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Development of Methods and Procedures for Monitoring Ambient Concentrations of Oxygenated Hydrocarbons

CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY

AIR RESOURCES BOARD
Research Division

Development of Methods and Procedures for Monitoring Ambient Concentrations of Oxygenated Hydrocarbons

Final Report

Contract No. 92-306

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DISCLAIMER

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The work described below was the result of a collaboration between AeroVironment, Inc., AtmAA Inc., and the California Air Resources Board. In particular, Dr. Kochy Fung of AtmAA was responsible for much of the development and evaluation of the described monitoring methodology.

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ABSTRACT

Oxygenated hydrocarbons (OHCs) in the ambient air are of concern because of their health effects and because they are a precursor to ozone. Since the introduction of methyl tertiary butyl ether (MTBE) as an addition to gasoline, the importance of measuring OHCs has increased. Previous measurements for OHCs have used gas chromatography (GC) methods that have made quantification and qualification of OHCs difficult, as these methods do not separate the OHCs from the rest of the volatile organic compounds (VOCs). In order to have a method for better determining OHCs in ambient air, the Air Resources Board (ARB) sponsored this ambient OHC collection and analysis development program.

The goal of this project was to develop and evaluate a method for measuring ambient air concentrations of oxygenated hydrocarbons (including carbonyls, alcohols and ethers) at the ppb level. The method developed involved collecting a sample on a sorbent tube, extracting the sample with a solvent, and analyzing the sample through injection into a two-dimensional gas chromatography with intermediate cryogenic trapping and detection by an oxygen specific detector (O-FID). With this method all of the relevant oxygenated hydrocarbons can potentially be analyzed on one sample medium with a single analysis. The samples are easily collected at variable intervals in a routine field monitoring program and may be stored indefinitely.

In general, results of the project indicate that routine analysis of OHCs is possible using the developed methodology. The methodology was tested using six OHC species, representing all of the target OHC classes, and a combination of charcoal and silica gel sorbent tubes. The six species were acetaldehyde, methanol, acetone, MTBE, butanal, and methyl ethyl ketone. With the possible exception of methanol, all of the species were accurately detected using the methodology. The detection of methanol using the silica gel tubes showed considerable variability at lower concentrations, most likely due to high methanol background concentrations in the elution solvent. Methanol detection may be improved by finding ways to lower the background concentrations in the solvent.

While the investigated methodology appeared to work satisfactorily, O-FID analysis is more labor and resources intensive than traditional FID analysis. The O-FID detector must be regularly primed with hydrocarbons, and large amount of N_2 and H_2 are required to operate the system. Thus, to remain economically feasible, the described methodology should be limited to large batch jobs, during which the system can be continuously operated. In addition, an O-FID provides specificity to the method, but at a greatly reduced sensitivity for OHCs of two or more carbons. Continued investigation into the use of O-FID detectors is recommended.

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Section 1

SUMMARY AND CONCLUSIONS

1.1 SUMMARY

The measurements of carbonyls over the past decade point out the deficiencies of the current emission inventory data base for these compounds. Levels of other oxygenated hydrocarbons (OHCs) are expected to rise with the use of oxygenated fuels due to either direct emission or photochemical formation. It is anticipated that the curtailment of OHCs will be an important aspect of the ozone control strategies in urban areas, expecially California. Thus, it is essential to establish the current baseline ambient levels of these OHCs against which future measurements can be compared.

The objective of this study was to develop, validate, and finalize a practical sampling and analysis method to routinely determine ambient concentrations of oxygenated hydrocarbons for use in regional programs. A usable method must analyze OHCs encompassing several chemical classes, including alcohols, ethers, carbonyls, carboxylic acids, and esters. Hydrocarbons are typically analyzed using FID detectors In order to achieve the specitivity required to accurately analyze the OHCs, an oxygen-specific detector is desirable. Use of an O-FID was therefore investigated as a potential analytical method for OHCs.

The sampling media chosen for investigation was solid sorbents. Sorbent tubes as sample media have several advantages including low cost, commerical availability, compactness, and sample stability. The breakthrough volumes for methanol, acetaldehyde, and acetone were determined for several commerically available sorbent tubes. Results indicated that a combination of sorbent tubes would be required to collect the several classes of OHCs required for this program. The recommended combination consists of a silica gel sorbent tube to collect primarily alcohols, and a charcoal tube to collect the aldehydes and ketones.

Sample analysis was performed using a Hewlett Packard 5840A gas chromatograph (GC) equipped with an auto sampler and valve board. Two-dimensional chromatography was used during analysis. The use of two columns allowed for a larger sample aliquot injection, improving both the sensitivity and selectivity of the analysis. Using a freeze-out trap, the GC automatically performed the analysis using heart-cutting and cryogenic trapping of target compounds form the first column, back flushing to eliminate solvent peak and residual injected species, and re-injection of the trapped species to the second colum for separation and detection. Tests of several different GC columns revealed that the combination of a J&W DB 624 column and a Restek Rtx 1701 column provided the species resolution required for this program.

One of the major challanges of the investigation was to identify a solvent which would not interfer with the wide spectrum of target compounds. Out of the several polar solvents evaluated, only n-butyl cellusolve, benzyl alcohol and dioxane were found to elute after the target compounds. Due to a lack of volatility and a high viscosity, both n-butyl cellusolve and benzyl alcohol had a tendancy to contaminate subsequent analysis. Therefore, dioxane appeared to be the most appropriate solvent for this method. Analysis of samples collected by the sorbent tubes, however, revealed that dioxane could not extract compounds such as methanol well from silica gel or acetaldehyde from charcoal. Improvement in the extraction efficiency were obtained when benzyl alcohol was mixed with dioxane, with improved results obtained using a 50:50 mix.

The above sampling and analytical methodologies were tested in several ways. First, samples of known OHC concentrations were obtained in a smog chamber using the sorbent tube combinations presented above. Sample concentrations of 100 and 250 ppb were generated using the smog chamber for compounds representing the five major groups of OHCs. OHC samples were also generated with 100 ppb concentrations of NO_2, SO_2, and ozone in order to investigate possible interference caused by other pollutants. Second, long term stability tests were performed by storing spike sorbent tubes for a period of up to three months and noting the difference in the analyzed concentration as a function of time. Finally, ambient samples were obtained at two sites over a period of two to three days to see if the method was suitable for field use.

1.2 CONCLUSIONS

In general, results of the project indicate that routine analysis of OHCs is possible using the methodology described in this report. The methodology was tested using six OHC species, representing all of the target OHC classes. The six species were acetaldehyde, methanol, acetone, MTBE, butanal, and methyl ethyl ketone. With the possible exception of methanol, all of the species were accurately detected using this methodology. The measurement of methanol using the silica gel tubes was adequate for higher concentrations, but showed larger variability at lower concentrations, most likely due to high methanol background levels relative to the concentrations being measured in the elution solvent. Methanol detection could be improved by having an extraction solvent with lower background.

A paired sample train of silica gel and charcoal sorbent tubes was proposed and evaluated against each sorbent used singly. The tandem arrangement was thought to be necessary because charcoal was shown to have larger breakthrough volumes than silica gel for most species except methanol and acetaldehyde. The combination would then provide adequate sampling air volume without breakthrough for the measurement of the OHCs at the low levels expected in ambient air. Experiments performed at the University of California at Riverside (UCR) for this project provided some valuable information and potential problems with this sampling arrangement. Firstly, the silica gel tube has to precede charcoal. When they are used in the reverse order, as was inadvertently done during the UCR experiments, some species, such as butyraldehyde may be collected, but not recovered from the charcoal. Secondly, with strong sorbents and/or solvent background, blank correction and analytical errors are essentially doubled, thereby raising the lower quantifiable limit of the OHCs. Finally, the UCR work showed breakthrough volumes at 40% relative humidity to be much larger than those determined at >80% relative humidity. Silica gel alone worked well in the UCR experiments when the relative humidity used was at 40%. For future sampling, it is advisable to use silica gel and charcoal tubes in parallel, unless high humidity conditions are expected.

Field measurements using the method yielded concentrations consistent with those expected for the monitoring sites chosen. High background levels in the silica gel tubes continued to affect the detection limit for several compounds. In addition, the field data indicates that silica gel tubes may have an additional source of methanol and acetone which influences measurement results.

An O-FID provides specificity to the method, but at a greatly reduced sensitivity for OHCs of two or more carbons. Routine maintenance is high compared to a flame ionization detector (FID). Highest purity gases (helium, hydrogen, and air) should be used and the unit should remain on for long-term stability. Priming with a hydrocarbon solvent such as hexane should be repeated until a stable baseline is obtained prior to performing any calibration or sample analysis. Thus, this detector is best used when samples are analyzed in large batches.

Section 2

RECOMMENDATIONS

Further investigation into the use of an O-FID is recommended. When using an O-FID, analytical sensitivity is sacrificed for increased specificity. An effort was made for this project to devise a sampling and analytical methodology that would detect a wide spectrum of OHCs using only one sample train and one analytical system. Considerable time was spent attempting to identify and match sorbent tubes, solvents, and GC columns that would work for all of the target OHCs. This project has demonstrated the feasibility of measuring oxygenated hydrocarbons using an O-FID. Using the methodology described in this report, alcohols up through C2, ethers through C5, and ketones and aldehydes through C4 can all be potentially analyzed. Analysis of some species, such as methanol, are only marginally possible. Therefore, it may be appropriate to consider using two analytical methods in order to achieve the required sensitivity over the entire target species range.

Additional work is required to improve the accuracy of the analytical method. Results from this project have demonstrated the need for using an elution solvent that has low levels of background concentrations of the species to be analyzed. To improve the performance of the methodology, further investigation in solvents and solvent preparation is required.

The precision and accuracy of the method will improve significantly when a solvent of high extraction efficiency and low background concentrations is identified. As the target species involved are reduced, the selection of extraction solvents becomes easier. For example, CS_2 can be used as the extraction solvent for charcoal, and analyzed with a FID for C4 or higher aldehydes and ketones, C5 or higher ethers, C3 or higher alcohols using a polar column I (OV275 or TCEP) and a DB-624 (J & W Scientific) as column II (30-m). Silica gel can be extracted with a mixture of n-propanol and water and analyzed using a protocol similar to the present study for the lower alcohols and aldehydes not covered by charcoal.

There appeared to be a problem with recovering butyraldehyde consistently from charcoal. It is unclear if the compound is lost due to reaction or decomposition on the surface of charcoal, or poor extraction efficiency of the solvent used. Further evaluation using a solvent known to work well with charcoal (e.g., CS_2) should help to resolve this issue.

Field tests using the described method indicate that there may be a source of methanol and possibly acetone in the silica gel tubes in addition to the background levels observed in the silica gel. The spun glass plugs used to hold the silica gel in place are the most likely source. Additional investigation into this apparent problem should be performed.

Section 3

PROJECT SCOPE AND PURPOSE

3.1 BACKGROUND AND STATEMENT OF THE PROBLEM

Volatile organic compounds (VOCs) in the atmosphere are of concern due to their role in the photochemical production of ozone and potential health effects. Ambient VOCs consist primarily of hydrocarbons (HCs) and oxygenated hydrocarbons (OHCs), and also some sulfur- and nitrogen-containing hydrocarbon species. OHCs consist of several classes of compounds, including alcohols, aldehydes and ketones, ethers, esters, and carboxylic acids. Measurements of VOCs in the urban environment in the 1960s and 1970s were focused on nonmethane hydrocarbons (NMHC). With the development of the DNPH method (Fung & Grosjean, 1981; Fung & Wright, 1990), the measurement of aldehydes and ketones (carbonyl compounds) become feasible. These compounds are emitted directly by mobile and stationary sources, as well as being intermediates of photochemical oxidation of hydrocarbons. They were routinely measured in major air quality studies, such as the South Central Coast Cooperative Aerometric Monitoring Program (SCCCAMP) in 1985 (Fung & Wright, 1987), the Southern California Air Quality Study (SCAQS) in 1987 (Fung, 1989), the Sacramento Air Quality Studies in 1989 (Fung, 1990a), and 1990 (Fung, 1991a), the San Diego Air Quality Study in 1989 (Fung, 1990b), the Bay Area Air Quality Study in 1989 (Fung, 1990c), the San Joaquin Valley Air Quality Study/AUSPEX in 1990, the Lake Michigan Ozone Study in 1991 and 1992, and the Los Angeles Free Radical Experiment performed in Clairmont in 1993. The studies conducted since 1989 measured carbonyls aloft as well using an adaptation of the DNPH method (Fung et al., 1991b).

These studies found an abundance of C1-C7 aldehydes and ketones in the atmosphere. Formaldehyde, acetaldehyde, acetone, methyl ethyl ketone (MEK), and up through benzaldehyde (C7) were routinely measurable, with acetone being the most abundant. The SCAQS data show that C4+ carbonyl compounds accounted for a larger fraction of the carbonyls and total VOC than expected (on the basis of photochemical modeling). Even the remote site at San Nicolas Island showed a mean total carbonyl concentration measured in clean samples of 27 ± 22 ppbC (Lurmann and Main, 1992).

In a subsequent study funded by the South Coast Air Quality Management District to establish clean air boundary conditions for VOC (NMHC + carbonyls), NO_X, and ozone, the mean NMHC concentrations (from speciation data) measured in the clean offshore Southern California Air Basin samples was 9.3 ppbC, lower than the clean SCCCAMP (16 ppbC) and Santa Barbara (28 ppbC) NMHC values. The mean total carbonyl concentration at 24 ± 11 ppbC was similar to that observed during the SCAQS. The total carbonyl concentration was greater than the NMHC total in 13 out of 18 samples. Higher carbonyls (>C2) were surprisingly abundant (Main et al., 1991). Results from the 1993 CARB-funded Clairmont Study, however, showed lower C5+ carbonyls.

Many of the high levels of carbonyls observed consistently in these studies suggest that there are, as yet, uncharacterized sources. It is known that plants emit a large variety of aldehydes. Schauenstein et al. (1977) noted a wide variety of aldehydes in fruits like pineapple, apple, grapefruit, lime, banana, pear, peach, lemon, blackcurrant, strawberry, orange, grape, and raspberry. Strawberry and pear were found to contain as high as 13-18 mg/kg of aldehydes in C2-C7 range. Common vegetables also were found to contain large C2-C4 aldehydes (SRI, 1978). Thirty-six plant volatiles, beginning with formaldehyde and other aliphatic, olefinic, aromatic, and cyclic aldehydes were cited by Graedel (1979). Microbial decomposition of biomass could also be a significant source of these OHCs. For example, Lurmann and Main found landfill gas to contain C2-C7 carbonyls at tens of ppm levels (Lurmann and Main, 1992). Landfill gas was also found to contain C1-C4 esters of C1-C4 carboxylic acids (Porter, 1992). Molding cheddar cheese emits a variety of OHCs including low molecular weight alcohols, ethers and carbonyl compounds (Pleil, 1991). Stack concentrations of ethanol and acetaldehyde at tens of ppm levels were measured at a commercial bakery (Fung, 1992). Apparently, the ethanol produced by yeast in the dough is released during baking, and acetaldehyde is formed from the ethanol released inside the oven.

The energy crisis of the 1970s has generated much interest in the use of methanol and ethanol as alternate fuels for the automobile. Because methanol can be produced economically with current technologies from a variety of abundant sources such as natural gas and coal found in the United States, it has been perceived as a way to lessen the nation's dependence on foreign energy sources (Gray and Alson, 1989). High oxygen fuels (gasoline blended with alcohol or other oxygenates, e.g., MTBE) have been in use for reducing tailpipe CO emissions during the wintertime in some urban areas of the western United States where increased woodburning has led to frequent violations of the CO standard. In California, methanol is considered as a cleaner fuel that will ease the ozone problem. Test fleets of vehicles using M-85 or M-100 fuels have been under evaluation by the California Air Resources Board and the South Coast Air Quality Management District.

The Clean Air Act Amendment 1990 has mandated 2.7 percent by weight (w/w) of oxygen in gasoline to be sold in CO nonattainment areas starting November 1, 1992. In February 1991, the EPA allowed the oxygen content requirement to be met by co-blending of ethanol and ethers into unleaded gasoline. ARCO took advantage of this ruling to produce wintertime EC-1 gasoline by blending 1.7 percent w/w of oxygen from ethanol and 1 percent w/w from MTBE.

The use of such oxygenated fuels may result in increased emissions of the alcohols and other oxygenates used in these fuels. There is also the potential for associated increase in the levels of formaldehyde and acetaldehyde in the atmosphere. Photochemical oxidation of MTBE was shown to produce other OHCs. Major products include t-butyl formate (~76 percent ±7 percent) and formaldehyde (~37 percent + 6 percent - 1 percent), with methyl acetate and acetone accounting for the balance (Tuazon et al, 1991). Consequently, the atmospheric concentrations of OHCs are likely to increase, as reformulated gasoline and alcohol fuels become more widely available.

The measurements of carbonyls over the past decade point out the deficiencies of the current emission inventory data base for these compounds. Levels of other OHCs are expected to rise with the use of oxygenated fuels due to either direct emission or photochemical formation. It is anticipated that the curtailment of OHCs will be an important aspect of the ozone control strategies in urban areas, especially in California. Thus, it is essential to establish the current baseline ambient levels of these OHCs against which future measurements can be compared. To do so, a method for routine analysis of OHCs needs to be developed.

3.2 PROJECT GOALS AND DESCRIPTION

The objectives of this study were to develop, validate, and finalize a practical sampling and analysis method to determine ambient concentrations of oxygenated hydrocarbons for use in routine regional programs. Specifically, the method should be able to analyze for a wide range of alcohols, ethers, and carbonyls.:

3.3 SCOPE OF WORK

The scope of work for this project was as follows:

1. Test sorbent tubes to find viable tubes for collection of ambient air levels of OHCs.
2. Test solvents to find a viable solvent for extracting the OHCs for the sorbent tubes which is compatible with the GC column.
3. Test chromatography columns to find a viable column for separation of OHCs which is compatible with the solvent.
4. Install an O-FID system (high temperature catalyst for "carbonizing" non-OHCs followed by "methanizing" the OHCs) in a GC with flame ionization detection (FID).
5. Test the system within the laboratory.
6. Generate OHC concentrations in a smog chamber and collect samples to verify the method.
7. Perform ambient measurements using the method to further evaluate its performance.

Section 4

TECHNICAL APPROACH

OHCs encompass several chemical classes, of which alcohols, ethers, and carbonyls (aldehydes and ketones) are of primary interest because they are directly linked to the use of oxygenated fuels. Carboxylic acids are the end products of photochemical oxidation of HCs, while esters can be formed from photochemical oxidation of ethers like MTBE. Hence, the ideal method for OHCs is one which is capable of measuring as many, if not all, of these five classes of compounds with specificity and adequate sensitivity. Such a method will potentially be more cost effective than individual methods for each class of compounds.

The following section describes the equipment and procedures used for the evaluation of one possible method for measuring OHCs. This method is designed around detection using an oxygen specific detector (O-FID).

O-FID

The O-FID is a flame ionization detector incorporated with two catalytic convertors. The first is a cracking reactor with a Pt/Rh catalyst maintained at 1100°C or higher to convert hydrocarbons to elemental carbon, and oxygen containing hydrocarbons to one CO molecule for each oxygen atom the compound contains. The second convertor is a methanizer, which uses a Ni catalyst in the presence of hydrogen to convert the CO into CH_4 for detection by a FID. This detector is commercially available from Siemans (distributed by ES Industries, Voorhees, NJ). For this project, the catalytic convertors were purchased and interfaced to the Hewlett Packard gas chromatograph for evaluation.

The advantage of the O-FID is its specificity for oxygen-containing compounds. In a complex mixture, the determination of OHCs in the presence of high levels of hydrocarbons would be difficult unless adequate resolution of the compounds is achieved. Two-dimensional GC was used to measure alcohols and MTBE in ambient air (Fung, 1991). Specificity was achieved by using two high resolution capillary columns of opposite polarity to separate interfering compounds coeluting from the first column (DB-624, slightly polar) by a second (TCEP, highly polar). With a single column approach, hydrocarbons will interfere, and the O-FID provides the needed specificity. The O-FID is the detector chosen in an ASTM procedure for determining oxygenates in fuel.

Another advantage of the O-FID is its uniform response of OHCs solely according to the number of oxygen atoms the compound contains. Thus, for example, alcohols and carbonyls, each with a single oxygen atom giving rise to one CO (subsequently reduced to one CH_4), have the same response. The disadvantage is that OHCs of more than one carbon can no longer be detected as sensitively by the FID. In essence, it is a trade-off of sensitivity for specificity. In the case of an oxygenated fuel sample, the amount of alcohols or MTBE are in percent levels. There is no problem with detection, and specificity is paramount.

For ambient air application, the issue of sensitivity versus specificity is readily apparent. We decided to evaluate the O-FID in conjunction with two-dimensional GC to see if this detector could be used to our advantage in this setting. Figure 4-1 is an example of analyzing our target compounds and detected by the O-FID. The respective concentrations (ug/ml) and peak areas of the MTBE (6.98, 13160), butanal (9.19, 71780), and MEK (9.6, 83860). Species of similar concentrations produced similar peak size indicating that the detector was performing as expected. The extraneous peaks at the early portions of the chromatogram in Figure 4-1 were absent when the standard was analyzed and detected by FID; there is no apparent explanation.

On a long-term basis, the O-FID requires significantly more attention than the almost maintenance-free FID. Due to the limited capacity of the reactors, it cannot be overloaded by a sample component. The O-FID needs to be primed with a hydrocarbon, such as hexane, to build up an elemental carbon deposit before giving a stable baseline and uniform response, and this process needs to be performed after the detector has been idled for a day or more. Furthermore, due to the limited capacity of the catalytic process, the detector cannot handle prolonged high concentrations. Finally, to assure long-term stability, the detector should remain turned on. This requires that significant amounts of N_2 (for purging the oven) and H_2 (for the nickel catalyst) be consumed.

4.1 SAMPLING AND ANALYSIS TECHNIQUE

o Sampling

One of the objectives of this project was to identify a method to store samples for up to three months with acceptable stability. Collection of OHC using sorbents was considered to be the most promising in fulfilling this objective. Other advantages of sorbent tubes include the low cost of commercially available, prepackaged sorbent tubes and compactness of the samples, needing very little storage space. The sorbent samples were frozen in an air tight container until analysis.

o Analysis

Two-dimensional chromatography was investigated as a method suitable for analyzing OHCs. This method allowed injection of a larger aliquot of the sample extract, resulting in higher method sensitivity and improved selectivity than if a single column was used. The set up, as shown in Figure 4-2, used a 4-port and a 6-port valve to perform several functions that constitute the essence of this approach: heart-cutting and cryogenic trapping of target compounds eluting from the first column, back flushing to eliminate solvent peak and residual injected species, and re-injection of trapped species to a second column for separation and detection. The system operated as follows:

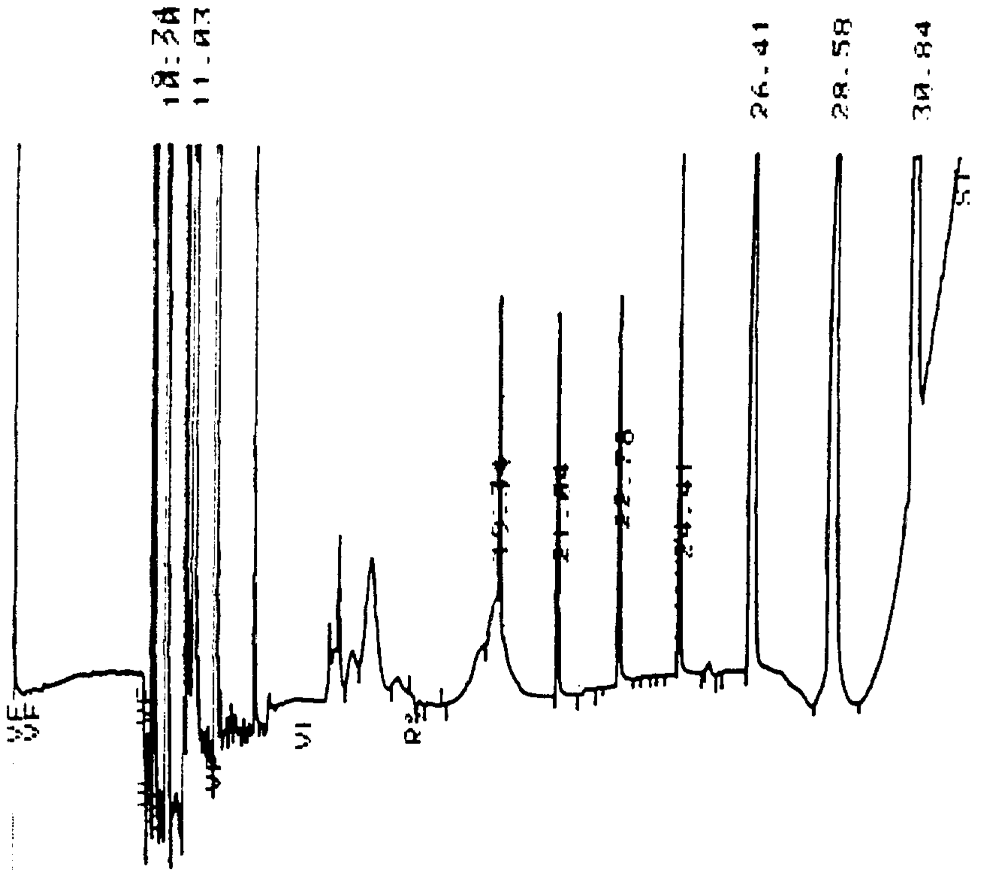


FIGURE 4-1. Analysis of some oxygenated hydrocarbons with O-FID detection. Peaks are: acetaldehyde (19.34 min), methanol (21.04 min), acetone (22.78 min), MTBE (24.41 min), butanal (26.41 min), MEK (28.58 min), and dioxane (30.84 min, solvent).

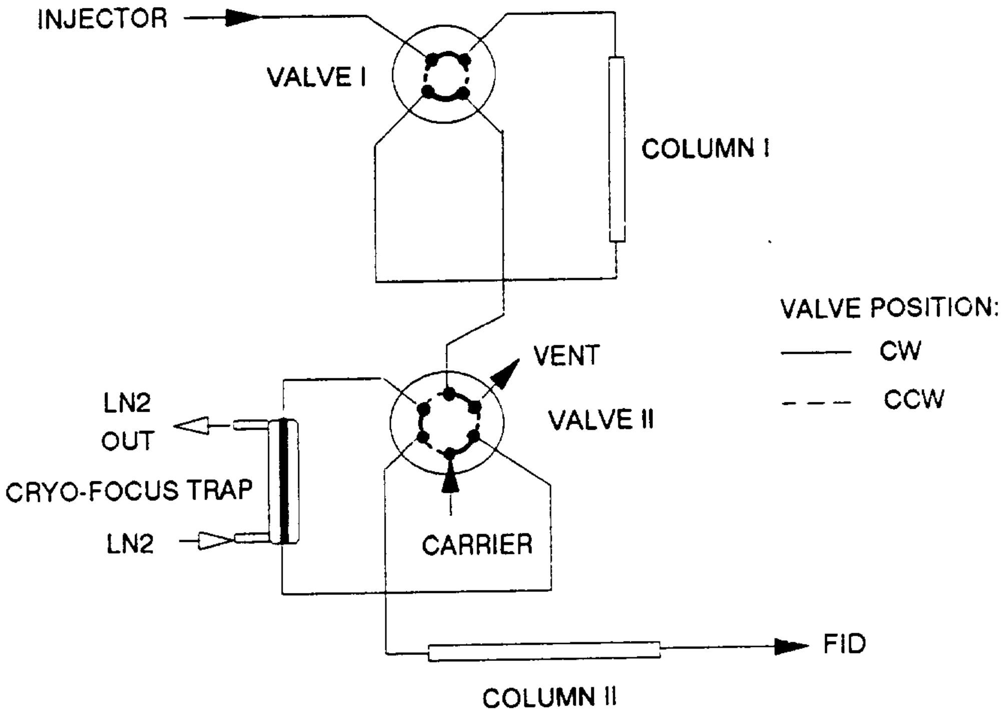


FIGURE 4-2. Valve plumbing diagram for two-dimensional gas chromatography analysis of OHCs.

An aliquot of extract was injected into the Column I via Valve I. Compounds eluting from the column were vented (or optionally monitored by an FID) through Valve II. Just before the first target species eluted, Valve II was actuated (dotted line) to divert the compound and other subsequent eluting species to a freeze-out trap maintained at -185°C by liquid N_2. After the last target compound had eluted, Valve I was actuated to backflush Column I, and Valve II, deactuated (solid line) to connect the trap to Column II. A cartridge heater was turned on to re-volatilize the trapped material for injection into Column II. When this re-injection took place, the column oven was cooled to cryofocus the species. Then the oven temperature was raised to elute the species. The temperature ramp used depended on the column used.

A Hewlett Packard 5840A gas chromatograph (GC) equipped with an auto sampler and a valve board was used to perform the analysis. The entire injection and valve sequences was automated by the gas chromatograph. The auto sampler performed the injection. The valve board permits automation of four solenoid operated valves and four contact closures. Valve I and II were controlled by solenoids. Cooling and heating of the freeze-out trap were controlled through the contact closures to turn on and off of the solid state relays in the respective Omega CN9000 temperature controllers (Omega Engineering, Stamford, CT), which powered the cryogenic valve for liquid nitrogen (LN_2), or the heater cartridge, respectively.

Freeze-out Trap

The trap was constructed from 9 inches of 1/16-inch o.d., 0.050-inch i.d. stainless steel tubing, which was packed with 80 mesh glass beads. The tubing was coiled tightly against a 3/4-inch diameter, 2¼-inch long 200-watt cartridge heater, with a Type K thermocouple wedged between the heater and the tubing, and a 1-inch long, 1/8-inch diameter Series Ke RTD (resistance temperature detector) secured against the coiled tubing with Nichrome wire. The temperature sensors were connected to respective CN9000 temperature controllers for heating (thermocouple) and cooling (RTD) of the trap. All of the above hardware were purchased from Omega Engineering, Stamford, CT. The entire trap assembly was housed in an aluminum box (4" x 5" x 2") insulated on the inside with 3/4-inch thick E felt (fiber glass). Two 1/4-inch Swagelok bulkhead union fittings, located approximately one inch from the top and bottom edge of the box, served as inlet and exhaust of LN_2, respectively, from the cryogenic valve.

The cryofocusing assembly (Part No. 354-A) or the cryotrap (Part No. 352-D) used in the 3550A Cryogenic Concentrator (Graseby Nutech, Durham, NC) may be adapted for use in place of the hardware described above.

Sample Extraction

The sorbent in the sample tube was transferred to a 2-ml or larger septum vial (Part No. 98133, Alltech Associates, Deerfield, IL) by removing the glass wool or foam plug using a hook, and gently tapping the sorbent tube with the open end inside the vial. The vial was then capped and labeled. While the vial can hold both front and back section of the sorbent, it is better to have the sections in different vials. Samples not extracted immediately were placed in a freezer for storage. It should be noted that chilling may cause the cap to come loose. The septum cap of each sample was checked for tightness before putting the sample into storage.

One milliliter of the extraction solvent was dispensed using a 2-ml pipette (Part No. 050-10-952-6, Brinkman Instruments, Westbury, NY). A 26-gauge needle was fitted to the end of the dispenser tip to allow solvent to be dispensed via piercing through the septum. Alternatively, a gas tight syringe could be used for the same purpose. if an If an open vial is used, activated charcoal gives off sufficient amount of heat upon solvation to cause a possible loss of sample. Therefore, the sample was first chilled by immersing the bottom section into liquid N_2 for approximately a minute. Then the septum was pierced with a small gauge (30 or 32) hypodermic needle to relieve the vacuum within the vial developed upon chilling, and to act as a vent when solvent was added into the vial through the septum with the dispenser while the vial remained in liquid N_2. A new septum cap was installed and the sample was sonicated for approximately 20 minutes, followed by mechanical shaking for approximately five minutes and sonication for an additional 20 minutes. The extracts should be filtered or the samples centrifuged to settle the fines, removing the clear extracts to a separate vial for injection. Otherwise, the injection syringe needle may be clogged and cause spurious results. If the samples were not analyzed immediately after extraction, they were stored in a refrigerator.

Silica gel does not gives off heat to the same extent as charcoal, so the above procedure was not necessary for the silica gel tubes. The extraction solvent was dispensed into an open vial after it was briefly chilled with liquid N_2, and the sample was similarly sonicated and shaken to complete the extraction.

4.2 SORBENT TUBE EVALUATION

Sorbent Evaluation

A variety of sorbents are available for the collection of organic compounds. The most common are coconut charcoal and silica gel, both of which have been used extensively in NIOSH procedures for industrial hygiene applications. Charcoal is used typically for the non-polar organic compounds, including those under investigation in this program, such as acetone, methyl ethyl ketone (P & CAM Method 127). Silica gel adsorbent is reserved for the more polar compounds, such as alcohols (P & CAM Method 247). The breakthrough volume, as defined by NIOSH, is the volume that has passed through a sorbent when the effluent concentration reaches 5% of the influent concentration. For a given sorbent, the breakthrough volumes increases as the molecular weight of the compounds of a homolog series increases. Thus, when sampling for a given class of compounds, the breakthrough volume will be dictated by the lowest member of the series. The breakthrough volumes of several commercially available sorbents were evaluated using the lowest molecular weight homologs. Methanol, acetaldehyde, and acetone were used to represent alcohols, aldehydes, and ketones respectively.

A gas chromatograph was used to perform the evaluation. The carrier gas (N_2) flow was set at 25 and 50 ml/min, respectively, dependent on the experiment. The higher flow was used to reduce the amount of time needed to observe breakthrough. The carrier was humidified in a water-filled impinger heated by a thermostated water bath at a temperature approximately 10 degrees higher than the sorbent test temperature. As the carrier gas entered the test chamber (GC oven) at the test temperature, a second impinger was used to allow the excess moisture to settle out prior to entering the injector where the sorbent tube was attached using two O-rings to replace the ferrules of the Swagelok connector. As such, the breakthrough volumes were evaluated at essentially 100% relative humidity. For a lower percent relative humidity, the water bath was operated at a temperature lower than the test temperature, and the percent relative humidity was calculated by assuming complete saturation of the carrier at the lower temperature. The ratio of the amount of water at the lower temperature to that needed for complete saturation gave the percent relative humidity of the test.

Interference Evaluation

Sorbents that are good in terms of background, sampling capacity, and recovery were evaluated further for interference and storage stability testing. Interference testing was accomplished by injecting the sorbent tube with a gaseous standard mixture and then purging the sorbent tube with air containing various atmospheric pollutants such as ozone, nitrogen dioxide, and sulfur dioxide at concentrations appropriate to ambient conditions. The purge (i.e., sampling) flow rate was based on the determined breakthrough volume and intended sampling duration of 1-3 hours (typical anticipated sampling times). The experimental control was a sorbent tube charged with the standard mixture and purged with pure air at identical conditions. After the exposure, the tubes were analyzed as usual to determine the extent of loss, if any. Inferences that cause the measured value to change less than 20 percent were considered acceptable.

Nitric acid may be an interferant, but ambient concentrations of nitric acid are usually low. The generation of known nitric acid at ppb levels in a test atmosphere is not easily accomplished. Extensive wall losses can make the actual test atmosphere concentration difficult to assess without extensive prior characterization. To investigate this, an evaluation at the Statewide Air Pollution Research Center at U.C. Riverside was performed using the 5800-liter evacuable smog chamber equipped with a long-path Fourier transform infrared spectrometer (LPFTIR).

The smog chamber/LPFTIR system was used to prepare and validate dilute mixtures of OHCs, including acetaldehyde, acetone, butanal methanol, methyl ethyl ketone, and MTBE. These compounds cover the spectrum of OHCs (alcohols, ethers, aldehydes and ketones). These mixtures were sampled using the proposed method at the same time the concentration was determined by the LPFTIR. Mixtures of oxygenated hydrocarbons were prepared at nominal concentrations of 100 and 250 ppb, and as mixtures with and without the addition of pollutants typically found in urban atmospheres. Concentrations of 100 ppb for nitrogen dioxide, sulfur dioxide and ozone were generated for this test. The addition of these pollutants allowed the detection of potential interferences. Possible interferences to the analytical methods which can arise from species that are photochemically generated in the troposphere (for example, the organic nitrates and peroxynitrates) were examined by carrying out chamber simulations of the relevant photochemical reactions and subsequent addition of known amounts of the oxygenated compounds to the photolyzed air mixtures.

The air mixtures of oxygenated compounds were prepared in an evacuable and thermostatted Teflon-coated chamber with a volume of 5,970 liters. The chamber is equipped with a set of *in situ* 1.3 meter basepath, multiple-refection optics interfaced to a Nicolet 7199 FTIR spectrometer. The sampling mandifold for the series of sorbent tubes was attached to a 9 mm diameter Pyrex tube which extended to 0.5 meters inside and near the middle of the chamber. Six sample trains were attached to the manifold, as described below:

1 & 2 Charcoal tubes (SKC #226-09, 600 mg of coconut charcoal divided into two section with foam separators and a glass wool end)

3 & 4 Silica gel tubes (SKC #226-10-04, 450 mg of silica gel divided into two section with glass wool separators)

5 & 6 Charcoal front tube and silica gel back tube attached in series using a Teflon union

Sorbent tubes were attached to the ports using Teflon unions. Flow rates through the sorbent tubes were maintained at 50 cc/min using individual rotameters and metering valves at the outlet of each sorbent tube. A certified mass flowmeter was used to verify the flow rates through the sample lines. Approximate 200 cc/min of additional air was drawn through the manifold to keep "fresh" sample in the manifold.

Prior to each run, the chamber was pumped down to <0.1 Torr and filled with diluent air from an air purification system. The purified air was at less than 3% RH; therefore, its water content was adjusted to approximately 40% RH at 298° K by introducing water through an atomizer with the chamber's two Teflon-coated mixing fans turned on. The adjustment of the air's water content was monitored by a Vaisala HMI 32 humidity sensor. No adjustment in CO_2 was made since the air pufication system does not alter significantly the CO_2 content of the input ambient air.

The caluculated amounts of SO_2 and NO_2 were measure separately into calibrated 0.5 liter Pyrex bulbs using an MKS Baratron capacitance manometer (100 Torr sensor) and expanded into the chamber by flushing with a stream of N_2 gas. O_3 was next flushed into the chamber from a calibrated 0.05 liter Pyrex bulb containing the sample of O_3-O_2 mixture (with approximately 11,700 ppm O_3 content) generated by a Welsbach ozonizer at a precalibrated voltage and input flow of O_2. Vapors of the oxygenated organic voltage compounds, also separately measured in calibrated 0.5 liter Pyrex bulbs with the capacitance manometer, were then individually injected into the chamber. The mixing of components for all runs was carried out to an initial pressure of 740 Torr, but reduced to prevailing barometric pressure (730 - 735 Toor) to avoid singnificant flow through the sorbent tubes during setup of the sampling train. The chamber temperature was maintained at 298 +/- 2° K for all runs.

The concentrations fo the organic compounds were monitored before and after the sampling on sorbent tubes and at 30 minute intervals during the 2-hour sampling period by FTIR spectoscopy, using a pathlength of 62.9 m and resolution of 0.7 cm^{-1}. GC-FID analysis of the mixture was also performed before and after the sampling period as an additional check for any significant change in the concentrations of the organic compounds.

A total of six gas mixtures were sampled in this manner, consisting of the following:

1. Pure air (with 350 ppm CO_2 and 40% relative humidity).
2. Air with criteria pollutants. About 100 ppb ozone, 100 ppb SO_2 and 100 ppb NO_2 added to the air/CO_2/H_2O mix.
3. Air (including CO_2 and H_2O) with approximately 250 ppb of each of the OHCs.
4. Air (including CO_2 and H_2O) with approximately 100 ppb of each of the OHCs.
5. Air (including CO_2 and H_2O) with approximately 250 ppb of each of the OHC plus 100 ppb of each of the pollutants.
6. Air (including CO_2 and H_2O) with approximately 100 ppb of each of the OHC plus 100 ppb of each of the pollutants.

Storage Stability Evaluation

Sorbent tubes were charged with known amount of gas standards with a gas tight syringe, capped and stored in a freezer inside closed containers for up to three months. Canning jars were used as storage containers because they are air tight. The experiment was conducted at three concentration levels. At each level, triplicate tubes were prepared. A total of 72 tubes were prepared, with the first three sets (concentrations) of three analyzed at the beginning to indicate the "time zero" concentrations. The process was repeated at the end of each consecutive month for the three-month duration.

4.3 FIELD TESTING

To field test the developed method, samples were obtained at two sites where concentrations of oxygenated hydrocarbons were likely to exist. Three days of sampling were performed in Monrovia, California, which was considered to be representative of typical urban air. Two days of sampling were performed on top of the Kiefer Landfill near Sacramento, California. The Kiefer Landfill is one of the last remaining large landfills without a vapor recovery system. Two sets of three-hour samples were obtained during each day of sampling. Each set consisted of both a charcoal and silica gel sorbent tube sampled individually. In addition, a six-hour sample set was collected at each site concurrent to the two three-hour samples. At Monrovia, the six-hour charcoal and silica gel tubes were sampled individually. At the Kiefer Landfall, the six-hour tubes were sampled in series, with the silica gel tube located in front of the charcoal tube. In addition to the samples, at least two sets of blanks were obtained at each site.

Sample flows for the field testing were controlled using needle rotameters at nominal flow rates of about 50 cc/minute. Exact flow rates were measured at the beginning and end of each sample period using a certified mass flowmeter or bubblemeter.

4.4 AUDITS

A systems audit of the development laboratory was performed by an outside contractor that specialized in the auditing of laboratories. The auditor visited the laboratory and examined the facilities and methods used to receive and extract samples, and reviewed data reduction, validation and reporting activities. A performance audit was not considered cost effective, since preparation of the specialized low concentration standards and high purity solvents required for this method were beyond the capabilities of the audit contractor and the scope of the audit task.

Section 5

METHOD EVALUATION AND DISCUSSION

The following section describes in more detail results of the investigation into several aspects of the proposed method.

5.1 SAMPLING AND ANALYSIS TECHNIQUE

Elution Solvent

Since the method described above is intended for measurement of several classes of oxygenated hydrocarbons, which include alcohols, aldehydes, ketones and ethers, such as methyl tert-butyl ether (MTBE), the solvent chosen must be one that would not interfere with (mask) the target compounds in the analysis. The broad range of elution times for these compounds precludes the use of common solvents such as carbon disulfide or methylene chloride. Another problem with carbon disulfide is poisoning of the reductive catalyst in the O-FID. Solvent volatility and viscosity, which can affect the method's precision and carry-over in sample injection, also had to be considered.

Several potential polar solvents were evaluated: ethyl carbonate, tetrahydrofuran, ethyl cellusolve, butyl cellusolve, acetonitrile, benzyl alcohol, and dioxane. On the basis of their retention times in a 2.4-m long, 3 mm i.d. stainless steel packed column of 25% 1,2,3-tris-cyanoepoxypropane (TCEP) on 60-80 mesh Chromosorb PAW (Analab, No. Haven, CT). or a 20-m long, 0.53 mm i.d., 3 um d.f. fused silica megabore DB 624 (J & W Scientific, Folsom, CA) capillary column, only butyl cellusolve, benzyl alcohol and dioxane were found to elute after the target compounds, which included acetaldehyde, butanal, acetone, methyl ethyl ketone (MEK), methanol, isopropanol, and MTBE. Other compounds such as benzaldehyde, pentanal, hexanal, o-tolualdehyde and 2-pentanone were found to elute earlier than n-butyl cellusolve in the TCEP column. However, further tests with standard solutions revealed that sample carry-over was a problem with this solvent because of its lack of volatility and high viscosity. There was always sufficient residual sample left in the syringe to contaminate the next sample. Since a low initial column temperature was needed to allow some retention of our target species, a solvent with high boiling point would coat the inside of the column until the over temperature was sufficiently high for it to elute. Insufficient removal of this film resulted in shifting retention times of our target species. Also, there were adsorptive losses of methanol with the TCEP column such that reproducibility of the low standards was poor.

Benzyl alcohol has a similar sample carry over problem due to its viscosity and high boiling point. For this reason, dioxane was chosen as the solvent for evaluation with the megabore column. However, further extraction efficiency determination revealed that dioxane could not extract compounds like methanol well from silica gel, or acetaldehyde from charcoal. Improvements in the extraction efficiency were obtained when benzyl alcohol was mixed with dioxane. Table 5-1 shows the extraction efficiency of the selected compounds at 10% and 50% benzyl alcohol in dioxane, which ranges from approximately 60% to 100%. The solvent blend did not have the carry-over problem. Thus, a 50:50 mix of benzyl alcohol and dioxane was chosen as the solvent for further development evaluation with the megabore column.

All of the solvents used were the highest purity grades available, with purities 99% or better. However, their high purity solvents still contained significant levels of impurities and varying levels of the target species. Dioxane was redistilled before it could be used for the quantitative work. Even then, the levels were still measurable, and background correction was necessary. The precision of the auto sampler was very good, such that the correction process did not cause much scatter to the calibration data. The impurities in the solvents necessitated a "cook-out" step after the last target species has been eluted, thereby lengthening the analysis time by approximately 18 minutes.

The solvent chosen for the extraction dictates the type of columns, and conditions that are needed to perform the analysis. In the present study, dioxane/benzyl alcohol mixed solvent represents a compromise to obtain reasonable extraction efficiencies for the species analyzed under the same conditions. Ideally, a more polar solvent such as water or in combination with a low molecular weight alcohol would have been a better solvent for silica gel, and carbon disulfide (CS_2) for charcoal. Background levels of oxygenated hydrocarbons in CS_2 are very low and that should significantly improve the LQLs. But the analysis would have to be performed under two different analytical conditions, and the O-FID would be unsuitable as the detector due to poisoning of the nickel catalyst by sulfur when CS_2 is used. Figure 5-1 is a chromatogram of CS_2 extract for MEK, MIBK (methyisobutyl ketone), and other air contaminants such as benzene, toluene, 1,1,1-trichloroethane, and perchloroethylene (PERC) analyzed using two-dimensional GC procedure with flame ionization detection. The first column was a 2-m TCEP packed column and the analytical column was a 10-m, 0.25mm i.d. 007-624 capillary (Quadrex) with a 2u film thickness.

While the 007-624 column is less polar (6% cyanopropylphenyl compared to 14% cyanopropylphenyl polysiloxane, the balance being dimethyl polysiloxane), and shorter than the Rtx 1701 used in this study (10 m vs 30 m), the elution order of compounds in both columns are similar. If this analytical set-up (i.e., TCEP in combination with Rtx 1701) is used to analyze the present target compounds extracted in CS_2, only MTBE, butanal, and MEK and, perhaps, methanol can be measured. Acetaldehyde and acetone co-elute with CS_2 in the TCEP column and methanol may be masked by CS_2 in the Rtx 1701 if the solvent peak is not sufficiently removed by the initial cutting process. In switching over to CS_2 for the extraction of charcoal tube, it allows higher molecular weight OHCs to be measured because they all elute *after* CS_2 in the TCEP column. MIBK in the above example clearly demonstrates this feasibility. With the dioxane/benzyl alcohol solvent, there is insufficient resolution of MIBK from the solvent peak in the TCEP to allow the cutting process to work correctly. In essence, this approach is suitable only for alcohols, and carbonyl and other oxygenated compounds with four or more carbons. However, this is not necessary a detriment because

TABLE 5-1. Extraction efficiency of selected oxygenated hydrocarbons from silica gel nts and charcoal adsorbents using benzyl alcohol/dioxane mixtures.

10% BenzylOH:90%Dioxane

	Acetal.	MeOH	Acetone	MTBE	Butanal	MEK
Sil. gel	0.6106	0.4729	0.7018	0.9760	0.9212	0.8900
Charcoal	0.4552	0.7481	0.6178	1.0370	0.7062	0.7438

50% BenzylOH:50%Dioxane

	Acetal.	MeOH	Acetone	MTBE	Butanal	MEK
Sil. gel	0.6779	0.5703	0.6557	1.0070	0.9390	0.8440
Charcoal	0.6217	0.8328	0.6677	1.0787	0.8260	0.7784

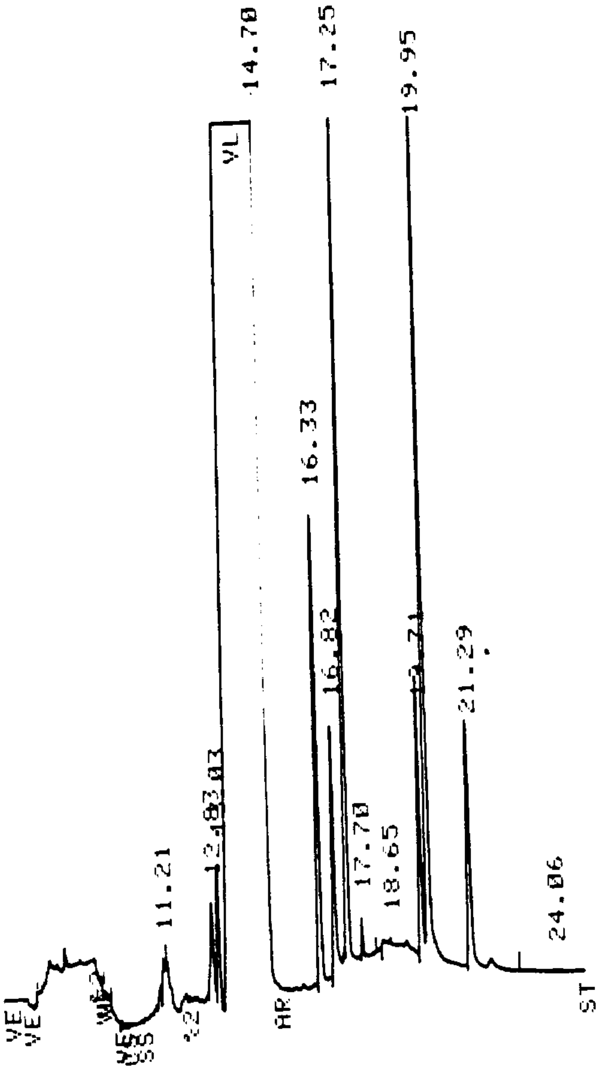


FIGURE 5-1. Analysis of some oxygenated hydrocarbons and air contaminants from charcoal strips using CS2 extraction solvent and two-dimensional gas chromatography. Peaks are: trichloroethane (16.33 min), MEK (16.82 min), benzene (17.25 min), MIBK (19.71 min), toluene (19.95 min), and PERC (21.29 min).

charcoal has only small breakthrough volumes for low molecular weight alcohols and aldehydes, such as methanol and acetaldehyde. Silica gel is a more appropriate sorbent for these compounds.

Analytical Column Selection

The following capillary columns, were evaluated for use as column II in the current analytical scheme:

- 12-m, 0.32 mm i.d. PoraPLOT U (Chrompack, Raritan, NJ)
- 30-m, 0.25 mm i.d., 1 um d.f., Rtx 200 (Restek, Bellefonte, PA)
- 30-m, 0.25 mm i.d., 1 um d.f., Rtx 1701 (Restek, Bellefonte, PA)

All the columns are of moderate polarity. The PoraPLOT U is capillary column has a layer of solid adsorbent deposited onto the inner wall to serve as the stationary phase. It was tested to determine if the cryofocussing step upon reinjection from the freeze-out trap can be eliminated. Rtx 200 and Rtx 1701 have bonded stationary phase of (1) trifluopropylmethyl polysiloxane, and (2) 14% cyanopropylphenyl, 86% dimethyl polysiloxane, respectively.

Standard solutions with acetaldehyde, methanol, acetone, MTBE, butanal, and MEK in dioxane were analyzed according to the present scheme, using the megabore column as column I, and the column under evaluation as column II. The results showed that the Poraplot U column was inadequate in resolving species such as methanol from n-butane, but needed high temperature ramp to elute the higher molecular weight species. Both Rtx columns had good resolution except that the methanol peak was broad with the Rtx 200. Thus, Rtx 1701 column was chosen as column II.

Analytical Conditions

The GC was fitted with the 20-m DB 624 megabore capillary column as column I, with the 30-m Rtx 1701 used as column II. Using this configuration, the analytical conditions such as carrier flows, temperature ramps, and injection volume, were fine tuned. The reiterative evaluation process produced the optimal system and operating conditions presented in Table 5-2.

Figure 5-2 is an example of a chromatogram obtained from analyzing 10 µl of a 1 µg/ml standard solution with this technique. The large acetaldehyde peak was due to a large acetaldehyde background in the dioxane. Standard solutions of the six selected O-HC in the range of approximately 0.2 to 10 µg/ml were analyzed to obtained linear calibration curves, all with correlation coefficient of 0.994 or better. Calibration curves are presented in Figure 5-3, with the results presented in Table 5-3.

TABLE 5-2. Optimal System and Operating Conditions.

	HP GC Address		Address Description
Oven:			
	Temp 1	35	Initial temperature at 35°C
	Time 1	2	Isothermal at 35°C for 2 minutes
	Rate	2	Increase oven temperature at 2° / min.
	Temp 2	49	Ramp temperature to 49°C
	Time 2	99	A setting to allow for the following steps on Temp 2 to take effect.
9	Temp 2	-40	At 9 min. change to oven to -40°C
13	Temp 2	100	At 13 min. raise temperature to 100°C at the rate of 10° / min
13	Rate	10	
17	Rate	5	Change the rate to 5° / min to reach 100°C
30	Temp 2	220	At 30 min. raise temperature to 220°C at the rate of 30° / min. to reach 220°C
30	Rate	30	
45	Stop		Run ends at 45 min.
Valve Timing:			
0.0	VLV/EXT	4	Turn LN_2 valve (4) on to cool trap to -185°C
1.2	VLV/EXT	1	Switch Valve II (1) to trapping position
9.0	VLV/EXT	0	Switch Valve I (0) to backflush column 1
9.1	VLV/EXT	-1	Return Valve II to initial position (vent / inject)
11.5	VLV/EXT	-4	Turn LN_2 valve off
11.5	VLV/EXT	6	Turn on trap heater (6) to heat trap to 140°C
14.0	VLV/EXT	-6	Turn off trap heater

Column Flows:

Column I - nitrogen carrier at 4 ml / min
Column II - helium carrier at 12.0 psi
FID Make-up gas - nitrogen, 14 ml / min

Detector Gases:

Hydrogen - 35 ml /min
Air - ~375 ml / min

Auto sampler Injection Volume:

The auto sampler was set to inject 1, 4, and 10 microliters of sample for an analysis. For the 10 µl injection, the auto sampler was modified to incorporate a switch to deactivate the 4 µl syringe plunger stop such that the full stroke was achieved.

Signal Processing:

The HP 5840A GC does not have an analog output from its FID. To allow the signal to be processed by an external data system and to achieve better sensitivity, the original FID was replaced with a FID and electrometer from Shimadzu (Columbia, MD) . A Shimadzu CR-4A Data Processor was used for peak recording, integration and identification.

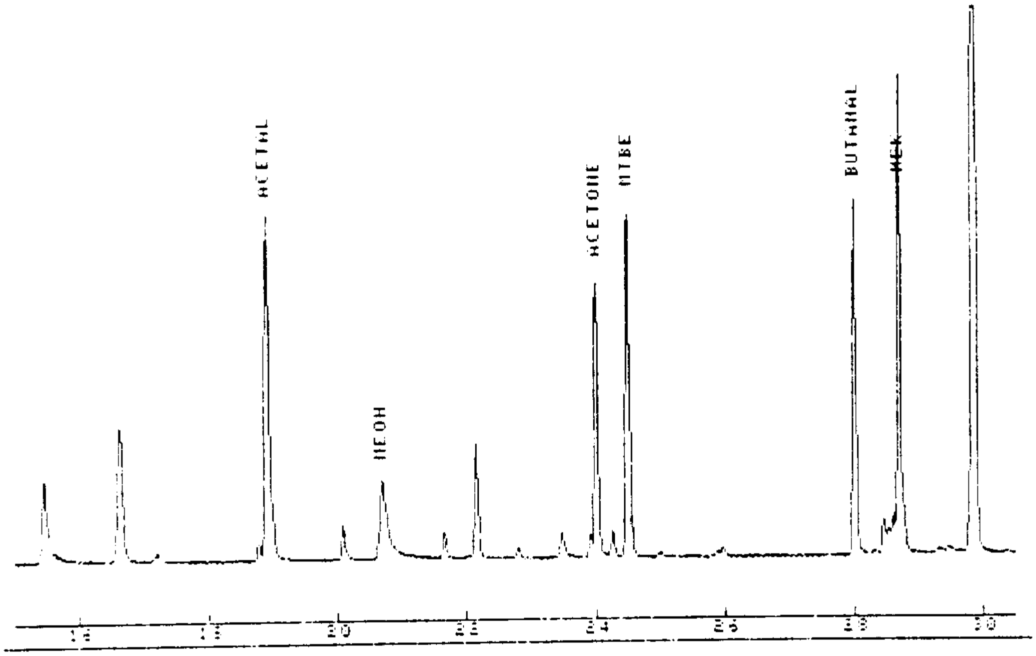
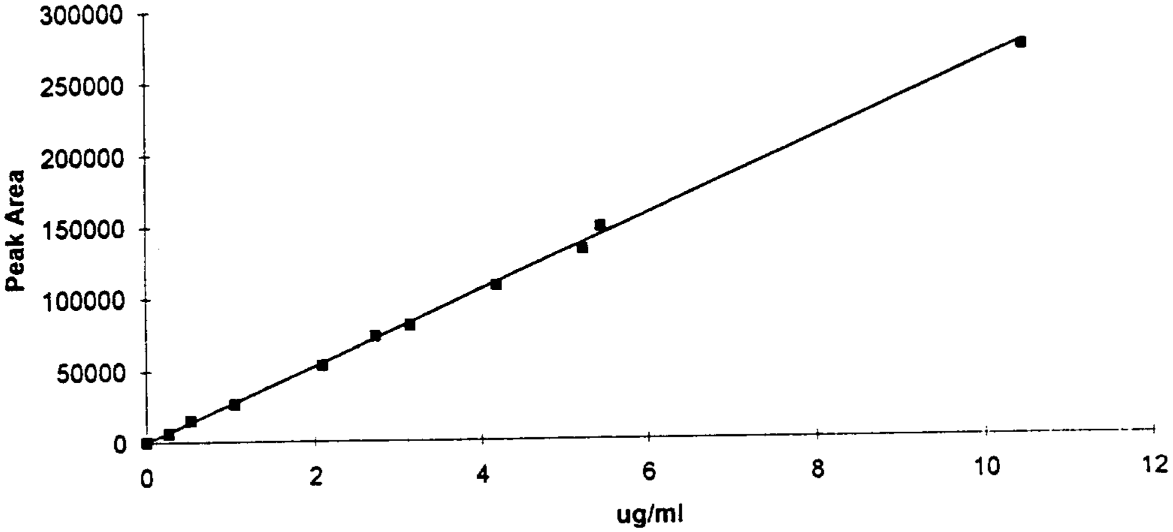


FIGURE 5-2. Analysis of selected oxygenated hydrocarbons (approximately 0.01 ug each) using two-dimensional gas chromatography.

Acetaldehyde Calibration



MEK Calibration

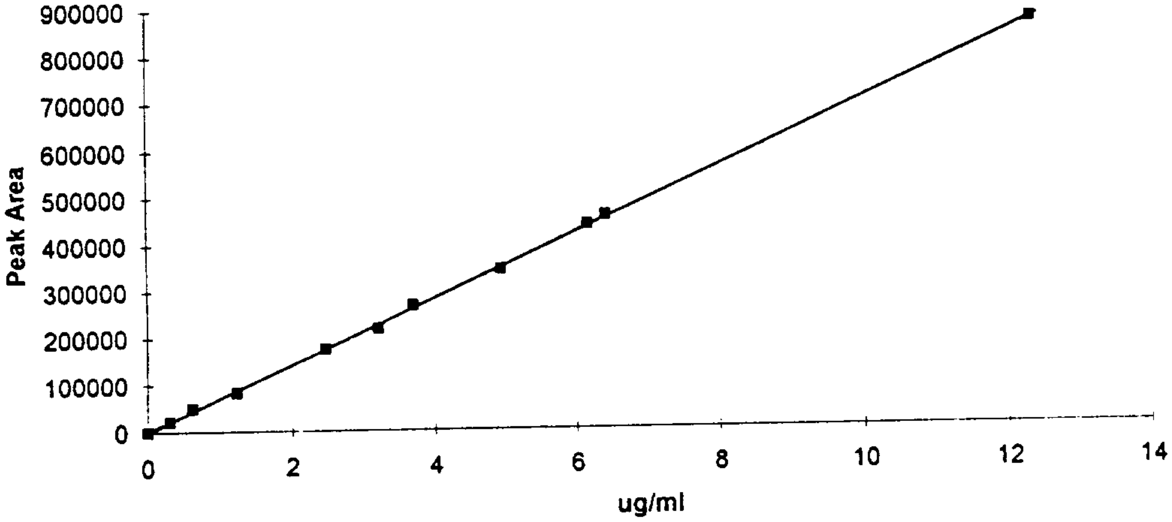
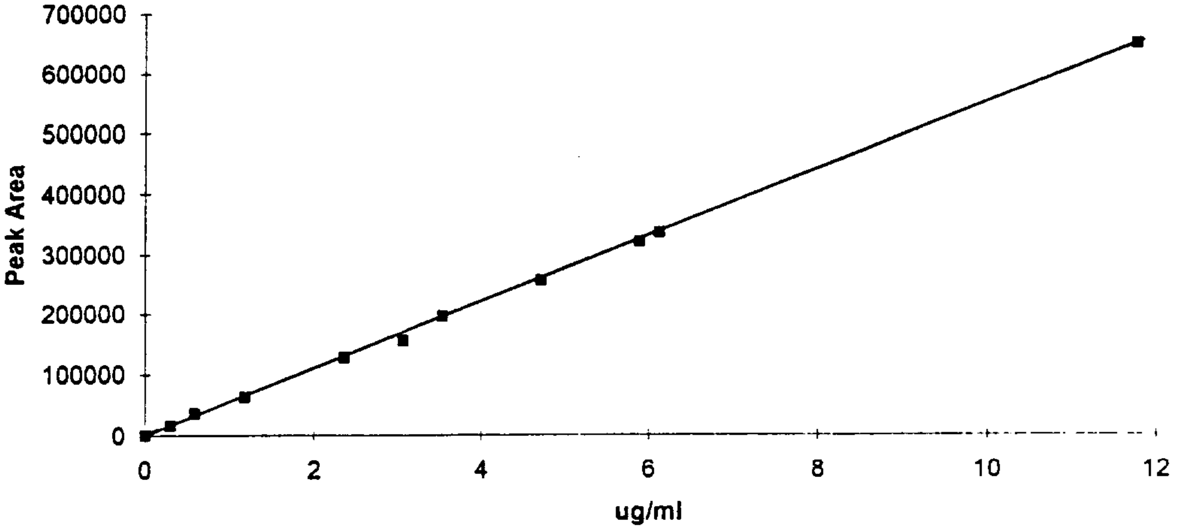


FIGURE 5-3. O-FID calibration results.

n-Butanal Calibration



MTBE Calibration

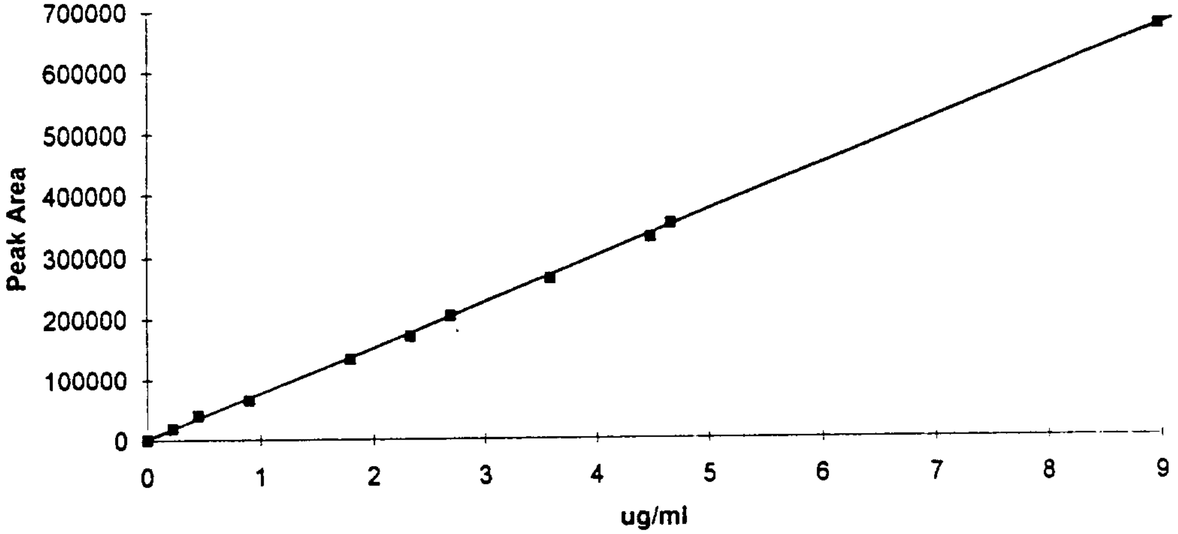
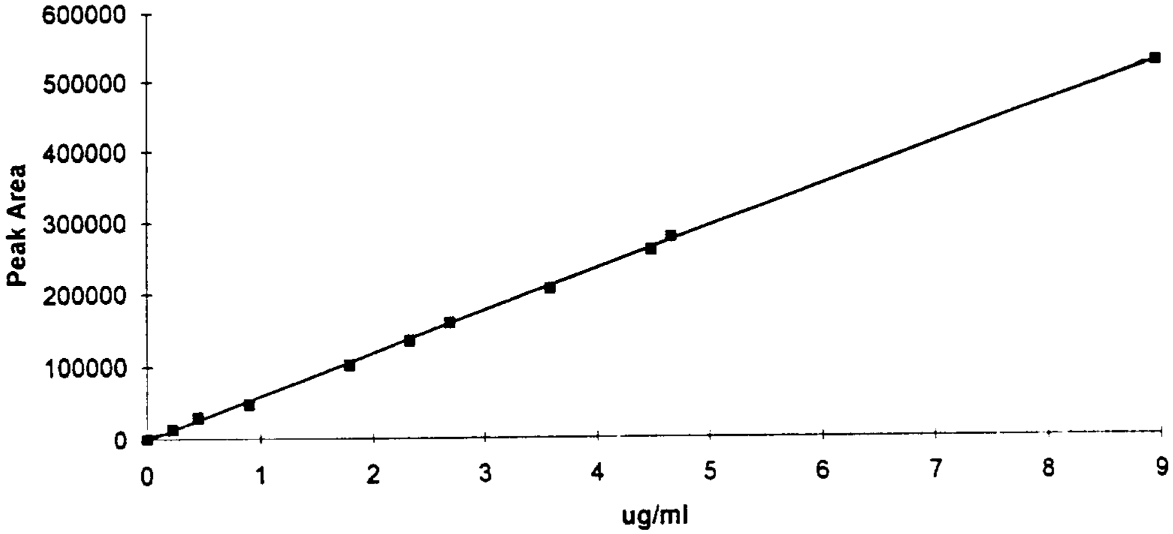


FIGURE 5-3. O-FID calibration results (continued).

Acetone Calibration



Methanol Calibration

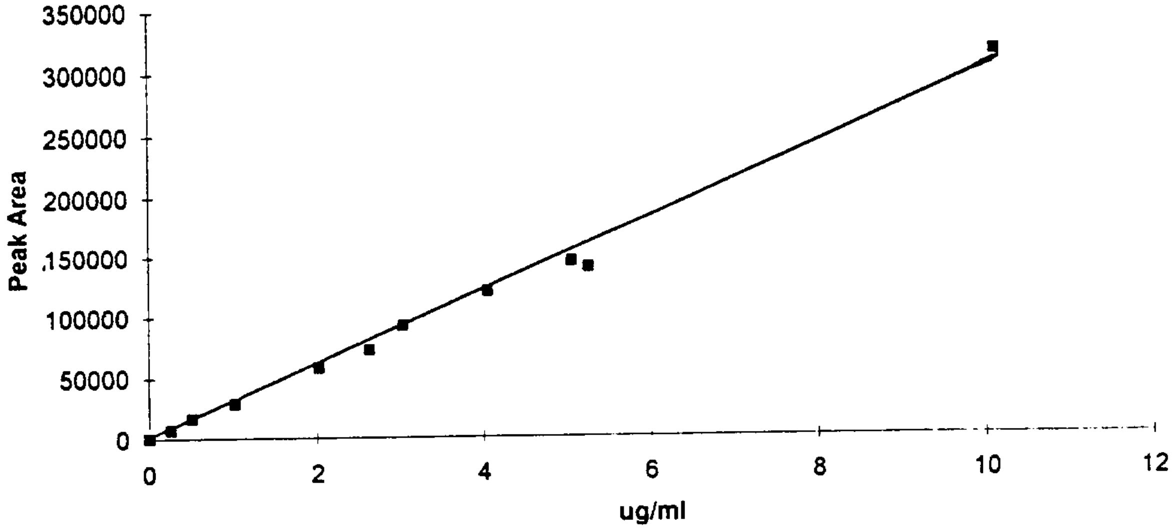


FIGURE 5-3. O-FID calibration results (continued).

Table 5-3. FID Calibration Results

	Intercept	Slope	R Square
Acetaldehyde	0.0018	3.82E-05	0.998781
MeOH	0.128626	3.25E-05	0.994032
Acetone	0.029268	1.7E-05	0.999510
MTBE	0.00414	1.33E-05	0.999638
Butanal	0.038521	1.81E-05	0.999401
MEK	-0.00308	1.41E-05	0.999685

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ug/ml = Peak Area x Slope + Intercept

Lower Quantifiable Limit

The method measures the concentration of an OHC species by drawing a volume of air through the sorbent tube, and analyzing for the mass of the OHC species collected. The concentration is calculated using the following equation:

$$C_i = (M_i - B_i) / V \tag{1}$$

where:

C_i = concentration of species, i
M_i = amount of i found
B_i = amount of i in blank sorbent
V = volume of air sampled

The relative precision of the measurement is given by Watson et. al. (1989):

$$\frac{S_i}{C_i} = \sqrt{\frac{{S_{Mi}}^2 + {S_{Bi}}^2}{(M_i - B_i)^2} + \frac{{S_{Vi}}^2}{V_i^2}} \tag{2}$$

The precision, S_{Mi} can be calculated from duplicate analyses of a sample, or estimated from the average standard deviation of pairs duplicate analyses of a sample set, and S_{Bi} from the standard deviation of a set of blank sorbent tubes. While S_{Vi} is the standard deviation determined from repeated measurements of V, it can be approximated by the precision of sampling flow rate, as time is measured much more precisely.

Detection limit is different than lower quantifiable limit (LQL) in that as long as a species is measurable by the instrument above its noise level, it is detected. LQL is the level when the difference between the sample mass and the blank is no longer statistically significant. LQL under most conditions is always greater than the detection limit. Only when the blank level and sample volume error is negligible that the two are equal.

If one defines the LQL of the measurement as the level at which the measured sample mass equal to three times the standard deviation of the blank (i.e. (M-B) is statistically significant at the 99.7% confidence level), the uncertainty at the detection limit can be calculated using equation (2) by substituting (M-B) equals $3S_{Bi}$. Table 5-4 summarizes the precision estimates derived from analyses of spiked standards.

Table 5-4 highlights the importance of having low blank levels in achieving low detection limits. The solvent has significant levels of contaminants on acetaldehyde, methanol, and MTBE despite the effort of distillation purification. As a result, the LQL for those compounds comparing to acetone, butanal and MEK are much higher due to the larger blank variability (S_{Bi}). The LQL can be improved significantly if a clean solvent can be identified or prepared.

TABLE 5-4. Statistical parameters relating to the measurement of OHCs.

Parameter	Acetal.	MeOH	Acetone	MTBE	Butanal	MEK
sMi (µg)	0.33	0.49	0.07	0.24	0.04	0.18
sBi (µg)	0.31	0.17	0.04	0.61	0.01	0.06
Lower Quantifiable Limit*						
(µg/M3)	95.0	52.3	12.8	190.2	2.1	17.8
(ppb)	52.8	40.0	5.4	52.9	0.7	6.1
% Rel. std. dev. at det. limit	37.8	50.4	8.1	45.3	4.6	18.5

* Assume sampling 6 liters of air, sample mass is three times the blank variability.

5.2 SORBENT TUBE EVALUATION

Sorbent Evaluation

A sorbent tube was charged with a gas standard using a gas tight syringe injected into the GC injector, and the effluent from the sorbent tube was continuously monitored with a flame ionization detector (FID). The baseline rose as breakthrough occurred. The breakthrough volume was calculated from the volume of carrier (flow rate x time) that had passed through the sorbent when the baseline was at 5% of the peak maximum. Table 5-5 shows the breakthrough volumes determined for several commercially available sorbents. Not all the compounds were tested for breakthrough volume. As the experiment progressed, it was apparent that methanol would be the compound with the smallest breakthrough volume and effort was concentrated in identifying a sorbent with a larger methanol breakthrough volume. Ambersorb, which is graphitized carbon, was not as good as charcoal for our test compounds, even though they are of similar nature. Two bulk silica gel sorbents were included in this test to determine if they would be significantly better than the pre-packaged tubes. A weighed amount of these sorbents were packed into 1/4-inch glass tubes and heated at 100°C with dry carrier overnight prior to conducting the experiment. Silica gel is deactivated by moisture, and the conditioning process allowed a uniform starting point of the experiment.

The results in Table 5-5 indicate that it would take a combination of sorbents to collect the several classes of oxygenated hydrocarbons in this program. Silica gel is better for the collection of alcohols, and charcoal the other classes. The suitable combination would be a silica gel sorbent tube to collect primarily alcohols and a charcoal tube to collect the aldehydes and ketones that break through the silica gel tube.

Smog Chamber Results and Interference Evaluation

In addition to investigating possible interference from criteria pollutants, the U. C. Riverside (UCR) smog chamber tests also provide information regarding the functionality of the investigated method and an estimate of the analytical accuracy of the method. Results from the analysis of the smog chamber samples at first did not show particularly good agreement with the concentrations injected into the smog chamber, with a large amount of variation in the analysis results. Ongoing analysis of the storage stability of samples soon revealed that suspended particulates within the elution fluid obtained from the samples was clogging the injection needles. This, in turn, was decreasing the volume of liquid injected into the GC, affecting the analytical results. The clarification procedures described in prior sections were used to reanalyze several of the UCR samples, providing much more consistent results. While investigating this problem, a peak in the chromatograph trace was identified between MEK and Butanal (at 28.4 minutes) that was unique to the elution solvent. The area of this peak gives an accurate measurement of the volume of elution liquid injected into the GC. Analysis of samples using the methodology presented in this paper takes approximately 1 hour per sample. Therefore, as an alternative to re-analyzing all of the samples, data from the original analysis was recomputed, compensating for the change in area of the 28.4 minute peak. This method was used to correct the analytical data.

TABLE 5-5. Breakthrough Volumes of Sorbents on Selected Compounds

Sorbent Tube	Breakthrough Volumes Liters/gram Sorbent		
	Methanol	Acetaldehyde	Acetone
Applied Science, Silica Gel Tube			
50deg. C, 100%RH	5	-	-
40 deg., 45%RH	7	-	8.96
Orbo 52, 250mg Silica Gel tube 40deg C, >80%RH	13.42	-	-
Applied Science, Si Gel bulk[*]			
40deg C, >80%RH	14.8	-	8.87
Merck "High Capacity" Si Gel bulk[*]			
40deg C, >80%RH	11.7	-	-
	10.2	-	-
Supelco Orbo 92, 160mg Ambersorb tube, 80mg backsection			
50deg C, 100%H	<1	-	-
Supelco Ambersorb XEN 572			
40deg C, >80%RH	2.63	9.6	29.6
SKC Charcoal tube, 226-09			
40deg C, >80%RH	7.96	14.32	-

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[*] Silica gel is sensitive to deactivation by moisture. Bulk material after heating showed higher capacity.

Tables 5-6 through 5-11 present the UCR smog chamber data. In order to calculate concentrations using the analytical data, it is necessary to correct the data for background concentrations that may exist in the tubes. Ideally, blanks obtained during sampling would provide this background correction. In the case of the smog chamber samples, this background correction is calculated using the data from the two pure air tests. The blank correction value for each sorbent tube type was calculated for each OHC species as the average of all of the pure air results for that species and sorbent tube, both with and without the addition of criteria pollutants. This blank or background value was then subtracted from the analysis results for the remaining tests.

Results demonstrate that it is possible to analyze for a wide range of OHC species when a combination of charcoal and silica gel sorbent tubes are used. All of the tested species were successfully collected and analyzed using either the charcoal tubes or the silica gel tubes, and in some cases both. Individual results, by species, are discussed below:

Acetaldehyde - Acetaldehyde results for charcoal were poor, with only a small portion of the total concentration identified at either level. Results for silica gel, however, were good, with calculated concentrations within 21 percent of true for all tests.

Methanol - Neither charcoal nor silica gel provided particularly good results for methanol, though concentrations obtained from the charcoal tubes were in general quite good for the higher level (260 ppb). The poorer results are most likely due to a combination of problems. First, the background level of methanol in the solvent is high, as is demonstrated by the significantly higher intercept for the methanol O-FID calibration equation (Table 5-3). Second, the measured background amounts are significantly higher for methanol than for other species. Background values of 0.76 µg/tube for charcoal and 2.65 µg/tube for silica gel were observed. High solvent and measured background values allow for increased variability during analysis, as exact background amounts can vary. The high silica gel background values are even more curious when compared with the values obtained from the back silica gel tubes which were paired with front charcoal tubes. Methanol is effectively scrubbed by the front charcoal tube, allowing virtually clean air to enter the silica gel tube. Thus, the values obtained from the silica gel tubes can essentially be considered blank data. These "blank" data, however, are significantly lower than the background reading obtained during the first two experiments involving pure air, questioning the validity of the silica gel data from the first two experiments. Assuming that the back silica gel values accurately represent background values, data for the four OHC experiments were recalculated, using the average of the two back silica gel results to correct the single tube results. Results were as follwows:

Experiment	Tube 1 (ppb)	Tube 2 (ppb)	Average	% Diff
Air + 260 ppb	301	253	277	7%
Air + 107 ppb	207	7	107	0%
Air + poll. + 260 ppb	200	219	210	-19%
Air + poll. + 107 ppb	-25	105	40	-62%

TABLE 5-6. Results of UCR smog chamber test.

						Acetaldehyde				92.59					
		Charcoal				**Silica gel**				**Pair 1**			**Pair 2**		
		Tube 1	**Tube 2**	**Avg.**	**% Diff.[2]**	**Tube 1**	**Tube 2**	**Avg.**	**% Diff.[2]**	**Charcoal**	**Silica**	**Total**	**Charcoal**	**Silica**	**Total**
Pure Air (ug)		0.24	0.99			0.92	0.24			0.46	1.71		0.07	1.00	
Pure Air + pollutants (ug)		0.26	0.65			0.65	1.18			0.71	0.75		-0.30	0.54	
Blank correction amount (ug) [1]	Charcoal	0.39													
	Silica gel	0.87													
Air + 264 ppb	Analyzed (ug)	0.64	0.71			4.29	4.35			0.95	0.79		1.11	0.71	
	Blank corrected (ppb)	24	30	**27**	**NA**	317	322	**319**	**21%**	52	-8	**45**	67	-15	**52**
Air + 108 ppb	Analyzed (ug)	0.67	0.47			2.44	1.67			0.08	0.21		0.37	0.79	
	Blank corrected (ppb)	26	8	**17**	**NA**	145	74	**110**	**1%**	-28	-61	**-89**	-1	-8	**-9**
Air + pollutants + 265 ppb	Analyzed (ug)	0.62	1.02			4.48	3.79			0.66	-0.09		0.25	-0.03	
	Blank corrected (ppb)	22	59	**40**	**NA**	334	270	**302**	**14%**	25	-89	**-64**	-12	-83	**-96**
Air + pollutants + 109 ppb	Analyzed (ug)	0.95	0.85			1.92	2.68			2.15	1.02		2.39	0.75	
	Blank corrected (ppb)	52	43	**48**	**NA**	97	167	**132**	**21%**	163	14	**177**	186	-11	**174**

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[1] Blank correction amounts calculated as the average of all pure air readings (with and without pollutants).

[2] Percent difference calculated as the average of the analyzed amount relative to the UCR's reported input amount. If the sorbent was clearly not working for a particular compound, the percent difference is reported as NA.

TABLE 5-7. Results of UCR smog chamber test.

		Methanol								127.39					
		Charcoal				Silica gel				Pair 1			Pair 2		
		Tube 1	Tube 2	Avg.	% Diff.[2]	Tube 1	Tube 2	Avg.	% Diff.[2]	Charcoal	Silica	Total	Charcoal	Silica	Total
Pure Air (ug)		1.33	1.33			3.66	3.09			0.70	2.47		0.20	2.46	
Pure Air + pollutants (ug)		0.84	1.08			2.37	3.01			0.66	1.70		-0.03	2.46	
Blank correction amount (ug) [1]	Charcoal	0.76													
	Silica gel	2.65													
Air + 260 ppb	Analyzed (ug)	2.57	2.72			3.99	3.61			2.47	1.47		2.59	1.78	
	Blank corrected (ppb)	230	249	**240**	**-8%**	170	122	**146**	**-44%**	217	-151	**67**	233	-111	**121**
Air + 107 ppb	Analyzed (ug)	0.91	0.98			3.14	1.57			1.09	1.26		0.82	1.77	
	Blank corrected (ppb)	19	28	**23**	**-78%**	62	-138	**-38**	**-135%**	42	-177	**-136**	7	-112	**-105**
Air + pollutants + 260 ppb	Analyzed (ug)	2.35	3.22			2.61	2.76			2.72	1.31		3.01	0.77	
	Blank corrected (ppb)	202	313	**257**	**-1%**	-5	14	**4**	**-98%**	249	-171	**78**	286	-240	**46**
Air + pollutants + 107 ppb	Analyzed (ug)	2.24	2.92			1.36	2.38			2.38	1.67		2.75	1.44	
	Blank corrected (ppb)	188	275	**231**	**116%**	-165	-35	**-100**	**-193%**	206	-125	**81**	253	-154	**99**

[1] Blank correction amounts calculated as the average of all pure air readings (with and without pollutants).

[2] Percent difference calculated as the average of the analyzed amount relative to the UCR's reported input amount. If the sorbent was clearly not working for a particular compound, the percent difference is reported as NA.

TABLE 5-8. Results of UCR smog chamber test.

		Acetone								70.27					
		Charcoal				Silica gel				Pair 1			Pair 2		
		Tube 1	Tube 2	Avg.	% Diff.[2]	Tube 1	Tube 2	Avg.	% Diff.[2]	Charcoal	Silica	Total	Charcoal	Silica	Total
Pure Air (ug)		-0.02	-0.02			2.17	2.66			0.15	2.13		0.07	2.67	
Pure Air + pollutants (ug)		0.03	0.09			2.85	2.86			0.07	2.48		0.02	1.93	
Blank correction amount (ug) [1]	Charcoal	0.05													
	Silica gel	2.47													
Air + 265 ppb	Analyzed (ug)	2.23	2.30			6.36	6.66			2.32	2.54		2.27	2.48	
	Blank corrected (ppb)	153	158	156	-41%	273	295	284	7%	160	5	165	156	1	157
Air + 109 ppb	Analyzed (ug)	1.19	0.92			3.58	5.21			1.50	2.60		1.37	2.75	
	Blank corrected (ppb)	80	61	71	-35%	78	193	135	24%	102	9	111	93	20	113
Air + pollutants + 265 ppb	Analyzed (ug)	2.49	2.79			8.30	6.95			2.26	2.22		2.41	1.88	
	Blank corrected (ppb)	172	193	182	-31%	410	315	362	37%	155	-17	138	166	-41	125
Air + pollutants + 109 ppb	Analyzed (ug)	0.89	1.07			3.49	2.23			0.90	2.08		0.93	1.27	
	Blank corrected (ppb)	59	72	65	-40%	72	-17	27	-75%	60	-27	32	62	-84	-22

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[1] Blank correction amounts calculated as the average of all pure air readings (with and without pollutants).

[2] Percent difference calculated as the average of the analyzed amount relative to the UCR's reported input amount. If the sorbent was clearly not working for a particular compound, the percent difference is reported as NA.

TABLE 5-9. Results of UCR smog chamber test.

		MTBE								46.3					
		Charcoal				Silica gel				Pair 1			Pair 2		
		Tube 1	Tube 2	Avg.	% Diff.[2]	Tube 1	Tube 2	Avg.	% Diff.[2]	Charcoal	Silica	Total	Charcoal	Silica	Total
Pure Air (ug)		-0.56	-0.48			-0.07	-2.00			-0.21	-0.12		-0.61	0.04	
Pure Air + pollutants (ug)		-0.63	-0.36			-0.36	-1.20			-0.07	-0.80		-0.97	-1.80	
Blank correction amount (ug) [1]	Charcoal	-0.49													
	Silica gel	-0.79													
Air + 261 ppb	Analyzed (ug)	6.00	5.83			5.48	5.30			5.37	-0.58		6.80	-0.45	
	Blank corrected (ppb)	300	292	296	14%	290	282	286	10%	271	10	281	337	16	353
Air + 107 ppb	Analyzed (ug)	2.35	2.12			1.31	1.81			1.89	-0.43		2.28	-0.44	
	Blank corrected (ppb)	131	121	126	17%	97	120	109	1%	110	17	127	128	16	144
Air + pollutants + 261 ppb	Analyzed (ug)	6.05	5.86			6.22	5.73			5.07	-1.51		5.20	-2.18	
	Blank corrected (ppb)	303	294	298	14%	325	302	313	20%	257	-33	224	263	-64	199
Air + pollutants + 108 ppb	Analyzed (ug)	1.89	1.60			1.06	1.00			1.33	-1.46		1.88	-1.98	
	Blank corrected (ppb)	110	97	103	-3%	86	83	84	-21%	84	-31	53	110	-55	54

[1] Blank correction amounts calculated as the average of all pure air readings (with and without pollutants).

[2] Percent difference calculated as the average of the analyzed amount relative to the UCR's reported input amount. If the sorbent was clearly not working for a particular compound, the percent difference is reported as NA.

TABLE 5-10. Results of UCR smog chamber test.

						Butanal				56.59					
		Charcoal				Silica gel				Pair 1			Pair 2		
		Tube 1	Tube 2	Avg.	% Diff.[2]	Tube 1	Tube 2	Avg.	% Diff.[2]	Charcoal	Silica	Total	Charcoal	Silica	Total
Pure Air (ug)		0.09	0.11			0.11	0.12			0.09	0.10		0.10	0.09	
Pure Air + pollutants (ug)		0.09	0.10			0.11	0.14			0.09	0.09		0.12	0.08	
Blank correction amount (ug) [1]	Charcoal	0.10													
	Silica gel	0.11													
Air + 267 ppb	Analyzed (ug)	0.10	0.11			4.95	4.71			0.09	0.10		0.14	0.10	
	Blank corrected (ppb)	0	1	0	NA	274	261	267	0%	0	0	-1	2	0	2
Air + 110 ppb	Analyzed (ug)	0.10	0.10			1.70	1.91			0.11	0.10		0.10	0.13	
	Blank corrected (ppb)	0	0	0	NA	90	102	96	-13%	1	0	0	0	1	1
Air + pollutants + 267 ppb	Analyzed (ug)	0.13	0.11			5.07	4.77			0.12	0.11		0.11	0.11	
	Blank corrected (ppb)	2	1	1	NA	281	264	272	2%	1	0	1	1	0	1
Air + pollutants + 110 ppb	Analyzed (ug)	0.12	0.10			1.69	1.63			0.14	0.11		0.14	0.11	
	Blank corrected (ppb)	1	0	1	NA	90	86	88	-20%	2	0	3	2	0	3

[1] Blank correction amounts calculated as the average of all pure air readings (with and without pollutants).

[2] Percent difference calculated as the average of the analyzed amount relative to the UCR's reported input amount. If the sorbent was clearly not working for a particular compound, the percent difference is reported as NA.

TABLE 5-11. Results of UCR smog chamber test.

Methyl Ethyl Ketone 56.59

		Charcoal				Silica gel				Pair 1			Pair 2		
		Tube 1	**Tube 2**	**Avg.**	**% Diff.**[2]	**Tube 1**	**Tube 2**	**Avg.**	**% Diff.**[2]	**Charcoal**	**Silica**	**Total**	**Charcoal**	**Silica**	**Total**
Pure Air (ug)		0.26	0.27			0.32	0.32			0.30	0.42		0.25	0.40	
Pure Air + pollutants (ug)		0.33	0.35			0.41	0.51			0.22	0.42		0.27	0.49	
Blank correction amount (ug) [1]	Charcoal	0.28													
	Silica gel	0.41													
Air + 264 ppb	Analyzed (ug)	2.76	3.19			4.95	4.74			2.89	0.37		2.88	0.39	
	Blank corrected (ppb)	140	165	**152**	**-42%**	257	245	**251**	**-5%**	148	-2	**145**	147	-1	**146**
Air + 108 ppb	Analyzed (ug)	1.39	1.33			2.03	2.16			1.40	0.37		1.37	0.34	
	Blank corrected (ppb)	63	59	**61**	**-43%**	92	99	**95**	**-12%**	63	-2	**61**	62	-4	**58**
Air + pollutants + 263 ppb	Analyzed (ug)	3.76	3.72			5.86	5.83			3.41	0.31		3.57	0.35	
	Blank corrected (ppb)	197	195	**196**	**-26%**	308	307	**307**	**17%**	177	-6	**171**	186	-3	**183**
Air + pollutants + 109 ppb	Analyzed (ug)	1.35	1.90			2.83	1.75			1.87	0.29		1.89	0.30	
	Blank corrected (ppb)	60	92	**76**	**-30%**	137	76	**106**	**-2%**	90	-7	**83**	91	-6	**85**

[1] Blank correction amounts calculated as the average of all pure air readings (with and without pollutants).

[2] Percent difference calculated as the average of the analyzed amount relative to the UCR's reported input amount. If the sorbent was clearly not working for a particular compound, the percent difference is reported as NA.

In general, methanol results are significantly improved using this correction method, though there is still considerable variability in the results at the lower concentrations. This indicates that better quantification of background values would improve results.

Acetone - As with methanol, the measured silica gel background level for acetone (2.47 µg/tube) is much higher than those for other species. Consequently, acetone reading for the silica gel tubes show substantial variability. Concentrations obtained using the charcoal are on the average about 37 percent low, but show extremely good precision, with percent differences ranging from -31 percent to -41 percent. This suggests that an adjustment of the extraction efficiency for charcoal may be required. One should note that the good precision is accompanied by low acetone background for charcoal (0.05 µg/tube).

MTBE - Results obtained using the charcoal tubes were very good, with percent differences all within 17 percent of true. Results obtained using the silica gel tubes were also good, within 21 percent.

Butanal - No butanal was detected using the charcoal tubes. Results for the silica gel tubes were good, particularly for the higher level.

Methyl Ethyl Ketone - Results for the silica gel tube were good. Charcoal results showed good precision, but were approximately 35 percent low on the average. Again, a re-evaluation of MEK extraction efficiencies for charcoal may improve results.

Results for the paired tubes are compromised to a large degree by the fact that the charcoal tube was inadvertantly used as the front tube and the silica gel tube was used as the back tube during sampling. Species that could not be successfully extracted from the charcoal tubes were in many cases still removed by the charcoal tubes, preventing the species from reaching the silica gel tube, from which it could have been successfully extracted. This effect is clearly seen in the results for butanal. Results for the single tubes clearly show that butanal cannot be extracted from charcoal, but can be extracted from silica gel. However, for the paired tubes, no butanal is detected by the back silica gel tubes. It should be noted that the same effect may also occur for some species if the tubes were reversed. This is a potential disadvantage of using paired tubes. An additional disadvantage is that measurement precision will decrease as more sample and blank variability is present when two tubes are required to calculate a single value. For these reasons, it may be more appropriate to sample using individual silica gel and charcoal tubes.

No statistically significant changes in measured concentrations were note as a result of the addition of the criteria pollutants.

Storage Stability Evaluation

Results of the storage stability evaluation are presented in Table 5-12. Mean values for the triplicate results are compared against the analysis limits, computed as three times the standard deviation (sigma) from the Day 0 results.

TABLE 5-12. Stability study results. (Shaded areas indicate deviations of statistical significance.)

	Charcoal					Silica Gel			
Acetaldehyde									
Conc., ug	Day 0	Day 30	Day 60	Day 90		Day 0	Day 30	Day 60	Day 90
2.72	2.66	2.99	1.89	2.10		2.82	2.63	2.38	2.08
	2.59	2.81	1.77	2.14		2.63	2.20	2.23	2.32
	2.94	2.63	1.70	1.86		2.70	2.73	2.37	2.17
Mean	2.73	2.81	1.79	2.03		2.72	2.52	2.33	2.19
Std. Dev.	0.19	0.18	0.09	0.15		0.10	0.28	0.09	0.12
+3s	3.29					3.01			
-3s	2.17					2.43			
5.44	4.93	4.36	3.72	4.28		5.71	5.61	5.92	5.65
	5.07	4.45	3.73	4.46		5.21	4.96	5.36	5.08
	6.32	5.10	3.86	4.90		5.40	4.58	5.34	5.01
Mean	5.44	4.64	3.77	4.54		5.44	5.05	5.54	5.25
Std. Dev.	0.76	0.41	0.08	0.32		0.25	0.52	0.33	0.35
+3s	7.73					6.19			
-3s	3.15					4.69			
10.88	11.29	9.39	7.73	8.79		11.73	11.26	10.66	11.62
	10.57	9.91	8.11	10.33		9.42	13.41	9.98	11.69
	10.78	9.87	6.68	8.34		11.88	13.12	10.92	11.41
Mean	10.88	9.72	7.50	9.15		11.01	12.60	10.52	11.57
Std. Dev.	0.37	0.29	0.74	1.04		1.38	1.17	0.49	0.15
+3s	11.99					15.15			
-3s	9.77					6.87			
Methanol									
2.62	2.53	3.02	2.41	2.47		2.73	2.56	2.14	3.39
	2.25	3.04	2.51	2.67		2.53	2.25	2.44	3.85
	2.67	3.13	2.16	2.61		2.61	2.21	2.76	3.29
Mean	2.48	3.06	2.36	2.59		2.62	2.34	2.45	3.51
Std. Dev.	0.21	0.06	0.18	0.10		0.10	0.19	0.31	0.30
+3s	3.13					2.92			
-3s	1.84					2.33			
5.25	4.77	4.79	4.86	4.71		5.32	3.72	3.64	6.94
	4.80	4.70	5.01	5.35		5.05	3.81	4.62	5.05
	6.38	5.70	5.16	5.73		5.30	3.36	4.37	5.64
Mean	5.31	5.06	5.01	5.26		5.22	3.63	4.21	5.88
Std. Dev.	0.92	0.55	0.15	0.52		0.15	0.24	0.51	0.96
+3s	8.09					5.67			
-3s	2.54					4.77			
10.50	10.49	9.58	10.25	11.33		10.99	11.29	9.51	9.84
	10.02	9.53	11.79	11.28		10.70	13.36	7.57	10.44
	10.98	7.96	9.67	10.63		11.77	12.88	9.32	9.83
Mean	10.50	9.02	10.57	11.08		11.16	12.51	8.80	10.04
Std. Dev.	0.48	0.92	1.09	0.39		0.55	1.08	1.07	0.35
+3s	11.95					12.81			
-3s	9.04					9.50			

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TABLE 5-12. Stability study results. (Shaded areas indicate deviations of statistical significance.)

Acetone									
2.33	2.25	2.40	1.97	2.70		2.50	2.27	2.26	2.69
	2.09	2.21	2.08	2.69		2.26	2.16	2.24	2.97
	2.69	2.18	2.44	2.25		2.22	2.09	2.04	2.93
Mean	2.34	2.27	2.16	2.55		2.33	2.17	2.18	2.86
Std. Dev.	0.31	0.12	0.25	0.25		0.15	0.09	0.12	0.15
+3s	3.28					2.77			
-3s	1.40					1.89			
4.66	4.18	3.66	4.67	4.96		4.81	5.14	5.10	6.71
	4.20	3.80	4.48	4.99		4.52	4.68	4.68	6.81
	5.59	3.62	4.76	5.27		4.50	4.15	5.25	5.72
Mean	4.66	3.69	4.64	5.07		4.61	4.66	5.01	6.41
Std. Dev.	0.81	0.09	0.14	0.17		0.17	0.49	0.29	0.61
+3s	7.09					5.12			
-3s	2.23					4.09			
9.31	8.92	7.33	9.69	10.04		10.14	12.62	10.41	10.76
	9.44	9.62	10.50	10.54		7.26	14.78	8.71	10.78
	9.58	8.17	9.02	9.46		10.02	13.82	10.27	10.89
Mean	9.31	8.37	9.73	10.01		9.14	13.74	9.80	10.81
Std. Dev.	0.34	1.16	0.74	0.54		1.63	1.08	0.95	0.07
+3s	10.34					14.03			
-3s	8.28					4.25			
MTBE									
2.33	2.22	1.45	2.54	2.49		2.33	3.11	3.01	2.12
	2.41	1.79	2.42	2.34		2.29	2.80	3.03	2.35
	2.41	2.08	2.62	2.09		2.36	3.19	2.84	2.42
Mean	2.35	1.77	2.52	2.31		2.33	3.03	2.96	2.30
Std. Dev.	0.11	0.32	0.10	0.20		0.04	0.21	0.10	0.16
+3s	2.67					2.44			
-3s	2.02					2.22			
4.66	4.74	4.25	4.75	4.66		4.58	6.04	5.49	4.77
	4.59	3.97	4.74	4.58		4.59	5.07	4.70	4.87
	4.64	4.12	4.82	4.86		4.80	4.83	5.01	3.81
Mean	4.66	4.11	4.77	4.70		4.66	5.31	5.06	4.48
Std. Dev.	0.08	0.14	0.04	0.15		0.13	0.64	0.40	0.59
+3s	4.88					5.04			
-3s	4.43					4.27			
9.31	8.68	7.82	9.67	9.47		9.39	7.94	11.00	9.77
	9.64	10.26	9.73	9.44		6.21	9.37	9.58	9.59
	9.62	9.68	9.63	9.87		10.28	9.00	10.94	9.33
Mean	9.31	9.25	9.67	9.59		8.62	8.77	10.51	9.56
Std. Dev.	0.55	1.27	0.05	0.24		2.14	0.74	0.80	0.22
+3s	10.95					15.05			
-3s	7.67					2.20			

TABLE 5-12. Stability study results. (Shaded areas indicate deviations of statistical significance.)

Butanal									
3.06	2.48	3.03	1.03	2.39		3.24	3.64	2.73	2.70
	2.63	1.87	1.52	2.18		2.90	3.48	2.85	2.90
	3.49	2.05	2.04	1.03		3.05	3.47	2.62	2.95
Mean	2.87	2.32	1.53	1.87		3.06	3.53	2.73	2.85
Std. Dev.	0.55	0.63	0.50	0.73		0.17	0.10	0.11	0.13
+3s	4.51					3.57			
-3s	1.22					2.56			
6.13	4.09	3.05	3.68	4.41		6.29	6.96	6.18	5.93
	5.49	3.92	4.69	4.73		5.93	6.20	5.86	6.02
	8.81	3.63	4.26	4.86		6.16	5.88	5.84	5.92
Mean	6.13	3.53	4.21	4.66		6.13	6.35	5.96	5.96
Std. Dev.	2.42	0.44	0.51	0.23		0.19	0.55	0.19	0.05
+3s	13.40					6.69			
-3s	-1.14					5.57			
12.26	13.89	11.83	4.47	5.01		13.06	10.48	12.77	12.12
	11.26	7.40	8.64	10.78		8.38	12.77	11.65	11.71
	11.62	9.38	4.63	9.51		13.04	12.84	12.53	11.79
Mean	12.26	9.54	5.91	8.43		11.50	12.03	12.32	11.87
Std. Dev.	1.43	2.22	2.36	3.03		2.70	1.35	0.59	0.22
+3s	16.54					19.58			
-3s	7.97					3.41			
MEK									
3.20	3.24	2.67	2.63	3.48		3.60	3.56	3.24	2.60
	2.82	2.57	2.78	3.47		2.96	3.53	3.20	2.87
	3.53	2.63	3.69	2.35		3.03	3.72	3.14	2.87
Mean	3.19	2.62	3.04	3.10		3.20	3.61	3.19	2.78
Std. Dev.	0.36	0.05	0.57	0.65		0.35	0.10	0.05	0.16
+3s	4.27					4.25			
-3s	2.12					2.15			
6.40	5.90	4.62	6.25	6.62		7.23	7.24	7.37	7.42
	6.36	5.31	6.14	6.41		5.99	6.48	6.75	7.61
	6.94	5.24	6.29	6.55		5.98	6.47	7.00	7.01
Mean	6.40	5.06	6.23	6.53		6.40	6.73	7.04	7.35
Std. Dev.	0.52	0.38	0.08	0.11		0.72	0.44	0.31	0.31
+3s	7.96					8.57			
-3s	4.84					4.23			
12.80	12.08	10.60	11.61	12.26		14.21	12.38	13.75	13.97
	13.19	12.30	12.35	13.96		10.07	12.63	12.53	13.66
	13.13	12.47	10.90	13.18		13.56	12.95	13.39	13.04
Mean	12.80	11.79	11.62	13.13		12.61	12.65	13.22	13.56
Std. Dev.	0.62	1.04	0.73	0.85		2.23	0.29	0.63	0.48
+3s	14.67					19.29			
-3s	10.93					5.93			

The results reveal that, with only a few exceptions, sample concentrations for the compounds tested do not show any statistically significant losses over the course of 90 days. The exceptions are the lower carbon species such as acetaldehyde and methanol, where some losses were noted, though not at all levels tested.

Charcoal tubes showed sample losses at both the low and high concentrations, and possibly at the middle concentration, though results at the middle level are less conclusive due to the higher standard deviation for the Day 0 samples. It should be remembered, however, that the smog chamber results indicated that acetaldehyde was essentially undetectable using charcoal tubes and the extraction solvent chosen, so these results do not significantly affect the usefulness of this sampling method. Similarly, the erratic charcoal results for butanal are inconsequential, since smog chamber results have indicated that charcoal does not work as a sorbent tube for butanal.

Silica gel tubes also showed some sample loss for acetaldehyde, but only at the low concentration. This appears to be the only significant loss of consequence. Other individual instances where triplicate means exceed the sigma limits are noted. These cases typically have larger standard deviations, with lower means reported for Day 30 and Day 60 than for Day 90. The most notable example is methanol. Results for the middle concentration show a sizable decrease after 30 days, followed by increases in concentration reported after 60 and 90 days. The mean for Day 90 is actually higher than the initial input concentration. One possible explanation for these inconsistencies is that separate batches of distilled solvents were used to perform the analysis. Variability in background concentrations from batch to batch can cause variability in extraction efficiencies, affecting results.

Applicability to Other Species

While glycols and glycol ethers (e.g., Cellusolves) were not tested in this study, NIOSH of OSHA sampling procedures use either charcoal or silica gel as the collection medium for these compounds. The analysis uses GC with FID. Since these compounds elute late from the TCEP column (e.g., Butyl Cellusolve elutes at ~16 min compared to MIBK at ~8.5 min), the analytical scheme developed here would enhance the detection of these compounds by allowing a very large sample aliquot to be injected for the analysis. Solvent/sorbent blank and extraction efficiency need to be determined when extending such methods to measure ambient levels.

5.3 FIELD TESTING

Blank results from the field testing are presented in Table 5-13. Background levels are lower than those obtained from the smog chamber tests, especially for acetaldehyde, methanol, and acetone. Charcoal background values are low for all compounds. Silica gel background values, however, remain significant for acetaldehyde, methanol, and acetone. In general, the variability in the blank values was good, producing lower quantifiable limits (LQLs) lower than those observed during the UCR tests. LQLs were calculated by taking three times the variability of the blanks (sigma) and calculating an equivalent volume concentration in ppb assuming a nominal sample time of three hours and a flow rate of 50 cc/min.

Table 5-13. Field testing blank results.

			Acetal.	MeOH	Acetone	MTBE	Butanal	MEK
Monrovia								
	Carbon	Average (ug)	-0.08	-0.20	-0.05	0.03	0.01	0.05
		Sigma (ug)	0.05	0.04	0.01	0.01	0.01	0.06
		LQL (ppb)*	9.2	9.0	1.0	0.7	0.8	7.2
	Silica gel	Average (ug)	0.77	1.80	0.21	0.02	0.10	0.03
		Sigma (ug)	0.19	0.12	0.81	0.13	0.01	0.04
		LQL (ppb)*	35.4	30.7	113.5	11.8	0.8	4.0
Sacramento								
	Carbon	Average (ug)	0.03	0.06	0.00	0.03	0.01	0.00
		Sigma (ug)	0.08	0.06	0.01	0.00	0.01	0.02
		LQL (ppb)*	14.5	16.4	0.8	0.1	0.7	2.4
	Silica gel	Average (ug)	0.76	1.92	-0.36	0.02	0.09	0.11
		Sigma (ug)	0.37	0.46	0.59	0.05	0.00	0.15
		LQL (ppb)*	68.2	117.1	83.5	4.8	0.1	16.7

*Assuming 9 liter sample volume (three-hour sample at 50 cc/min).
Lower quantifiable limits for a six-hour sample would be half of those for a three-hour sample.

Results for the field sampling are presented in Table 5-14. All concentrations were calculated by first subtracting the blank background values presented in Table 5-13. Spring weather persisted at both the Kiefer Landfill (near Sacramento) and Monrovia sites, and low OHC concentrations were expected. In general, calculated concentrations are reasonable for the areas sampled, and the results are consistent with previous observations during the method evaluation and testing. Results obtained from the charcoal tubes appear to be more sensitive than those from the silica gel tubes, once again due primarily to the higher background levels and variability observed in the silica gel blanks. Results for each compound are discussed below:

Acetaldehyde - Contrary to the results from the smog chamber tests, the charcoal tubes appear to outperform the silica gel tubes for sampling of acetaldehyde. This appears to be due primarily to much improved background levels in the charcoal tubes, and continuing high background level and background variability in the silica gel tubes, resulting in high LQLs for silica gel. Results from the Sacramento site are very close to expected concentrations for urban areas. In contrast, the Monrovia concentrations seem unusually high. This is somewhat surprising, given that results from the smog chamber tests suggest that the carbon tubes underestimated acetaldehyde. However, the consistency of the Monrovia measurements and the fact that consistent, lower concentrations were measured at Sacramento implies that the Monrovia values are real, possibly due to local sources.

Methanol. Methanol concentrations for Monrovia produced by the charcoal tubes are consistent with expected concentrations for urban areas. In contrast, data from the silica gel tubes introduce several questions. In all cases, three-hour silica gel samples show methanol concentration of approximately 100 ppb or greater, whereas six-hour silica gel samples show concentrations below the LQLs. In most cases, the analyzed methanol concentrations in the six-hour samples were actually lower than the blank concentrations. Breakthrough volume tests during this study determined that breakthrough could occur after three hours of sampling at 50 cc/min. These results vividly demonstrate the role the breakthrough volume plays in this type of monitoring. Apparently, a significant amount of methanol is present in the silica gel tubes. This methanol is retained in the tube for at least three hours of sampling at 50 cc/min. However, after six hours of sampling essentially methanol-free air, the inherent methanol is pushed out of the tube. This concept is further demonstrated by reviewing the data obtained from the charcoal tubes at Sacramento. Unlike the six-hour samples at Monrovia, the six-hour samples at Sacramento consisted of a silica gel front tube in series with a charcoal back tube (identified in Table 5-14 by superscripts). Charcoal tube data from Sacramento show exactly the opposite trend of the silica gel data--no detectable methanol for the three-hour, individual samples, and high concentrations for the six-hour samples of essentially the same magnitude of the high silica values. This again is indicative of the methanol inherent in the silica gel tube being passed through the silica gel front tube into the charcoal back tube. The source of this apparent inherent methanol is the remaining question. Background concentrations of methanol in the silica gel have been taken into account, since all of the reported concentrations include subtraction of the background amounts observed in the blanks. The only other systematic source of methanol is the spun glass plugs that hold the silica gel in place within the tubes. Since the plugs were not included in the extraction process, methanol inherent in the plugs would not be analyzed in the blank, but would show up

Table 5-14. Field testing results.

Site	Tube	Date	Start Time	Duration (min)	Flowrate (cc/min)	Acetal. (ppb)	MeOH (ppb)	Acetone (ppb)	MTBE (ppb)	Butanal (ppb)	MEK (ppb)
Monrovia	Carbon	5/11/95	10:35	180	50	77.6	34.5	4.5	2.0	ND	ND
		5/11/95	10:35	360	50	83.4	27.0	5.5	2.4	ND	ND
		5/11/95	13:35	180	50	54.8	30.2	6.3	ND	ND	ND
		5/12/95	8:30	180	50	80.7	54.0	3.1	1.4	ND	ND
		5/12/95	8:30	360	50	83.7	34.7	4.8	2.4	ND	ND
		5/12/95	11:30	180	50	65.9	49.8	3.5	ND	ND	ND
		5/19/95	9:27	180	50	93.7	38.7	8.7	3.2	ND	ND
		5/19/95	9:27	360	50	112.1	19.8	11.4	4.1	ND	ND
		5/19/95	12:27	180	50	103.6	48.9	9.2	2.6	ND	ND
Monrovia	Silica gel	5/11/95	10:35	180	50	ND	115.3	ND	ND	ND	ND
		5/11/95	10:35	360	50	ND	ND	ND	ND	ND	2.7
		5/11/95	13:35	180	50	ND	195.2	ND	ND	ND	ND
		5/12/95	8:30	180	50	ND	167.2	ND	ND	ND	ND
		5/12/95	8:30	360	50	ND	ND	ND	ND	ND	ND
		5/12/95	11:30	180	50	ND	122.9	ND	ND	ND	ND
		5/19/95	9:27	180	50	ND	95.7	ND	ND	ND	ND
		5/19/95	9:27	360	50	ND	ND	ND	ND	ND	3.5
		5/19/95	12:27	180	50	ND	100.0	ND	ND	ND	4.7
Sacramento	Carbon	5/18/95	9:40	180	51.3	34.4	ND	5.6	ND	ND	ND
		5/18/95	9:40(b)	360	55.7	16.1	107.2	46.2	ND	ND	1.2
		5/18/95	12:40	180	51.2	19.3	ND	ND	ND	ND	ND
		5/19/95	9:00	180	42.2	21.3	ND	11.3	ND	1.0	2.8
		5/19/95	9:00(b)	360	48.5	16.6	113.9	52.1	ND	ND	ND
		5/19/95	12:00	180	42	11.8	ND	2.4	ND	ND	ND
Sacramento	Silica gel	5/18/95	9:40	180	55.5	ND	156.6	ND	ND	1.4	ND
		5/18/95	9:40(f)	360	55.7	ND	ND	ND	ND	ND	ND
		5/18/95	12:40	180	54.4	ND	97.2	ND	ND	ND	ND
		5/19/95	9:00	180	45.1	ND	176.7	159.2	ND	0.8	ND
		5/19/95	9:00(f)	360	48.5	ND	ND	ND	ND	0.4	ND
		5/19/95	12:00	180	44.5	ND	153.3	128.7	ND	0.8	ND

once air had passed through the tube, entraining the methanol into the silica gel. This would also explain why the zero air samples obtained from the smog chamber yielded higher background levels. The charcoal tubes have a foam plug, possibly explaining why they were not susceptible to this problem.

Acetone. Acetone concentrations obtained from the charcoal tubes at Monrovia are consistent with expected concentrations, as are the three-hour charcoal tube concentrations at Sacramento. The results from Sacramento imply that the silica gel problem noted for methanol may also exist for acetone.

MTBE. Measured MTBE concentrations are consistent with expected concentrations. The only source of MTBE is gas stations. Several gas stations are located in the vicinity of the Monrovia site. In contrast, the Kiefer Landfill is located approximately 10 miles from the nearest gas station. The results clearly demonstrate this difference in local sources.

Butanol, MEK. Very little of these compounds was measured at either site, so no additional conclusions can be made. However, the results seem consistent, with reasonably good LQLs calculated for both compounds.

5.4 AUDITS

The report from the laboratory audit is included in this report as Appendix A. The auditor found the development laboratory capable of performing the investigative analysis for this program. The only issue raised during the audit concerned a lack of formalized standard operating procedures (SOPs) for the analytical technique developed during the program. While the auditor felt that all of the pertinent parameters and information had been included in the final report, he noted that the procedures were not in a format that would constitute a useable SOP.

It has been noted previously in this report that further development of the method is necessary, particularly in the identification of a solvent that has sufficiently low background concentrations of all target species. Therefore, formalized SOPs are not considered appropriate at this time.

Section 6

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Appendix A

LABORATORY AUDIT REPORT

I INTRODUCTION

On May 22, 1995, a technical systems review was conducted on the project entitled Development of Methods and Procedures for Monitoring Ambient Concentrations of Oxygenated Hydrocarbons (OHC). This project is funded by the California Air Resources Board, under Contract 92-306, with AeroVironment, Inc. of Monrovia, California. AtmAA Inc., of Calabasas, California, serves as laboratory subcontractor, responsible for gas chromatography method development. Dr. Kochy Fung is AtmAA's principal investigator, responsible for developing, evaluating, and documenting the GC measurement method.

The technical system review was conducted by Dr. Tony Burns of Southwest Research Associates, (SRA), AeroVironment's Quality Assurance Subcontractor. Dr. Burns conducted a laboratory systems audit which examines the facilities and methods used to receive, extract, and analyze laboratory samples submitted under this project. In addition, the laboratory systems audit examined data reduction, validation, and reporting activities. A laboratory performance audit was not conducted due to the unavailability of commercially prepared standards for the target analytes. To analyze at the low levels in question, AtmAA redistills laboratory grade dioxane to obtain extremely high purity solvent. Duplicating this procedure would not be cost effective. Therefore, SRA focused on reviewing procedures, documentation, and vendor identification data for the methods and materials used.

II. BACKGROUND

The objective of this project is to develop, evaluate, and field test a method for measuring ambient air concentrations of oxygenated hydrocarbons (including carbonyls, alcohols, and ethers) at the ppb concentration level. The method developed involves sample collection using an adsorbent tube, sample extraction from the sorbent using a solvent, and analysis via solvent injection with two-dimensional gas chromatography and intermediate cryogenic trapping and detection by an oxygen-specific detector. Using this method, all of the relevant oxygenated hydrocarbons can be analyzed using a single analysis. The samples are easily collected in the field and demonstrate good storage stability.

The two-dimensional gas chromatographic method permits isolation and concentration of the analytes of interest prior to their introduction in the gas chromatograph and measurement by the oxygen-specific detector (O-FID) to provide higher sensitivity and specificity. The specificity of an O-FID is based on the principle that 1) hydrocarbons are pyrolyzed in the presence of a Pt/Rh catalyst to elemental carbon at approximately 1100° in an inert atmosphere, while 2) oxygenated hydrocarbons (OHCs) give off CO proportional to the number of oxygen atoms in the molecule. The liberated CO is converted to methane using a nickel catalyst in the presence of hydrogen for subsequent detection with an FID. This detector used in this system is manufactured by Siemans and marketed by ES Industries (New York).

The six specific analytes that were tested in detail during this project were: acetaldehyde, methanol, acetone, methyl *tert*-butyl ether, butanol, and methyl ethyl ketone. The measurements of carbonyls over the past decade point to the deficiencies of the current emission inventory database for these compounds. Levels of other oxygenated hydrocarbons (OHCs) are expected to rise with the use of oxygenated fuels due to either direct emission or photochemical formation. It is anticipated that the curtailment of OHCs will be an important aspect of the ozone control strategies in urban areas, particularly California. Thus, the findings of this project and the development of the method will be critical in establishing current baseline ambient levels of these OHCs against which future measurements can be compared.

III. QA AND PROJECT MANAGEMENT

AtmAA, Inc., is well equipped to perform the project. There was ample space and hardware to permit evaluation of a variety of GC column materials and configurations during the method development stage of the project. Dr. Fung has had considerable experience in the development and application of two-dimensional gas chromatography to measure trace OHCs in ambient air. In this prior work, Dr. Fung achieved specificity by using two high-resolution capillary columns of opposite polarity to separate interfering compounds collected from a first slightly polar column by a second highly polar column. In this fashion, problems attendant to interferences found with a single column approach are eliminated.

Dr. Fung appeared to be well qualified and knowledgeable concerning method requirements and the hardware innovations/modifications he has built into the two-dimensional gas chromatograph system. The only concerns noted in relation to this activity pertain to project documentation and development of the Standard Operating Procedure/Protocol.

Minor Issues

(1) Dr. Fung is well aware of the steps taken to develop the method and the equipment modifications required to support it. However, the documentation that describes these activities is not assembled in any one place or notebook. This makes it difficult for other investigators to duplicate the work and might even hinder AtmAA's ability to replicate the work in the absence of Dr. Fung.

(2) AtmAA is tasked with development of an SOP/Protocol that could be used to implement this method. The final report prepared for this project contains the necessary information, but it is not formatted to serve as an SOP, which must provide step-by-step instructions for performing the method.

IV. GC CONFIGURATION

Two-dimensional gas chromatography allows injection of a larger aliquot of sample extract, resulting in higher method sensitivity and improved selectivity in comparison to a single column. The AtmAA method uses a four-port and a six-port valve to perform several functions that are the basis of the approach: heart-cutting and cryogenic trapping of target compounds eluting from the first column, back flushing to eliminate residual injected species, and solvent peak and reinjection of trapped species to a second column for separation and detection.

In this method an aliquot of extract is injected into the first column of the two-dimensional gas chromatograph via valve I. Compounds eluted from the column are vented through valve II. Just before the target species are eluted valve II is actuated to divert the compounds and other subsequent eluting species to a liquid nitrogen freeze trap. Valve I is actuated to backflush column I after the last target compound is eluted. Valve II is deactivated to connect the trap to column II. A cartridge heater revolatilizes the trapped material for injection into column II. When this reinjection takes place, the column oven is cooled to cryofocus the target analytes. Oven temperature is then raised to elute target species.

The GC equipment used is current and reliable. A Hewlett Packard 5840A gas chromatograph (GC) equipped with an auto sampler and a valve board is used to perform the analysis. The entire injection and valve sequences are automated and controlled by the gas chromatograph. The valve board permits automation of four solenoid operated valves and four contact closures. Valves I and II are solenoid controlled. Cooling and heating of the freeze trap is controlled through the contact closures which operate solid-state relays in the respective Omega CN 9000 temperature controllers which power the cryogenic valve for liquid nitrogen and the heater cartridge, respectively. A Shimadzu data processor was used for peak recording, integration, and identification.

The analytical response of the FID output as a function of analyte concentration was linear in the concentration range of approximately 0.2 to 10 ug/ml. The GC peaks for all of the six OHC's tested were present and sharply defined. The correlation coefficient for the linear calibration curves was 0.994 or better. Dr. Fung estimated that the detection limit for the OHCs to be <0.1 ug/ml (equivalent to <0.1 ng on the column), although no formal detection limit study was conducted.

No concerns or minor issues were noted in relation to any of the analytical activities conducted.

V. COLLECTION OF AIR SAMPLES AND EXTRACTION SOLVENT MIXTURE

This project determined that solid sorbent sampling represented the most promising technique for collection and storage of OHCs. Data are presented that indicate sorbed samples are stable for up to 90 days. The sorbed samples are frozen in an air-tight container until analysis. A key part of this procedure is the solvent leaching (extraction) of the sorbed OHCs and other air constituents for subsequent GC analysis. Extraction is facilitated using a sonicator to improve solvent contact and analyte extraction.

Critical to the success of this project is the ability of the solvent to consistently extract the analytes from the sorbent tubes. A series of polar solvents were evaluated with a mixture of 50% benzyl alcohol and 50% dioxane being selected as the optimum solvent. AtmAA presented data that indicated the extraction efficiencies for each analyte were consistent, although the actual efficiency for each analyte varied as would be expected. Although all the solvents used were of the highest purity available, the solvents still contained significant levels of impurities and even target species. As a consequence, a background correction was always necessary. The use of a liquid extractant facilitated GC calibration, as there is no need for a special gas-handling system. Analyte standards are prepared gravimetrically as they are transferred into the extractant. As described above, a blank had to be run concurrently because of the presence of trace contaminants in the extraction solvent mixture.

In general, the storage stability study that was conducted demonstrated reasonable holding times for the extracted samples for up to 90 days. Although there is some variability in the results, it must be remembered that this is a research project and the analyst is dealing with very low levels of oxygenated hydrocarbon analytes. In general, the recovery of target analytes through measurements of spiked tubes was satisfactory.

No concerns or minor issues were noted in relation to the sampling and extraction is activity.

VI. CONCLUSIONS

During the course of method development, AtmAA has examined many factors relating to analysis of OHCs in air that may affect analytical results. Based on the results of this review, AtmAA appears to have optimized primary analytical conditions, sorbent configurations, and extraction solvent mixes. No concerns were identified that would or could affect the validity of the data generated. The minor issues identified can easily be corrected by generation of a method specific SOP and improved record keeping. This method itself provides a viable approach to analyzing low levels of OHCs in air using a single analytical method.