# DRAFT
# STANDARD PROCEDURES
# FOR CONDUCTING EPA CHAMBER EXPERIMENTS

## Appendix A to Quality Assurance Project Plan

**Version 0.3**

**Atmospheric Processes Laboratory**
**College of Engineering Center for Environmental Research and Technology (CE-CERT)**
**University of California, Riverside**

**Last Edited:**

**Bill Carter** **April 26, 2002**
**Claudia Sauer** **April 25, 2002**

## Preface

This document describes the standard operating procedures for carrying out experiments in the UCR EPA environmental chamber facility at CE-CERT. These procedures should be employed unless indicated otherwise in the instructions for the experiments provided by the Project Manager or Project Scientist. It is applicable for experiments carried out using this facility for the purpose of chemical mechanism evaluation and VOC reactivity assessment.

This document is intended for use by technicians and scientists who are experienced with the operations and instrumentation available at the CE-CERT Atmospheric Processes Laboratory. Separate Standard Operating Procedures (SOP) documents exist or are being prepared that give additional detail for operation of specific instruments or procedures, and details concerning data processing procedures for UCR EPA chamber runs are described in a separate Data Processing Procedures document. The overall quality assurance objectives and procedures for this project, and the list and locations of available specific SOP documents, are given in the Quality Assurance Project Plan for the UCR EPA chamber.

This current 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.

## Contents



# 1 Background

The current EPA chamber consists of a large hanging FEP Teflon pillowbag reactor located inside the temperature-controlled enclosure on the second floor of the Environmental Chamber Laboratory building at CE-CERT. During and between experiments the enclosure is continuously flushed with dry purified air supplied by the Aadco air purification system that also supplies the matrix air for the reactor. The enclosure currently has two light sources, a bank of blacklights mounted on the East wall inside the enclosure, and a Vortek 200 kW argon arc light on the North wall. The blacklights may be removed or reconfigured after the performance of the Vortek light source has been verified for routine operation. The configuration of the pillowbag reactor within the enclosure is also expected to be modified in the future. Most of the sampling instruments for this chamber are located in the first-floor laboratory underneath the chamber, with sampling lines running between the floors.

This document gives a summary of the procedures that should be carried out when conducting experiments in this facility, unless indicated otherwise in the instructions from the Principal Investigator

or Project manager. These procedures are applicable for EPA runs involving the current reactor and lighting configuration discussed above, unless indicated differently in the run instructions as indicated below. Reference is made in this document to standard operating procedure documents for various instruments or operations, and to the document describing the data processing procedures for UCR EPA environmental chamber experiments. The current location and versions of these documents are given in the folder \\ozone\aplshared\DOCs, which is accessible through the CE-CERT shared network.

# 2 Log Books

It is essential that all operations be documented in the appropriate log book at the time the operations are carried out or as shortly thereafter as possible. The log books that should be employed are described below.

Each log book will have an appropriate area where it will be located so it can be readily accessed for making entries when needed. The log books should not be removed from these areas during any period when operations are being carried out when entries to the log books may be appropriate. If the information in the log book is needed at a different location then the appropriate pages must be copied. In any case, anytime a log book is removed from its area, a note should be left indicating who has it and where it is.

All entries into the log books should indicate the date and time of the operation or observation to the nearest minute. The times should refer to Pacific Standard or Pacific Daylight time, as applicable depending on the time of year, with times given using either with a 24-hour format (preferred) or with "AM" or "PM" appended. The first log book entry made after daylight time begins or ends should indicate "PST" or "PDT" as appropriate. The times entered should be obtained using clocks that are within one minute of the correct time as determined by radio or internet connection to NIST clocks.

Notations referring to instruments should unambiguously indicate which instrument is being referred to. This could include either the model *and* serial number of the instrument or the 8-character ID string assigned to the instrument as given in the InstInfo.xls data set, as described in the UCR EPA Chamber Data Processing Procedures document.

Following is a description of the log books applicable for EPA chamber experiments, their appropriate locations, and the types of information they should contain.

## 2.1 Main EPA Chamber Run Log Book

This log book is used for noting the major operations for the EPA chamber experiments, and should contain all relevant information for the experiments that are not contained in the computer or hardcopy data files or the more specialized log books described below. The objective is that a person who was not involved with the experiments and does not have access to the people who were can use the log book to find out what was done during the experiment, and other relevant observations that may affect how the data should be interpreted.

The main EPA chamber run logbook should be located in the downstairs chamber lab, generally near the data acquisition computer.

Following is a summary of the types of information that should routinely be entered into this log book when applicable. Note that this does not cover all the types of information that may be appropriate. If is

unclear whether the information is appropriate, it is better to err by putting in too much information rather than too little.

- The EPA chamber run number, indicating when operations relevant to that run began, given with sufficient emphasis so that pages containing information for that run can be readily located at a later date.
- A brief summary of the run instructions and description for the experiments.
- All operations made to the reactor, such as when it is emptied, filled, flushed, etc.
- All injections made into the reactor, including all relevant information concerning how the reactants were injected and the amounts that were injected. At a minimum this should include the information needed to fill out the "Injections" sheet in the run file, as described in the UCR EPA Chamber Data Processing Procedures document.
- Major operations or changes made to the enclosure, such as changes to temperature set points, turning on or off temperature control, beginning or ending flushing, etc. Times when the enclosure is open for extended periods for maintenance, construction, or other purposes should also be indicated. The enclosure log book can be referred to for additional information when applicable.
- The times that the lights are turned on and off and the power levels or other relevant settings to the lights that affect the light intensity.
- All operations affecting what is being sampled by the analyzers employed for the run. Note that it is not necessary to indicate all sampling state changes if they are under computer control and the sampling state is being logged by the data acquisition system.
- Notations when manual samples are taken for GC analysis or any other purpose. The amount of sample or relevant sampling parameters should be noted where appropriate.
- Observations about the state of the reactor during the experiment, particularly noting if it has collapsed or has low volume due to leaks or excessive sampling.
- Any changes to which instruments are connected to the sample system, indicating when an instrument is added or removed from the sampling manifold.
- Times when an instrument collecting data for an experiment is known to be having problems or is non-operational, and times when normal operations for the instrument are restored.
- Times when instrument are being calibrated and either the relevant information and data for the calibration or an indication about where this information or data can be located.
- Results of flow rate measurements or other measurements affecting the operation of the sampling system.
- Documentation of maintenance, configuration, and calibration of instruments that are used for chamber experiments and that do not have their own instrument log book.
- Observations about problems or unusual conditions or events related to the reactor, lights, instruments, laboratory, etc., that may possibly have relevance to the quality of the data or the experimental conditions.
- Observations about any unusual or unexpected results or measurements that are noticed that may possibly have relevance to the quality of the data or the experimental conditions.

In addition to these routine observations, this log book should also contain a complete description of the configuration of the sampling system. The log book should contain a complete diagram of the existing sampling system indicating the length and volumes of all sample lines and how they are connected, and to which instruments, and indicating the normal flow rates through all lines. Any time changes are made a new diagram should be entered into the log book.

This log book should also contain an unambiguous list of all the instruments that are being employed. A complete list of the connected instruments should be given whenever the sampling system is changed and diagramed, and whenever changes are made to which instruments are routinely connected.

This log book should indicate whenever the reactor is changed and contain a summary of changes made to its configuration, and indicate where applicable where additional information can be found. Diagrams of the configuration may be appropriate if major changes are made. Although details concerning reactor construction and configuration go into the enclosure log book, this main chamber run log book should contain a summary indicating that these changes were made and indicate that additional information is available in the enclosure log book.

### 2.2 Enclosure Log Book

The enclosure log book is used to record operations and other information relevant to the enclosure and its associated lighting, temperature control and air handling systems, to the reactor within the enclosure and its associated framework and mixing, inlet, and exhaust systems, and to other items contained within the enclosure. It can also be used to enter run-relevant information by persons working near or within the enclosure when it is inconvenient to use the main run logbook downstairs, though major run-relevant information will eventually have to be copied or at least summarized in the main run log book.

This log book should be located on a table near the entrance of the enclosure.

Entries into this log book include the following.

- Notation of when flushing is turned on and off, and the flow rates used
- Operations of the light sources and the associated systems
- Operations of the temperature control and air handling systems
- Notations of when the doors are open for extended periods between experiments or when the doors are open even briefly during experiments or preparations for experiments
- Logs of maintenance, repairs, modifications, and adjustments of the temperature control or air handling systems
- Notations of when major repairs, modifications, or adjustments are made to the Vortek light and associated systems. Details should be in the Vortek log book, as discussed below.
- Notations of repairs or modifications made to the reactor(s).
- Documentation of operations and measurements made during experiments to map spatial variations of temperature and light intensity within the enclosure.
- Diagrams or notations giving the precise locations of all structures, instrumentation, light or temperature sensors, and sampling inlets within the enclosure. Measurements should be made in a 3-dimensional x,y,z coordinate system where the zero point is the corner on the South-West floor (the end of the wall with the door farthest from the Vortek light) Is that to the right or to the left side of the door? , the “x” dimension is from South to North, the “y” dimension is from West to East, and the “z” dimension is from down to up. Measurements should be made with a tape measure to the nearest inch or 2 cm. Again: how precise do you want these measurements to be. Estimates by eye, counting the number of reflective sheets, measuring with a tape measure to the inch
- Documentation of the construction and configuration of all reaction bags used in the enclosure
- Diagrams showing the framework and associated structures holding the reactors in place and controlling mixing and air handling within the reactors.

### 2.3 Vortek Light Log Book

Because of its complexity, a separate log book is maintained for the Vortek 200 kw arc light and associated systems. Details of a all tests, adjustments, modifications, repairs, problems, maintenance, and operations on this system should be noted in this log book. Any time the system is turned on and off should also be indicated there. The log book should also contain diagrams of the system as it is configured, and new diagrams should be added when the changes are made.

### 2.4 Instrument Log Books

Most major instruments or groups of instruments should have log books documenting the maintenance, configuration, and calibrations of the instruments. The SOP for the instrument should describe the types of information that should be contained within the log book, which generally should be everything that concerns the instrument. Note that if results of calibrations are contained in computer data files, the instrument log book should indicate the names and locations of those files, and, where appropriate, copies of relevant data tables or plots of calibration or other characterization results.

## 3 Procedures for Beginning Runs

### 3.1 Run Instructions

The instructions for conducting EPA chamber experiments should normally be given in the run instructions sheet as described in the EPA Chamber Data Processing Procedures document, though occasionally verbal or other means of communication may be used. At a minimum the instructions would indicate reactant injections and any procedures that should be followed that are different than described in this document.

The run instructions should be reviewed by the person responsible for the experiment and any uncertainties or potential problem areas should be resolved before proceeding. The operator should not make guesses as to the intent of the instructions if they are unclear, nor should he or she modify the procedures without consulting with the person who is responsible for the instructions. If modifications are made, they should be indicated in the run instructions sheet, if applicable.

A summary of the run instructions should be entered into the main EPA chamber log book about the time that the operations begin. It is not necessary to duplicate detailed instructions if they are contained on the run instructions sheet,

### 3.2 Preparation

#### 3.2.1 Log Book Notations

In the subsequent discussion, the term “log book” will refer to the main EPA chamber log book located in the downstairs laboratory, unless indicated otherwise.

Verify that the clocks or watches that will be used for noting the times when making notations into the log book during the preparations for the experiment are either properly linked to the NIST transmitter or are synchronized to clocks that are so linked. The synchronization should be to within 15 seconds. This includes personal watches if they will be used for this purpose.

The log book should note any instruments used for this experiment that are different from those used in the previous experiment. If an instrument that is normally used but was not used in the last experiment is still not being used, then this should be noted as well.

When beginning operations relevant to the experiment, write the run ID designation conspicuously in the log book (or use color highlighting) so one can readily locate information relevant to the experiment by thumbing through the book at a later date.

### 3.2.2 Initial Checks

All instruments to be used for the experiment should be checked for proper functioning and any problems encountered and corrective actions taken should be noted in the log book.

The sampling system should be checked for appropriate connections and flows prior to the experiment. Note in the log book any changes made to the sampling system since the previous experiment. If a non-standard configuration is used that was also used in the previous run, note in the log book that this non-standard configuration is still applicable.

### 3.2.3 Zero Air Sampling

The sample line for the continuous instruments should be set to pure air mode for at least 15 minutes prior to any span checks or reactor or enclosure sampling for the experiment. The zero air readings for all instruments should be checked to be sure they are in the appropriate range, and problems and any corrective actions taken should be noted in the log book. Note that high zeros may indicate problems with the sampling system that will have to be corrected before the run can proceed.

### 3.2.4 Span Checks

The instruments should be set to sample zero air immediately before span checks are conducted so the instruments will be in a reproducible initial state.

The following span checks should be conducted prior to the experiments if the relevant species are to be monitored during the experiments, unless the run instructions indicate that they are not necessary or measurements of the affected species are not important.

- Ozone using the GPT mode of the calibrator
- NO and CO using a certified calibration cylinder with known concentrations of NO and CO.
- $NO_2$ by using the GPT mode of the calibrator with the NO from the certified calibration cylinder
- Formaldehyde using the output of the calibrated formaldehyde source.
- $HNO_3$ using the output of the calibrated $HNO_3$ source if $HNO_3$ measurements are to be made and the run instructions indicate that $HNO_3$ should be monitored.
- $H_2O_2$ using the output of the calibrated $H_2O_2$ source if $H_2O_2$ measurements are to be made and the run instructions indicate that $H_2O_2$ should be monitored.

The $O_3$, NO and CO span sources should be sampled for at least 15 minutes, the GPT, formaldehyde and $H_2O_2$ span sources should be sampled for at least 20 minutes, and the $HNO_3$ span source should be sampled for at least 30 minutes. This is required to allow the span concentrations and instruments to completely stabilize and to allow for at least 5 minutes of averaging times for stabilized readings.

The times that the span checks are being conducted should be accurately noted in the log book. The log book should also indicate the span source being used and the concentration of the span gas, or given an indication of where the accurate span concentration can be obtained.

At the present time the data acquisition and sample valve control system is not configured to control or sense the states of the sampling system with regard to span checks. However, it is programmed to accept operator-input flags that indicate that a certain type of span check is being conducted. If this is the configuration, the operator should enter the flag for the appropriate span state change immediately *before* any manual change is made to the sampling state. The manual state change should be completed within two minutes of the time the flag is entered onto the data acquisition system.

Entries should be made into the log book whenever incorrect sample state information was entered into the data acquisition program or when the manual sampling state changes could not be made within two minutes of the change of the sample state on the computer.

Once the spans are completed the instruments should be set to sample zero air for at least 10 minutes prior to making measurements in the enclosure or reactor.

#### 3.2.5 GC Preparation

Signal baseline, flow rates and pressures should be checked for all GCs that will be used for the experiment.

Gas standard injection from the reference gas cylinder should be done to check for the response stability. The results should be added to the standard gas results spreadsheet (which is needs to be prepared)

### 3.3 Preparation of Enclosure and Reactor

The chamber enclosure should be flushed with Aadco air at a rate of ~1400 (or at least 1200) SCFH for at least 6 hours prior the beginning of the experiments.

A sign should be mounted conspicuously on the enclosure door stating that an experiment is in progress and that no one is to enter without permission from the person in charge of carrying out the experiment.

The contents of the enclosure should be monitored prior to the preparation of the reactor for the experiments. The $NO_x$ levels in the enclosure should be less than 2 ppb, the CO levels should be less than 0.25 ppb, and the formaldehyde levels should be less than 15 ppb. (The acceptable levels of formaldehyde will be reduced once the source of the formaldehyde contamination is identified and removed.)

IMPORTANT: Be sure that the pressure sensor that is used to prevent overfilling the reactor is operational before any operations involving filling the bag. If a pressure sensor is used to prevent excessive vacuum when emptying the bag, the proper operation of that sensor should be verified as well.

Prior to any experiment, the reactor should be emptied and filled completely at least three times, not counting the dump and fill that occurred after the previous run. The pressure sensor should be used to fill the reactor to a nearly reproducible volume.

Better mixing is obtained if the reactants are injected into a partially-filled reactor, with the final fill to the maximum volume being made after the reactants are injected and mixed. Therefore, if reactants are to be injected procedures involving flushing materials into the reactor and not involving fans, then for the final

fill the reactor should be inflated to at least one-half, but no more than three-fourths, of its maximum volume.

Note in the run log book the times the flushes started, the number of flushes, and the times the flushes ended. The enclosure log book can be used to enter this information if more convenient, but the run log book should indicate the fact that the flushes occurred and generally when.

### 3.4 Reactant Injections

The contents of the reactor should be monitored for at least 10 minutes prior to injection of any reactants. The NO, $NO_2$, $NO_x$, CO, and formaldehyde levels in the reactor should be no more than 0.2 ppb or below the detection limits of the available instrumentation, whichever is greater. If these levels are exceeded, the reactor should be emptied and filled again. If this is done, then the contents of the reactor should be monitored again prior to injection of any reactants.

The contents of the reactor should *not* be sampled while reactant injections are being made unless indicated otherwise in the run instructions.

The amounts of reactants to be injected should be calculated based on the run instructions and the estimated reactor volume as derived from results of the previous section.

The line used to inject the reactants should be different than the line used for sampling unless indicated otherwise in the run instructions.

Reactants should be injected using appropriate standard procedures established for each type of reactant, unless indicated otherwise in the run instructions. These are as follows:

- NO. The desired amount of NO should be prepared on the vacuum system by expanding the desired pressure of NO in a bulb of known volume. It should be previously purified by passing through Molecular Sieve using the established procedures. NO can be pre-purified and stored in a bulb on the vacuum system provided that the bulb is kept dark and free from air. The NO should not be exposed to air or $O_2$ at any time during its preparation The contents of the bulb should be flushed into the reactor using $N_2$, NOT AIR, using as high a flow rate as practical to achieve rapid dilution. The pressure of the NO in the bulb and the volume of the bulb should be recorded in the log book.
- $NO_2$. The amount of NO corresponding to the desired amount of injected $NO_2$ should be prepared as discussed above. The contents of the bulb should then be pressurized with $O_2$ before being flushed into the reactor. Either $N_2$ or air can be used. The NO or $NO_2$ should not be exposed to ambient air at any time during its preparation The pressure of the NO in the bulb and the volume of the bulb should be recorded in the log book.
- CO. CO must be purified prior to injection into the reactor to remove contaminants (probably iron carbonyl) that affect environmental chamber experiments. Evidence for the presence of these contaminants can be seen as an NO interference on chemiluminescent NO analyzers, which disappears upon irradiation. The most effective procedure to purify the CO is currently being investigated, so the standard procedure for injection of CO has not been established.
- Formaldehyde. The formaldehyde should be prepared from paraformaldehyde in the vacuum system using the established procedures, with the desired amount expanded into a bulb of known volume. The contents of the injection bulb can be flushed into the chamber with air or $N_2$. It should not be exposed to ambient air at any time during its preparation. The pressure of the formaldehyde in the bulb and the volume of the bulb should be recorded in the log book.

- Gaseous Organics. Organic reactants that are gases at ambient temperatures and pressures can either be prepared for injection by expanding the desired amount into a bulb of known volume using a vacuum system, or introducing the desired volume at atmospheric pressure in a gas-tight syringe. The contents of the bulb or syringe is then flushed into the chamber with air or $N_2$. $N_2$ should be used if the compound tends to oxidize rapidly. The pressure (if applicable) and the volume of gaseous reacted injected should be noted in the log book.
- Volatile Liquid Organics: Organic reactants that can be volatized with no or only mild heating in less than 10 minutes flushing can be injected by introducing the desired volume of liquid into a bulb designed for this purpose, whose contents are then flushed into the chamber with $N_2$ or air for a sufficient time to completely volatilize the liquid. The flushing time should be at least twice as long as it takes to remove all visible liquid. Care should be taken to avoid condensation of liquid on the inlet lines. The amount of liquid, the flushing flow rate, the flushing time, and the amount of heating (qualitatively at least) should be noted in the log book.
- Low Volatility Liquid Organics: The standard operating procedures for injecting low volatility compounds into this reactor have not yet been developed.
- Volatile Solid Organics: The standard operating procedures for injecting volatile solid materials into this reactor have not yet been developed.

The reactor should be thoroughly mixed before analyses are conducted to determine amounts injected. For pillowbag reactors that do not have internal mixing systems, this is accomplished by manually agitating the sides of the reactor before it is completely inflated.

After the reactor is thoroughly mixed, pure air should be added to achieve the maximum reactor volume, as controlled by the automatic shut-off valve.

Once the reactants are injected and mixed and the final fill has been completed, the contents of the reactor should be sampled by the continuous instruments until stable readings are obtained in all concentrations, and for at least 5 minutes after that. A minimum of 15 minutes should be allowed for mixing, even if the continuous analysis results indicate that stable readings have been obtained in much less time.

After complete mixing and stable readings are verified by the readings of the continuous monitoring instruments (or at least 15 minutes has passed, whichever is longer), then samples by GC analyses should be carried out. All GC instruments to be used for the run, including those only to be expected to be useful for product analysis, should be used.

Unless indicated differently in the run instructions, a second GC analysis at least for the injected VOCs should be carried out prior to irradiation, to assure stable readings to determine initial concentrations. If the results of the two analyses do not agree to within the expected precision of the measurement as determined by results of calibrations, then a third analysis should be conducted.

If supplemental injections have to be made, change to sampling zero air when the injections are being made, and note this in the log book. Put sampling back on the reactor after the injections are complete. Repeat all GC analyses after supplementary injections.

If the reactant injections required operator entry into the enclosure, an enclosure sample should be taken after all injections are complete but prior to the sampling preceding the initiation of the irradiation.

### 3.5 Initiating Irradiation

The continuous monitoring instruments should be set to sample zero air prior to the irradiation, with the zero air sampling ending approximately 15 minutes before the lights are turned on. Then the reactor should be sampled continuously for 15 minutes before the lights are turned on and about 30 minutes afterwards. The run instructions may indicate a longer or shorter period of post-irradiation is appropriate. The purpose of this procedure is to (1) get a zero reading before the relatively long continuous reactor sampling period, (2) get a stable reading of concentrations before the lights are turned on, and (3) get data reflecting any rapid processes that occur at the beginning of the irradiation.

Be sure the QSL monitor is logging the light intensity data prior to turning on the lights. The location and naming of the QSL data files should be as specified in the Data Processing Procedures document. (Not discussed in current draft. File naming conventions for the QSL PAR Radiation Sensor have not been established.)

Work lights in the enclosure should be turned off after the QSL logging has started and before the irradiation lights are turned on.

Note in the log book the time the light is turned on and any applicable power settings.

Verify that the light intensity is as expected based on measurements with previous experiments with this light setting (if applicable) by noting the QSL reading after the readings have stabilized. Note the QSL reading in the log book.

Switch to automated sampling after the 30 minutes (or instruction-specified) initial reactor sampling period, and not in the log book when this was done.

Take samples for GC analysis between 30 and 60 minutes after the beginning of the irradiation, or as directed in the run instructions.

### 3.6 Sampling Schedule Summary

An example of a sampling schedule that might be employed during a representative 24-hour irradiation, with the irradiation beginning and ending on noon of the consecutive days, is shown on Table 1. This indicates the full set of initial run sampling as discussed above, as well as sampling after and between experiments, as discussed in the following sections.

## 4 Procedures During Run

### 4.1 Enclosure Access

DANGER: Never enter the enclosure or expose yourself to radiation to the Vortek lamp if it is being operated without a spectral filter that cuts off the radiation above ~300 nm. Regardless of the spectral filter, wear proper eye and skin protection when looking into or entering the enclosure whenever the Vortek lamp is on, and never look towards the lamp. (Until determined otherwise, proper eye protection shall consist of a welders mask with a #12 or darker filter or equivalent.) The initial configuration of the Vortek is expected to be richer in UV radiation than natural sunlight. Until an appropriate eye and skin protection protocol has been established, entry into the enclosure when the Vortek lights are on is forbidden.

Even if appropriate eye and skin safety protocols are established, do not enter the enclosure unless necessary for the purpose of the experiment, which might include sampling or checking the state of the reactor. Be sure that the sign stating that an experiment is in progress is conspicuously posted by the enclosure door.

Minimize the length of time the door is open when entry to the enclosure is necessary. If the purpose of entry is for assessment of the reactor condition, it may be sufficient just to look through briefly into the reactor without actually entering.

Note all door openings into the reactor into the enclosure log book until such time that automatic logging of door openings have been implemented.

### 4.2 Reactor Inspection

Inspect the reactor at least twice a day during multi-day experiments and note in the log book the condition of the reactor in terms of bag volume. Inspect the reactor first thing in the morning if the run was carried out overnight. Attempt to estimate how far the reactor walls are apart at the farthest point and at the point where the sample is being withdrawn.

Terminate the experiment if the reactor has collapsed to such a low volume that the walls are closer than 2 feet apart at the widest point, or closer than 1 foot apart at the point where the sample is being withdrawn.

### 4.3 Equipment and Inspection

Inspect the performance of the temperature control and lighting equipment for proper operations at least twice a day during the experiments, or at the beginning and end of the working day for multi-day runs.

An examination of the performance of the temperature control system at a minimum consists of visually examining the concentration-time trace of the temperature data from the enclosure for consistent readings within the desired range. Examination of other relevant temperature traces indicators may also be appropriate.

An examination of the performance of the lighting equipment at a minimum consists of examining the QSL trace for consistent readings in the appropriate range. For the Vortek it may be appropriate to examine other indicators, as described in the SOP for the Vortek light source.

Examine concentration-time for the continuous instruments at least twice a day during the experiments, or at the beginning and end of the working day for multi-day runs to determine if they are obtaining data in the expected pattern. Particular emphasis should be on instruments that periodically enter obvious failure mode, such as the GC-Luminol $NO_2$ analyzers or Alpha Omega formaldehyde analyzer.

If TDLAS data are being collected, examine the spectra and other indicators and parameters for correct operation at least twice a day during the experiments, or more frequently if the run instructions indicate that the TDLAS data are of particular importance. The specific data quality verification procedures are described in the SOP for the TDLAS instruments.

Note in the log book any time problems are encountered and corrective action, if any, that is taken.

If inspections indicate that instruments went off line or stopped collecting valid data, provide estimates in the log book of approximately when the invalid data began. If the problem is corrected and the instrument is again collecting valid data, indicate in the log book the time that valid data begins.

### 4.4 Sampling

Each reactor employed should be sampled by the continuous instruments at least once an hour during the course of an experiment unless indicated otherwise in the run instructions.

The enclosure should be sampled by the continuous instruments at least once every four hours during the course of the experiment unless indicated otherwise in the run instructions.

Table 1 shows an example of a sampling schedule that can be employed during an experiment that is consistent with these procedures.

GC samples should be taken with a frequency indicated in the run instructions, or at least once every four hours during the working day. For overnight irradiations GC samples should be taken first thing in the morning. Not the time that the samples are taken as indicated in Section 6.

### 4.5 Span Checks

If the experiment is more than three days long then spans should be taken during the expected mid-point of the experiment unless indicated otherwise in the run instructions. The procedures should be the same as employed at the beginning of the experiments, as described in Section 3.2.4.

## 5 Run Ending Procedures

Note in the log book the condition of the reactor in terms of bag volume (as discussed in Section 4.2) at the time the run is to be terminated.

The sample line should be switched to continuous reactor monitoring mode at least 15 minutes before the lights are turned off, or for the time required to take the needed GC samples, which ever is longer.

GC samples should be taken for all instruments used during the experiment during the period when the final continuous reactor monitoring is being conducted.

If the run instructions indicate that final GC analyses are important, then at least two final GC analyses should be made. In this case, it may be appropriate to switch to zero air or automatic sampling mode for the time while waiting for the first analysis to complete.

Verify that the QSL is on and logging properly before turning off the lights. In doing so, note whether the readings are in the proper range and note any problems in the log book.

Note the exact time that the lights are turned off.

Continue monitoring the reactor for at least 15 minutes after the lights are turned off.

Monitor first zero air then the enclosure immediately following the period of continuous monitoring of the reactor following the lights off. Then switch the sample line to pure air to obtain zero readings for the final reactor and enclosure samples.

The reactor should be emptied and filled at least once immediately at the conclusion of each experiment, so it contains only pure air between experiments. This should begin immediately following the termination of the final monitoring of the reactor. If high concentrations of pollutants are used (above 250 ppb of NOx) then the reactor should be emptied and filled twice.

Unless indicted otherwise in the run instructions or this is a single day run *and* another run planned for the following day, span checks should be conducted on the continuous instruments. The procedures should be the same as employed at the beginning of the experiments, as described in Section 3.2.4.

Unless there is to be a significant gap of time between experiments, or there are other sampling needs, the automatic sampling should be set to sample the enclosure for each 15 minutes every two hours, with sampling on zero air for the remainder of the time.

Table 1 gives an example of run ending sampling procedures consistent with the procedures discussed above.

The sign stating that an experiment is in progress should be removed if in fact an experiment is no longer in progress.

# 6 General GC Analysis Procedures

Note in the log book the exact times the GC samples are withdrawn from the reactor, using a clock that has been synchronized as discussed in Section 3.2.1. If the sampling takes more than a minute, note beginning and end times in the log book, and use the mid-point time as the time of the sample for data processing purposes.

GC samples for species monitored using loop or trap sampling can be taken from any point on the sample line into the continuous instruments, provided that the line from the main sample lines to the GC sample port is no more than 6 inches long. In this case, sampling must be from the reactor for at least 5 minutes before GC samples are taken. The line between the main sample line and the GC sample port should be flushed with at least 3 volumes before the sample is taken for analysis.

GC samples for analysis using the Tenax method must be taken from a port connected directly to the reactor until alternative procedures are developed.

All GC data processed using the HP ChemStation software should be stored using the standard GC naming convention that was employed during previous DTC experiments, as described in the Data Processing Procedures document.

Data files from GCs processed using other software should be stored in using standard locations and naming conventions as specified in the Data Processing Procedures document, if such specifications have been made for this software. If not, the locations and names of the GC data files should be noted in the main run log book.

If GC instruments whose data are not computer processed or saved are used, the strip charts and printouts should be a folder labeled with the run ID, filed with the folders for the other experiments.

# 7 Data Processing

The data processing procedures are described in detail in the Data Processing Procedures document. As discussed there, a checklist for the data processing will be included in the run instructions file, and will be moved to the run data file once the run is completed. This checklist contains a list of all the items that have to be done, including any special additional data processing that must be done for the particular experiments, as entered by the Project Scientist when the run instructions were created.

The creation of the run data file, the entry of the major run times, comments and flags, and the loading of the raw data from the experiments should be carried out as soon after the run is completed as possible.

The items in the checklist in the run data file should be checked off once they are accomplished.

While processing the data check the results from the various instruments for reasonableness, to indicate whether any problems may be indicated. Take appropriate corrective actions if problems are found.

The Project Scientist who gave the instructions for the experiment should be notified that the data are ready for examination as soon as sufficient data have been processed that initial analysis or modeling of the results can be carried out.

Once the data processing for the experiment has been completed, all the data files for the experiment, which includes the run data file and all the raw data files and any associated data or analysis spreadsheets should be copied into a data archive directory. (Instructions for this have not yet been formulated)

Table 1. Representative sampling schedule for a 24-hour irradiation experiment beginning and ending at noon.

| Day | Time | Min | Sampling | Comments |
|---|---|---|---|---|
| 1 | 8:05 | 15 | Zero | Initial Zero preparing for run |
| 1 | 8:20 | 15 | NO / CO Span | Initial Spans |
| 1 | 8:35 | 20 | GPT | |
| 1 | 8:55 | 15 | O3 Span | |
| 1 | 9:10 | 20 | HCHO Span | |
| 1 | 9:30 | 20 | H2O2 Span | |
| 1 | 9:50 | 30 | HNO3 Span | |
| 1 | 10:20 | 15 | Zero | |
| 1 | 10:35 | 15 | Reactor | |
| 1 | 10:50 | 15 | Enclosure | |
| 1 | 11:05 | 15 | Zero | Injections |
| 1 | 11:20 | 15 | Reactor | Initial concentration measurements |
| 1 | 11:35 | 10 | Zero | |
| 1 | 11:45 | 15 | Reactor | Pre t=0 measurements |
| 1 | 12:00 | | Reactor | Lights on |
| 1 | 12:00 | 30 | Reactor | Post t=0 measurements |
| 1 | 12:30 | 15 | Zero | |
| 1 | 12:45 | 15 | Enclosure | |
| 1 | 13:00 | 15 | Zero | |
| 1 | 13:15 | 15 | Reactor | |
| 1 | 13:30 | 45 | Zero | Automatic Run Sampling Cycle for Experiment. Reactor sampled every hour; enclosure sampled every four hours. |
| 1 | 14:15 | 15 | Reactor | |
| 1 | 14:30 | 45 | Zero | |
| 1 | 15:15 | 15 | Reactor | |
| 1 | 15:30 | 45 | Zero | |
| 1 | 16:15 | 15 | Reactor | |
| 1 | 16:30 | 15 | Zero | Cycle repeats |
| … | … | … | … | … |
| 2 | 11:30 | 45 | Zero | Automatic cycle interrupted |
| 2 | 11:45 | 15 | Reactor | Sampling before lights off |
| 2 | 12:00 | | Reactor | Lights Off |
| 2 | 12:00 | 15 | Reactor | Sampling after lights off |
| 2 | 12:15 | 15 | Zero | Zero after lights off |
| 2 | 12.30 | 15 | Enclosure | Final enclosure sampling |
| 2 | 12:45 | 15 | Zero | Zero in preparation for spans -- Reactor can be emptied. |
| 2 | 13:00 | 15 | NO / CO Span | Final Spans |
| 2 | 13:15 | 20 | GPT | |
| 2 | 13:35 | 15 | O3 Span | |
| 2 | 13:50 | 20 | HCHO Span | |
| 2 | 14:10 | 20 | H2O2 Span | |
| 2 | 14:30 | 30 | HNO3 Span | |
| 2 | 15:00 | 15 | Zero | |
| 2 | 15:15 | 15 | Enclosure | Overnight automatic sampling of enclosure every two hours. |
| 2 | 15:30 | 105 | Zero | |
| 2 | 17:15 | 15 | Enclosure | Cycle repeats overnight |