

**EVALUATION OF ATMOSPHERIC IMPACTS OF
SELECTED COATINGS VOC EMISSIONS
AND
ENVIRONMENTAL CHAMBER STUDIES
OF VOC SPECIES IN ARCHITECTURAL COATINGS
AND MOBILE SOURCE EMISSIONS**

Combined Progress Report to

California Air Resources Board
Contract No. 00-333

And

California South Coast Air Quality Management District
Contract No. 03468

For the Period
September 16, 2003 through February 15, 2004

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Preface

This periodic report discusses progress both for the ongoing CARB contact 00-333 and for the new SCAQMD contract no. 03468, which was initiated during the period covered by this report. After discussions with the project officers for these two contracts, it was agreed that the reporting for these two contracts should be combined.

Summary

During the period of this report the methods for injecting and analyzing Texanol®¹ were developed and four environmental chamber experiments with this compound were carried out, additional chamber experiments were conducted with the selected petroleum distillates for the CARB project, methods for injecting and analyzing ethylene and propylene glycol were worked on, and chamber experiments with these glycols were begun. The results of the added Texanol® experiments were used to derive preliminary measurements of the rate constants for the reactions of OH radicals with the two Texanol® isomers. PM measurements were made during most of the chamber experiments during this report, but a discussion of these data will be deferred to a later report. The chamber experiments are discussed further below.

The work plan for the SCAQMD project is also discussed. It is proposed that Task 1, the “Evaluation of ROG and NO_x Surrogates,” be modified to incorporate experiments with a more complex and representative ROG surrogate than employed previously. Task 2, “Reactivity Assessment for Selected Coatings and Mobile Source VOCs,” is currently underway with our experiments with propylene and ethylene glycols, but the additional compound(s) to study still need to be determined. Task 3, “PM Measurement Support for Reactivity Experiments,” is also underway, with PM measurements for most of our experiments, and control experiments for the PM measurements are now underway. A work plan for Task 4, “Assessment of Potential of Chamber for Availability Studies,” has not yet been developed.

Environmental Chamber Experiments

The environmental chamber experiments that were carried out for the projects and the period covered by this report are summarized in Table A-1 in Appendix A. No chamber experiments for these projects were carried out between September and November because the chamber was dedicated to the EPA OBM project, which involved a continuous series of experiments using radical measurement instrumentation from Penn State². Both Teflon® reactors were changed prior to the experiments for the OBM project, and these reactors remained for use in these experiments.

Base ROG Surrogate Modifications

Because of maintenance problems, the TDLAS instrument used for the analysis of formaldehyde was not always operational during the period of this report. This extended down time periods for this instrument made it difficult to do well-characterized experiments where formaldehyde is a reactant, which includes experiments with the 8-component ROG surrogate used in our previous reactivity studies. Removing formaldehyde from the surrogate it would improve productivity and reduce uncertainties in our reactivity studies. Model calculations were carried out to assess whether removing formaldehyde from the

¹ Texanol® is a registered trade name for a commercially-available mixture of 3-hydroxy-2,2,4-trimethylpentyl-1-isobutyrate and 1-hydroxy-2,2,4-trimethylpentyl-3-isobutyrate. Although strictly speaking the compound names should be used when referring to this material, the commercial trade name is used to refer to this substance throughout this report for the sake of brevity.

² The proposal for this project is available at <http://www.cert.ucr.edu/~carter/epacham/obmprop.pdf>.

surrogate would affect the results of the experiments to a sufficient extent that including it is mandatory to achieve the objectives of this project. It was found that if the formaldehyde is removed and the amounts of the other 7 surrogate components are increased by 10%, the ozone formed in the various types of base case and incremental reactivity experiments are essentially the same, with differences being less than experimental uncertainty and variability³.

Therefore, to simplify the experiments for this program and improve productivity, for the experiments during the period of this report we modified the base ROG surrogate by removing the formaldehyde and increasing the other seven components by 10%. The first two experiments during this period were side equivalency tests with the standard “MIR” and “MOIR/2” (MOIR with NO_x reduced by an additional factor of 2) experiments with this modification. The results were as expected. All the incremental reactivity experiments during this period employed these modified base case experiments.

Texanol® Injection Tests and Experiments

Prior to conducting chamber experiments with Texanol®, tests were carried out to assure we could quantitatively inject this compound into the gas phase and to assess our analysis capabilities. The injections into the gas phase were carried out by placing desired quantity of the liquid (measured using a microsyringe) in a Pyrex injection tube, flushing the tube with nitrogen heated to ~100°C at a flow rate of about 7 liters min⁻¹, and into the chamber through Teflon® tubes heated to ~120°C. The gas-phase material was analyzed by passing ~100 ml of air from the chamber through a Tenax cartridge, then desorbing the contents of the cartridge onto a GC column. The GC was calibrated by preparing liquid solutions of Texanol® in methanol and placing them on the Tenax cartridge for analysis.

Both the gas-phase analysis and the methanol liquid solution analysis indicated two peaks for the Texanol® sample used. Based on communications with Rodney J. Boatman of Eastman Kodak the first peak attributed to 1-Hydroxy-2,2,4-Trimethylpentyl-3-Isobutyrate (the SAPRC-99 detailed model species TEXANOL2) and the second to 3-Hydroxy-2,2,4-Trimethylpentyl-1-Isobutyrate (SAPRC-99 TEXANOL1). The relative peak heights differed somewhat in the gas-phase samples than the liquid analysis, with the relative area of the second peak (TEXANOL) being 68% of the total in the liquid analysis, while it averaged 59±2% in the chamber injection test and irradiation experiments. No effect of temperature on the isomer ratio was observed in injection tests where the temperature of the injection tube or injection line was varied. Although this phase difference in the isomeric ratios is not large, it is larger than the variability in the GC analysis, and probably should be taken into account when making reactivity estimates for the commercial Texanol® mixture from those calculated for its constituents.

A Texanol® injection test experiments was carried out to evaluate our ability to quantitatively inject and analyze this in the gas phase, and to determine how much flushing time is required for quantitative injections. This consisted of continuously flushing the injection tube with a measured amount of Texanol® into one of the reactors over a 15 hour period, and monitoring the gas-phase materials over time by GC and a total carbon analyzer. CO was also injected and monitored over time to provide data to correct for effects of dilution caused by the continuous injection process. The results are shown on Figure 1, which gives plots of the Texanol carbon as calculated from the amount injected and corrected for dilution using the CO data, the Texanol analysis by GC, and the total carbon analysis (calibrated using propane). The total carbon data show the increase in Texanol over time during the injection process, and indicate that essentially all the Texanol is injected in less than 5 hours. The GC measurements (calibrated using the methanol solution) are in excellent agreement with the amount of

³ The maximum change in maximum O₃ in making this change in the base case ROG surrogate was calculated to be less than 3% for base case standard MIR or MOIR/2 experiments and incremental reactivity experiments with 200 ppb added n-octane or 20 ppb added m-xylene.

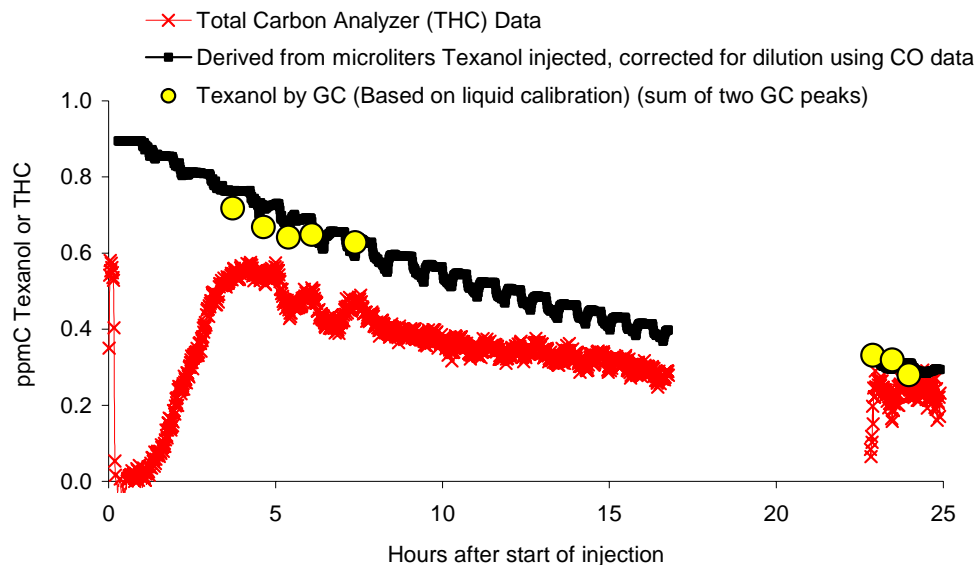


Figure 1. Experimental and calculated Texanol carbon levels in the Texanol injection test experiment.

Texanol® calculated from the volume injected and the dilution correction derived from the CO data, indicating that the GC analysis is quantitative and appropriately calibrated. The carbon as determined by the propane-calibrated total carbon analyzer was about 75% of the calculated or GC-determined value, suggesting that the propane calibration for the carbon response for this FID instrument is probably not quantitative. A low response would be expected because of the oxygen content of the Texanol® isomers, though probably not this low.

It was concluded that we were able to inject and analyze Texanol® quantitatively for the purpose of conducting reactivity chamber experiments. It was also found that a somewhat higher injection temperature could be used to reduce the amount of time required to inject the material into the chamber.

As indicated on Table A-1, a total of four chamber experiments with Texanol® were carried out during this period, two each with the two standard base case experiments. Representative results of one experiment of each type are shown on Figure 2. Results of model calculations using the current SAPRC-99 mechanism for the base components Texanol® representation are also shown on the figure. Results of the other two experiments are similar.

The results indicate that the added Texanol® cause relatively small changes in rate of NO oxidation and O₃ formation and amounts of O₃ formed in the experiments, but cause large decreases in rates of consumption of m-xylene, indicating an inhibiting effect on radical levels. Apparently the NO conversion and O₃ formation caused by the direct reactions of the Texanol® isomers just cancels the reduction in NO conversion and O₃ formation from the reactions of the other VOCs caused by its inhibition of radicals. These predictions are reasonably well simulated by the current mechanism. The underprediction by the model of O₃ formation in the MIR experiment is consistent with results of previous runs, and is discussed in more detail in the recently submitted report to the CARB on the “low NO_x mechanism evaluation” project (Carter, 2004).

Figure 2 shows that the precision of the measurements of the major Texanol® isomer is moderately good during the experiments, though the consumption rate is somewhat underpredicted. The

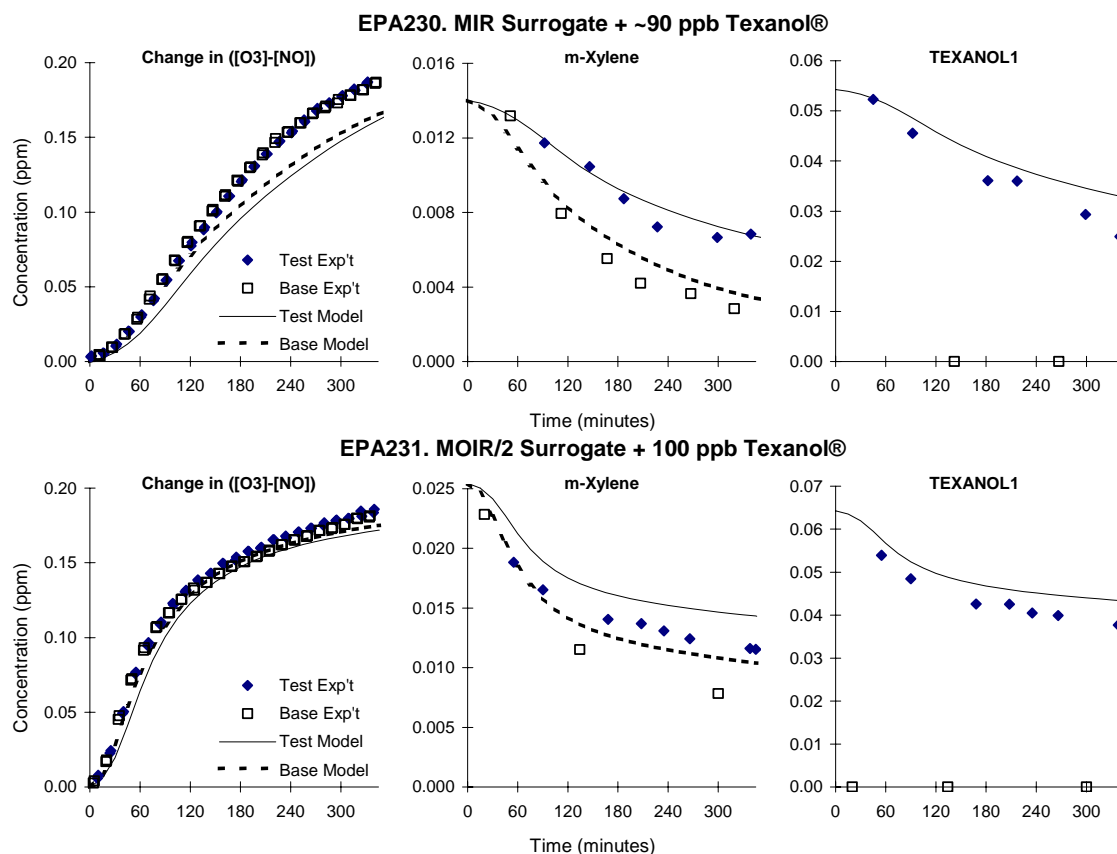


Figure 2. Experimental and calculated results for $\Delta([O_3]-[NO])$, m-xylene and 3-Hydroxy-2,2,4-Trimethylpentyl-1-Isobutyrate for representatives of the two types of surrogate + Texanol® experiments carried out during this period.

measurements of the other isomer (not shown) are comparable. Since the precision of these measurements are reasonably good, and since the Texanol® isomers are expected to react only with OH radicals, the Texanol® isomer and m-xylene data from these experiments can be used to determine the rate constants for the reactions of OH radicals with the isomers, using m-xylene as the reference compound. The relative rate constant measurement involves determining the slopes of plots of $\ln([isomer]_0/[isomer]_t)$ against $\ln([m-xylene]_0/[m-xylene]_t)$, which should be the rate constant ratio if reaction with OH radicals is the only consumption process for the compounds involved. These plots are shown for the measurements from all four experiments in Figure 3, and the results are summarized on Table 1. It can be seen that the results of these measurements are in remarkably good agreement with the estimated rate constants currently used in the SAPRC-99 mechanism for these isomers.

Additional Petroleum Distillate Experiments

As indicated on Table A-1 in Appendix A, additional incremental reactivity experiments were carried out for most of the petroleum distillates studied for this project during this period. This was to provide needed replicate runs for mechanism evaluation and data needed to assess effects of these materials on PM formation. These two experiments each with VMP Naphtha and Aromatic-100, and one experiment each with ASTM-1A, 1B, and 3C1. An analysis of the results of these experiments will be described in a subsequent report.

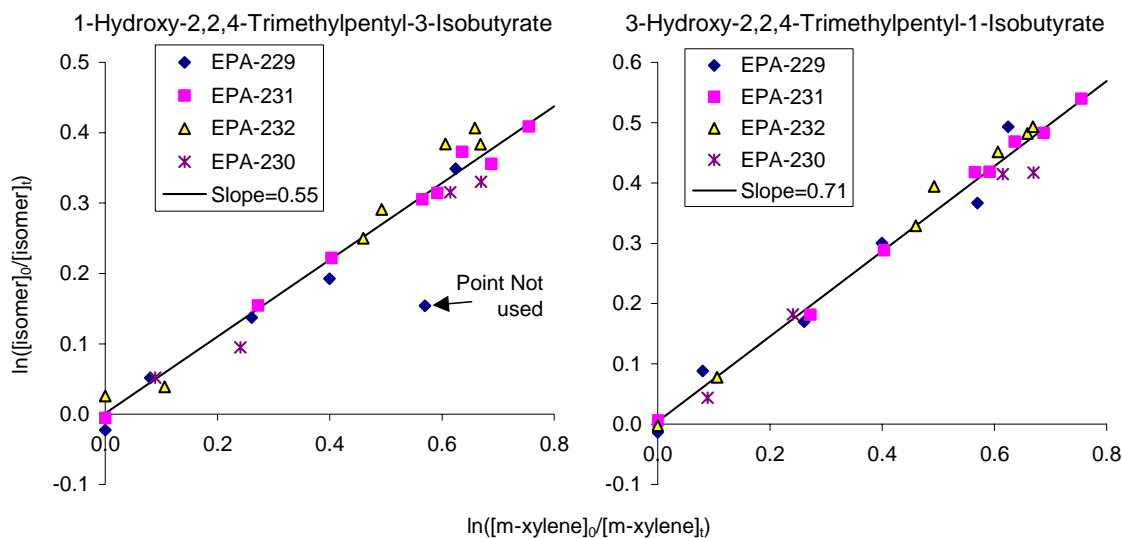


Figure 3. Plots of $\ln([\text{isomer}]_0/[\text{isomer}]_t)$ against $\ln([\text{m-xylene}]_0/[\text{m-xylene}]_t)$, for the added Texanol® incremental reactivity chamber experiments.

Table 1. Summary of results of OH rate constant measurements for the Texanol® isomers

Isomer	Relative to m-Xylene	$k(\text{isomer})$ ($\text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$)	
		This work [a]	Estimated [b]
1-Hydroxy-2,2,4-Trimethylpentyl-3-Isobutyrate	0.55	1.29e-11	1.29e-11
3-Hydroxy-2,2,4-Trimethylpentyl-1-Isobutyrate	0.71	1.67e-11	1.62e-11

[a] Based on m-xylene rate constant of 2.36e-11 (Atkinson, 1989)

[b] SAPRC-99 mechanism estimate (Carter, 2000)

Glycol Experiments

After discussions with the SCAQMD and CARB staff, it was determined that ethylene and propylene glycols will be among the compounds to be studied for the SCAQMD project. Work was carried out during this period to develop methods to inject and analyze these glycols, two incremental reactivity experiments were carried out with propylene glycol, and one with ethylene glycol. The injection method used for these glycols was essentially the same as that employed for Texanol®, which as discussed above gave good agreements between analyzed gas-phase concentrations of the Texanol® isomers and the calculated amounts injected. Unfortunately, the GC analysis methods for the glycols were found not to be of sufficient quality to be quantitative, so the success of the injection procedures for quantitatively introducing these compounds into the gas phase could not be verified. However in view of the fact the injection method worked well for Texanol®, whose isomers have lower vapor pressure than these glycols, we believe it is reasonable to assume that these glycols are also satisfactorily injected using this method. Therefore, for the purpose of mechanism evaluation we will estimate the initial gas-phase glycol levels from the calculated amounts injected.

Representative results of the MOIR/2 glycol experiments carried out during this period are shown on Figure 4, with results of model calculations also being shown. As with other MOIR/2 experiments, the model fits ozone formation and NO oxidation in the base case experiment reasonably well, though the consumption rates of m-xylene and other VOCs that react only with OH radicals are somewhat underpredicted. The two glycols have qualitatively similar effects on overall reactivity, increasing the amount of O₃ formed but decreasing the overall OH levels, as indicated by slower m-xylene consumption rates. The model gives fair prediction of the effects of the glycols on NO oxidation and O₃ formation, though the effect on O₃ may be underpredicted. This is despite the fact that the model is based on assuming that all of the injected glycol made it into the gas phase. If the model is assuming that more glycol is entering the gas phase than is actually the case, then it should overpredict the effect of the glycol on O₃ and other measures of reactivity, which is not what was observed in these experiments. Additional experiments will be needed to verify if the observed underprediction this is a consistent trend.

Updates to Work Plan for SCAQMD Project

The proposal and initial statement of work for the SCAQMD project had four major tasks, of which three involve conducting environmental chamber of the type discussed in this report. A description of these tasks, the number of experiments indicated in the proposal and carried out as of the date of this report⁴, and the status of these tasks are summarized on Table 2. These are discussed further below.

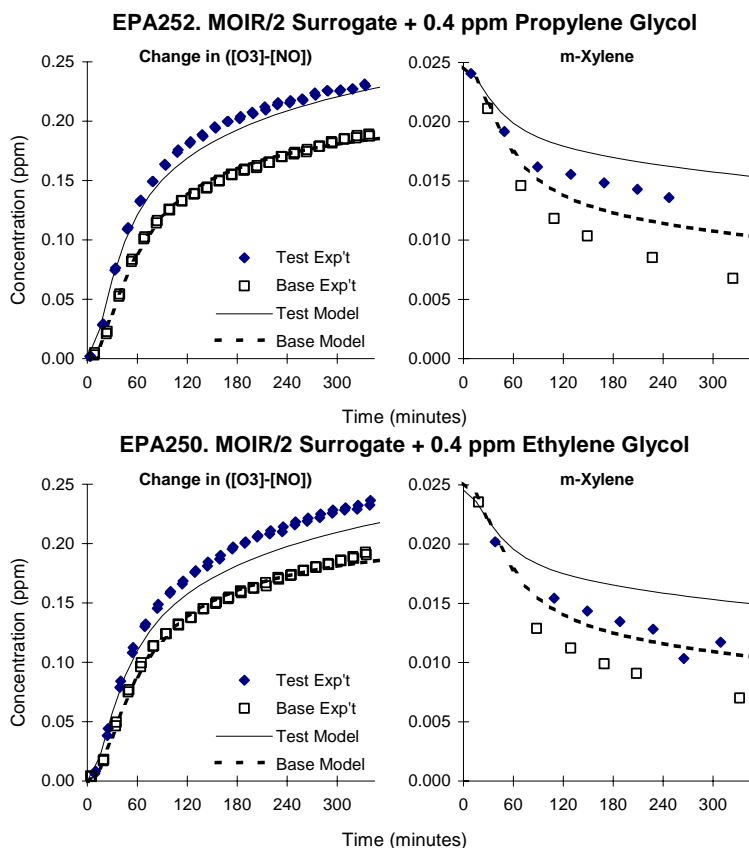


Figure 4. Selected results of propylene and ethylene glycol reactivity experiments

⁴ This includes experiments carried out subsequent to the period discussed in this report.

Table 2. Major tasks in work plan for SCAQMD project

Task	Description	Runs		Status
		Proposed	To date	
1	Evaluation of ROG and NO _x Surrogates	8	1	It is proposed to develop and conduct experiments with a more complex and realistic surrogate for this task. See Appendix B.
2	Reactivity Assessments for Selected Coatings and Mobile Source VOCs	22	11	Input is needed from SCAQMD and the ARB's RRAC as to additional compounds to study. Also, it is proposed that reactivity experiments with the more complex surrogate developed in Task 1 be included in this task.
3	PM Measurement Support for Reactivity Experiments	5	3	PM measurements are being made for most experiments. Control experiments are being conducted to investigate differences in PM formation between the two reactors in the current chamber.
4	Assessment of Potential of Chamber for Availability Studies	n/a		We have contacted Dr. Jon Kurland, the head of the RRWG Availability Task Group, concerning this matter, and requested that this be discussed among the group either in a conference call or at the next RRWG meeting.

Task 1. Evaluation of ROG and NO_x Surrogates. The proposal for this project discussed conducting experiments with the 8-component ROG surrogate used as the base case in our current reactivity experiments. The only experiment carried out thus far in this task was an experiment with formaldehyde removed from this surrogate, to be used as a replacement for the reactivity studies to simplify the experiments as discussed above.

An extensive amount of experiments with this 7- or 8-component surrogate have already been carried out under separate funding. In view of the results of these experiments and other considerations, we recommend that the remainder of the work on this task focus on the development and use of a more realistic surrogate than employed previously. The background and rationale for this proposal is given in Appendix B to this report. Because of the effort required, we would like to have the approval of the SCAQMD staff before proceeding on this effort. We recommend that this be discussed at the next ARB RRAC meeting if such a meeting can be arranged in a timely manner.

Task 2. Reactivity Assessment Experiments. The proposal indicates that the compounds to be studied in this task will be determined after discussions with the SCAQMD staff and the ARB's Reactivity Research Advisory Committee (RRAC). After initial discussions, it was decided that experiments with ethylene glycol and propylene glycol be given priority for this project. At the time of the preparation of this report, we have conducted the experiments needed to assess the reactivities of propylene and ethylene glycols for the two base case conditions employed thus far for reactivity studies in this chamber. Additional reactivity experiments will need to be carried out with the more complex surrogate if it is developed under Task 1. This should include at a minimum experiments with at least two representative petroleum distillate studied for the CARB project representing different levels of aromatic content, and at least one of the glycols.

However, even if we receive approval modify task 1 to evaluate a new ROG surrogate, we expect to be able to conduct reactivity experiments for at least one other representative compound within the

scope of this project. We need to have this discussed at the next RRAC meeting and have the approval of the SCAQMD staff before proceeding on this effort.

Task 3. PM Measurement Support. As part of this task, PM measurements are being made for all of the chamber experiments during and subsequent to the period discussed by this report, and for many carried out previously. The results of side equivalency tests indicate that reactor “A” has greater PM formation than reactor “B”, indicating unequal background effects. For this reason, each reactor needs to be considered independently when assessing PM effects. During the period subsequent to that discussed in this report we have begun to carry out experiments to investigate the source of this inequivalency, but the cause has not yet been identified. The remaining work on this task will consist of continued experiments to assess the cause of this background effect in addition to continuing to make PM measurements during the reactivity and surrogate evaluation experiments. This will be discussed further in subsequent reports.

Task 4. Assessment of Potential of Chamber for Availability Studies. We have initiated informal discussions with the RRWG work interested in availability studies, but have relatively little progress to report thus far. We have requested that this matter be discussed in a teleconference with the RRWG availability task group or be an agenda item at the next RRWG meeting. The work plan for this task will depend on the results of these discussions.

Future Schedule

During the current and upcoming period we are continuing with the chamber experiments with the glycols and have conducted some control experiments to assess background effects for PM formation in our reactors. During the coming period we will also work on analysis and modeling of the results of the petroleum distillate experiments to determine which, if any, additional experiments are necessary and their implications on the mechanisms used to model their ozone impacts.

We have received funding for the CARB project “Updated Chemical Mechanism for Airshed Model Applications” (CARB Contract 03-318) that includes, among other tasks, improving the performance of the SAPRC mechanism for predicting ozone formation in low ROG/NO_x surrogate - NO_x experiments. This is relevant to this project because the ozone underprediction in the relatively low ROG/NO_x “MIR” experiments complicates the test compound mechanism evaluation using the results of those experiments. We will attempt to expedite this effort in order to have a better base case mechanism to evaluate the reactivity experiments for this project.

The work on Task 1 and the remaining experiments on Task 2 for the SCAQMD project will have to be deferred until we get input from the SCAQMD staff regarding the proposed modifications of Task 1 and the priority for additional compounds to study for Task 2.

References

- Atkinson, R. (1989): “Kinetics and Mechanisms of the Gas-Phase Reactions of the Hydroxyl Radical with Organic Compounds,” J. Phys. Chem. Ref. Data, Monograph no 1.
- Carter, W. P. L. (2004): “Development and Evaluation of a Gas-Phase Atmospheric Reaction Mechanism for Low NO_x Conditions,” Draft report to the California Air Resources Board for Contract 01-305, March 10. (Currently Under review by the CARB Research Screening Committee).

Appendix A. Tabulation of Chamber Experiments

Table A-1. Summary of UCR EPA chamber experiments carried out during the period of this report that are relevant to this project.

Run	Date	Type [b]	Purpose and Conditions.	Results
169 - 225	9/03 - 11/03	Runs for other projects	New reactors were installed then the chamber was used for experiments for the EPA OBM project. Several blacklight experiments for PM studies conducted in November.	
226	12/11/03	New Standard MIR Surrogate Side Equivalency Test	Test side equivalency for O ₃ and PM for the new standard "MIR" base case surrogate experiment. 30 ppb NO _x and 0.55 ppmC (nominal) ROG surrogate (without formaldehyde) injected into both reactors.	Good side equivalency for Ozone. Model underpredicted O ₃ to about the same extent as with previous "MIR" base case experiments. PM data only obtained for last few hours of experiment. About 25% more PM volume on Side A than B. Higher PM on Side A is consistent with results of previous experiment.
227	12/12/03	New Standard MOIR/2 Surrogate Side Equivalency Test	Test side equivalency for O ₃ and PM for the new standard "MOIR/2" base case surrogate experiment. 25 ppb NO _x and 1.1 ppmC (nominal) ROG surrogate (without formaldehyde) injected into both reactors.	Good side equivalency for Ozone. Results in good agreement with model prediction, as is the case with previous "MOIR/2" base case experiments. No valid PM data.
228	12/15/03	CO - NO _x	Control experiment to test chamber radical source. 25 ppb NO _x and 50 ppm CO added to both reactors.	Results reasonably consistent with standard chamber model. Somewhat more O ₃ on Side A, consistent with previous such experiments.
229	12/16/03	Standard MIR surrogate + Texanol	New standard MIR incremental reactivity experiment for Texanol. Estimated 90 ppb Texanol injected into Side A, but amount injected uncertain because of operator error. Texanol isomers measured by GC was ~70 ppb.	Texanol addition had almost no effect on O ₃ but caused a reduction in m-xylene consumption rate. Observed effect of Texanol addition reasonably consistent with model predictions. More PM formation on Side A.
230	12/17/03	Standard MIR surrogate + Texanol (repeat)	Repeat previous experiment because of uncertainty in Texanol injection, except in this case the Texanol was injected into Side B. Calculated 95 ppb of Texanol injected, in reasonably good agreement with GC analysis of Texanol isomers.	Effect of Texanol on O ₃ and other gas-phase species essentially the same as the previous experiment. More PM formation on Side A.
231	12/18/03	Standard MOIR/2 Surrogate + Texanol	New standard MOIR/2 incremental reactivity experiment for Texanol. 90 ppb Texanol injected in Side B.	As with MIR experiments, the added Texanol had relatively little effect on O ₃ but caused a reduction in the m-xylene consumption rate. Results generally in agreement with model predictions.

Table A-1 (continued)

Run	Date	Type [b]	Purpose and Conditions.	Results
232	12/19/03	Standard MOIR/2 Surrogate + Texanol	MOIR/2 incremental reactivity experiment with Texanol with larger amount of injected Texanol. 140 ppb Texanol injected into Side B.	As with previous experiments, the added Texanol had relatively little effect on O ₃ but caused a reduction in the m-xylene consumption rate. Results generally in agreement with model predictions.
233	12/23/03	Standard MOIR/2 Surrogate side equivalency test	Assess side equivalency after Texanol experiments and obtain comparison and base case data for PM data in each reactor. MOIR/2 base case surrogate - NO _x mixture injected into both sides.	Good side equivalency for O ₃ . Approximately twice as much PM formed in Side A as B, consistent with previous runs.
		Inactive	The chamber was inactive for the Christmas and new-years breaks.	
234	1/7/04	CO - NO _x	Control experiment to test chamber radical source. 25 ppb NO _x and 50 ppm CO added to both reactors.	Somewhat more O ₃ formed in Side A than B, consistent with previous runs. However NO oxidation and O ₃ formation rates somewhat lower than predicted by standard chamber model.
235	1/8/04	Standard MIR Surrogate side equivalency test	Assess side equivalency after break and obtain comparison and base case data for PM data in each reactor. MIR base case surrogate - NO _x mixture injected into both sides.	Good side equivalency for O ₃ . Approximately twice as much PM formed in Side A as B, which is a greater difference than previous runs.
236	1/9/04	NO _x - Air	Control experiment to test background effects. 25 ppb NO _x injected into both sides.	Slightly faster conversion of NO to NO ₂ on Side A than B. In order for model to fit the NO to NO ₂ conversion rates, it was necessary to assume the equivalent of 1 ppm CO on each side.
237	1/13/04	Standard MOIR/2 Surrogate + ASTM IIIC1	Additional reactivity experiment for ASTM IIIC1 petroleum distillate. 1.2 ppmC distilled added to Side B.	Added distillate had relatively little effect on O ₃ but caused decreased the m-xylene consumption rate.
238	1/14/04	Standard MIR Surrogate + VMP Naphtha.	Additional reactivity experiment for VMP Naphtha petroleum distillate. 1.2 ppmC distilled added to Side A.	Added naphtha caused a decrease in the amount of O ₃ formed.
239	1/15/04	Standard MOIR/2 Surrogate + Aromatic-100	Additional reactivity experiment for Aromatic 100 petroleum distillate. 0.8 ppmC distillate added to Side A.	Added Aromatic-100 caused a large increase in the initial NO oxidation rate but a decrease in the final O ₃ concentration.
240	1/16/04	Standard MOIR/2 Surrogate + ASTM-1A	Additional reactivity experiment for ASTM 1A petroleum distillate. 1.2 ppmC distillate added to Side A.	Added distillate caused reduction in amount of O ₃ formed and rate of consumption of m-xylene.

Table A-1 (continued)

Run	Date	Type [b]	Purpose and Conditions.	Results
241	1/21/04	Formaldehyde - CO irradiation	Control experiment to test for NO _x offgasing effects and also formaldehyde actinometry experiment.	The formaldehyde consumption rate was about 40% higher than expected based on the assigned NO ₂ photolysis rate and calculated rate ratios. Essentially the same O ₃ formation on each side. O ₃ formation slightly greater than predicted by standard chamber model.
242	1/27/04	Standard MOIR/2 Surrogate + ASTM-1B	Additional reactivity experiment for ASTM 1B petroleum distillate. 0.9 ppmC distillate added to Side B.	Added distillate caused reduction in amount of O ₃ formed and rate of consumption of m-xylene.
243	1/28/04	Standard MOIR/2 Surrogate + VMP Naphtha	Additional reactivity experiment for VMP Naphtha petroleum distillate. 0.9 ppmC distillate added to Side B.	Added distillate caused slight reduction in O ₃ and reduced rate of toluene consumption. (Effect on m-xylene consumption could not be determined because of GC interferences.)
244	1/29/04	Standard MIR Surrogate + Aromatic-100	Additional reactivity experiment for Aromatic 100 petroleum distillate. 0.3 ppmC distillate added to Side B.	Added distillate caused large increase in initial NO oxidation and O ₃ formation rates but had relatively little effect on final O ₃ .
245	1/30/04	Standard MOIR/2 Surrogate + Propylene Glycol	Incremental reactivity experiment for propylene glycol for SCAQMD project. 0.4 ppm glycol injected into Side B.	Added glycol caused increase in O ₃ formation and decrease in m-xylene consumption rate. Results generally consistent with model predictions, though calculated effect on O ₃ was somewhat lower than experimental.
		Runs for another project	Blacklight experiments were carried out for another project.	
250	2/11/04	Standard MOIR/2 Surrogate + Ethylene Glycol	Incremental reactivity experiment for ethylene glycol for SCAQMD project. 0.4 ppm glycol injected into Side B.	Added glycol caused increase in O ₃ formation and decrease in m-xylene consumption rate. Results generally consistent with model predictions, though calculated effect on O ₃ was somewhat lower than experimental.
251	2/12/04	CO - Air	Control experiment to test for NO _x offgasing effects. 50 ppm CO injected in both sides.	Approximately the same amount of O ₃ formed on both sides. Amount of O ₃ formed somewhat higher than predicted by standard chamber effects model.
252	2/13/04	Standard MOIR/2 Surrogate + Propylene Glycol	Repeat of the previous experiment with propylene glycol except that the 0.4 ppm glycol was injected into Side B.	Result essentially the same as the previous propylene glycol experiment except for PM formation.

Appendix B. Proposed Modification of Surrogate Evaluation Task

One of the objectives of our current environmental chamber program for SCAQMD is to evaluate the organic surrogates we use in environmental chamber experiments to represent the reactive organic gas (ROG) in urban atmospheres. Environmental chamber experiments with ambient ROG surrogates are used for testing model predictions for ozone and (eventually) PM formation under controlled but chemically realistic conditions and also to serve as the “base case” in the incremental reactivity experiments where effects of VOCs on O₃ and (eventually) PM formation is determined.

The experiments we have carried out thus far employed a simplified 8-component surrogate that we determined was adequate for use in a base case for incremental reactivity experiments for testing mechanisms for effects of VOCs on O₃. This employed essentially the same degree of lumping in terms of representing VOC classes as current airshed models (each compound corresponding to a model species), which means that use of a more complex surrogate would not necessarily be represented by more complex models. Use of a simplified surrogate such as this was an advantage for this purpose, since it simplified the experiments and the mechanism evaluation process. The relative composition of this surrogate was derived based on analysis of air quality data carried out by Jeffries in 1989⁵, which in turn was based on morning measurements in various cities by Lonneman in the 1980's⁶.

We have conducted a number of chamber experiments with this surrogate at varying ROG and NO_x levels with this mixture, primarily under EPA funding. The results indicate that there is a consistent bias in the SAPRC-99 mechanism towards underpredicting O₃ at low ROG/NO_x ratios, and this bias is even worse for CB4⁷. This bias was not evident in modeling studies of previous chamber experiments because of the relatively large amount of scatter in the chamber data, which at best was ±30% in predictions of O₃. However, the bias is evident in modeling the data from the new UCR EPA chamber because of the greater precision of the data, and perhaps also because of the lower reactant concentrations that were employed, which are more representative of current atmospheric conditions.

Although probably suitable for as a base case mixture for mechanism evaluation of O₃ reactivities of added VOCs, there is a concern about whether this adequately represents the mixture of VOCs in actually emitted into urban atmospheres today. Also, when designing this surrogate no effort has been made to obtain a mixture that represents the PM forming potential of ambient VOCs, and probably it doesn't adequately represent this because generally the lowest molecular weight compound is used to represent all compounds of a given type.

One of the objectives of this SCAQMD project is to conduct experiments with mixtures representing current mobile source emissions. Since mobile source emissions are a major component of the ambient VOC mixture, this objective is consistent with the objective of conducting experiments with more realistic surrogates.

Therefore, as a component of this SCAQMD project we propose to design a new, more complex ROG surrogate to more closely represent current emissions, both in term PM formation potential as well

⁵ Jeffries, H. E., K. G. Sexton, J. R. Arnold, and T. L. Kale (1989): “Validation Testing of New Mechanisms with Outdoor Chamber Data. Volume 2: Analysis of VOC Data for the CB4 and CAL Photochemical Mechanisms,” Final Report, EPA-600/3-89-010b

⁶ Lonneman, W. A. (1986): "Comparison of 0600-0900 AM Hydrocarbon Compositions Obtained from 29 Cities," Proceedings APCA/U.S. EPA Symposium on Measurements of Toxic Air Pollutants, Raleigh, NC

⁷ Carter, W. P. L. (2004): " Development and Evaluation of a Gas-Phase Atmospheric Reaction Mechanism for Low NO_x Conditions," Draft report to the California Air Resources Board for Contract 01-305, March 10. (Currently Under review by the CARB Research Screening Committee).

as reactivity to form ozone. A limited number of chamber experiments will be conducted using this surrogate to determine to evaluate the performance of the SAPRC-99 mechanism in predicting O₃ formation at various ROG, NO_x, and ROG/NO_x is comparable to or different than the results obtained with the larger body of experiments with the simpler surrogate. Incremental reactivity experiments will also be carried out with at least one petroleum distillate and propylene glycol, to determine whether there is any difference in mechanism performance in simulating incremental reactivities of these different types of VOCs, compared to the experiments with the simpler surrogate. These data will be useful to assess the relevance of the larger data of ambient surrogate and incremental reactivity experiments that have already been conducted.

PM formation will also be measured during these surrogate experiments, and the results will be compared with the PM formed in the experiments with the simpler surrogate. Significantly more PM may be formed when this surrogate is used, since it will have more high molecular weight compounds, which may have higher PM formation potential. These data may be potentially more useful for evaluating mechanisms for PM formation under more chemically realistic atmospheric conditions.

Although we will seek guidance from the SCAQMD and the CARB staff whether it is better to base the surrogate on ambient air measurements or emissions data, based on input we have obtained previously, we would expect the surrogate would be based on emissions data. Assuming that this is the case, we will obtain from the SCAQMD, CARB and EPA emissions speciation profiles (or distributions of profiles) that they consider to best represent current anthropogenic emissions into urban areas into California. We will also seek guidance from the SCAQMD and CARB staff as to whether it is appropriate to include biogenics in this surrogate, and if so how much and what speciation.

Once a design ambient ROG profile is obtained, we will derive a mixture of organic compounds to use to represent it in experiments. Obviously it will not be practical to include every single compound in the design profile, of only because many are not resolved by GCs, and/or are only identified by generic type (e.g., C9 branched alkane, C12 aromatic, etc.) However, the goal would be for the experimental mixture to match the design profile in terms major identified components present, and in terms of distributions of carbon number and general chemical type. The level of detail or representativeness obtained in practice will depend on cost and experimental considerations that have not yet been fully analyzed. We expect that the experimental surrogate would consist of three components that would be injected separately: formaldehyde, a gas mixture, and a liquid “cocktail” containing the liquid or lower volatility components in the appropriate amounts. The possibility of including petroleum distillates or gasoline samples in the “cocktail” to obtain the desired composition distributions will be investigated.

Other than using this more complex mixture, the experimental procedures employed will be similar to those in experiments with the surrogate currently in use. A minimum of 7 dual-reactor experiments using this surrogate will be carried out, including experiments with varying ROG and NO_x levels, and at least 3 experiments with added petroleum distillate or propylene glycol. The type of petroleum distillate to be studied will be determined in consultation with the SCAQMD staff and the CARB's RRAC.