

**EVALUATION OF ATMOSPHERIC IMPACTS OF  
SELECTED COATINGS VOC EMISSIONS**

**Revised and Corrected  
June 7, 2002**

Progress Report to the  
California Air Resources Board  
Contract No. 00-333

For the Period  
June 30, 2001 through March 15, 2002

William P. L. Carter  
Principal Investigator

Center for Environmental Research and Technology  
College of Engineering  
University of California  
Riverside, California 92521

## Summary of Progress

During this reporting period progress on this made in several areas. The Principal Investigator attended a meeting of the CARB's Reactivity Research Advisory Committee in which priorities for this project were discussed. The consensus was that Texanol and petroleum distillates that are representative of those used with coatings should be the priorities for study. Data were obtained concerning representative petroleum distillate compositions from the study of Censullo et al (2001) and a preliminary reactivity analysis of these data were carried out. Progress was made in preparing the new UCR EPA environmental chamber for experiments for this program, but a number of problems have been encountered and the project is currently behind schedule. Progress up to January 2002 is discussed in detail in the report to the EPA, and progress since then is briefly summarized here. Most of the effort for this CARB program consisted of work on developing a total carbon analysis method that can be used in conjunction with the direct reactivity method developed previously under CARB contract 97-314. Progress in these areas is briefly summarized below.

## Analysis of Reactivity Data for Representative Petroleum Distillates

One of the tasks for this project is to analyze available data concerning compositions of petroleum distillates that are currently used, and develop systematic procedures to assess their reactivities and reactivity uncertainties. An important part of this effort is compiling available data that can be used for this purpose. Discussions were held with representatives of the ACC Hydrocarbon Panel concerning making representative data available, and as part of this we were provided examples of compositional information concerning ~30 representative products. The types of information provided were sufficient to make reactivity estimates, though at present the data are still proprietary and cannot be reported here. We believe that there is a good chance the ACC will permit us to use these data since the manufacturers and product names are not identified. We will be holding further discussions with the ACC hydrocarbons panel representatives concerning availability and use of their data.

Also during this period we were provided the draft report of Censullo et al (2001) in which the results of analyses of 42 different petroleum distillate products were summarized. The summary compositional information gave carbon number distribution and general chemical class information; the detailed speciated analyses upon which these were based were not available at that time. This summary information was sufficient to make reactivity estimates, though as discussed below the estimates for the aromatic solvents are highly uncertain. The reactivity analysis from the summary compositional data consisted of (1) assigning ARB bin numbers to the solvents and deriving their corresponding MIR's from the bin MIR assignments used by the CARB, and (2) estimating the MIRs based on the compositional data provided by Censullo et al (2001) and the MIRs for the SAPRC-99 model species corresponding to this composition. The following assumptions were made concerning uncertain species categories.

- The branched and cyclic alkane reactivities were derived from the generic branched and cyclic alkane model species (e.g., BR- $C_n$  and CYC- $C_n$ , where  $n$  is the carbon number), whose assumed compositions are given by Carter (2000).
- The unspciated alkanes were assumed to consist of 50% branched and 50% cyclic alkanes, which were represented by the corresponding generic species as indicated above.
- The aromatics labeled "xylenes" (or portions thereof) were assumed to consist of equal parts of o-, m-, and p-xylene.
- The other unspciated aromatics were represented by the by three different alternative methods, as follows:

- Set 1. Representing using SAPRC-99 the generic unspciated aromatic model species, which are assumed to consist of ~50% monoalkyl benzenes and the remainder di- or tri-alkylbenzenes, with no naphthalenes (Carter, 2000).
- Set 2. The unspciated aromatics were assumed to be primarily monoalkylbenzenes
- Set 3. The unspciated aromatics were assumed to be primarily di-or trialkylbenzenes.

Subsequent to the period discussed in this report, the final data of Censullo et al (2002) became available, which included more detailed compositional information, particularly for the aromatics. These were assigned to SAPRC-99 detailed model species using the updated emissions assignment procedures being developed under contract for the University of Houston (Carter, unpublished results, 2002). These were used to derive improved reactivity estimates for these solvents.

A summary of the results of our reactivity analysis of these petroleum distillates is given in Table 1, which shows the descriptions, bin assignments, bin MIR assignmnets, and MIR values calculated using the detailed speciation data given by Censullo et al (2002). Note that the draft report of Censullo et al (2001) had erroneous boiling point range data, as indicated by a lack of correlation between the reported boiling point and carbon number ranges. However, the boiling point range given in the final report (Censullo et al, 2002) are much more reasonable, giving a good correlation with the carbon number. This is shown on Figure 1.

Figure 2 shows plots of MIRs calculated from the summary compositional data against the MIRs calculated using the ARB's binning method, with the aromatic reactivities calculated using the three different sets of assumptions, as indicated above. It can be seen that the MIR's agree reasonably for the mostly alkane materials, but significantly different results are obtained for the aromatics, depending on the assumptions made. The ARB's binning assignments seem to be based on assuming the most reactive aromatics are present in the mixtures. This shows that summary compositional information is not sufficient to characterize reactivities, particularly for high aromatic mixtures. However, the estimates based on summary compositional data could probably be improved by using different mixtures to represent the unspciated aromatic classes.

Figure 3 shows plots of the MIRs calculated from the detailed compositional dta against the MIRs calculated using the ARB's binning method. It can be seen that considerably better agreements between the calculated and bin MIR's are obtained when the detailed compositional data are used, particularly for the high aromatic solvents. This shows that the ARB binning method performs reasonably well against MIRs derived using detailed compositional information for these solvents.

### **Progress in Preparation of the UCR EPA Chamber**

The statement of work for this project calls for conducting environmental chambers using the new environmental chamber being constructed under EPA funding. This is referred to as the "UCR EPA" chamber, or just the EPA chamber, in the subsequent discussion. Progress on the construction and characterization of this facility through January is described in the report to the EPA on this project, which was also distributed to the CARB staff (Carter, 2002a). Although progress was made since then towards completing this chamber so it could be used for this project, several delays were encountered that put us behind the target schedule given in the report to the EPA. A brief summary of the current situation is as follows.

- As discussed in the EPA report (Carter, 2002a), the argon arc light as initially installed did not have the correct spectral filter, and had insufficient intensity in the 300-400 nm region. A further setback was suffered when the spectral filter broke when the vendor was attempting to replace it, due apparently to an engineering error. This resulted in an inability to use the light for

Table 1. Summary of petroleum distillate solvents studied by Censullo et al (2001) and results of reactivity analysis Bin Assignments, distillation ranges and calculated MIRs corrected. (6/3/02)

ID	Description	Avg Carbons	Dist Range (°F) [a]	Bin	Bin MIR	Calc MIR [b]
0-1% Aromatic						
CP04	aliphatic petroleum distillates	8.3	240-285	6	1.41	1.42
CP14	aliphatic petroleum distillates	8.3	244-287	6	1.41	1.48
CP24	aliphatic petroleum distillates	8.4	244-287	6	1.41	1.58
CP23	aliphatic petroleum distillates	8.5	260-288	6	1.41	1.57
CP29	aliphatic petroleum distillates	9.3	285-335	6	1.41	1.30
CP43	aliphatic hydrocarbons, Stoddard type	10.0	300-365	6	1.41	1.09
CP38	synthetic isoparaffinic hydrocarbon, ASTM Designation: Type III (Odorless), Class C Mineral Spirits (0-0.25% aromatic); Stoddard Solvent	10.7	320-351	7	1.17	[c]
CP18	aliphatic petroleum distillates	11.3	312-387	11	0.91	0.88
CP33	solvent naphtha (petroleum), medium aliphatic	10.4	324-402	11	0.91	1.09
CP16	aliphatic petroleum distillates	11.3	351-415	11	0.91	0.88
2-8% Aromatic						
CP05	aliphatic hydrocarbon	7.3	185-220	4	2.24	1.86
CP28	solvent naphtha light aromatic(94%), toluene (6%), benzene (<0.1%)	7.5	195-225	9	1.62	1.61
CP30	aliphatic petroleum distillates	8.5	240-285	9	1.62	1.76
CP11	aliphatic hydrocarbons, Stoddard type	9.9	300-365	9	1.62	1.33
CP12	aliphatic hydrocarbons, Stoddard type	10.0	300-365	9	1.62	1.33
CP03	distillates (petroleum), hydrotreated light	11.6	379-405	14	1.21	0.97
8-23% Aromatic						
CP35	solvent naphtha, light aliphatic	8.4	247-282	10	2.03	2.04
CP01	petroleum hydrocarbon naphtha, ASTM Designation: Type I VM&P Naphtha, Regular, 20 vol % max aromatics	8.4	240-305	10	2.03	2.72
CP26	aliphatic petroleum distillates	10.1	307-389	15	1.82	2.02
CP10	aliphatic hydrocarbons	10.1	307-389	15	1.82	1.83
CP25	aliphatic petroleum distillates	10.2	318-380	15	1.82	1.82
CP20	aliphatic petroleum distillates	10.1	312-387	15	1.82	1.81
CP02	paraffinic petroleum distillate	9.9	310-400	15	1.82	2.22
CP39	paraffinic petroleum distillate	9.9	315-397	15	1.82	2.19
CP06	solvent naphtha (petroleum), medium aliphatic	10.2	324-402	15	1.82	1.75
CP15	aliphatic petroleum distillates	10.1	351-415	15	1.82	1.95
100% Aromatic						
CP40	aromatic hydrocarbon	8.0	280-286	21	7.37	7.51
CP34	xylene(79-82%), ethylbenzene(18-20%), toluene (0-1%)	8.1	280-286	21	7.37	7.55
CP41	aromatic hydrocarbon	8.2	280-286	21	7.37	7.34
CP19	aromatic hydrocarbon	8.4	280-286	21	7.37	7.51
CP27	aromatic hydrocarbon	8.9	280-286	21	7.37	7.48
CP31	aromatic hydrocarbon, xylenes, trimethylbenzene, cumene	9.0	320-348	22	7.51	7.27
CP36	light aromatic solvent naphtha, 1,2,4-trimethylbenzene, mixed xylenes, cumene	9.1	320-348	22	7.51	7.31
CP21	light aromatic solvent naphtha	9.1	320-348	22	7.51	7.20
CP07	light aromatic solvent naphtha, 1,2,4-trimethylbenzene, mixed xylenes, cumene	9.1	320-348	22	7.51	7.35

Table 1 (continued)

ID	Description	Avg Carbons	Dist Range (°F) [a]	Bin	Bin MIR	Calc MIR [b]
CP42	light aromatic solvent naphtha, 1,2,4-trimethylbenzene, mixed xylenes, cumene	9.1	320-348	22	7.51	7.42
CP13	aromatic hydrocarbon	9.1	320-348	22	7.51	7.29
CP22	heavy aromatic solvent naphtha	10.0	343-407	23	8.07	7.72
CP08	heavy aromatic solvent naphtha	10.0	343-407	23	8.07	7.23
CP32	aromatic hydrocarbon, naphthalene, trimethylbenzene	10.0	343-407	23	8.07	7.23
CP17	aromatic hydrocarbon, naphthalene, trimethylbenzene	10.1	343-407	23	8.07	7.77
CP37	heavy aromatic solvent naphtha	10.1	343-407	23	8.07	7.40

[a] Corrected data as given by Censullo et al (2002). Note that the boiling range data given in the draft report (Censullo et al, 2001) are erroneous.

[b] Calculated using detailed speciation data provided by Censullo et al (2002). See Figure 1 for MIRs estimated from the summary compositional information provided by Censullo et al (2001).

[d] No compositional data provided.

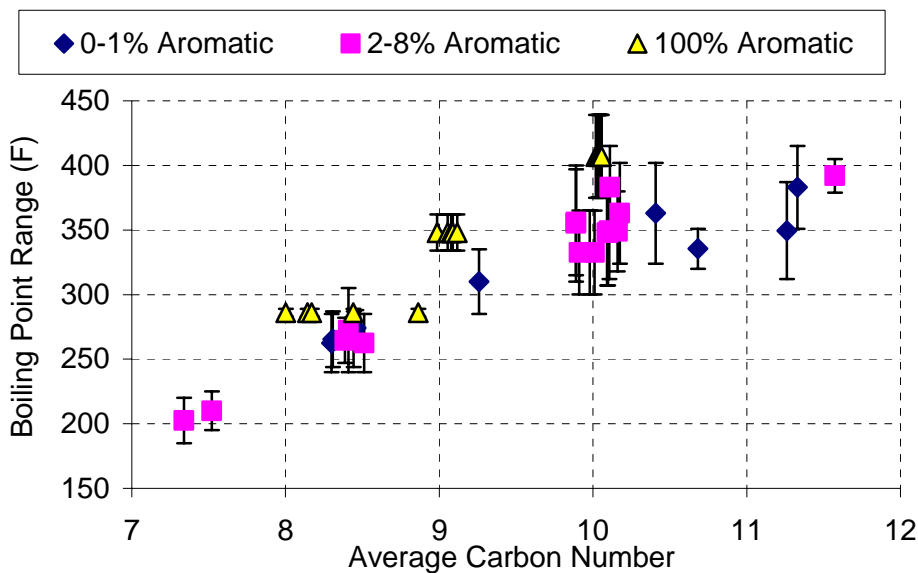


Figure 1. Plots of boiling point ranges against average carbon number from the petroleum distillate data tables given by Censullo et al (2002).

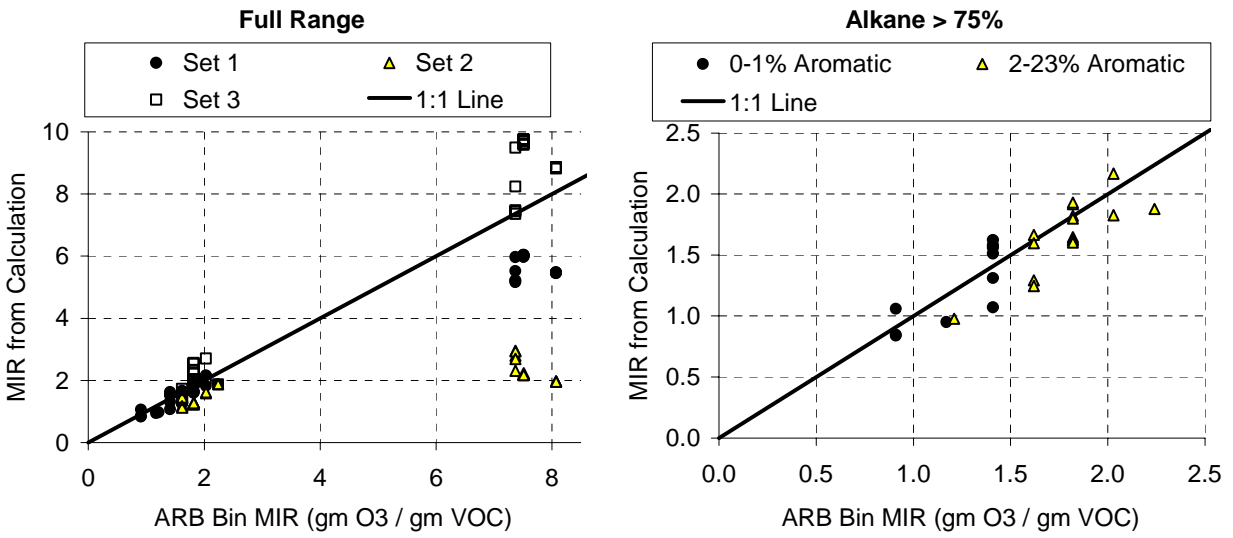


Figure 2. Plots of MIR's estimated from the summary composition data for the petroleum distillates provided by Censullo et al (2001) against the MIRs derived using CARB's binning method.

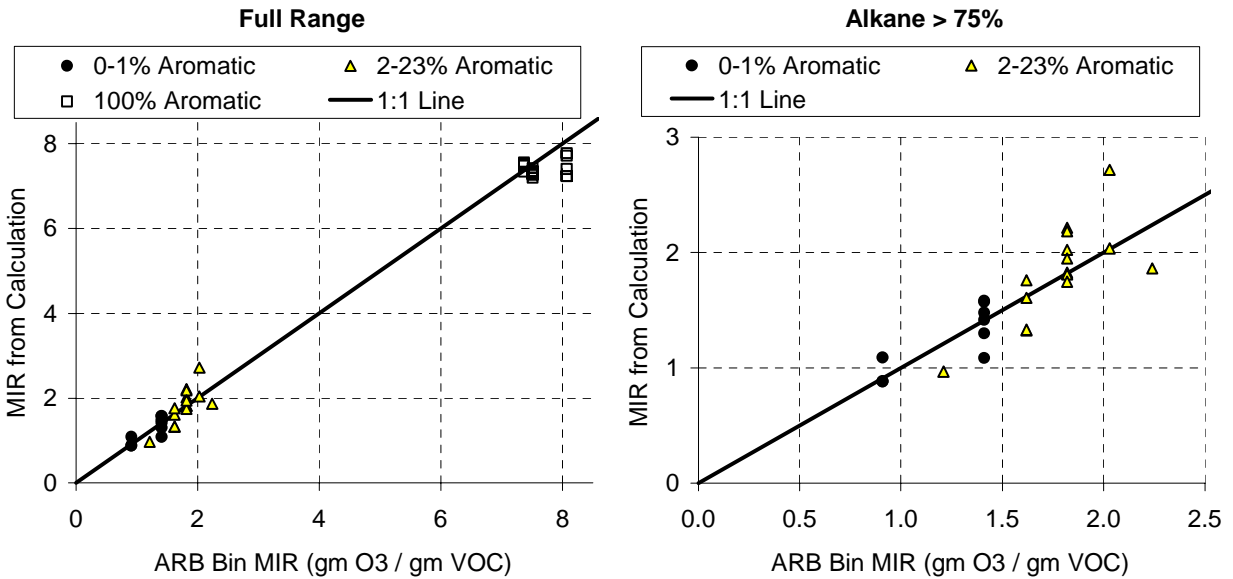


Figure 3. Plots of MIR's derived from the detailed composition data for the petroleum distillates provided by Censullo et al (2002) against the MIRs derived using CARB's binning method.

experiments at least through the end of April. A number of spectral tests were made to elucidate the filter problem, and discussions are being held with the vendor and their subcontractors concerning this. Because it may take some time to develop a suitable filter material to meet all our specifications, in the meantime we will install a temporary uncoated filter system that has the correct cutoff at 300 nm, but is somewhat rich in the UV at 300-400 nm. This temporary system, which will be satisfactory for the initial characterization instrumentation evaluation runs, should be in place by mid-April

- Because of the need to start tests and characterization experiments using a large reactor in the new chamber enclosure, we decided to temporarily install blacklights inside the enclosure. The “BTC” chamber that was used in the characterization tests for the EPA discussed by Carter (2002a) was dismantled and the modular blacklight panels were moved to the EPA chamber enclosure. Initial tests indicates that this system gives an NO<sub>2</sub> photolysis rate of ~0.3 min<sup>-1</sup> in the portion of the enclosure opposite the lights.
- Essentially all of the instruments to be used for the EPA chamber except for the GC’s were moved to the new laboratory building and connected to a sampling system that can select sampling from the reaction bag, the enclosure room, zero air, or various span sources under computer control. Although this is simpler and has more limited flexibility than the more comprehensive sampling system being constructed for the final configuration, the current sampling system will serve for the initial characterization tests. Most of these instruments are now operational, though a component needed for the NO<sub>2</sub> channel on the TDLAS broke down and had to be shipped back to the vendor for repairs.
- A new formaldehyde analysis system based on wet chemical methods that we had ordered previously from Alpha-Omega was finally delivered (a previous version was unsatisfactory and had to be returned to the factory for redesign) and is being evaluated against the TDLAS formaldehyde analysis. It appears to be more sensitive than the TDLAS but its reliability is still uncertain.
- A large (~50,000-liter) pillow-bag was constructed and installed inside the new enclosure for use with the temporary blacklight system. Pure air and other characterization runs are being conducted, but analysis of the results is not complete. Because of leaks, runs longer than 24 hours cannot be conducted using the present reactor. We are working on improving the design of the reaction bags to reduce the leakage problems.
- Formaldehyde and NO<sub>x</sub> offgasing was observed inside the EPA chamber enclosure, with formaldehyde levels of ~10 ppb and NO<sub>x</sub> levels of ~3 ppb occurring during the most recent experiments. Although this may not be high enough to cause significant contamination of the inside of the reactor (as long as it is under positive pressure and does not have large leaks), it is still considered to be unsatisfactory. Tests using components of the temporary blacklight system inside pillow bags suggest that the temporary blacklight system may be introducing much of the contamination. It will be removed as soon as the interim spectral filter for the Vortek lights is in place, probably in mid-April.
- A considerable effort was made in developing procedures, file formats, and computer programs or macros for processing and managing data from the experiments in the new chamber. The objective was to develop a system that takes advantage of the capabilities of current spreadsheet and database programs to expedite the timely and accurate processing of the data for modeling while also implementing appropriate quality assurance procedures and checklists. (The existing procedures used out-of-date programs that would require significant modification to work with

the variety of instruments and sampling modes currently being used. It was decided that the effort in developing a new system that meets our needs would probably take less time and yield more satisfactory results than attempting to upgrade the old Fortran-based system that only the Principal Investigator understood.)

- A major effort is underway to develop a comprehensive quality assurance plan for the EPA chamber experiments. A draft Quality Assurance Project Plan (QAPP) was written, along with standard operating procedures for the overall experiments, data processing, and operations of specific instruments and components. Although we had stated in the January report to the EPA that the draft QAPP would be submitted in January, the effort involved to prepare a comprehensive plan turned out to be much more extensive than anticipated. We hope to have a draft plan available to submit to the EPA during the coming quarter, at which time it will also be made available to the CARB for their review and comments.
- Work is continuing on the design and construction of the sampling and mixing system for the dual reactors that will be used when the Vortek light becomes operational. The mixing system has been designed and is being constructed. The sampling system has been designed and the major parts are being ordered. However, work is still continuing on developing methods to seal the reaction bags to minimize leakage. Experience with the large pillow bag currently in use is providing useful information in this regard.

We had attempted to have the chamber operational with a pillow-bag system with the Vortek lights with the temporary spectral filter system by mid April, but operational problems with the Vortek caused delays. In order to expedite construction of the final reactor so we can proceed with this project, the decision was made to remove the temporary system and begin construction of the final reactor assembly. We hope to have this completed and the begin evaluating this system by July. In the meantime, characterization and instrumentation evaluation experiments are being carried out using a smaller reactor that has been constructed in the new laboratory building.

### **Development of a Total Carbon Analysis Method for Use with Direct Reactivity Measurements**

One of the objectives for this project is to adapt the direct reactivity measurement method developed under CARB contract 97-314 so it can be used for evaluating reactivities of major types of coatings VOCs, particularly Texanol and the various types petroleum distillates. As discussed in the draft final report for that project (Carter, 2002b), the GC methods currently used for determining how much VOC has been injected into the reactor are not satisfactory for evaluations of evaluation of complex mixtures or low volatility materials, and total carbon analysis method is needed for this purpose. Work has progressed in developing such a method for this purpose during the latter stages of Contract 97-314 and the initial stages of this project, and the current progress in this effort is briefly summarized below.

The total carbon analysis method being evaluated is based on using a catalytic combustor to convert all organic compounds to CO<sub>2</sub>, then using a high sensitivity CO<sub>2</sub> analyzer to measure the amount of carbon combusted. CO<sub>2</sub>-free air needs to be used in the experiments because the relatively high level of ambient CO<sub>2</sub> would otherwise swamp the signal from the combustion of the test VOCs. Initial tests of the concept were carried out using a Byron Model 15 taken from a Byron Model 301 total carbon analyzer, and a high sensitivity CO<sub>2</sub> analyzer on loan from API, and the results indicated that the method should be feasible. Therefore, an API Model 360 ultra high sensitivity CO<sub>2</sub> analyzer was purchased for this project using remaining gift funds provided by the ACC for the purpose of expediting work on the direct reactivity measurement method for contract 97-314.



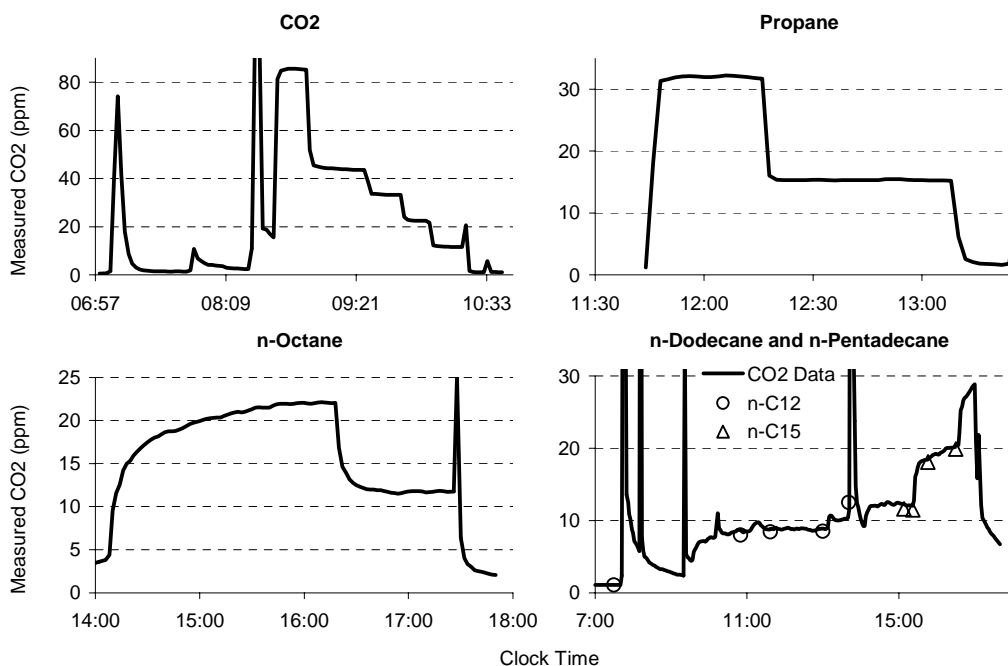


Figure 4. Concentration – time plots of measured CO<sub>2</sub> during the evaluation of the total carbon analysis system using representative compounds.

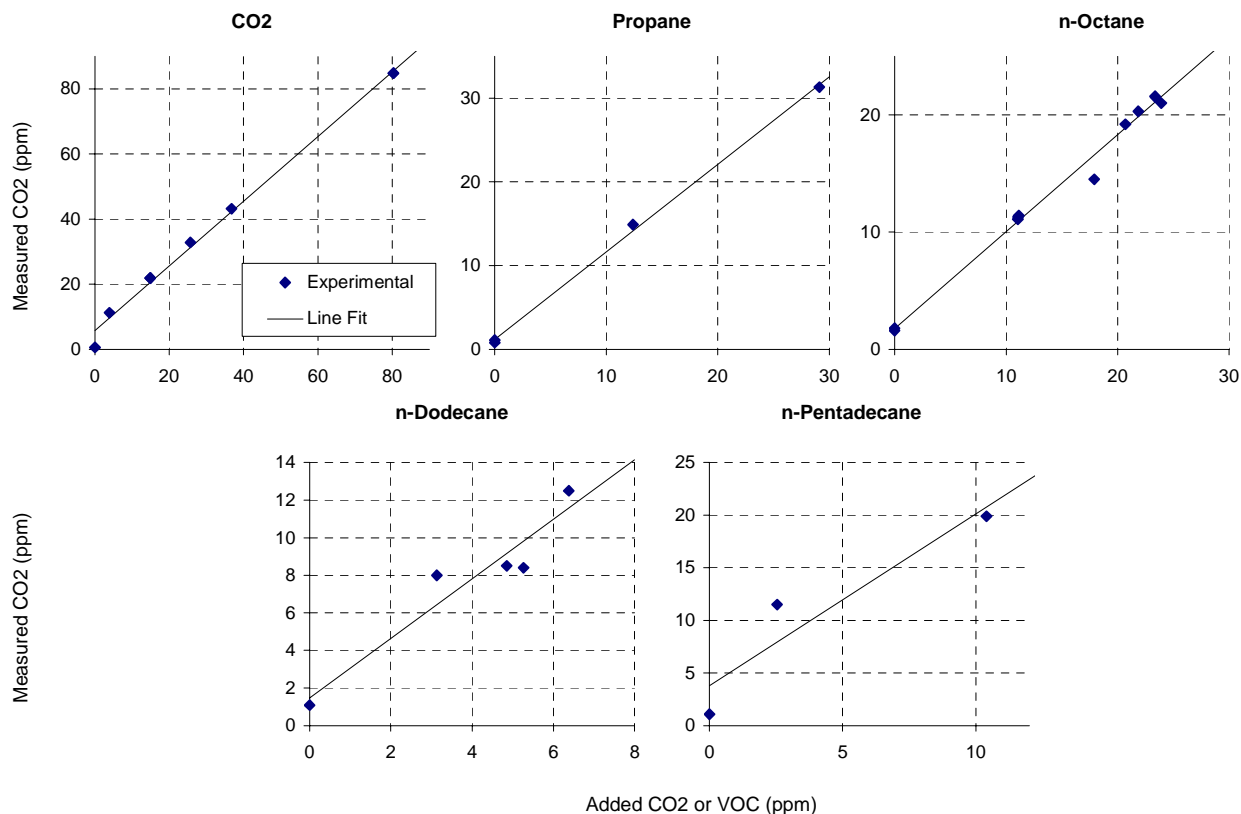


Figure 5. Plots of CO<sub>2</sub> signal against amounts of CO<sub>2</sub> or test VOC added during the evaluation of the total carbon analysis system.

Once the new CO<sub>2</sub> analyzer was finally delivered, tests were conducted to determine if other combustion catalysts would give equivalent or better results than the Byron Model 15, but of the systems we tried the best results were obtained by continuing to use the Byron catalyst. Tests were conducted using various temperatures for combusting ~30 ppm of propane, and essentially complete combustion was obtained at temperatures greater than ~300°C. Since using an excessively high temperature makes it difficult to interface the combustor to the flow system, for most experiments the catalyst temperature was held in the 350-370°C range.

Calibration tests were conducted using CO<sub>2</sub>, propane, and n-octane injected using prepared gas cylinders, and using n-dodecane and n-pentadecane injected using the syringe pump. The results are shown on Figure 4 and Figure 5, where Figure 4 shows the concentration-time plots of the CO<sub>2</sub> data obtained and Figure 5 shows plots of the CO<sub>2</sub> signal against the amount of compound present. The amount of CO<sub>2</sub> added was determined by flow rate measurements when diluting a standard gas cylinder, and the amounts of alkanes present were determined by gas chromatography. Tests were also carried out using methane (not shown) and generally satisfactory results were obtained.

The results indicate that the catalyst system quantitatively converts the alkanes to CO<sub>2</sub> and that the system is probably sufficiently sensitive to measure VOCs at 1 ppmC or less. The more scattered results with the higher alkanes is probably due to imprecisions in the GC measurement of the amount of compound added, but additional evaluations with those compounds will be needed. The reason for the long stabilization time in the initial n-octane experiment is uncertain, but it may be due to hang-up of n-octane in the inlet lines. The inlet system was heated to 100 or 150°C when conducting the tests with n-dodecane and n-pentadecane, and this was sufficient to give relatively rapid stabilization times when the concentrations were changed, as is shown on Figure 5.

The tests discussed above were carried out using CO<sub>2</sub>-free purified air obtained from a local supplier. Because of limited tank capacities, it would be more convenient for routine operation of the system to be able to remove CO<sub>2</sub> on a continuous basis from the output of our own pure air system. Alternative methods were evaluated based on using soda lime, ascarite, and molecular sieves to remove the CO<sub>2</sub>. The best results were obtained with ascarite but results with soda lime, which is much less expensive, were also satisfactory. None of the systems we tried removed the CO<sub>2</sub> to the level in the tank air, but most gave CO<sub>2</sub> levels that were about ~1 ppm higher. However, the data suggest that the baseline should be sufficiently stable for our purposes. We are currently evaluating use of soda lime to remove the bulk of the CO<sub>2</sub>, with Ascarite in series to hopefully remove additional CO<sub>2</sub> and yield more stable results.

The use of the total carbon analyzer is requiring a re-design of the flow reactor configuration because the CO<sub>2</sub> analyzer requires a flow rate of ~0.8 liters/minute, and in the previous setup the total reactor flow was only about 0.5 liters/minute. This required a modified setup involving higher flow through the HONO generator, and splitting the flow between the reactor and the CO<sub>2</sub> analyzer, as shown on Figure 6. Initial tests with this setup were unsatisfactory, probably because of leaks. A number of leaks have been found and corrected, but the system has not yet been completely evaluated. Work on this has been relatively slow because of demands on the technician's time due to the work on the EPA chamber program, and also because the NO<sub>x</sub> analyzer used for the HONO system has needed to be repaired.

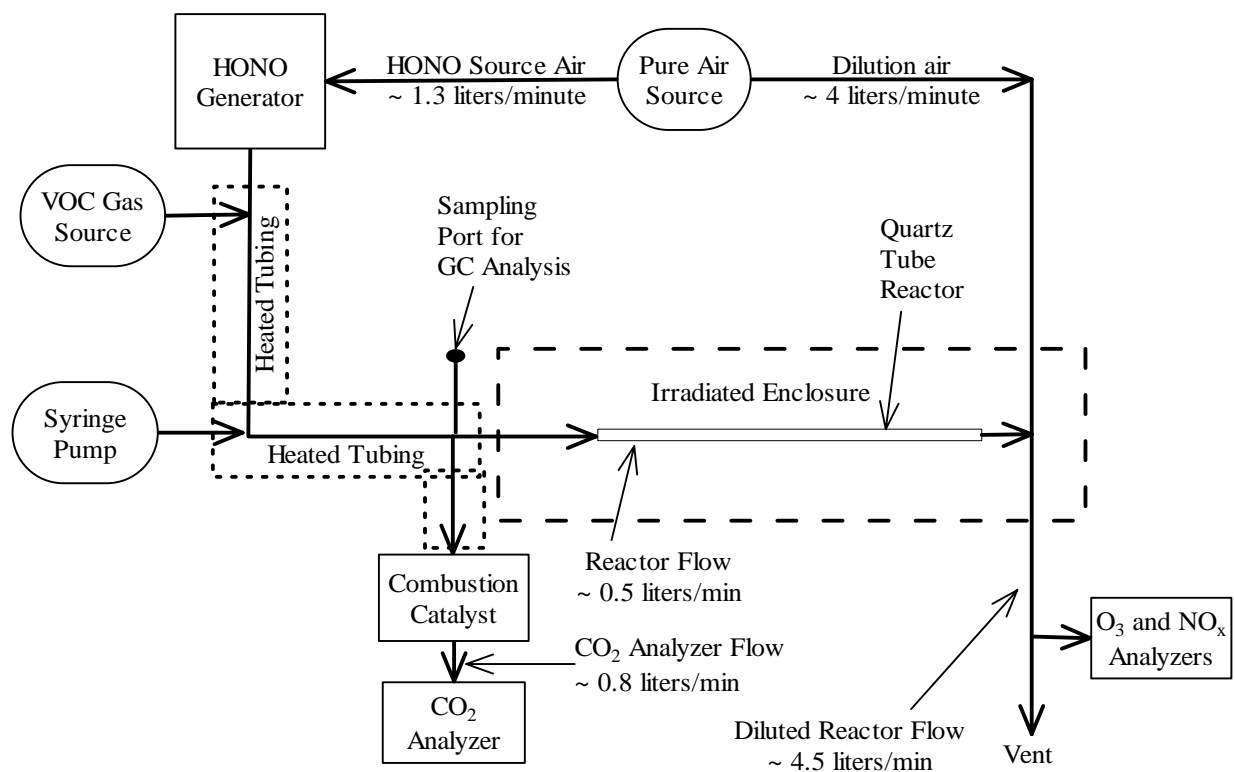


Figure 6. Diagram of setup for plug flow reactor being evaluated for use with the total carbon analysis system.

### Future Schedule

During the upcoming quarter, work will continue on evaluating the modified HONO flow system with the integrated total carbon analyzer. We hope we can complete this evaluation during this quarter and make the final decision on whether this system can yield adequate data with the low volatility compounds and complex mixtures of interest to this project.

Work is continuing on preparing the EPA chamber so it can be used for this project. We hope that by the end of the next quarter we will finally have the reactor, and sampling system in their near intended final configuration, and be able to operate using the Vortek lights, though perhaps with the temporary spectral filter system with the high intensity in the 350-400 nm region. This can then be used to begin the full chamber characterization experiments and evaluating the new instrumentation used.

Work will also continue during the coming quarter in completing the draft QAPP and its associated standard operating procedures for overall experimental operations and data processing. We hope to reasonably comprehensive draft that we can submit to the EPA and the CARB sometime during the coming quarter.

Work on the analysis of the petroleum distillate compositions will depend on the availability of additional data and discussions with the ACC hydrocarbon panel. Progress in this area will probably require having an RRAC meeting where petroleum distillate issues and data availability are discussed.

## References

- Carter, W. P. L. (2000): "Documentation of the SAPRC-99 Chemical Mechanism for VOC Reactivity Assessment," Report to the California Air Resources Board, Contracts 92-329 and 95-308, May 8. Available at <http://www.cert.ucr.edu/~carter/absts.htm#saprc99>.
- Carter, W. P. L. (2002a): "Development of a Next-Generation Environmental Chamber Facility for Chemical Mechanism and VOC Reactivity Research," Draft Research Plan and First Progress Report to the United States Environmental Protection Agency Cooperative Agreement CR 827331-01-0. January 3.
- Carter, W. P. L. (2002b): "Development and Application of Improved Methods for Measurement of Ozone Formation Potentials of Volatile Organic Compounds," Draft Final Report for California Air Resources Board Contract 97-314, February.
- Censullo, A., C., D. R. Jones, and M. T. Wills (2001): "Investigation of Low Reactivity Solvents," Draft Final Report for California Air Resources Board Contract 98-310, December.
- Censullo, A., C., D. R. Jones, and M. T. Wills (2002): "Investigation of Low Reactivity Solvents," Final Report for California Air Resources Board Contract 98-310, May 10.