol formation, and other pollutants under low-NO_x conditions
- Providing information needed to evaluate whether control strategies aimed at replacing reactive VOCs with less reactive but more persistent compounds may adversely affect ozone or other pollutants when they are transported downwind.
- Determining major oxidation products formed by organics when they react under low-NO_x conditions. This is important to developing scientifically based models for low-NO_x reactions of VOCs, as well as to understanding the ultimate environmental fates and impacts of these compounds, which in some cases may affect global climate change.
- Determining the effects of temperature on secondary pollutant formation and VOC reactivity. Current environmental chamber facilities are not adequate to evaluate these effects, but limited studies of temperature effects indicate that temperature effects are probably significant.
- Determining the effects of temperature and humidity on secondary organic aerosol formation from various VOCs. The results will be compared with data obtained using outdoor chamber systems to evaluate the range of applicability of those data.
- Evaluating the budgets of HO_x and NO_y, and evaluating the usefulness of indicators of O₃ and P(O_x) sensitivity to precursors for conditions typical of ambient atmospheres.
- Evaluating the impacts of various types of VOC sources, such as architectural coatings, on formation of O₃, secondary PM, and other pollutants in various environments.
- Testing equipment to be used for monitoring pollutants in ambient air under controlled conditions where the actual pollutant concentrations, and the history and source of the air mass being monitored, are known.

2 PROJECT MANAGEMENT

2.1 Personnel Qualifications

The project team has extensive experience in making measurements of gaseous and particulate air pollutants in a research environment and in managing research projects. Further, CE-CERT has developed specific sampling devices for several major air quality studies and has previously designed sampling systems for mobile platforms.

The Principal Investigator (PI) for this project will be Dr. William P. L. Carter. Dr. Carter has been involved in environmental chamber research since 1979 and chemical mechanism development research since 1974. More recently, he has been conducting experimental and modeling studies of VOC reactivity. Chemical mechanisms developed by Dr. Carter are widely used in research and regulatory applications. Environmental chamber data from his compilations or programs have been used in the evaluations of the other mechanisms in use in the United States. He is responsible for the compilation of the UCR environmental chamber database (Carter et al, 1996) and participated in developing the proposed protocol for evaluating mechanisms using environmental chamber data (Jeffries et al, 1992). Dr. Carter has a joint appointment with both the Air Pollution Research Center (APRC) and CE-CERT. APRC is the site of the original UCR environmental chamber facility, and remains a leading facility for basic kinetic and mechanistic studies.

CE-CERT co-investigators for this project will be Mr. Dennis R. Fitz and Dr. Gail S. Tonnesen. Mr. Fitz was formerly a member of the APRC research team, where he managed the Outdoor Chamber Facility, and is currently the manager of the Atmospheric Processes and Stationary Source Emission Control Group at CE-CERT. He specializes in the measurement of trace atmospheric pollutants, especially the minimization of gas-particle sampling artifacts. Dr. Tonnesen developed a process analysis method for analyzing model simulations with Professor Jeffries at the University of North Carolina, and she has continued to apply this method to the evaluation of photochemical models in research with Dr. Robin Dennis at the U.S. EPA.

Each member of the CE-CERT project staff has extensive experience in their particular disciplines. All project personnel will be familiar with the content of this QAPP, thus obtaining a project overview, including information on all functions of the measurement systems, from experimental design, objectives, sampling, and data validation and reporting. Where applicable, project personnel must be familiar with the SOPs applicable to their areas of responsibility. In addition, if major revisions or enhancements are made to the QAPP and/or SOPs, all affected individuals must review those revisions at that time.

2.2 Project Responsibilities

Organizational commitment is an essential element for developing and implementing a successful research project. At CE-CERT the Principal Investigators are kept apprised of all research program activities, from identifying the need to develop sound experimental designs to delivering data reports. Commitments to research activities, such as those described in this QAPP are made only after the activities are thoroughly reviewed and approved by the Principal Investigators. Figure 1 presents the organizational chart that shows the

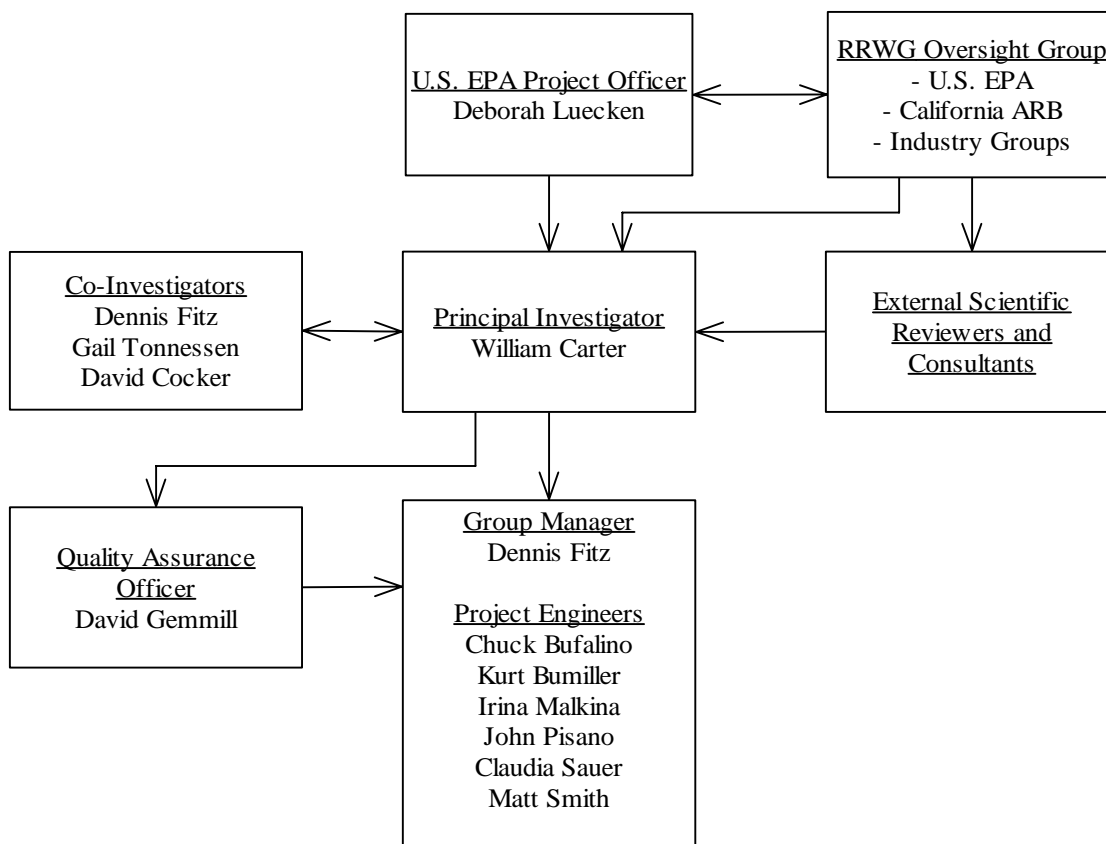


Figure 1. Project Organization Chart

lines of responsibility and information flow for activities under this project. A listing of specific responsibilities of each position for this project follows.

2.2.1 Principal Investigator

The Principal Investigator is responsible for the overall conduct of the project, experimental design, reporting of the results, and interacting with the project officer, co-investigators, and oversight groups. Specific responsibilities include, but are not necessarily limited to, the following:

- Direct, integrate, and schedule experiments and other activities of CE-CERT project team;
- Primary responsibility conducting project within available budget and approval for major expenditures;
- Work with the Group Manager in assuring that needed personnel are available for this project and in assigning tasks and responsibilities;
- In collaboration with the co-investigators, guide the overall approach for performing the experiments and reviewing their results;

- Keep current on project status and issue quarterly progress reports to the EPA and oversight groups;
- Interact with Research Advisory Committee, external scientific reviewers, collaborators, and co-investigators in the development of study priorities, reporting of results, and obtaining external input;
- Evaluate overall data quality, characterization results, and overall system performance for suitability to meet project objectives;
- Assure that the QAPP serves the needs of the project in terms
- Interpret the results, use the results for model evaluation and to address other objectives of the project; and
- See that results are appropriately reported in peer-reviewed scientific publications.

2.2.2 Co-Investigators

The project co-investigators are responsible for the conduct of specific aspects of the project that are within their expertise or interest. These include, but are not necessarily limited to, the following:

- Work with the Principal Investigator in developing the experimental design in areas of their interest;
- Interact with external scientific reviewers, collaborators and other external groups in their area of interest in the development of study priorities, reporting of results, and obtaining external input;
- In collaboration with the Principal Investigator, guide the overall approach for performing the experiments and reviewing their results;
- Assist in oversight and supervision of personnel working on this project where appropriate;
- Assist in interpreting and reporting the results where appropriate; and
- See that results are appropriately reported in peer-reviewed scientific publications.

2.2.3 Group Manager

The Group Manager (who is also a co-investigator and therefore has other responsibilities as indicated above) has overall responsibility for the management of the personnel and resources at the CE-CERT Atmospheric Processes (AP) group, which conducts a number of other research projects besides this one. His primary responsibility in this capacity is to assure that available resources are utilized effectively to implement all projects, and be responsible for the management of these resources. Specific responsibilities as they relate to this project include the following:

- Work with the Principal Investigator in developing an implementation plan for this project that is feasible given the resources and personnel available;
- Assign personnel responsible for the various tasks based on input and needs communicated by the Principal Investigator and co-investigators for this project;
- Conduct weekly AP group meetings where the status and tasks for this and the other AP projects are discussed, and work for the coming week is coordinated; and
- Assist Principal Investigator with administration and fiscal management of project.

2.2.4 Project Engineers and Technicians

The project engineers and technicians are the personnel who carry out the experimental work for this project, operate and maintain the instrumentation and facility, and who do the initial data collection,

verification, and processing. Specific responsibilities are allocated among individuals depending on the needs of the project. These responsibilities include, but are not necessarily limited to, the following:

- Perform chamber experiments as directed by the Principal Investigators;
- Obtain, inspect, and prepare the measurement instruments;
- Install, configure, calibrate, and maintain the instruments according to protocols;
- Obtain, test, assemble, and configure all ancillary and support equipment;
- Maintain log books and records of experimental operations, facility and instrument modifications, calibrations, etc.;
- Maintain calibration databases;
- Validate and deliver the data from the chamber experiments the Principal Investigators; and
- Assist investigators in reporting results concerning experimental and data validation methods.

2.2.5 Quality Assurance Officer

The Quality Assurance officer is primarily responsible for the development and implementation of the Quality Assurance Plan and Standard Operating Procedures, assuring that they meet EPA and NARSTO standards, and assuring that they meet the objectives of this project. Specific responsibilities include:

- Leads the development and implementation the Quality Assurance Project Plan and Standard Operating Procedures
- Reviews the test protocols and test matrices with particular emphasis on its quality control components
- Reviews the fabrication, assembly, and operation of the test systems
- Conducts performance and system audits of the measurement and data validation systems
- Follows up on all unsatisfactory performance to ensure that the appropriate corrective actions have been performed

2.2.6 Run Modeler

The Run Modeler is responsible for assuring that the results of the experiments are processed so that they can be used for modeling, and also for providing input on the experimental design so that the experiments have the desired utility for mechanism evaluation to satisfy the objectives of this project. Specific responsibilities include:

- Provides guidance on the types of experiments and measurements most useful for mechanism evaluation and characterization of chamber conditions
- Designs the data processing procedures so that the information needed for modeling is of the necessary quality and in a useful format for modeling
- Verifies that the processed data files for experiments appropriately represent their conditions for modeling and have all the information needed.
- Analyzes results of characterization experiments and data to derive appropriate model input parameters or provide guidance concerning uncertain inputs.
- Maintains databases of experimental and characterization results for modeling purposes
- Conducts initial modeling or analysis of experiments to determine if inconsistencies or unexpected results suggest possible experimental or measurement problems.

- Conducts the modeling analysis of the experiments for the project reports.

Currently the Run Modeler and the Principal Investigator is the same person, but this does not necessarily have to be the case.

2.2.7 EPA Project Officer

The EPA Project Officer is the primary person responsible for the oversight of this project by the EPA, and assuring that the EPA provides appropriate and effective input in the way this project is conducted. Note that since this project is a cooperative agreement, the EPA is a partner in the ongoing design and conduct of the project. The specific responsibilities include, but are not necessarily limited to, the following:

- Assure that the contractual and requirements of the EPA for this project are met, and communicating with the Principal Investigator in a timely manner when action is needed to meet these requirements;
- See that the results and issues in the project are communicated within the appropriate groups and offices in the EPA and that their appropriate input is communicated back to the Principal Investigator;
- Serve as chair or co-chair of the RRWG oversight group for this project and assist the RRWG in assuring that the group functions effectively in providing external input for this project;
- Works with the Principal Investigator, oversight groups, collaborators, etc. in assuring that the interests and concerns of the EPA are appropriately represented as project priorities are developed or modified due to external input;
- Provide input as needed to assure that the project has effective and appropriate peer review;
- Reviews the QAPP and conducts critical project reviews;
- Interacts with the Principal Investigator as needed; and
- Performs other functions required of the EPA for project officers.

2.2.8 RRWG Oversight Group

As discussed in the “External Input” section, below, the Reactivity Research Working Group (RRWG) will serve as the primary vehicle for providing external input and oversight for the overall project. Their role will include, but not necessarily be limited to, the following:

- Provide the Principal Investigator and the EPA Project Officer input on the research plan and its ability to meet the needs of the various stakeholders relevant to the overall objectives of the project;
- Review the overall performance of the project and provide input on problem areas;
- Select independent peer reviewers for this project, receive and review their reports, and receive and review responses by the Principal Investigator and the EPA Project officer;
- Make the Principal Investigator and EPA Project Officer aware of other projects that may be of relevance to the project; and
- Assist in organizing and conducting workshops where this and related projects are discussed.

2.2.9 External Reviewers and Consultants

As discussed below, external reviewers will be used to provide independent peer review of the various aspect of the project, and provide constructive criticism and recommendations to the investigators and the Oversight Group. They will be consultants funded either as part of the project or other sources of funding

coordinated by the RRWG oversight group, but in any case they will be selected by the RRWG oversight group. Their contracts should include the following specific responsibilities:

- Review the research plan for the project and provide constructive criticism and recommendations for improvement;
- Performs independent reviews of experimental designs, characterization tests, progress reports, and other project documents and reports yet to be determined;
- Make the investigators and the Oversight Group aware of other projects, results, or available methods and approaches that may be relevance to this project; and
- Provide a written report on findings and recommendations.

2.3 External Input

Various means of external input are used to assure that this project represents the state of the art in environmental chamber research and that maximum advantage is taken of the unique characteristics of the facility to address mechanism evaluation issues of greatest relevance to regulatory assessment and control strategy development. During the initial stages of this project, external input has primarily been through an international workshop held at the beginning of the project, consultation with the California Air Resources Board staff and various industry groups concerning research needs that can be addressed using the facility, and informal discussions with the EPA/ASRL staff and other researchers. However, a more comprehensive process for external input is needed to review the draft research plan given in this report.

It is planned that the Reactivity Research Working Group (RRWG) will serve as the primary vehicle for providing external input and oversight for the overall project, with additional input being provided by the California Air Resources Board's Reactivity Research Advisory Committee (RRAC) and selected experts in atmospheric chemistry and environmental chamber research being added as consultants, as discussed below. The RRWG is considered to be appropriate for the primary vehicle for external input and oversight for the following reasons:

- The RRWG is was formed to coordinate reactivity-relevant research, and the overall objectives of this project directly address important components of the RRWG's medium and long-term research objectives.
- The EPA/ASRL staff and contractors responsible for oversight of this project, the head of the Atmospheric Processes group in the CARB Research Division, and the Principal Investigator are active in the RRWG, as are the industry groups that have shown the greatest interest in the need for VOC reactivity research, and an improved environmental chamber facility for this purpose.
- The RRWG science team includes technical experts in various areas of reactivity-related research, and previously prepared an assessment of the state of the science concerning VOC reactivity and reactivity models who can provide input on technical aspects of this project.
- The RRWG policy team includes representatives of regulatory agencies and regulated industries and can provide needed input on policy-relevance of proposed research for this project.
- The RRWG is a division of NARSTO, which provides guidance and resources for technical review, quality assurance, and data archiving and distribution.

- Informal discussions with EPA staff and consultants and with Dr. Don Fox, the chairman of the RRWG, indicate that there is a desire and willingness for the RRWG to participate in this manner. Dr. Fox is planning to put discussion of this project on the agenda for the next meeting, scheduled for January 16-17, 2002.

The mechanism for the RRWG oversight and input is currently being formulated. The expected approach will be to form a sub-group that would include appropriate technical experts, the EPA project officer, project officers for other projects using the chamber (currently only the CARB), and representatives of industry groups interested in this project, with those actually funding RRWG research projects being given priority. This group would review the research plan for this project and provide input and recommendations to the Principal Investigator through teleconferences and email, and present its overall recommendations and criticisms at the following RRWG meeting, which probably would be in the Spring of 2002. Updates on the project, and comments on its outputs and modified research plans would then be discussed at the approximately quarterly RRWG meetings. The general RRWG meetings probably provide the best vehicle to provide input on policy-relevance of the research plan, though it is expected that at least some members of the oversight group for this project would also be members of the RRWG policy team.

It is also recommended that the RRWG oversight group select two or three scientists with appropriate expertise and understanding of the research objectives to serve as *paid* peer reviewers for this project. Although the Principal Investigator can suggest names for possible reviewers, the choice should be up to the EPA project officer in consultation with the RRWG oversight group. It is important that the reviewers be paid for their efforts, to assure that they give the project the attention it requires, and that the input is provided in a timely manner. However, an industry group or a regulatory agency could provide in-kind support by assigning this task to an appropriate expert in their employ. Fairly obvious candidates for peer reviewers include the membership of the CARB's Reactivity Science Advisory Committee, and the CARB may wish to consider using this committee for this purpose.

The first task of the reviewers should be to review and criticize the work carried out thus far on this project and the draft research plan. They would then be retained to periodically conduct reviews of outputs of this project or provide recommendations to the RRWG and the Principal Investigator concerning the progress and current research plans. Although the Principal Investigator would obviously prefer it if the EPA or RRWG could find a source of funds to cover the costs of this review effort, if necessary (and with the approval of the EPA project officer) it could come from the funds for this cooperative agreement. The level of effort and funding needed should be discussed at the upcoming RRWG meeting.

The California Air Resources Board's Reactivity Research Advisory Committee (RRAC) is already overseeing the Principal Investigator's projects concerning architectural coatings reactivity, which includes experiments to be carried out in this facility. It is expected that this group will continue in this advisory and oversight capacity for the CARB projects. Although many of the industry participants in the RRAC are also active in the RRWG, the RRWG and RRAC meetings would probably have to continue to be separate because the CARB meetings must be in California, and the EPA participation in the RRWG meetings require that most RRWG meetings be on the East Coast.

2.4 Management Assessment

2.4.1 Assessment Responsibilities

The point of contact for managerial project assessment is that of the Principal Investigator and other investigators, as described above. These investigators will be linked to the Research Advisory Committee and the external reviewers and consultants. These links will provide timely reviews of the project experimental design, implementation, and interpretation of experimental results.

2.4.2 Assessment Types and Usage

The assessments of overall project quality will be provided from a number of different sources. Informal review of selected components of this project will be obtained periodically from internal staff experts not routinely associated with the program. The Oversight Committee and external reviewers described in Section 1.7 will provide external review of quarterly progress and other reports. The Principal Investigator will provide the RRWG oversight group with timely updates on the status of the project at the regular RRWG meetings (which are held 3-4 times a year) and receive external input during this process. Workshops will be held when appropriate to review research progress and plans for future experiments.

Internal quality assurance performance and system audits will be performed by the project QA Officer. The first audit will be conducted after the new chamber system has been fully characterized. Additional audits will be performed at one-year intervals thereafter, for a total of three audits through July 2004. The focus of these audits will be in the accuracy of the measurement systems used to measure reaction chamber concentrations, critical components of the experimental setup, uncertainty analysis of selected data, and data validation methodology. Where applicable, adherence to SOPs and protocols will be evaluated. The results of these audits will contain any suggested corrective actions, and be appended to the data interpretation reports generated in this study.

In addition, it is expected that EPA will perform periodic system audits of this project.

2.4.3 Assessment Criteria

The assessment criteria for the overall research plan will concern the extent to which the proposed experiments will provide data needed to address the overall objectives of this project, as discussed in Section 1.3. Since major objectives of this project concern provide data needed for evaluating and improving models for predicting effects of emissions on air quality, the criteria will include considerations such as the importance of the model uncertainty being addressed and the extent to which the proposed research, if successful, can reduce the uncertainty, and the probability of success of the research in obtaining data of the type and quality needed.

Criteria for assessment of the experimental design and approach will concern the extent to which it will yield data of maximum utility to address the objectives of this project. Since most of the data are to be used for model evaluation, criteria for assessing data utility and quality will include the following:

- Utility of the type of measurements for model evaluation. For example, are model predictions of the measurements sensitive to the uncertainties in the mechanism that are being evaluated? Are the available resources being applied to the highest priority types of measurements?
- Degree of characterization of experimental conditions for modeling. For data to be useful for model evaluation, experimental conditions need to be sufficiently well characterized that the data can be used for model evaluation without characterization uncertainties dominating the results. Types of characterization information needed and characterization quality goals for this project are discussed in Section 5.
- Accuracy, precision, and sensitivity of the measurement data. The measurements in the concentration region of interest should be sufficiently accurate and precise to provide a meaningful test of model predictions. Accuracy and precision goals for various types of measurements are discussed in Section 4.
- Extent of biases and interferences in the measurements.
- Degree to which unavoidable characterization uncertainties and known or suspected measurement biases are bounded or quantified. The experimental design must be such that effects of unavoidable uncertainties or measurement biases are minimized or can be quantified.
- Procedures used to assure data quality, identify data not meeting quality objectives, and to minimize errors and other data quality problems.
- Degree to which appropriate operating procedures are used in making the measurements, assuring data quality, identifying when data are not meeting quality objectives, and minimizing errors and other data quality problems.
- Degree to which the modeling appropriately incorporates the characterization results in the inputs, and the analysis of the modeling results appropriately take into account characterization and measurement uncertainties and biases.
- Degree to which the experimental procedures, measurement methods, and data processing and analyses, and modeling methods are documented.

Assessment criteria for the internal audits for the various types of specific measurements are documented in the corresponding SOPs. Generally, the criteria will reflect the data quality objective criteria presented in Section 4.

The criteria for the testing of new measurement methods will be assessed and documented on a case-by-case basis through specially designed experiments. Generally the applicable the criteria will be based on the criteria for overall data quality and utility as discussed above. The criteria will not necessarily be associated with specific pass/fail limits; rather the emphasis will be on characterizing the performance of the candidate method under controlled conditions, and determining whether any unavoidable uncertainties and biases can be bounded or quantified to a sufficient extent that the data meets the criteria discussed above.

2.4.4 Assessment Documentation

Progress Reports will be issued by the Principal Investigator approximately once per calendar quarter. These reports will summarize the work carried out since the previous report, problems encountered, and work anticipated for the upcoming period. Results of any assessments, audits or peer reviews carried out during the

project period will also be summarized, though detailed reports will probably not be incorporated in the quarterly reports. Instead, these assessment documents or reports will be posted at the project web site at <http://www.cert.ucr.edu/~carter/epacham/>, and their availability there will be noted in the quarterly reports. The progress reports themselves will also be made available on the project web site.

An interim report on the project will be prepared approximately annually if requested by the EPA project officer and a final report will be prepared at the end of the project. These reports will contain summaries of each experiment performed during the reporting period, similar to that provided by Carter (2002). The summary will contain a table that indicates the consecutively numbered runs, type of run, conditions, results, and discussion. In addition, the summary will contain major sections organized by type of run that present the experimental details with concentration-time plots, where appropriate. The interim reports will also present a research plan for the remainder of the project. Results of quality assessment evaluations and audit audits will also be discussed, and either attached as appendices to the report or made available on the project web site. The interim and final reports will also be posted on the web site.

2.5 Communications Plan

2.5.1 Internal Communications

The project team members are located at CE-CERT and those involved in ongoing experiments generally communicate on a daily basis concerning the project developments and information. The team members are also linked by e-mail correspondence, and also use this as a means to communicate and exchange data, either as email attachments or by network-accessible files. Weekly Atmospheric Processes Group meetings are held where the status and activities for this and other projects are discussed, and project direction is assessed. Periodic meetings are also held concerning specific issues as the need arises.

2.5.2 External Communications

Periodic progress reports summarizing progress, problems, and results from the project will be prepared on approximately a quarterly basis and submitted to the EPA project officers and the RRWG oversight group for review and comments. The status of the project will also be discussed at the RRWG meetings, which are generally held approximately 3-4 times a year. It is expected that the RRWG will form a panel or subgroup of technical experts who will review these reports and provide input on their technical merits or problems. The RRWG as a whole, and its policy team in particular, will provide input on the overall priorities for experiments and compounds to be studied.

The Principal Investigator has requested that the RRWG or the EPA find the resources to pay for the time of selected technical experts to critically review the reports and other outputs of the project, and communicate with the Principal Investigator, the RRWG, and the EPA project officer concerning any problems or input. If such funds are not forthcoming, then the Principal Investigator may use of project funds for this purpose. This mechanism is considered necessary to ensure rigorous peer review of the project.

The status of the project and the most recent or applicable progress reports and research plan will also be posted at the project web site, which is at <http://www.cert.ucr.edu/~carter/epacham/>. Contact information for the Principal Investigator and relevant collaborators is also given at that web site.

When appropriate, results of the project will be written up for publication in peer reviewed journal articles. The EPA, the RRWG oversight group, and any other applicable funding agencies will be provided drafts of any proposed manuscripts resulting from this project, and will have at least 30 days for review and comments prior to submission for publication. This input will be taken into account when preparing the manuscript for final submission to the journal.

2.6 Technical Assessment and Response

Maintenance and regular system checks will be performed according to a routine schedule for each instrument according to its specific SOP. Review of these checks will be performed at the time of the checks so that corrective actions can be promptly initiated and the checks can be repeated before the experimental run is begun. Technical assessment of the downloaded data will be performed after each sample run. This assessment will consist of review of the calibration results and corresponding control charts, and an examination of time series data plots to identify any potential problems or questions to be resolved. If problems are encountered the PI will be contacted and a recommended approach will be developed and implemented.

The periodic reports for this project will include a discussion of the applicable quality assurance activities carried out during the reporting period. This discussion may incorporate the following topics, as appropriate:

- Summary of quality assurance and quality control activities
- Summary of all quality assurance and quality control problems encountered
- Corrective actions taken and lessons learned
- Certification of the implementation of QAPP quality management activities
- Technical and statistical evaluation of the quality control data
- Audit results
- Summaries of measurement uncertainties
- Summary of success/failure to meet data quality objectives

Internal technical performance and systems audits will be performed approximately yearly. The systems audits will be done to verify that procedures are being followed according to the SOPs. A detailed checklist will be developed in order to conduct this audit. The performance audits will be conducted to evaluate the accuracy of the measurements by comparing instrument performance against different standards that are used to perform the routine calibrations. The detailed procedures used to perform these audits will be documented in an SOP. The criteria for satisfactory audit results are presented in the accuracy column in Table 5. If unsatisfactory audit results are encountered the appropriate troubleshooting will be undertaken in order to determine the cause of the discrepancy, followed by the indicated corrective actions. A formal audit report will be presented within 30 days after the audit.

3 FACILITY AND INSTRUMENTATION

3.1 Facility

Environmental chamber experiments will be carried out at the CE-CERT facility located at 1086 Columbia Avenue, Riverside California, 92507. The major components are the laboratory building, the environmental chamber enclosure and associated components such as the light sources and air purification systems, and the sampling and data acquisition systems. These are briefly described below.

3.1.1 Laboratory Building

A two-story laboratory building was designed and built at CE-CERT to meet the specific needs of this project. The temperature-controlled enclosure with that will house the reactors and the light source is located on the second floor, with most of the sampling instrumentation, except for those that must be closely coupled to the reactor, being maintained on the first floor. The chamber enclosure has dimensions of 20 ft. wide x 20 ft. high x 40 ft. long, and is capable of housing two Teflon® reactors. Sampling from the reactors is done at a point along the centerline between the reactors. A pad to the side houses an air purification system, water chiller, compressed air cylinders, and cryogenics. These components are described in more detail in the following sections.

3.1.2 Environmental Chamber Enclosure

All experiments will be carried out using large FEP Teflon® reactors located a temperature-controlled irradiation enclosure that is continuously flushed with purified air Schematics of the enclosure. The purpose of the enclosure is to supply the light to the reactor at the desired intensity and uniformity, to maintain the reactor at a controlled but variable temperature, and to maintain the reactor in an environment of purified air, to avoid introduction of contaminants into the reactor by diffusion through the reactor walls or leaks. A diagram of the enclosure, showing the approximate dimensions relative locations of the reactors, light source, and sample lines, is shown on Figure 2. As discussed below, different reactor setups and light sources will be used during the course of this project. The major characteristics of the enclosure are as follows:

- The temperature control system is designed to maintain the temperature to within $\pm 1^\circ\text{C}$ at set points ranging from 4 to 50°C . It must be able to recover temperature control to within desired range within 5 minutes after the heat load changes by $\pm 100\text{ KW}$.
- Polished aluminum panels, *Alcoa Everbright*, are installed on all interior surfaces. This material was found to have the best UV reflective capability.
- In order to preclude potential contamination from the materials and sealants used in the construction of the interior enclosure walls, materials containing polymeric diphenylmethane diisocyanate (MDI) and a silicone sealant were used. The MDI MSDS gives a vapor pressure of approximately 5 ppb at 20°C .

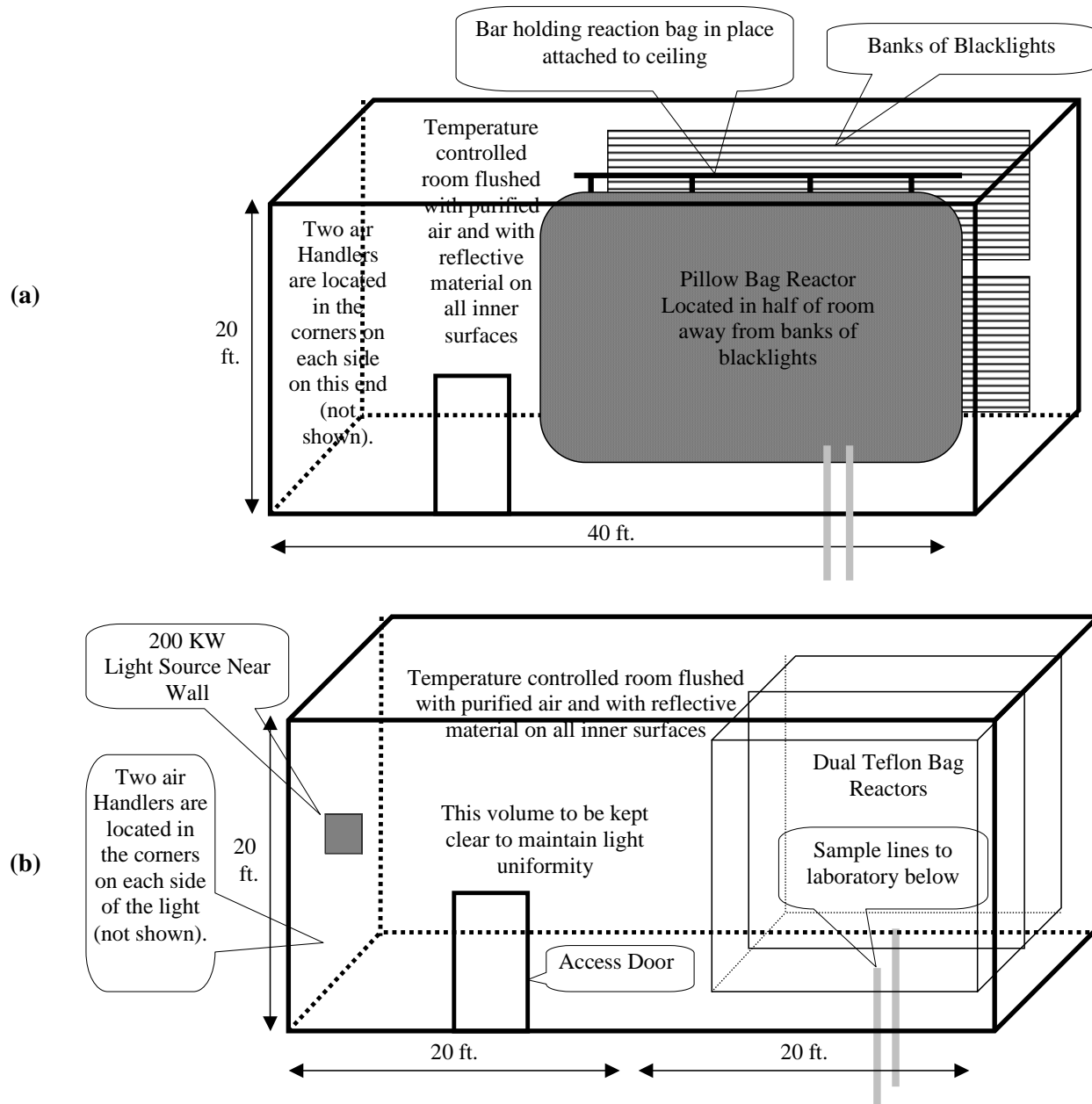


Figure 2. Schematic of the temperature-controlled enclosure showing the locations of the reactors, light source, and sampling lines. (a) Setup for the initial experiments using the temporary blacklight light source. (b) Setup that will be used once the 200 KW Argon Arc light source becomes fully operational.

- The enclosure is designed to maintain an internal positive pressure of 1 inch of water, with a leak rate of no greater than 5% per hour with the access openings closed. Because of the relatively airtight construction of the enclosure, a pressure release system has been provided to avoid the enclosure imploding or exploding due to pressure changes caused by sudden changes in temperature. The pressure relief system includes both coarse and fine filtration for PM as well as a Purafil bed.
- An air scrubbing system is used to keep the enclosure air clean. This is done in order to preclude exposure of contaminants to the reactor bags.

3.1.3 Light Sources

The primary light source for this project will be a single 200 KW argon arc light manufactured by Vortek, located at one end of the enclosure as shown on Figure 2 (b). The use of a single light and its particular location with respect to the reaction chambers was based upon light intensity distribution calculations that were provided by Vortek, based on an assumed 15% reflectivity of the Everbright® panels within the reactor. This design provides for the maximum uniformity in light intensity across the reaction chamber area, with no more than a theoretical 6% difference between the sides of the reactor closest to or farthest from the light. The source will be fitted with the appropriate filter(s) in order to provide the desired spectra. After construction of the laboratory is completed the light source will be periodically tested for intensity uniformity and spectrum.

Because of manufacturing delays, the Vortek 200 KW light system will not be fully operational until around April 2002 or later. Therefore, the initial experiments in this facility will be conducted using banks of blacklights that are temporarily installed on the East wall, as shown on Figure 2 (a). Measurements indicated that the light intensity in the area occupied by the reaction bag varied by no more than $\pm 10\%$.

3.1.4 Reaction Chambers

The reactors utilized in the experiments for this project will be constructed of flexible and collapsible 2 mil FEP Teflon® film and located inside the chamber enclosure discussed above. The reactors will have large volumes to minimize chamber effects and wall losses of aerosols, to provide sufficient volume for sampling using instruments with high sample flow rates, and to maximize path lengths for in-situ spectroscopic analysis methods. Since permeation through this 2-mil film can be significant, the reactors will be maintained inside a clean air enclosure during the experiments, as described above. The reactors will be built and leak-tested at CE-CERT. After each experiment they will be cleaned by emptying and flushing with clean air. Complete details describing the reaction bag construction and testing are presented in the SOP for reactor construction, which is in preparation.

For the initial experiments utilizing the temporary blacklight light source, the reactor will consist of a single pillow-shaped bag that is approximately 24ft. long and with a maximum inflatable diameter of approximately 10 ft. It will be attached to a rod running the length of the top of the reactor, with the rod in turn attached to the ceiling of the enclosure. Sample lines will be attached to the bottom. This is shown on Figure 2 (a), above.

Once the Vortek 200 KW light source becomes operational, dual reactor bags will be utilized in the initial experiments in this program, located as shown on Figure 2 (b), above. Each reactor will have dimensions

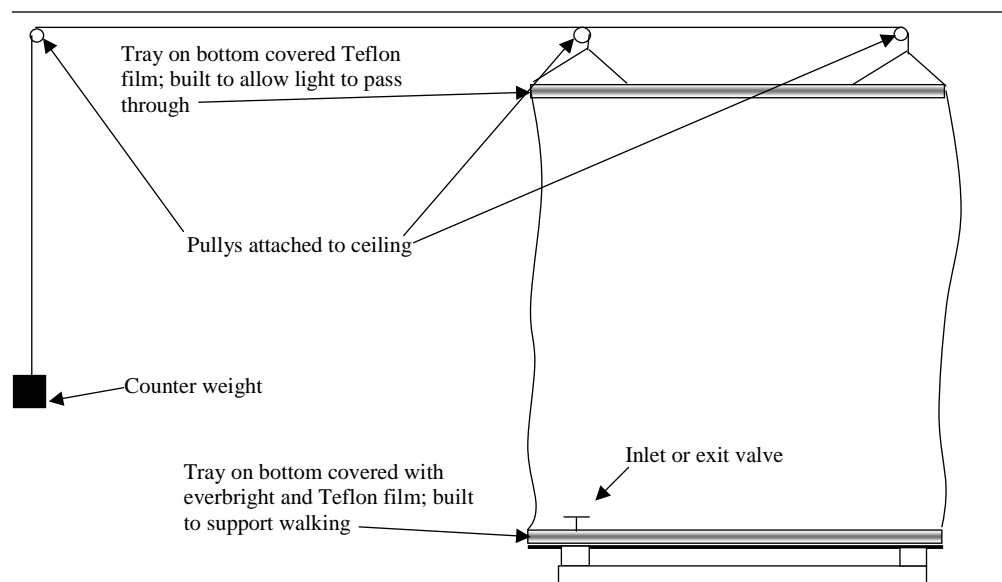


Figure 3. Diagram of configuration currently planned for reactor construction for use with the 200 KW Vortek lights

of 9 ft. x 18 ft. x 16 ft., with a volume of about 73m^3 . They will be attached to rigid frameworks on the top and bottom, with the top framework being moveable up and down to allow the reactor to collapse for emptying and purging, and with the bottom framework attached to the sample lines, air inlets and exits, and the mixing system. A diagram of the configuration as planned is shown on Figure 3.

3.1.5 Air Purification System

Pollution-free air will be used to fill and flush the chambers, as well as the larger enclosure to preclude contamination of the reaction chambers by permeation or through leaks, and to provide dilution air for instrument calibration purposes. An Aadco Instruments, Inc. Model 737 Pure Air Generator will be utilized. This system has a capacity of 1000 liters/minute, and consists of adsorption towers that are used to remove nitrogen oxides, heavier hydrocarbons, and CO. The system also contains a catalytic oxidizer to remove CH_4 and other light hydrocarbons. The air is then passed through packed towers containing Purafil and heated Calulite.

3.1.6 Air Mixing and Reactant Injection System

High-volume air re-circulation and mixing systems have been developed to mix the contents of the reaction chambers to assure uniform concentrations after the reactants are injected, and to assure that the common reactants in the two reactors are present at the same concentration. The system consists of four 8" Teflon Chemduit ducting. Teflon-coated blowers are used to exchange the air within and between the reactors. The system has the provision for injecting low volatility material when needed or for mixing within the reactor

after injections are made. Injection will be accomplished by delivering known quantities of the undiluted compound into a glass vessel of known volume and pressure. Then the contents of the vessel will be injected into the reaction chamber. Valves will close off and isolate this system from the circulation ducting during experiments.

3.2 Sampling and Data Acquisition Systems

The instruments for monitoring the gas-phase species, and their associated calibration and data acquisition systems are maintained in a room directly beneath the chamber enclosure. Sampling from the reaction chambers is accomplished by means of a dedicated sampling system. The system contains an array of computer controlled solenoid valves so that the sample mode for each instrument can be manually or automatically switched between the reaction chambers and the respective instrument calibration sources. It also provides the zero air to purge the enclosure and reaction chambers. A dedicated computer equipped with LabView data acquisition and control software operates the system. The data acquisition system will collect data from the gas analyzers in one-minute averages.

The solenoid valve status is stored with the analyzer response data so that a permanent record of the sampling mode is continuously maintained. This feature was provided to simplify the data validation process and to avoid miss-direction of data. In addition, the data are processed directly into a format that enhances the analysis, mechanism evaluation, and planning processes. This will include, to the maximum extent possible, automated calibration and zeroing procedures, as well as flagging and rejecting spurious or transitional data.

The sampling system for the aerosol instruments has not yet been constructed. The current plan is to locate the aerosol equipment on the facility's second floor, immediately adjacent to the enclosure for the reactors, and located to provide equal access to each reaction chamber. It will be maintained at the same temperature as the reactors by air exchange with the chamber enclosure. Data acquisition for the continuous methods will probably be accomplished using a separate computer.

Samples for analysis of low volatility materials will be collected by manual extraction on sample media such as Tenax and DNPH cartridges using short sample lines. Access to the reaction chambers for these measurements will be through the opening in the enclosure that provides samples for the aerosol instruments.

3.3 Measurement Methods

Table 1 presents the list of the gaseous and aerosol measurement methods currently planned for this project, and Table 2 gives a equipment necessary to support the measurements. Brief descriptions of the methods, and the procedures utilized to perform calibrations of the instruments are presented below. Operating procedures for most of these instruments or measurement methods are or will be described in more detail in Standard Operating Procedure (SOP) documents that are described in Section 6.3, below.

Table 1. Summary of measured species or parameters, instrumentation used, and associated measurement objectives.

Species	Instrumentation			Measurement Objectives		
	Make and Model	Principle	Comments	Det'n Lim.	Accuracy	Precision
O ₃	Dasibi Model 1003-AH	UV absorption	Standard ambient monitoring instrument for O ₃ measurements.	2 ppb	±10%	±5%
O ₃	Monitor Labs Model 8410	Chemiluminescence	Provides for comparisons between UV and chemiluminescent methods.	2 ppb	±10%	±5%
NO	Eco-Physics Model CLD 780 TR	Chemiluminescence	Low range analyzer for NO only.	40 ppt	±10%	±10%
NO	TEI Model 42C	Chemiluminescence	Standard ambient monitoring instrument for NO/NO _x measurements.	1 ppb	±10%	±10%
NO _x				1 ppb	±15%	±15%
NO	TEI Model 42C with external converter	Chemiluminescence	External converter to reduce losses of HNO ₃ before reaching converter	1 ppb	±10%	±10%
NO _y					±15%	±15%
NO ₂ , PAN	CE-CERT NO ₂ /PAN GC	GC separation and Luminol detection		200 ppt	±20%	±20%
				100 ppt	±30% [b]	±20% [b]
NO ₂ , HNO ₃	Unisearch	Tunable Diode Laser	Research grade instrument	0.5 ppb	±10%	±10%
				1 ppb [a]		
HCHO, H ₂ O ₂	Unisearch	Tunable Diode Laser	Research grade instrument	200 ppt	±15%	±15%
				1 ppb [a]	±25%	±25%
CO	TEI Model 48C	Gas correlation IR	Standard ambient monitoring instrument for CO measurements.	50 ppb	±10%	±10%

Table 1 (continued)

Species	Instrumentation			Measurement Objectives		
	Make and Model	Principle	Comments	Det'n Lim.	Accuracy	Precision
HCHO	Alpha Omega Model MA-100	Wet chemical		1 ppb [a]	±15% [b]	±15% [b]
VOCs	HP 5890 with loop injectors	GC Separation with FID detection	Various megabore columns available for different sets of VOCs. Loop injection suitable for low to medium volatility VOCs. Trap analysis used to increase sensitivity.	10 ppb	±10%	±10%
VOCs	HP Model 5890 set up for Tenax cartridge sampling	GC Separation with FID detection	Various megabore columns available for different sets of VOCs. Tenax cartridge sampling used for low volatility VOCs that cannot go through GC valves, but can elute through GC columns.	1 ppbC	±15%	±15%
VOCs with nitrogen or halogens	HP Model 5890 with loop injectors	GC Separation with ECD detection	The performance of this instrument has not been satisfactory in recent years and it may not be used for this project.	Varies	±30% [b]	±15%
Aldehydes	Shimadzu (hybrid of components)	HPLC	For analysis using DNPH cartridges.	0.04 µg/cartridge	±15%	±20%
Total Carbon	Byron Model 301	FID	Under evaluation; may be suitable for CH ₄ analysis only.	100 ppbC	±30% [b]	±25% [b]

Table 1 (continued)

Species	Instrumentation			Measurement Objectives		
	Make and Model	Principle	Comments	Det'n Lim.	Accuracy	Precision
Aerosol size and distribution	CE-CERT SEMS	Scanning Electrical Mobility Spectrometer	Research grade instrument. See Cocker et al (2001)	N/A	±25%	±25%
Temperature	Various type J thermocouples, radiation shielded housings	Thermocouples	Covers expected operational range of chambers	Change of 0.1°C	±0.2°C	±0.1°C
Relative Humidity	General Eastern HYRO-M1 chilled mirror	Dew Point	Dew point range: -40 to 50C			
Light Spectrum	LiCor LI-1800 Spectroradiometer		Spectrum in 300-850 nm region covers spectral region of interest. Calibrated at factory. Cosine response.		±10%	±10%
Light Intensity					[c]	±15%
Light Intensity	Biospherical QSL-2100 PAR Irradiance Sensor		Measures integrated radiation in UV-visible region over ~85% of a sphere.		±15%	±2% [a]

[a] This is an estimated value that is subject to change.

[b] It has not yet been determined if this system can meet these objectives.

[c] Measurement useful only for determining relative differences.

Table 2. Support equipment

Measurement or Device(s)	Make, Model, or Description	Comments
Dilution Calibrator	TEI Model 146C or CSI 1700 Dynamic Gas Calibrator. $\pm 3\%$ accuracy for measurement of dilution flows.	Used to dilute standard gas cylinders for calibration of instruments
O ₃ Primary Standard	Dasibi Model 1003-AH	Set up as a primary standard to calibrate O ₃ monitoring instruments
Calibration Gas Cylinders	Scott Marrin for NO, NO ₂ , and CO calibration gases; Puritan-Bennett for fuel and carrier gases for GCs	All calibration gases will be EPA Protocol
Calibration systems for HCHO, H ₂ O ₂ , and HNO ₃	Specially fabricated containment devices for permeation sources and diffusion tubes maintained at constant temperature	Accuracy of each system will be independently verified
Data Acquisition System	Windows PC with LabView software. 16 analog input, 32 I/O, 16 thermocouple, and 10 RS-232 channels	Collects data from most monitoring instruments, controls sample modes, initiates calibrations, and carry out initial data processing.

3.3.1 Gas Analyzers

Dasibi Model 1003-AH O₃ Analyzer. This is a commercially available instrument that is routinely used for the ambient monitoring of O₃. This analyzer utilizes the same UV measurement principle as is used in over 98% of the national monitoring network, and is an EPA-equivalent method for the monitoring of O₃. This analyzer will be used as the principal O₃ measurement device on this project. The instrument is calibrated using the primary standard for O₃ as described in the SOP for the instrument. This primary standard will be periodically referenced against the Standard Reference Photometer maintained by ARB in Sacramento.

Monitor Labs Model 8410 O₃ Analyzer. This instrument is no longer commercially available, but is an EPA reference method for the ambient monitoring of O₃. The analyzer utilizes the chemiluminescence method by reaction with ethylene. This instrument may become useful for intercomparisons with the UV method, particularly since there have been concerns raised within the monitoring community with regard to the UV method being subject to interferences from a variety of hydrocarbons and other compounds. The instrument is calibrated using the primary standard for O₃ as described in the SOP for the instrument.

Eco-Physics Model CLD 780 TR NO Analyzer. This is a research grade, low-range, NO-only analyzer. It is sufficiently sensitive to detect steady-state NO levels in the presence of NO_x and O₃ in light, and the commercial NO/NO_x analyzer does not have this capability. The analyzer is calibrated using the gas dilutor

to dilute an EPA-Protocol NO cylinder to the desired concentrations, as described in the SOP for the instrument.

TEI Model 42C NO/NO_x Analyzer. This is a commercially available instrument that is routinely used for the ambient monitoring of NO and NO₂. The analyzer utilizes the same chemiluminescent method as is used in virtually all the National monitoring network, and is an EPA-reference method for the monitoring of NO₂. The analyzer is calibrated using the gas dilutor to dilute an EPA-Protocol NO cylinder to the desired concentrations. In addition, the analyzer's NO₂ converter is periodically checked by the gas phase titration procedure, which consists of adding a known amount of NO to excess O₃ using the calibrator.

TEI Model 42C NO/NO_y Analyzer with External Converter. This commercially available analyzer uses an external converter in order to minimize losses of HNO₃ in the NO_y channel. However, there is a growing body of evidence that indicates that this analyzer's responses to HNO₃ are vary considerably, and the NO_y data are not necessarily useful when HNO₃ or complex or uncharacterized mixtures are present. Consequently it has been postulated that the NO_y data are only useful if denuders are used to remove the HNO₃. The analyzer is calibrated using the gas dilutor to dilute an EPA-Protocol NO cylinder to the desired concentrations. The analyzer's NO_y converter is periodically checked using NO₂ generated by the gas phase titration procedure.

CE-CERT NO₂/PAN GC. This analyzer was designed and developed by CE-CERT. It uses luminol detection combined with a GC column to separate NO₂ from PAN and other species that are then detected by luminol to provide a specific analysis for NO₂. The sample air is drawn through the instrument by a micro pump and flows across a fabric wick wetted with Luminol solution. The central portion of the wick is viewed by a photomultiplier, the signal of which is proportional to the NO₂ concentration. Its sensitivity to NO₂ at low concentrations is at least equal to that of the TDLAS, but the possibility of interferences at low concentrations has not entirely been ruled out. It will also provide data for PAN, though its reliability and accuracy for this purpose has not yet been fully established. The analyzer is calibrated by dilution of an NO₂ cylinder.

Unisearch NO₂/HNO₃ and HCHO/ H₂O₂ Tunable Diode Laser Absorption Spectroscopy Systems (TDLAS). These research grade analyzers (2) are based on measuring single rotational - vibrational lines of the target compounds in the near to mid infrared using laser diodes with very narrow line widths and tunability. The sample for analysis is flushed through closed absorption cells with multi-pass optics held at low pressure (~25 Torr) to minimize spectral broadening. Because of the narrow bandwidth of the diode lasers required to obtain the highly species-specific measurement, separate diode lasers are usually required for each compound monitored. However, both TDLAS systems acquired for this project have two lasers and detection systems, permitting analysis of up to four different species. These instruments will be calibrated using internal calibration cells. In addition the NO₂ channel will be calibrated by dilution of an NO₂ cylinder, and the other channels will be calibrated using the specially fabricated permeation and/or diffusion systems described in the SOP for the instrument or the calibration source (see Section 6.3).

The first TDLAS system for NO₂ and HNO₃ will utilize a heated sample line at low pressure to minimize HNO₃ line losses. This instrument has been upgraded for use in this project. The second instrument can be operated on a single mode if greater sensitivity is required.

TEI Model 48C CO Analyzer. This is a commercially available instrument that is routinely used for the ambient monitoring of CO. The analyzer utilizes the same gas correlation IR method as is used in virtually all the National monitoring network, and is an EPA-reference method for the monitoring of CO. The analyzer is calibrated using the gas dilutor to dilute an EPA-Protocol CO cylinder to the desired concentrations.

Alpha Omega Power Model MA-100 HCHO Analyzer. This continuous formaldehyde analyzer is based on the wet chemical method of Dasgupta and others. This analyzer is in the development and testing phase, and will be used as a backup and/or a replacement for the TDLAS if proved sufficiently reliable. The analyzer will be calibrated using the specially fabricated permeation system described in the SOP for the permeation source.

Hewlett Packard Model 5890 Gas Chromatographs. The first two HP 5890 instruments listed in Table 1 are standard laboratory GC-FID systems. They will also be used to monitor at least some of the oxidation products, such as simple aldehydes, ketones, and organic nitrates, provided that their identities are established by other means. The loop sampling method is currently used for the more volatile and less sticky compounds is sufficient for monitoring reactant VOCs, but it may not be sensitive enough for monitoring trace VOCs for pure air experiments or to verify the performance of the air purification experiments. The trap sampling method (Carter et al, 1996) will be employed when more sensitive analysis is required.

The Tenax cartridge sampling method used for the lower volatility or more “sticky” VOCs (Carter et al, 1996) will be adapted for more sensitive analysis by sampling larger volumes of air through the trap. The GCs as currently configured allow use of three different columns for loop or trap sampling, and a fourth column for Tenax cartridge sampling. This permits a variety of types of compounds to be separated. These GC systems will be operated and calibrated according to CE-CERT SOPs.

A third HP 5890 GC is fitted with ECD detection for more sensitive monitoring of organic nitrates and certain other types of compounds for which ECD detection is sensitive. Experience with this system over the years indicates that it has problems with obtaining consistent data and at present it probably does not meet our measurement objectives. It may be suitable for some purposes that do not require high accuracy and precision.

3.3.2 Particle Measurements

Scanning Electrical Mobility Analyzers (SEMS). Two of these instruments have been designed and built by CE-CERT to simultaneously measure size and number distributions of aerosols formed in each reactor. Separate instruments have been provided for each reactor because aerosol materials will not pass through solenoid valves without undergoing modification that is difficult to characterize. The aerosol sizes and number distributions are the primary physical measurements needed to determine amounts of aerosol formed and how they grow or are removed during an experiment. The instrument measures in the range of 0.03 μm to 0.8 μm electrical mobility diameter, and consists of three major components: a Thermo Systems Inc. (TSI) model 3077 ^{85}Kr neutralizer which generates a Fuchs charge distribution, a TSI model 3081 differential mobility analyzer long column which selects for particle sizes based on the voltage applied and the particles electrical mobility, and a TSI model 3760A condensation particle counter (CPC) used to detect particles. The analyzer's four gas flows are calibrated using a primary flow calibrator and the particle size is calibrated using aerosolized polystyrene latex spheres. Further information on these SEMS analyzers is presented in Cocker et al (2001).

The SEMS can be modified to serve as a **Tandem Differential Mobility Analyzer (TDMA)**. This is done by configuring the SEMS to measure the size and number distribution of particles within a single size range, then passing the sample through a chamber exposing the particles to humidity, heat, or other conditions of interest. The principle of operation and further information about this instrument, which is based on the design of Rader and McMurry (1986), is given by Cocker et al (2001). The instrument can therefore be used to determine the effects of humidity, temperature, or other changes to the environment to aerosol size and number distributions. This information is useful to investigate important aerosol properties such as hygroscopicity and volatility, and thus gives an indication of their major chemical characteristics.

3.3.3 Ancillary Measurements

Included in Table 1 is a listing of the major support equipment utilized in the facility. This equipment provides the measurements to characterize the conditions that may affect the results of mechanism evaluation. Brief descriptions of these instruments, and the procedures utilized to perform calibrations of the instruments are presented below.

Temperature. Type J thermocouples attached to thermocouple boards on the computer data acquisition system provide the temperature measurements. In order to maximize measurement accuracy the thermocouples are shielded from the light and flushed with air from the experiment being monitored. During experiments at least one thermocouple will be located inside each reactor bag. A meteorological grade insulated temperature sensor will serve as a standard to reference the accuracy of the thermocouples. This sensor will be located inside the chamber enclosure during the experiments.

Relative Humidity. The relative humidity is measured using a General Eastern Model Hygro M1 chilled mirror dew point sensor. Its lower limit of -40°C is above the expected dew point of the purified air and is adequate for chamber experiments for determining humidity effects. The measured dew point temperature will be converted to relative humidity using an algorithm supplied by General Eastern. The sensor will be calibrated using a certified psychrometer.

Light Spectrum and Intensity. The spectrum in the 300-850 nm region will be measured using a LiCor Model 1800 spectroradiometer. Spectra will be measured inside and outside the reactors with the sensor head pointing at and away from the direct light beam. The manufacturer will certify the device on a yearly basis.

Light Intensity. A number of different methods will be used to measure the spherically integrated intensity in the reaction chambers and assess light uniformity. However, the primary means of measuring total light intensity will be at least three Biospherical Instruments, Inc. QSL 2100 PAR irradiance sensors. These sensors measure near-spherical irradiance in the 300-700 nm region, with the spectral and directional response curves and calibrations supplied by the manufacturer. These sensors will be used to check for light uniformity and how the intensity varies with time and location within the enclosure. Measurements will also be made inside and outside the reactor bags. The sensors can be located within the reactor bags, and thus will be used to measure changes in transmission through the chamber walls.

The responses from these sensors will also be compared to results of collocated NO_2 actinometry runs at various light intensities and using different light sources. Steady state actinometry measurements will be

made using data from experiments with appropriate NO_x and O_3 levels, with corrections being made for dark reactions in the sample lines. With an absolute calibration and a known spectral response of the instrument, and the known relative spectral distribution of the light source, the spherically integrated absolute intensity at a function of wavelength will be calculated.

4 QUALITY OBJECTIVES FOR MEASUREMENT DATA

The data quality objectives associated with the various types of measurement data include accuracy, bias, precision, detection limits, completeness, representativeness, and (where applicable) comparability. These indicators are described in more detail in the following sections. Provisional objectives for each indicator and type of measurement have been established, are presented in Table 1. However, these may be refined as the project progresses based on our experience with the measurement and how the data are used for model evaluation. These indicators will be measured, recorded, analyzed, and re-assessed on many of the methods by means of repeated calibrations, special tests, and audits as discussed below. Some of the indicators will be measured during sampling configuration experiments and actual chamber runs. The typical criteria will be used as indicators of error or bias in a data set.

4.1 Accuracy

Accuracy refers to the difference between the measured concentration or parameter value and the measurement or parameter value as derived from some standard independent traceable method that is taken as representative of the “true” value. Note that the accuracy of calibration method used as the standard also needs to be assessed, and the considerations discussed below is also applicable to those methods.

The accuracy standards currently set for each measurement are given in Table 1. These are based on considerations of the capability of the instruments together with the accuracy needs for the project. Although extremely high accuracy is obviously always desirable, in practice because of characterization uncertainties accuracies of ± 5 -10% are generally quite sufficient for using the data for model evaluation, and improving them beyond this level generally does not significantly improve the utility of the data. This level of accuracy (and precision) is not attainable for all instruments, and the values in Table 1 reflect levels that should be attainable and yet are sufficient to provide data of at least some utility for mechanism evaluation. If we find that the performance of the instruments with the lower accuracy standards can be improved, the standards may be improved so they are closer to the desired ± 5 -10% level. If the performance does not meet the standards on Table 1, a decision will be made either to reduce the standards or discontinue use of the measurement, depending on whether it is judged that the lower accuracy data will still have utility for the objectives of this project.

Quantifying the range of uncertainty of the in the data whose accuracy uncertainties is greater than $\pm 30\%$ is important if the data are to be used to evaluate model performance, since at that level the measurement uncertainty may be non-negligible compared to uncertainties in the model or the model inputs. The accuracy measures, discussed below, will be used as one of the factors to determine whether the model fits the data to within measurement uncertainty, along with considerations of bias and model input uncertainties.

The accuracy of the instruments will be determined from performance audit results. These tests will consist of challenging the instrument with a test atmosphere from an independent, traceable source not routinely used for calibrations. If possible, a minimum of four different audit gas concentrations, including zero ppm will be delivered to each concentration measurement instrument over its operational range. In some cases it may not be possible to provide more than one concentration. The test gas concentrations will enter each instrument through the same sampling system normally used during experimental runs. After the instrument

response has equilibrated, its output will be read from the data logger and, if necessary, corrected to reported engineering units.

The percent difference at each measurement will be calculated using the following equation:

$$\%Dif. = [(Y - X)/X] * 100$$

where X is the test value taken as the “true” value and Y is the corresponding reported instrument response. If the test consists of a multipoint comparison, the resulting data will be used to generate a linear regression equation in the following form:

$$Y = \text{Slope (X)} + \text{Intercept}$$

The deviation of the slope from unity will be the indicator of the relative accuracy of the instrument. The standard deviations of the slopes and intercepts will also be computed.

For concentration measurements, the intercept will provide an indication of the quality of the zero air used to calibrate the instrument, or other factors such as instrument drift or leaks in the sampling system. For these and other measurements that should in principle have zero intercept a satisfactory intercept is one whose that is no more than two standard deviations from away from zero, or no more than 3% of the maximum value, whichever is larger.

The nature of how the data deviate from a straight line fit will be taken as an indication of the linearity of the measurement. Indications of nonlinearity will be significant nonzero intercepts for measurements where the intercept should be zero, or the data deviating from the line at the high or low values in a consistent manner that is outside the level of uncertainty indicated by a statistical analysis of the scatter of the data. Where feasible, steps will be taken to assure that all measurements are in the linear range. Where this is not feasible, either non-linear calibration curves will be derived, or separate calibrations will be conducted for each concentration range.

Accuracy is particular concern for measurements where the sensitivity or response of the measurement varies over time. Records of calibration results will be maintained and statistical measures and plots will be maintained to track response stability in this regard. Instruments where this is a particular concern include the following:

- TDLAS, all species
- GC-Luminol, NO₂ and PAN
- Formaldehyde by Alpha Omega MA-100 (not yet evaluated – may not be a problem)

At the present time, the response stability is sufficiently questionable that it is considered necessary to span the instruments at least several times during the course of an experiment. This will be assessed by tracking the span stability over time, and if necessary the frequency of the span checks will be increased to achieve the desired performance objectives for accuracy.

4.2 Precision

Precision is a measure of the variability of replicate measurements of the same quantity. The precision standards currently set for each measurement are given in Table 1. The considerations involved in setting standards of precision include those involved in setting accuracy standards, as discussed in the previous section. However, although improving accuracy beyond $\pm 5\%$ generally does not significantly increase the utility of the data, greater levels of precision can be quite useful in some cases when evaluating model predictions of relative changes, either over time or when reaction conditions are modeled. Therefore, higher precision standards are set whenever this is considered to be attainable.

Precision can be determined from data in replicate calibration tests, as follows. Replicate calibration tests for all gas instruments will be assimilated and %Dif values will be provided using the following:

$$\%Dif = [(A - C)/C] * 100$$

In this equation, C is the concentration delivered by the standard calibration system and A is the analyzer response. The standard concentration must be at least 10 times the detection limit and at least five data points must be recorded before calculating the precision for each method. An average and standard deviation of all the %Dif values for each instrument are then calculated to provide precision estimates for each instrument. The results of these precision tests will be plotted on dedicated control charts, providing up-to-date evaluation of whether or not the performance of each instrument is within its established control limits. The precision will be determined as a percentage of the average concentration of the span check standard using the following:

$$\text{Precision} = \{x\}_{\text{avg}} \pm 1.96 * s$$

Where $\{x\}_{\text{avg}}$ is the average of the %Dif values, and s is their standard deviation. The upper and lower 95% probability limits are established using this statistical test. Provisional probability limits for each method are presented in the precision column in Table 1. The degree of adherence to these limits for each method will be periodically evaluated. If appropriate, these limits will be refined, and Table 1 in this QAPP document will be modified accordingly.

If necessary, the precision of selected methods can occasionally be determined from analyses from collocated data. In this case, two instruments that measure the same species will be calibrated and used concurrently. In this case the 95% limits for precision will be determined from calculation of the %Dif from each collocation run using the following equation:

$$\%Dif. = 2(A - B)/(A + B) \times 100$$

In this equation, A is the value from instrument A, and B is the corresponding value reported from collocated instrument B. A series of replicate collocation checks will be assimilated and an average and standard deviation of all the %Dif. values will be calculated for each measurement to provide a refinement of the precision estimates presented in Table 1.

In addition, this approach can be used to establish the repeatability for selected experimental runs, as appropriate. In this case the measured concentrations from each reaction chamber for a given method would be compared over selected time periods.

4.3 Measurement Bias

Bias refers to the measurement tending to err more in one direction than the other. Sources of bias might include interferences (positive or negative), sample line losses, converter inefficiencies in methods that require conversions, erroneous calibration standards, etc. It is essential that biases be minimized if the data are to be used for model evaluation, since bias in model simulations of measurement data is often the primary measure of model performance.

The bias standard for all instruments for this project is that the magnitude of the bias be no greater than $\frac{1}{2}$ the magnitude of the accuracy standard for the instrument. Bias is more of a concern for some measurement methods than for others. The measurements where bias is a potential concern are as follows.

- NO_x and NO_y measurements using converters for chemiluminescent detection of NO. The converters have variable efficiency and therefore the measurements are always subject to being biased low. However, if the “NO_x” or “NO_y” data are being used to derive concentrations of specific compounds, the possibility of unsuspected species being converted and detected as the target compound introduces a possible positive bias. For these reasons, NO_x or NO_y data will not be used for mechanism evaluation purposes only if no better alternatives are available, ideally only with pure compounds, and always with great caution.
- HNO₃ Measurements. HNO₃ is subject to line losses and therefore measured concentrations may be biased low or line losses during calibration may cause biases in the other direction. Steps must be taken to assure that line losses are not significant. Note that this is applicable both for specific HNO₃ measurements by TDLAS as well as for attempting to infer HNO₃ concentrations from NO_y data. It is probably not possible to measure HNO₃ in humidified samples except using in-situ methods.
- H₂O₂ Measurements. The possibility for line losses of H₂O₂ also needs to be evaluated, especially in humidified air.
- Formaldehyde Measurements. Line losses of formaldehyde are not considered to be significant when sampling dry air but may be a source of bias when sampling humidified air. The possibility of interferences in the wet chemical Alpha Omega method is also a concern.
- NO₂ by GC-Luminol. Data obtained in the first phase of this project (Carter, 2002) indicate that the GC-luminol method may have interferences in the measurements of NO₂, particularly in the presence of HNO₃. This has not been adequately evaluated.
- Low Volatility or “Sticky” Organics. Line or sampling losses may be non-negligible depending on the sampling method employed. This will need to be evaluated before conducting experiments where such measurements may be used.
- Spectral Interferences on TDLAS measurements. Biases may be introduced in TDLAS measurements if the spectral line being used has interferences from lines from other species. Generally this would yield positive biases because the lines are calibrated using pure species. This can be assessed by using different lines for measuring the species and seeing if the same results are obtained.

The research plan will include tests to characterize potential line losses for species of concern under the temperature and humidity conditions of the experiments to be carried out. Conducting calibrations using various sample line lengths and conditions is one approach that can be employed in this regard. Modifications

of the sample lines (such as heating) or moving the instrument or sampling point closer to the reactor may be necessary to reduce these biases to acceptable levels.

As indicated above, potential biases in the wet chemical formaldehyde measurement and NO₂ measurement by GC-luminol will be evaluated by comparing their measurements with the TDLAS measurement of the same species under various conditions. This will include, but not be limited to, measurements made during irradiations of complex simulated atmospheric mixtures where the greatest variety of potential interfering species may be present. If interferences are found to be significant, then use of the instrument may be discontinued, or the measurement may be used only for determining upper limit concentrations.

If two measurements of the same species are available, biases (or at least lower limits thereof) can be quantified in two possible ways, depending on the relative level of confidence we have in the different methods. If one of the method is considered to be the standard that is most likely to be unbiased, then the bias for the other measurement can be calculated using

$$\text{Bias} = [(X - S)/S] * 100$$

where S is the standard value and X is the value from the method being evaluated. If neither method is considered to be less likely to be biased than the other, then the bias for each measurement is calculated using

$$\text{Bias} = 2 (A - B)/(A + B) * 100$$

where A and B are the values of the respective methods. In either case, the bias over a particular sample run is then assessed by taking the average and standard deviation of these discrete quantities. The average is taken as the measure of the bias, and the standard deviation can be used to assess the significance of this bias measure. Obviously if the standard deviation is large compared to the average then the bias is low compared to the precision, and is either not of concern or needs to be assessed using a more precise standard method.

4.4 Minimum Detection Limits

Detectability is the low range critical value that a method-specific procedure can reliably discern, at a specific probability, from a zero concentration. For many species it is of critical importance to this project since a major research objective is obtaining data at lower pollutant levels than previously studied.

Analytical procedures and sampling equipment impose specific constraints on the determination of minimum detection limits (MDLs). For the continuous gas analyzers, MDLs are determined by repeatedly challenging the instrument with zero air, and for methods requiring sample collection and subsequent laboratory analysis the MDLs are determined by the use of laboratory blanks. Besides providing MDL information the use of blanks provides essential laboratory measurement control data. Generally, the MDL for measurements on this program is determined as three times the standard deviation of laboratory blanks or three times the standard deviation of the instrument response when subjected to zero air.

The MDL for each continuous gas analyzer has been well characterized; this information can be found in the appropriate analyzer manual. This information can be verified through statistical evaluation of data from zero air checks, using the following:

$$\text{MDL} = t_{(n-1, 1-a = 0.99)} * s$$

In this equation, s is the standard deviation of the replicate zero analyses; t is the student's t value appropriate to a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom.

The determination of MDLs for discrete measurements involves a different approach. The samples are collected at a location away from where the analysis is performed. Standards for the determination of detection limits for the laboratory analytical instruments are prepared in the laboratory and therefore are not subjected to the same procedures and equipment as the reaction chamber samples. This detection limit is referred to as the instrument detection limit (IDL). The IDL is indicative of the ability of the instrument to differentiate, at a specific probability, between zero and at a specific concentration. It should be noted that the determined IDL does not include the sampling and handling process. However, the IDL for each laboratory analytical method will be determined through statistical evaluation as described in the equation above.

The MDLs associated with the various instruments employed in this project are given in Table 1. Note that some of the values given there are estimates and subject to change as the instrument or method is evaluated. These cases are noted in footnotes to the table.

4.5 Completeness

Completeness refers to the ratio of the number of valid measurements to the number of measurements called for in the experimental protocol or sampling schedule. Completeness objectives depend on how the measurements are used and the extent to which the sampling schedule reflects changes in the measured species or parameter. The following considerations are used when assessing whether completeness is adequate for a particular measurement in a particular experiment, given in approximate order of importance:

- The sufficiency of the measurements to establishing the conditions of the experiment for modeling. For example, completeness in data to determine initial reactant concentrations is critical and the run may be useless if such data are lacking. When possible, at least two measurements of important initial reactants are desirable for verification and to reduce characterization uncertainties.
- Whether the measurements are sufficient to establish how conditions of the experiment vary with time. The number of measurements required will depend on the extent to which the parameter vary during the course of the experiment or from run to run and the sensitivity of the model simulation to the variation. If experience indicates that variation during an experiment is sufficiently minor then only a few measurements may be sufficient, and if run-to-run variation is sufficiently small then missing data may be acceptable in a limited number of experiments, particularly if they are replicate or control runs.
- How rapidly the concentration of the measured species varies throughout the course of the experiment. Missing data during periods when the species concentrations are rapidly changing can reduce the utility of the experiment for model evaluation, while data when concentrations are relatively constant or below the MDL have relatively small or no impact.

The protocol or sampling schedule set by the investigators for the experiments is designed to provide sufficient data density to achieve these standards and, to the maximum extent feasible, sufficient redundancy to minimize losses in data utility due to bad samples or malfunctions.

Nevertheless, even if relatively low levels of completeness can be acceptable in many circumstances, poor instrument performance in this regard increases the probability of unacceptable omissions and need to be corrected. Corrective action will be taken if data losses occur with unacceptable frequency or if instrument performance is considered to be such that this is likely to be the case.

4.6 Representativeness

Representativeness generally expresses how closely a measurement reflects the characteristics of the environment being monitored. In the context of these experiments, this includes, but is not necessarily limited to, the following considerations:

- whether the sample probes are sampling material representative of the bulk of the reactor;
- the times associated with each sample;
- whether the sampling from the reactor has occurred for a sufficient period of time for the values to be representative of the reactor; and
- whether dark reactions occurring in the sample lines may be affecting the measurements.

Note that the possibility of biases of individual types of measurements due to sample line losses has already been discussed in Section 4.3, above.

Experience suggests that the reactors used in environmental chamber experiments are generally well mixed and thus sample probe placement is not critical. However, this will be verified by conducting experiments with probes in different locations, and alternatively or simultaneously sampling from the different probes.

A minimum requirement for representativeness in terms of sample times associated with the data is that all clocks used to enter sample times or experimental operations be synchronized. This is done by having wall clocks at critical locations in the laboratory and the computers used for data collection or acquisition all synchronized to the NIST time standard. The SOPs for conducting experiments and sampling call for the operators assuring synchronization of all clocks used and only referring to such clocks when making lab book or data entries.

The sampling time for data taken manually will be recorded in the log book using a NIST-synchronized wall clock and entered into the run database along with the measurement results. However, the sampling time for data collected automatically and logged by the data generally reflect the ending period of a sampling period over which the data are averaged. In addition, some instruments, such as Alpha Omega formaldehyde analyzer, have significant lag time between sample collection and data reporting. In these cases, an appropriate offset time will be derived for each instrument based on its sampling lag and averaging times, and the correction will be applied so the time associated with the data represents the mid-point of the sampling period.

Generally, most continuous monitoring instruments will be alternatively sampling different sources over a regular cycle as determined by the sampling protocol for the experiments. Since eventually the chamber will have a dual reactor configuration (see Section 3.1.4, above) this would involve sampling alternatively from the different reactors, as well as from zero air and (from time to time) calibration sources and the chamber

enclosure. For the data to be representative of the various sources the sample line must be flushed completely with the air being sampled and the instruments must have sufficient time to respond to the change and stabilize on the appropriate levels. Experiments will be conducted to determine the time required for the instruments to respond to changes and achieve stable readings with the sampling configuration employed. This will be used to derive a minimum data stabilization time, which will be equal to the equilibrium time for the slowest responding instrument on the sampling manifold, multiplied by a factor of 2 to assure complete stabilization. The sampling schedule will be set such that the time for sampling from each source is at least this minimum stabilization time plus the longest minimum averaging time for the instruments, and data collected before the minimum stabilization time has passed will be flagged as “transitional” and not used in the final reported data set.

The lengths of the sample lines will be minimized to the extent possible to minimize sample losses and dark reactions in the lines, but because of the configuration of the laboratory relatively long lines will still have to be used. Issues of sample line losses were already discussed in Section 3.1.4 as a type of bias. Sample line reactions are probably not significant for most species currently planned to be monitored, because of the relatively short residence times compare to the time scale of most reactions. The major exception is dark reaction of O₃ with NO, which is sufficiently fast that measurable losses may occur. This is often dealt with in model evaluation studies by using [O₃]-[NO] as the primary measurement for model evaluation, since this quantity is unchanged by this reaction and is influenced by the same mechanistic characteristics. However, simultaneous measurements of O₃ and NO are useful for some purposes, such as determining light intensity using the photostationary state method (Carter et al, 1996). In this case, corrections to the data may have to be made using the sample line residence time and the rate constant for the O₃ + NO reaction. The sample line lengths and the flow rates will be measured with sufficient accuracy that the residence times data needed for such corrections can be determined.

4.7 Comparability

Comparability refers to how confidently one data set can be compared with another. It is the objective of this study that the generated data will be of sufficient quality to facilitate comparison with similar experiments performed at other locations. This will require adherence to the data quality objectives of each criterion listed above.

5 CHARACTERIZATION OF EXPERIMENTAL CONDITIONS

Adequate characterization of experimental conditions is necessary for the data obtained to be useful for model evaluation, which is a major objective of this project. Experimental conditions include not only directly measurable physical parameters such as temperature and light characteristics, but also reactor conditions such as dilution and chamber effects such as wall offgasing and loss processes and the chamber radical source. A summary of the types of characterization information that is considered to be important, how this information will be obtained, and the associated characterization quality objectives and acceptance limits are discussed below.

5.1 Physical Parameters

5.1.1 Temperature

As indicated in Table 1, the temperature in the reactor is measured with various thermocouples, with accuracy and precision objectives of ± 0.2 and $\pm 0.1^\circ\text{C}$, respectively. The characterization objectives are that the temperature be accurate to within $\pm 0.5^\circ\text{C}$, and that the temperature during an experiment be constant and uniform to within $\pm 1^\circ\text{C}$. Initially each thermocouple will be calibrated a standard temperature sensor. The temperatures in the reactor enclosure will be measured as a function of time and location at selected temperature settings. These tests will be performed when the enclosure is new and after any modifications are made to the temperature control or air handling systems. During actual experiments the temperature will be measured at a set location in each reactor, and if any spatial variability is observed the variability relative to this set location will be determined.

5.1.2 Light Intensity

The absolute light intensity inside the reactor will be determined by conducting various types of NO_2 actinometry measurements such as discussed by Carter et al (1996). The various types of available NO_2 actinometry measurements include the quartz tube measurements using the method of Zafonte et al (1977) modified as discussed by Carter et al (1996) and the NO , NO_2 , O_3 steady state method as discussed by Carter et al, 1996, 1997). The latter method has the advantage of measuring the light intensity within the volume of the reactor, which is the primary measure of interest, which is a significant advantage over the quartz tube method that measures the light intensity only in a single location, usually outside the reactor. However, data obtained previously in our laboratories (Carter et al 1996, 1997) indicate that this does not always yield reproducible results, and is subject to uncertainties due to reactions in the sample line and also measurements near the detection limits in many cases. Therefore, the principal method for establishing absolute intensity will be the quartz tube method, but in conjunction with relative light intensity measurements to assess light uniformity and variability.

The primary means for assessing light uniformity and variability will be use of the QSL PAR radiation sensors, which provide a relatively high precision measurement of near-spherically integrated intensity on a continuous basis. Although the absolute accuracy is uncertain, this measurement appears to be highly precise and the sensor heads are easy to relocate, making them well suited for uniformity measurements. These measurements will be placed on an absolute basis by making co-located NO_2 actinometry measurements using

the quartz tube method, using the same light source that will be used in the experiments. The PAR radiation sensors are also supplied with absolute calibration information that can be used for a consistency check, though the chemical actinometry measurement will continue to be used as the primary standard unless there is some reason to re-evaluate this. The PAR measurements will then be used to assess light uniformity within the portion of the enclosure where the reactor is located, and also measure the difference in light intensity inside vs. outside the reactors.

During most experiments the sensors will be located at a standard position within the reactors to determine variation of light intensity with time. This will provide information not only on changes in intensity due to any changes in the light source, but will also characterize the effects of ageing of the reactor walls on intensity within the reactors. The sensors will be periodically compared with results of NO₂ or other actinometry measurements, and will be periodically recalibrated by the manufacturer.

The objectives for light uniformity within the space where the reactor will be located is $\pm 5\%$, and if that cannot be achieved with the current reactor design then the reactor volume may be decreased. The objective for stability in light intensity over time is $\pm 15\%$. The accuracy objective that is achievable will depend on the achievable accuracy of the quartz tube NO₂ actinometry measurement, which we estimate to be on the order of 15%. Light intensity measurement accuracy of 5-10% is desirable, but it is unclear at present whether this is attainable.

5.1.3 Light Source Spectrum

The spectrum of the light source will be measured as a function of time and orientation using the LiCor LI 1800 spectroradiometer. The spectra will be measured in the enclosure prior to installing reaction bags, with the sensor head oriented in different directions (facing the light, away from the light, or towards the other walls, ceiling or floor) to determine the extent of variability due to orientation. After reaction bags are installed, the spectrometer will be placed inside the reactor and spectra will again be measured as a function of orientation. The latter measurements will be made from time to time as the reactor ages or when new reactors are installed. During most experiments, the spectrometer will be placed on a standard location facing the light, so changes over time can be measured and tracked. Spectral measurements will be periodically made with the spectrometer in a standard location behind the reactors, where light reaching it passes through both reactor walls.

The LI 1800 will be calibrated annually at the factory using a standard light source. The possibility of obtaining a standard lamp for more frequent calibrations in house will be investigated.

The LI 1800 does not measure the light spectrum below 300 nm. Although the light source with appropriate spectral filters does not have significant intensity at wavelengths lower than that, it may be that the LiCor may indicate measurable intensity at lower wavelengths. In this case, we will employ the Spex spectrometer system available at our facility to measure the spectrum at lower wavelengths. This also provides data at higher spectral resolution, and was used to derive the recommended spectrum we use for modeling blacklight light sources (Carter et al, 1996). However, because it is less portable it is not as well suited as the LI 1800 for assessing how the spectrum changes on a routine basis.

5.1.4 Humidity

Although most of the experiments for this project will be conducted using dried purified air, some experiments, particularly those involving measuring aerosol formation, will involve use of humidified air. As indicated on Table 1, a dew point hydrometer, which is interfaced to the data acquisition system will be used to monitor the humidity in all experiments using humidified air. The hydrometer is also on line during most dry air experiments, to confirm that the matrix air is indeed dried. The specification for unhumidified experiments is for the dew point to be below -40°C , the minimum dew point that can be measured using this instrument.

5.1.5 Dilution

Dilution of reactants will occur if the bag leaks in such a way that outside air enters the reactor, or if the experimental or reactant injection procedure involves flushing additional matrix air into the reactor during the course of the experiment. Dilution by external air is undesirable because it may introduce contaminants, so a design objective for the reactor configuration is to have the reactor always under a slight positive pressure so any leaks would be outward rather than inward. In this case, leaks will be manifested by reactor collapse but not cause significant dilution. However, this needs to be periodically verified.

The dilution rate can be determined either by injecting inert species and monitoring their concentrations over time, or by monitoring relative consumption rates of reactive species and correcting for their known relative rates of reaction, as discussed by Carter et al (1993). The former method will generally yield more accurate and precise dilution information, while the latter can be used for most experiments where a variety of reactive species are present. Although carbon monoxide is not totally unreactive in irradiation experiments, it is sufficiently slowly reacting that the correction due to reaction is small or negligible. Since carbon monoxide - NO_x irradiations are also useful for assessing the chamber radical source (see Section 5.2.3), the data from those experiments can be used to assess whether dilution is in an acceptable range. The goal is to have dilution rates of less than 0.1 %/hour, and if dilution rates of greater than ~ 0.20 %/hour are observed, then corrective action will be taken.

If the experimental plan calls for continual dilution and CO is not suitable either because its presence is not desired or it could be formed in chemical reaction, then an unreactive or low reactive organic will be added and will be monitored by gas chromatography to measure dilution. The optimum compound and analysis method to use for this purpose has not yet been determined.

5.2 Chamber Characterization

Chamber wall effects and (in some cases) background species can generally not be avoided in environmental chamber experiments, and need to be adequately characterized for the data from the experiments to be useful for model evaluation. The types of wall effects that are currently being considered, and the approaches and characterization quality standards that will be used to assess them are summarized in this section.

5.2.1 Background Offgasing and Contaminant Levels

Background levels of contaminants in the reactors will be assessed by utilizing our available analytical equipment to measure potential species in the reactor after injection with pure air, both in the dark and upon irradiation. For NO_x , CO, formaldehyde, and organics other than methane and ethane the objective is for the background level of these species to be below the detection limits of our current instrumentation, as indicated in Table 1. The objectives for methane and ethane will be established once the performance of the methane combustor in the pure air system can be assessed (it is currently back at the factory being repaired), but it is hoped that methane can be reduced to below 10 ppb and ethane can be reduced to below the current GC-FID detection limits.

Much more sensitive indications of background offgasing and contaminant effects can be obtained by appropriate characterization experiments, which in some cases can yield measurable responses to levels of background NO_x or VOC levels that are below the detection limits of our current instrumentation. O_3 formation in CO – air or aldehyde – air are extremely sensitive to NO_x offgasing in trace levels, and O_3 formation in pure air irradiations are very sensitive to trace VOC as well as trace NO_x . Therefore, NO_x offgasing and background VOC effects will be evaluated using such experiments and determining the offgasing rates that are required for model simulations to be consistent with experimental results, as discussed in the first interim report for this project (Carter, 2002).

As part of the initial reactor characterization, a comprehensive set of background offgasing tests will be performed at various temperatures and following various types of experiments in the reactor. Since new reactors appear to have higher background effects than ones exposed to repeated pure air irradiations, the reactor will be conditioned by flushing with the lights on and replicate experiments will be conducted to assure they have attained consistently known values. The effect of HNO_3 , H_2O_2 and nitrate aerosol on NO_x offgasing will also be determined, though the aerosol experiments will not be part of the initial assessment.

These background offgasing tests will be performed periodically during the course of conducting these mechanism evaluation experiments to assure that they are within the previously established acceptable range, as measured during the initial evaluation process. This will be important when conducting very low NO_x experiments that may be sensitive to such offgasing.

The results of the initial characterization experiments will be used to determine the acceptable range of NO_x and background VOC offgasing effects, which will probably be expressed in terms of O_3 formation rates in standard pure air and VOC – air experiments. Once these have been established, the characterization experiments will be used to determine whether it is acceptable to continue to use this reactor, or whether corrective action, such as additional flushing or other cleaning procedures, or replacing the reactor entirely, are needed.

5.2.2 Wall Loss Measurements

Ozone and HNO_3 are known to be destroyed or absorbed on chamber walls, and this may be the case for H_2O_2 and (under humidified conditions) formaldehyde as well. Dark decay tests will be performed for O_3 , HNO_3 , H_2O_2 and formaldehyde when the reactors are newly conditioned and periodically once they are in use. Possible interactions of these species in affecting their dark decays will be assessed by measuring their dark

decays when mixed together as well as each separately in pure air. The effects of varying temperature, humidity, and (eventually) the added aerosols will also be assessed. During the initial evaluation period they will be preceded and followed by NO_x offgasing or radical source experiments to determine if they have any effect on the results. The effect of light on HNO₃ wall losses will be determined from the data taken during the experiments assessing the effects of HNO₃ on NO_x offgasing and the radical source.

The results of these experiments will be used to establish acceptable limits of wall loss rates. Corrective action will be taken if wall loss measurements indicate that these standards are not being met with a particular reactor.

Wall losses may also be a concern in experiments with low volatility materials. This will be assessed by injecting the materials into the reactors and monitoring their changes in concentration in the dark, when chemical reactions consuming them should not be occurring.

5.2.3 Radical Source Measurements

The chamber radical refers to a heterogeneous reaction or offgasing process that results in higher radical levels in irradiation experiments than can be accounted for by known homogeneous processes (Carter et al, 1982, 1996). As discussed by Carter et al (1996), the magnitude of the chamber radical source can be assessed by conducting n-butane - NO_x and/or CO - NO_x irradiations to determine which radical input rate is needed for the model to fit the experimental results. Such experiments will be conducted at various NO_x levels, temperatures and humidities as part of the initial characterization experiments. The effect of added HNO₃ and (eventually) aerosols on the magnitude of the radical source will also be assessed.

The acceptable limits for the chamber radical source is tentatively set as the range obtained in the "pillowbag" experiments discussed by Carter et al (2002). This may be reduced if the initial characterization experiments indicate that lower radical source levels are achievable with the larger reactor.

Radical source measurement experiments for the appropriate conditions will also be carried out in conjunction with mechanism evaluation experiments, to assure that the conditions of the reactor are not changing in this regard. If the results indicate that the radical source is outside the expected range based on the initial characterization experiments with well-characterized reactors, then corrective action will be taken.

5.2.4 Side Equivalency Tests

The enclosure will be equipped with dual reactors to increase productivity and to provide a precision dimension to reactivity assessment data. Side equivalency tests consist of conducting the same experiment in both reactors to assure that the same results are obtained. Most of the characterization tests discussed above will consist of the same test in both reactors, allowing side equivalency (or precision) for each test to be determined. Side equivalency tests between the reactors will also be determined by conducting various types of standard or control experiments to determine precision under conditions representative of mechanism evaluation. Note that this will be done only after it is demonstrated that the sampling systems for each reaction chamber are equivalent.

5.2.5 Aerosol Effects Characterizations

The effects of the reaction chamber on wall losses of aerosol materials will be determined by adding aerosols of appropriate types and measuring changes in size and number distribution over time. This will be done both in the dark and with the light on, and in the temperature and humidity ranges that are associated with the experiments where aerosol effects or secondary organic aerosol (SOA) formation is measured.

5.2.6 Additional Characterization Experiments

The tests described above will not necessarily be the only types of characterization and/or control experiments that will be performed. Additional experiments or characterization tests may be necessary, based on results of the ongoing project results and external inputs.

5.3 Control Experiments

Various types of standard VOC - NO_x tests will be initially performed and at least every six months thereafter to assure that reproducible conditions are obtained within the reactors and for quality assurance for the various measurement methods. These will represent NO_x conditions and O₃ levels characteristic of the mechanism and reactivity evaluation experiments of interest. These tests will include as a minimum: 1) standard propene - NO_x experiments at ~10-20 ppb, and 2) surrogate - NO_x experiments of the type used for the base case in the reactivity experiments.

Standard aerosol-forming experiments will also be used for control purposes in conjunction with studies of particulate formation; the type of experiment most appropriate in this regard has not yet been determined, and more than one type may be appropriate.

6 STANDARD OPERATING PROCEDURES

The procedures to be employed when conducting chamber experiments this project, operating the associated equipment, and processing the data obtained are or will be described in various standard operating procedure (SOP) documents, which are listed in Table 3 and discussed below. The personnel responsible for carrying out the experiments are required to follow these procedures unless indicated otherwise in the instructions for the experiments provided by the Project Manager or Project

Given below is a brief summary of the standard operating procedures documents that have been prepared, their objectives and current status.

6.1 Standard Procedures for Conducting EPA Chamber Experiments

The overall procedures and operations that should be followed when carried out carrying out chamber experiments using this facility, unless instructed otherwise by the project scientist, is described in the “Standard Procedures for Conducting EPA Chamber Experiments” document, which is included as Appendix A to this QAPP. This is referred to as the “Chamber SOP” in the subsequent discussion. This describes in general terms the major of operations and protocols that need to be carried out when conducting experiments, and is intended for use by the technicians and scientists who are experienced with the operations and instrumentation available at our facility. Separate SOP documents exist or are being prepared that give additional detail for operation of specific instruments or procedures that can be used for training personnel not familiar with the equipment or procedures involved. Although this Chamber SOP was prepared to address the specific objectives of this project, it is also applicable for all experiments to be carried out for the purpose of mechanism evaluation and chamber characterization.

The objectives of the Chamber SOP is to describe default procedures that will result in experiments being carried out under appropriate and well-characterized conditions, and with the needed measurements being made at the appropriate times, with the measurements, operations and conditions being well-characterized and documented. Reproducibility of conditions when appropriate is also an objective. The scope of the chamber SOP includes the following:

- Maintenance of log books
- Procedures for preparing the enclosure and reactor for experiments
- When and how span and zero checks should be conducted in conjunction with experiments
- How reactants should be injected
- When measurements should be made and how frequently at various times during the experiment, such as immediately before and after major operations such as turning on or off the lights or injecting reactants.
- How the irradiation should be initiated and terminated
- Procedures for accessing the enclosure during experiments
- General GC analysis procedures

Table 3. List of Standard Operating Procedure (SOP) documents for the UCR EPA chamber and associated equipment and operations

Description or Title	Status
<u>General</u>	
Standard Procedures for Conducting EPA Chamber Experiments	Draft written by PA and under review. Included as Appendix A. See Section 6.1
Data Processing Procedures for UCR EPA Environmental Chamber Experiments	Draft written by PA and under review. Included as Appendix B. See Section 6.2.
<u>Operations</u>	
Construction of Rectangular Reaction Bags	Draft written
Operation of the Vortek Lamp	Preliminary draft written but additional detail required
Operation of Chamber Enclosure Cooling System	Preliminary draft written but additional detail may be required
Operation of Air Purification System	Not completed
Operation of Vacuum System	Not started
Operation and Calibration of Dilution Calibrators	Not started
Certification of Ozone Transfer Standard	Status unknown
Singer gas dry meter calibration	Not started
Bubble flow meter calibration	Not started
Calibration of HNO ₃ Trace Gas Sources	Draft written
Calibration of H ₂ O ₂ Trace Gas Source	Draft written
Preparation of Calibration Standards for Gas Chromatography	Status unknown
<u>Individual Instruments</u>	
Teco NO-NO _y Analyzers	Drafts written for various field projects need to be modified to be appropriate for operations with chambers
Eco-Physics NO Analyzer	Draft written
Ozone Analyzers	Not started
CO Analyzer	Not started
GC-Luminol NO ₂ and PAN analyzers	Draft written for a field project needs to be modified to be appropriate for operations with chambers
Operation of TDLAS #1	Not completed
Operation of TDLAS #2	Not completed

Table 3 (continued)

Description or Title	Status
Operation of FID GC analyzers	Not completed
Operation of Alpha-Omega Formaldehyde Analyzer	Draft written
Calibration and placement of temperature sensors	Not started
Operation and maintenance of the Li-1800 spectroradiometer	Not started
Operation and maintenance of QSL PAR radiation sensors	Not started

The current version of the Chamber SOP document is applicable for the chamber when configured with pillowbag reactors and the sampling system as of April 2002. Revisions are anticipated when the larger dual reactors are installed and the final sampling is completed.

6.2 Data Processing Procedures and Documentation

The procedures, programs, and files to be used for data processing for the chamber experiments for this project are described in detail in the “Data Processing Procedures for UCR EPA Environmental Chamber Experiments” document, which is included as Appendix B to this QAPP. Responsibilities of personnel with regard to data input, documentation, processing and quality assurance are also described. The functions, formats, and locations of the various computer files involved are documented, and relevant checklists and standard operating procedures with regard to data processing are summarized. It also describes the procedures that should be used to communicate and document instructions for the procedures for the experiments to be carried out.

The Data Processing Procedures document is intended for use by the technicians and scientists familiar with the types of data being generated, and assumes a knowledge of how to access and use the CE-CERT computer network and other basic computer skills, such as knowledge of Microsoft Excel, which is used as the primary means for working with the data obtained. However, it assumes no prior knowledge of the data files and custom macros and programs employed, nor where the files should be located on the CE-CERT network. The document discusses the following

- Personnel involved with data processing, and their responsibilities. This is consistent with the personnel description given in Section 2.2, but with a greater emphasis on specific data processing tasks.
- Formats, naming conventions, and the network locations of the various types of data files involved with the experiments. This includes various types of raw data files, the run data files that contain the raw and processed data for each experiment, templates, macro, and plotting files, and various types of summary information files that are used for data processing or documentation.

- Operation of the various programs and macros that have been developed to load raw data files into the run data file and processing the data for viewing and modeling. A number of Excel macros have been developed for this purpose, and this section documents the operation of these macros.
- Step-by-step data processing procedures that should be employed for each experiment, including a checklist to assure that the necessary procedures are followed. This includes procedures for preparing, reviewing and revising run instructions as well as data processing procedure during and after experiments.

The current Data Processing Procedures document is still a draft. Some files and procedures have not been implemented, and these cases are indicated by comments given in read font in the draft.

6.3 SOPs for Specific Instrumentation and Operations

As indicated on Table 3, Standard Operating Procedure documents are being prepared or will be prepared for describing how to operate specific instruments or carry out specific procedures for this project. These SOP documents serve several objectives, including

- assure safety of personnel when operating the equipment or procedures;
- document procedures carried out for reporting purposes and so that results can be reproduced;
- assure that appropriate procedures are followed on a consistent basis;
- assure that calibrations and needed quality assurance checks are conducted at appropriate intervals;
- assure that the equipment is properly maintained; and
- assist in training personnel who are unfamiliar with the procedures and equipment employed in our laboratory.

Personnel working on this project will be expected to follow these SOPs except in cases where they are instructed otherwise due to special requirements of the experiments or are otherwise inappropriate.

The objective is to have SOP documents for all the types of analytical equipment employed for this project and for operation of complex equipment where inappropriate procedures may affect data quality, proper equipment operation, or safety. The list of SOPs on Table 3 is probably not comprehensive, and additional SOPs will be added as the need becomes evident, or new equipment is acquired.

As indicated in Table 3, the process of preparing specific SOPs is currently underway but is far from complete. The priority has been to adopt existing SOPs from field projects to the purpose of this project and to prepare SOPs for new equipment and procedures at the time the appropriate procedures are being developed. SOPs for equipment and procedures where appropriate procedures have been well established at our laboratory by long practice are given somewhat lower priority, but are being developed as time permits.

7 DATA ACQUISITION AND MANAGEMENT

7.1 Data Acquisition

The data acquisition system for this project has been designed to acquire the continuous raw data from all the continuous analyzers and ancillary measurement equipment. The system contains a dedicated desktop computer configured with Labview software. The system contains 16 channels for thermocouple temperature measurements, 10 RS-232 digital input channels, and 16 analog input channels. The system converts all input channels into digital format for validation, use, and storage. The computer will record and store the responses from all the analyzers and other equipment, and store the results on raw data computer files. These raw data computer files are then used as input for the data processing procedures discussed in Appendix B.

The data acquisition system is configured to register the value of each measurement channel and average these values each minute. The concentrations recorded by the data logger are only delayed from real-time by the measurement delay inherent to each specific instrument. (These instrument-specific measurement delays can be separately specified for each instrument for the purpose of data processing, as discussed in Appendix B.) The clock on the computer running the data acquisition system linked to the correct time using a program that accesses reference universal time over the internet. The data acquisition system will record data in one-minute averages for all gas analyzer channels during that period, and the reported concentration for that period is defined as the last one-minute average during that period.

The sampling mode varies depending on the objectives of the experiment as discussed in Appendix B, but generally a source is sampled for a minimum of 10 minutes to allow the data to stabilize. The data acquisition system provides the information sufficient in most cases to determine what is being sampled when the data are being collected (e.g., a reactor, enclosure, zero air or a calibration source), which it determines either by sensing the states of the valves, or reading input from the valve control program, or by accepting manual input from the operator. In cases where this is not sufficient, the operator records what is being sampled in the log book (using the exact time using a wall clock referenced to universal time by radio signal), which is entered into the run data file when the data are processed as discussed in Appendix B.

7.2 Data Recording and Identification

The Project Engineers are required to maintain detailed measurement system and/or instrument log books which detail operating conditions, calibrations, audits, maintenance, and any exceptions to normal operation of the measurement system. In addition, as discussed in Appendix B, the file \\ozone\apl\data\instruments\instinfo.xls contains a worksheet that should clearly identify each instrument with its associated data input channel number, and the Project Engineers are required to keep this worksheet up-to-date at all times. Log book recorded information is required to be at a level of detail sufficient to identify all periods of normal data collection; and all periods during which known problems exist for one or more instruments. In addition, all periods of data collection, including the specific sampling mode and any known problems with any of the instruments, will be logged at a sufficient level of detail in order to preclude misdirection of data.

Electronic data from the data collection computer at least once a week as discussed in Appendix B. In addition, as also discussed in Appendix B the data management software enables downloading of the raw data directly into Excel spreadsheets, within which the data will be validated, analyzed, and archived. During the data validation process the level of validation and the experimental test number will be clearly identified with the data set from each sample run.

As discussed in Appendix B, each chamber experiment will have an Excel file that contains the loaded and processed data, the comments and flags for the experiments, and parameters used to process the data. This file will identify all processed data arrays in terms of terms of which species it measures, which instrument is used, the units of the data, corrections made to the raw data, if any, and the locations of the raw data files, if applicable. A standard set of species or measured parameter names will be used, as indicated in the file \\ozone\apldata\chambers\ exptspec.xls. This file also indicates the units that should normally be used when processing data for those species or parameters (see Section 7.3). A standard set of unique instrument designations will also be used, as indicated in the file \\ozone\apldata\instruments\instinfo.xls. That file lists all instruments that have been or are being used to make measurements in the chamber (if only for a single experiment), and indicates the manufacturer, model, and serial numbers, and other relevant information for that instrument. This can be used to obtain information about the instrument based on its designation as given in the run data file.

7.3 Data Units

A consistent set of units will be used to report measurement data, as specified in the file \\ozone\apldata\chambers\ exptspec.xls referenced above and in Appendix B. Units of major types of measurements are as follows:

- Gas Concentration Parts per million by volume (ppm) at 298.15 K and 1 standard atmosphere (760 torr) total pressure (see below)
- Temperature Degrees K
- Volume Liters
- Light intensity by radiometer **To be determined. Probably mw/cm².**
- Light intensity as NO₂ photolysis rate Min⁻¹
- Clock time Local standard or daylight time as determined by clock linked to standard universal time by radio or internet
- Elapsed time Minutes
- Injected liquid concentration Microliters

The gas concentration measurements will be reported in parts per minutes (ppm) units to be consistent with the units generally used when modeling gas-phase chemical processes in ambient air and environmental chamber experiments. However, to avoid conversion problems and ambiguities resulting from use of units that depend on ambient conditions, these will be placed on a molecular basis by using ppm at standard temperature and pressure. Standard temperature is defined as 25 degrees C or 298.15 K and standard pressure is 1 standard atmosphere or 760 torr. By this definition, 1 ppm is always 4.0873×10^{-8} moles/liter regardless of the ambient

temperature and pressure. By this definition, conversions of reported ppm to molecular or mass based units will not depend on ambient conditions.

Appropriate corrections will be made when conducting calibrations to assure that the reported units are ppm at standard temperature and pressure, which may be different than ppm under the conditions of the calibration. Note that our laboratories in Riverside, California are at an altitude such that the ambient pressure is generally ~97% of a standard atmosphere, so this pressure difference will need to be taken into accounts in some types of calibrations to avoid introduction of a consistent ~3% bias in our data.

7.4 Control of Erroneous Data and Data Validation

Power failures, instrument or computer failures, operator intervention for maintenance and calibration, deviation of the instrument calibration results outside the acceptable limits, deviations of the QC checks outside the acceptable ranges, problems with the sample runs, or other problems are all factors can potentially compromise data validity. The Project Engineers will identify those periods during which specific data may be considered unreliable by the use of notations in the log book. These notations will then be used to flag periods of problem or unusable data in the processed data file produced during data processing as discussed in Appendix B.

As discussed in Appendix A, most experiments will involve alternating sampling inputs from several different sources. This will necessarily involve periods when the source being samples is not well defined, or when the sample lines and/or instruments are stabilizing because the concentrations are changing due to changes in the source being sampled. To account for this, as discussed in Appendix B the Excel macros that process the continuous monitoring data automatically exclude all data for set amounts of time after the sample state has changed. This transition time for which data are excluded can be set for each measurement type and instrument and also for each sampling state. Based on experience from examining stabilization times on various instruments, this ranges from 3 to 10 minutes, depending on the stabilization time of the instrument or (for span sampling) how long it takes for calibration source concentrations to stabilize. As discussed in Appendix B, the default stabilization times can be changed or flags can also be entered manually in the data processing process if examination of the data indicate that the default stabilization times are not adequate.

The data processing procedures discussed in Appendix B also include inspecting data graphically, which often very useful in making and discrepancies and inconsistencies evident. Preliminary modeling of the experimental results, involving comparing experimental measurements with model predictions, is also carried out at the later stages of the data processing procedure, and experience has indicated that is also useful in suggesting where possible experimental problems may exist. Such problems will be resolved by discussion within the project team and/or by reference to the raw data and the project logbook, and the results will be reflected by comments and flags in the run data file as discussed in Appendix B.

As discussed in Appendix B, some of the data processing involves taking averages of data for the purposes of conducting span or zero checks or determining initial or average conditions for modeling. As indicated above the data processing procedures involve visual examination of data plots to determine if anomalous or invalid data exist, and flagged data are not used when computing these averages. In addition, to avoid the need to manually flag all clearly spurious data points before computing these averages, the data processing programs discussed in Appendix B will not include data in the averages that are more than three

standard deviations from the averages. These are computed in an iterative process by computing the average, determining if any points are more than three standard from this average, and re-computing the average excluding them, then repeating this process until such points are no longer found.

7.5 Data Management

Data management, formatting, and archiving is described in the Data Processing Procedures document given in Appendix B.

8 RECORDS MANAGEMENT

CE-CERT will maintain a records management system specifically dedicated to this project. The objective is to provide efficient retrieval of all experiments performed, along with all supporting documentation, which include all pertinent records, logs, files, and reports from all tests. In the case where the records are in electronic format, they will be stored in a dedicated LAN system share drive folders at CE-CERT as discussed in Appendix B. Hard-copy records will be maintained in a dedicated cabinet. These records will be maintained in the project files for a period of not less than five years after the completion of the tests. Although not necessarily identified by a specific form, in addition to the raw and validated data, data validation and evaluation reports, and project correspondence, the following project information will be maintained:

- **Test and Laboratory Logs.** These records will describe the test matrix and related sampling modes and how they were followed. They will include the specific instrument identification, Project Engineers, test numbers, dates, sampling start and stop times, calibration information, temperature, humidity, any problems encountered, and all other operational parameters that are specific to each test.
- **Instrument Calibrations.** These records document the calibrations of all measurement instrumentation, including flow rate calibrations where applicable. The record will include the Project Engineer, the date, time, and location of the calibration, identification of the instrument, the ambient barometric pressure and temperature, identification of the reference standard that is used for the calibration and, if applicable, its traceability to NIST standards. The record will also include any calibration information necessary to convert instrument responses to corrected reported values for each experiment.
- **Analytical Laboratory Records.** These records document all pertinent operational conditions and procedures in the analytical laboratory at the time the calibrations of the instruments utilized were performed. As a minimum these records include dates and times, technician, temperature, humidity, filter conditioning periods, QC checks and detailed calibration results, and any other information pertinent to the laboratory analyses presented.
- **Performance Evaluations.** These records will contain all performance evaluation documentation. This will include performance and system audit reports, results of laboratory round robin intercomparison tests, and the results of any other on-site testing performed. All reports will include the name of the responsible parties, the date, time, and location of the audit or tests, a complete description of the audit or test results, along with any problems encountered and the resulting corrective actions undertaken.
- **Outside Peer Reviews.** These records will include all reports generated by the Research Advisory Committee and others that have provided peer reviews of project reports, individual experimental plans and/or experimental test results. These records will also contain all associated correspondence, including responses to comments from the Principal Investigators.

9 ROUTINE CONTROLS AND PROCEDURES

Control over the handling and operation of the equipment and materials have been established and will be maintained throughout this project. This section presents the types and levels of controls that have been incorporated into the project process where routine procedures are followed. Non-routine activities such as research methods will be covered by research protocols or experiment descriptions presented in the progress reports. Where applicable, the instrument and equipment manuals and/or SOPs will be utilized. A list of SOPs and manuals to be followed in the execution of this project is presented in Table 3, above. These documents present the detailed descriptions of the routine operation of all measurement instruments, including routine quality control procedures. The instrument operating manuals contain information concerning periodic maintenance and instrument troubleshooting, and are referenced by section in the project SOPs. Checklists have been developed for these instruments to document operations. In the event that procedures are developed that are not included in the manuals, they will be detailed in the SOPs.

9.1 Documentation and Chain-of-Custody Procedures

A logbook will be maintained with the instruments and all relevant calibrations, experimental procedures and observations will be recorded. Separate data sheets or files will be maintained for collected samples and instrument QC checks. For integrated measurements, sample data sheets will contain a chain-of-custody log for documenting the movement of the sample media, from preparation of the media cartridge, to the particular experimental run, analysis, data validation, and entry of the concentrations into the project database.

9.2 Calibration and QC Checks of Measurement Equipment

The precision and detection limits objectives presented in Table 1 define the provisional control limits for this project. Zero and span checks of each continuous analyzer will be performed before and after each experimental sample run as discussed in Appendix A. The results of these calibrations will be summarized in the log book and file for the instrument and also in an Excel file containing the calibration data for the instruments as indicated in Appendix B. Complete calibration records and control charts for each analyzer will be maintained in these files. When instrument performance is outside the established limits, the following actions will be taken:

- The appropriate troubleshooting will be conducted in order to determine the cause of the discrepancy. The items investigated will be the instrument, its sampling system, and its calibration system. If necessary the calibrations will be repeated.
- When the cause of the problem is isolated, it will be re-calibrated or repaired. The description, operation, and maintenance of calibration standards are included as part of the calibration procedures in the SOPs.
- If the cause is found to be instrument drift, data from the experimental run may be corrected per the calibration results.

Multipoint calibrations of each instrument will be performed on a regular basis as indicated in the instrument's to document instrument linearity and response. Each of these calibrations will include an ongoing

records management system will be maintained so that the calibration status of all instruments is readily available and easily retrievable. This will include maintaining the raw and summarized calibration data in electronic format in the calibration data files for the instruments as described in Appendix B.

9.3 Evaluation of the Adequacy of the Calibration and QC Check Strategy

Periodic evaluations of the above calibration and QC check strategy will be undertaken, for the purpose of refining the strategy in order to achieve all data quality objectives. Within this evaluation, instrument performance versus calibration frequency will be analyzed. If it is found that a particular instrument frequently performs outside of its established control limits, the appropriate corrective actions will be undertaken. These actions may include repair or modification of the instrument, evaluation of the control limits themselves, or replacement or elimination of the instrument. On the other hand, if the instrument performs consistently well within its control limits, the frequency of calibration and/or QC checks may be reduced.

Some of the instruments in use are of new technology or experimental in nature, and consequently do not have well established SOPs and performance criteria. As the performance database for these instruments is developed, periodic evaluations of these data will be conducted. Thus, as more is learned about the performance of these instruments, the SOPs and performance criteria may be refined.

9.4 Maintenance of Equipment

Procedures for routine, frequently conducted maintenance of the instruments are described in the SOPs. More complicated, less frequently performed maintenance items are included in the operating manuals and referenced in the SOPs. A maintenance and repair log will be maintained for each instrument. This log will provide a continuous record of the status of each instrument.

9.5 Quality of Consumables

The calibration sources for all appropriate instruments will be certified according to the EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards (Revised September 1997). Otherwise, NIST-traceable standards will be used as a calibration source whenever possible or available. All sampling media will be obtained and prepared following existing EPA protocols and accepted methods. Each calibration source method utilized is described in the appropriate SOP.

9.6 Labeling

In cases where discrete measurements are performed, unique sample numbers will be associated with each sample cartridge and sample custody forms will be used.

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