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Detection and Quantification of Atmospheric Carbonyl Compounds

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DETECTION AND QUANTIFICATION
OF ATMOSPHERIC
CARBONYL COMPOUNDS

BY

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ABSTRACT

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Ambient air aldehyde analysis was performed in Schenectady, N.Y. and on Whiteface Mtn. in Wilmington, N.Y. The technique, as prescribed by Kuntz et. al. (7), entailed the trapping of the volatile aldehydes as their 2,4-dinitrophenylhydrazone derivatives in an acetonitrile solution. The derivatives were then separated on a reversed phase HPLC column and detected by UV absorption at 254 and 360 nm., simultaneously. The air in Schenectady was found to contain formaldehyde and acetaldehyde at concentrations which ranged from 0.70 to 30.5 ppb and below that of detection to 1.6 ppb, respectively. Formaldehyde's daily average in Schenectady was 7.6 ppb. The formaldehyde and acetaldehyde levels at Whiteface Mtn. ranged between 0.61-2.6 ppb and 0.33-0.80 ppb, respectively. In addition, hourly sampling at both locations showed a diurnal variation in formaldehyde.

My thanks to Professor Hull, whose knowledge, patience, and humility have given me the opportunity to experience scientific research. From which opportunity, I have developed the curiosity to know why and the fortitude to search for an answer. And to my parents, I express my most sincere gratitude for without their sacrifices and support none of this could have been possible.

Sincerely,

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INTRODUCTION

The atmosphere is continually being contaminated with chemical waste. Carbonyl compounds, aldehydes and ketones, is one such group of pollutants. Of this group, the two most prevalent compounds in the troposhere are formaldehye and acetaldehyde, which have the following structures:

CH_2O	CH_3CHO
formaldehyde	acetaldehyde

The major sources of these pollutants are engine exhaust, industry, and power plants. As much as 12 to 14 percent of the unburned hydrocarbons from engine exhaust contain aldehydes and ketones (1,4). In industry, aldehydes and ketones are employed in manufacturing as industrial reagents. For example, formaldehyde is used in the manufacturing of urea, phenolic, melamine, and acetal resins present in insulating materials, particle-board, plywood, textiles, and adhesives. Many of these products, upon saturation with water, undergo reverse polymerization, thereby, releasing the volatile aldehydes. Moreover, aldehydes can be produced in the atmosphere by the photooxidation of gas phase hydrocarbons. A simple example is:

$$\mathrm{CH2{=}CH2 + O3 \longrightarrow \underset{formaldehyde}{OCH2} + X} \qquad (1)$$

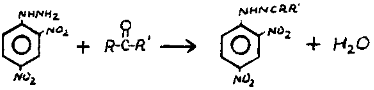
The aldehydes, once having entered the atmosphere, are responsible for a number of deleterious effects. They are contributors to photochemical smog, as exemplified by equation one (1,5). In addition, aldehydes can be precursors to organic aerosol formation (3). For example the vapors of benzaldehyde can react with a hydroxyl radical yielding an acyl radical. This radical goes on to react with molecular oxygen producing benzoic acid. Benzoic acid is a solid and contributes to particulate matter build-up in the atmosphere.

It should also be stated that, carbonyl compounds are a major source of free radicals, important intermediates in many atmospheric reactions.

As well as having deleterious effects on the atmosphere, aldehydes have been found to be harmful to one's health. Formaldehyde, for instance, is an irritant to the skin, eyes, and nasopharyngeal membrane. The compound can be detected by the sense of smell at levels below .061 ppm and it becomes an irritant at concentrations ranging between .061 and .122 ppm (1). The current Occupational Safety and Health Administration (OSHA) eight hour exposure limit for formaldehyde is 3 ppm (5). The potential health hazard of carbonyl compounds, therefore, has ellicited the need for an effective assay of ambient air.

In an attempt to stabilize and trap aldehydes and ketones a myriad of derivative techniques have been proposed. Many of them, however, are subject to significant interferences or are unable to differentiate the different aldehyde derivatives, thereby, making them less useful for atmospheric sampling. Two derivative methods which do not allow for carbonyl differentiation are MBTH and bisulfite addition. The nonselective MBTH method involves the formation of an azine derivative which then undergoes a color forming reaction that can be used for quantitation. The colorimetric measurement results in a total aldehyde concentration in terms of formaldehyde equivalents (5,6). The bisulfite addition method is also restricted since it determines only total carbonyl concentrations (6). Another method of analysis involves the absorption of the gas sample into a chromotropic acid solution. This method, however, is limited to formaldehyde and is susceptible to interferences from nitrates, phenols, alcohols, and nitrogen dioxide (6,8,9).

A different approach involves the oxidation of the aldehyde to its carboxylic acid by injection into a basic peroxide (H2O2) solution. The carboxylic acid is then separated by ion chromatography using a dilute bicarbonate eluent (6). This method, however, is subject to significant interference from alcohols. Currently, the most viable method for trapping aldehydes and ketones is as 2,4-dinitrophenylhydrazone (DNPH) derivatives.



(2)

Once an effective derivative reagent has been found, the efficiency of the assay becomes dependent upon the methods of separation and identification of the carbonyl derivative. In a paper published in 1979, Kuwata and his coworkers introduced reversed phase HPLC as a method of separating the DNPH derivatives (4). Previous work attempted to use gas chromatography as a method of separation, but, GC analysis resulted in poor resolution between carbonyl compounds of the same molecular weight. Also, thermal degradation of the derivatives contributed to the formation of double peaks which led to misinterpretation of complex samples (1,4). By using the HPLC, the double peaks originating from thermal degradation were eliminated since the analysis was carried out at ambient temperatures. Moreover, because of the small particle packing, the HPLC obtains effective separation with reasonable retention times (1,4). Until recently, the most widely accepted method for detecting the carbonyl derivative was by UV absorbance at 360 and 254 nm. In 1982, however, Jacobs and Kissinger reported electrochemical detection limits for DNPH derivatives of carbonyl compounds 20 times lower than those obtained with UV absorbance (10).

Prior to 1980, the derivative forming step took place in an aqueous medium. As a result of the aqueous medium, the derivative required extraction into an organic layer, evaporation to dryness, and dissolution in a suitable solvent. An inconvenience justified by an organic reaction presumably proceeding to 100 percent completion. In 1980, however, Kuntz, Lonneman, Namie, and Hull identified a water interference. Having noted this, Kuntz and his coworkers described a method by which the DNPH is used as an acetonitrile solution (7). This technique eliminates the extraction steps required by an aqueous medium, removes a water interference, and allows for direct injection into an HPLC since acetonitrile is a standard mobile phase.

The validity of the DNPH-acetonitrile system has been examined by Lipari and Swarin. In order for the derivatization step to be analytical in an acetonitrile solution the reaction must proceed analogously to that in an aqueous medium. Lipari and Swarin first examined the rate of the acid catalyzed reaction in acetonitrile by varying the concentration of HCl(1-4 drops of 1-12N acid). The test revealed that the derivatives were formed in less than five minutes independent of the acid concentration (5). Next, they examined the efficiency of the technique by employing a gas permeation generator to provide a formaldehyde atmosphere of known concentration. Other aldehydes were generated using a technique outlined by Graham (12). As a basis for comparison, test were run determining the collection efficiency of the derivatizing step in an aqueous medium. The results, as reported by Lipari and Swarin, are as follows (5):

COLLECTION EFFICIENCY(%)

	Acetonitrile-DNPH	Aqueous-DNPH
Formaldehyde	97.5+/-1.0	86+/-10
Acrolien	95.0+/-4.0	9+/-4
Butyraldehyde		80+/-14
Benzaldehyde		102+/-7

The apparent negative deviation in the collection efficiency for an aqueous medium may be due to lose of derivatives during the extraction and drying steps. Thus, the DNPH-acetonitrile system not only proves to be a viable alternative to the aqueous system, but also a better analytical technique.

The DNPH-acetonitrile system, however, required atmospheric testing also, because the test conditions up till now have been free of pollutants. In 1980, Lowe et al. verified that formaldehyde sampling with DNPH was not subject to interference from ozone (up to 100 ppb) and sulfur dioxide (up to 90 ppb), two common air pollutants (3). Grosjean has also reported finding that the presence of other aldehydes does not affect the trapping of formaldehyde, acetaldehyde, and benzaldehyde. In addition, the derivatives were found to be stable when exposed to air containing 150 ppb NO2, 200 ppb ozone, hydrocarbons, free radicals, SO2, and other pollutants (16). Hence, atmospheric sampling employing DNPH as the derivatizing agent appears to be analytically valid.

The derivatizing agent, DNPH, has provided a simple, analytical technique for determining the aldehyde make-up of the troposphere. As a result, Grosjean has reported having detected six aldehydes in the Los Angeles area using the aqueous-DNPH system. The carbonyl compounds were; formaldehyde (<70 ppb), acetaldehyde (<56 ppb), propanal (<37 ppb), butanal (<8 ppb), butanone (<15 ppb), and benzaldehyde (<2 ppb) (15). Diurnal sampling revealed a variation in aldehyde concentration which corresponded to ozone levels with a maximum occurring in the late afternoon (3). Kuwata et al. have also compiled atmospheric aldehyde concentrations in Osaka, Japan. The data reported formaldehyde and acetaldehyde concentrations which ranged between 20 to 35 ppb and 1 to 8 ppb, respectively (4).

In 1983, Kuwata reported a revised technique for assaying air for carbonyl compounds based on the derivatization of aldehydes with DNPH. The method allows for sampling with a C18 cartridge impregnated with DNPH (a dry medium), rather than an impinger containing a DNPH-acetonitrile solution (11). The technique not only promises a simplified procedure, but it also has the potential of increasing sensitivity 400 fold.

This paper will report the examination of the derivatization step of gas phase carbonyl compounds with DNPH in an acetonitrile solution. The protocol will be that as outlined by Kuntz et. al (7). This study will be divided into two segments. First, parallel testing of the technique with a literature method using a permeation generator as the source of the aldehydes. Second, actual atmospheric sampling with the technique in Schenectady, NY and Wilmington, NY on Whiteface Mountain. Also, a brief evaluation, with some results, will be presented on the most recently developed method of sampling, employing Sep-PAK C18(SP) cartridges (11).

EXPERIMENTAL

CHEMICALS:

HPLC grade acetonitrile was obtained from Burdick and Jackson and used both as a mobile phase for HPLC analysis and as a solvent.

The derivatizing agent, DNPH, was purchased from Eastman Organic Chemicals. Purification by recrystalization was repeated until a 1.26X10-3 molar solution of the solute in acetonitrile was found clean of any aldehyde hydrazones by HPLC analysis.

Aldrich Chemical Company supplied the 4,5-Dihydroxynaphthalene-2,7-disulfonic acid, disodium salt dihydrate (chromotropic acid).

The Sep-Pak C18 cartridges were purchased from Waters Associates of Milford, Massachusetts.

ABSORBING REAGENTS:

DNPH Impinger Reagent

The concentrated stock reagent was a 2.5X10-3 molar solution of DNPH in acetonitrile. In order to prevent contamination, the hydrochloric acid catalyst was not added until the solution was diluted (2).

The absorbing reagent was prepared by diluting the stock solution 1:2 with acetonitrile. To this solution, the concentrated hydrochloric acid catalyst was added (30ul per 200ml of reagent).

Chromotropic Acid Reagent

The stock solution was prepared by dissolving 0.35 grams of chromotropic acid (CA) in 100ml of concentrated sulfuric acid (8.74X10-3 molar).

The absorbing solution contained 5 parts stock solution, 4 parts concentrated sulfuric acid, and 1 part deionized water.

Cartridge Preparation

The Sep Pak C18 cartridges were prepared for sampling by first washing each cartridge with 2 ml of acetonitrile. The cartridges were then saturated with 2 ml of a 0.2% DNPH and 1% phosphoric acid solution in acetonitrile at a rate of 2 ml/min. Next, they were dried under reduced pressure in a nitrogen atmosphere. The apparatus consisted of a desiccator with both an inlet and an outlet. A nitrogen stream (20-30 ml/min) was connected to the inlet. The outlet was attached to an aspirator. The cartridges were dried for 1 hour under these conditions and then connected directly to a nitrogen stream (50-100 ml/min) for an additional 30 minutes. The prepared cartridges were capped with glass rods and stored in nitrogen containing-brown jars at 3-5 degrees(°C) (11).

STANDARDS:

Standard Aldehyde Hydrazones

0.5 grams of the aldehyde was dissolved in 20 ml of 95% methanol. The aldehyde solution was then mixed with a solution of 2,4-dinitrophenylhydrazine. The DNPH solution was prepared by adding 2 ml of concentrated sulfuric acid to 0.4 grams of DNPH. Next, water (3 ml) was added dropwise until solution was complete. The mixture was then diluted with 10 ml of 95% methanol (13).

In order to assure complete crystal formation, the solution was allowed to stand for 24 hours. The derivative was collected by suction filtration and then redissolved in hot methanol while stirring and heating.

In order to facilitate solution, ethyl acetate can be added. Recrystallization was repeated until a melting point comparable to literature values was obtained (12).

The standard hydrazones were used in constructing calibration curves based on detection with UV absorbance at 360 and 254 nm, as well as determining retention times on a reversed phase HPLC column.

Calibration of the Chromotropic Acid Assay

Stock formaldehyde solutions were prepared from 96% paraformaldehyde. A stock concentration of 6.1X10-2 molarity was obtained by diluting .1919 grams of paraformaldehyde with 10% sulfuric acid in a 100 ml volumetric flask. With the aid of a magnetic stirrer, the paraformaldehyde took approximately 24 hours to go into solution. Standard solutions of varying concentrations were obtained by simply diluting the stock solution. The formaldehyde solutions are stable for only one or two days (8).

The standard reaction products were obtained by combining 5 ml of the chromotropic acid reagent with 1 ml of a formaldehyde stock solution in a 10 ml volumetric flask. The solution was then brought to volume with concentrated sulfuric acid. Even though the reaction color is fairly stable, the calibration curve obtained from fresh solvents should not be used for reaction products older than 24 hours (8).

The absorbance of each standard mixture was then measured at 580 nm. A calibration curve was constructed by plotting absorbance versus concentration (Figure 1).

Standard Aldehydes In The Gas Phase

A Metronics Dynacalibrator permeation based generator supplied a source of gas phase carbonyl compounds. The generator quantitatively produced an aldehyde at known part per million concentrations from a permeation tube. Through the work of Professor Hull, a calibration curve plotting flow rate versus meter reading was constructed. Knowing the flow rate of the generator, one can then calculate the ppm emission of a standard aldehyde at 1 L/min by the following equation:

$$C=(P*Km)/(Fd+Fc)$$

where,

P is the permeation rate (ng/min-cm)

Km is the molar constant=molar volume/molecular weight

The molar volume(V/n) =RT/P

Fd is the dilution flow rate

Fc is the carrier flow rate which was preset at 177cc/min.

Example: Calculate the concentration in ppm of acetaldehyde being emitted by a permeation device (10 cm long), where P=360 ng/min-cm at 30^{O}C and knowing Fd is set at 1000 cc/min.

P=(permeation rate)X(device length)=3600 ng/min

V/n=RT/P=(.0821 l-atm/K-mole)(303K)/(1atm)=24.89l/mole

Km=(V/n)/MW=24.89/44.05=.5647

Fd= 177 cc/min

Fc= 1000 cc/min

C=PKm/Fd+Fc= 1.73 ppm

Note: The appendix contains the permeation rates for various aldehyde permeation tubes and the table which converts meter reading to dilution flow rate.

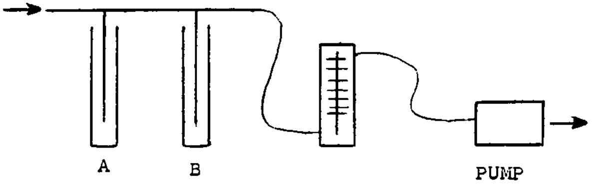
The concentration at any other dilution flow rate is a fraction of that at 1 l/min. For example, at a flow rate of 6 l/min the expected concentration of acetaldehyde is .288 ppm (i.e. 1.73 ppm/6). Therefore, knowing the correlation between flow rate and concentration and flow rate and meter reading, one can calibrate the generator to produce a known concentration of an aldehyde.

When sampling from the generator one has the option of sampling using the generator as both a pump and a source or just as a source. The generator is equipped with an overflow valve which allows for a zero or finite flow of the sample gas at the outlet port. By connecting a "Y" to both the outlet port and the overflow valve, the generator will pump the sample carbonyl gas at the rate of dilution flow, Fd. A zero flow rate, however, can be obtained by simply connecting the analyzing apparatus to the outlet port, thereby, leaving the overflow valve open to the environment. As a result, the generator will require the sample gas to be pulled out by an external pump. Both procedures were experimentally tested and found to be equivalent.

SAMPLING PROCEDURES:

Impinger Technique

Both the chromotropic acid and the DNPH techniques employ the same sampling apparatus. That is, two impingers, a pump, and a flow meter connected in series.



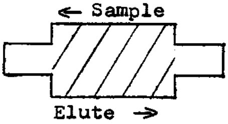
Impinger B is used to check sampling efficiency by determining the amount of aldehyde overflow.

For the chromotropic acid technique 10 ml of sampling reagent was added to each impinger. After sampling, the absorbance of the colored reaction product was measured at 580 nm (8). The concentration was then obtained from the calibration curve (Figure 1).

The DNPH technique required 4 ml of reagent in each impinger. When sampling the atmosphere, however, it was discovered that the acetonitrile evaporated readily. In order not to interrupt sampling every hour, one can add an additional 8 ml of acetonitrile (more or less depending on the length of time of sampling and the temperature) to the 4 ml of reagent. At the end of sampling, the solution was quantitatively transferred from the impinger to a 10 ml graduated cylinder and brought up to a volume of 4 ml with acetonitrile. An aliquot of this solution was then injected into an HPLC for analysis.

Cartridge Technique

Sampling with the SP cartridges was very similar to sampling with impingers, rather than two impingers there were two cartridges in series. Upon completion of sampling, the hydrazones were eluted from the cartridge by 2 ml of acetonitrile. The only criteria when sampling with cartridges is that sampling is performed in one direction and elution in the other, that is:



An aliquot of the eluent was then injected into the HPLC for analysis.

In both the cartridge and impinger techniques, sampling was performed at a rate of .5 l/min.

INSTRUMENTATION:

CA Absorbance Measurement

The absorbance of the colored reaction product was measured on a Varian-Aerography Cary 118 UV/VIS absorption spectrophotometer.

DNPH Hydrazone Separation and Detection

The DNPH hydrazones were analyzed on a Varian-Aerograph 5000 HPLC which was attached to a 254 nm UV detector and a Tracor 970A variable wavelength detector set with the UV lamp at 360nm (14). The analytical column was an Alltech C18 10 ul 25cmX4.6mm reversed phase HPLC column. The mobile phase was 65 percent acetonitrile and 35 percent water. The program was isocratic with a flow rate of 1.5 ml/min.

ANALYTICAL PROCEDURES:

Chromotropic Acid

The absorbance obtained from the Cary 118 was converted to a concentration by the calibration curve (Figure 1). The concentration was then interpreted as a ppm value by the following calculation:

moles of formaldehyde= conc(moles/1)X(.010 1)

moles of air sampled= PV/RT

where,

P= atmospheric pressure (atm)

V= volume of air= (sampling time)X(pump rate=.5 1/min)

R= .0821 1-atm/K-mole

T= temperature (K)

formaldehyde conc (ppm)=(moles of form/moles of air)X10E6

DNPH

The hydrazones trapped both by the impinger and the cartridge techniques were separated on the HPLC. The derivatives were identified by their retention times (Table 1). The peak areas, computed by measuring the height and multiplying it by the width at half height, were converted to concentrations by response factors which had units of conc(mole/liter)/area(mm^2) (Table 1). The response factors were ascertained through the work of Clyde A. Kelly in which he synthesized and analyzed hydrazone standards (14). From the concentration of the hydrazone, the number of moles of aldehyde were calculated by knowing the volume to which the derivative was diluted after sampling (4 ml for impinger technique and 2 ml for cartridge method). The concentration of the aldehyde, in ppm, was then determined by using the same method as outlined for the chromotropic acid assay.

Limit Of Detection

Limits of detection (LOD) for the DNPH-acetonitrile technique were determined according to a paper written by Gary L. Long and J. D. Winefordner. The method involved analyzing a series of reagent blanks from which data the background levels of aldehydes were calculated based on a 90 liter air sample diluted to 4 ml. The standard deviation for each aldehyde detected was then calculated. And, the limit of detection was defined as a signal which was greater than three standard deviations from the average background signal. The limit of quantitation was defined as a signal greater than ten standard deviations from the average background signal (15).

RESULTS AND DISCUSSION

The first project undertaken involved the comparison of the DNPH and the CA techniques in sampling formaldehyde from a permeation generator. The reason for doing this was to confirm the analytical accuracy of the DNPH-acetonitrile method since the CA technique is a proven assay.

The test consisted of determining a series of formaldehyde concentrations ranging from 0.04-1.4 ppm. The source of formaldehyde was a Metronics Permeation Generator. Sampling was not simultaneous, rather it was sequential. That is, at one concentration the formaldehyde was measured with the DNPH technique and then the CA technique. Consequently, there may have been some variation in the sampling conditions. Regardless, the data shows excellent correlation between the two techniques (Figure 2).

Having confirmed the validity of the technique, a procedure for actual atmospheric sampling was established.

Initial sampling was performed in Schenectady, N.Y. from the third floor of the Science and Engineering building. The campus is isolated from the city and contains only secondary access roads along its perimeter. As a result, the concentration of aldehydes present at this location would appear to be representative of an urban area without the direct interference from auto emission. The apparatus was similar to that mentioned in the experimental. The only addition was a long glass tube which extended out of the window and was attached to the inlet port of the apparatus.

Sampling was performed twice a day during the months of June, July, and August. Samples were run between 9:00-12:00 in the morning and 1:00-4:00 in the afternoon. Since the flow rate was 0.5 liters/min., the volume of air being sampled was 90 liters.

Before the data could be interpreted, analytical criteria had to be established. Blanks taken during later sampling at Whiteface Mountain (Table 2) were used to determine the background levels of aldehydes in the reagent. According to the method prescribed in the experimental, detection limits for a 90 liter sample were found to be as follows:

	Detection Limit(ppb)	Quantitation Limit(ppb)
Form.	0.10	0.32
Acetald.	0.16	0.53

With the exception of acetone, the other aldehydes were not found in the reagent. Acetone was found in the reagent at exceedingly high and unstable concentrations. The contamination of the reagent, apparently due to the acetonitrile, led to the inability to monitor acetone levels.

The data obtained in Schenectady is represented in Table 3. The data shows formaldehyde concentrations which range between 0.70 and 30.5 ppb and acetaldehyde concentrations between levels below that of detection and 1.6 ppb. Formaldehyde's daily average was 7.6 ppb. Acetaldehyde, however, was far less detectable and only a few of the days had levels in the range of quantification.

In order to examine the daily variation in formaldehyde, the concentration was monitored over a 36 hour period with sampling occurring every 3 hours. The formaldehyde concentration ranged between 1.7 and 8.1 ppb. Maxima occurred between 7:00-10:00AM and

6:00-10:00PM (Figure 3). These peaks are most likely due to commuter traffic.

In an attempt to determine the significance of the concentrations found in Schenectady, sampling work was undertaken on Whiteface Mountain in Wilmington, N.Y. The work was performed at the SUNY Atmospheric Sampling Station located at the summit (4,900 ft.). It was hoped that the air at the peak would be less contaminated by traffic, thereby, providing atmospheric background levels of ambient aldehydes.

Sampling was performed for about one week. The air was sampled by drawing it in through a large diameter pipe (3 inches) at a rate of 100 liters/min. The impinger apparatus was connected directly to the pipe at a point above the pump.

The data which was in the range of quantitation ranged between 0.61-2.6 ppb and 0.33-0.80 ppb for formaldehyde and acetaldehyde, respectively (Table 4). The acetaldehyde levels again were less than formaldehyde and many of the samples did not contain concentrations in the range of quantitation. During this period, ozone concentrations were also monitored and recorded with an apparatus in the station. The ozone concentration varied from 30-70 ppb (Table 4). In an attempt to correlate this data a plot was constructed with both aldehydes and ozone on the y-axis and time on the x-axis (Figure 4). As expected, all three concentrations varied in a similar manner. The only difference was that ozone appeared to be a precursor to aldehyde formation since it peaked 3 to 6 hours before formaldehyde. A plot of formaldehyde concentrations delayed 3 hours versus ozone (Figure 5) seems to show an apparent correlation. This observation is theoretically explicable since ozone can react with alkenes yielding aldehydes (equation 1 Introduction).

Next, diurnal sampling was performed over a two day period by sampling every 3 hours. The formaldehyde ranged between 0.61 and 2.6 ppb with maxima occurring between 10:00-12:00PM and minima between 12:00-2:00 in the afternoon (Figure 6). This was different than that observed in Schenectady where traffic apparently is the most significant source of aldehydes. At Whiteface Mountain one notes a minima during the daylight hours rather than a maxima as in Schenectady. One may reasonably conclude that at Whiteface, where the likelihood of traffic-emitted aldehydes is low, the effects of aldehyde photolysis are more obvious.

An overview of the data collected at Whiteface and Schenectady along with the work done by Grosjean in Los Angeles allows for a comparison of rural, small city, and large city aldehyde concentrations. The averaged data for formaldehyde and acetaldehyde concentrations is as follows:

LOCATION	FORM.(ppb)	ACETALD.(ppb)
Whiteface Mtn.	2.0	0.30
Schenectady	7.6	0.46
Los Angeles	23.8	9.3

Unsurprisingly, the formaldehyde and acetaldehyde concentrations appear to increase as the city size increases. This effect is to be expected if the major sources of aldehydes are the internal combustion engines, traffic, and industry, which increase with increasing city size. The relatively high acetaldehyde concentrations for Los Angeles along with the presence of propanal, n-Butanal, methyl ethyl ketone, and benzaldehyde indicate significant differences between the air in the East and the West. There appears, however, to be no obvious reason for this. It would be useful to examine a large eastern city.

As mentioned in the introduction, the cartridge technique, a recent discovery, is presently being tested. A comparison with the impinger technique has already been performed. The method was somewhat similar to that used to compare the impinger technique with the CA procedure. The only difference was that the two tests were run simultaneously. That is, both apparatuses were connected to the aldehyde generator outlet with a "Y". This was done in order to lessen experimental error due to fluctuations in sampling conditions. The results (Figure 7 and Table 5) were very encouraging with formaldehyde. Not only were the values for each dilution run comparable, but it appeared that the cartridge technique is more efficient since the chromatograms for cartridge B were cleaner than the chromatograms for impinger B. Further testing with other aldehydes is planned.

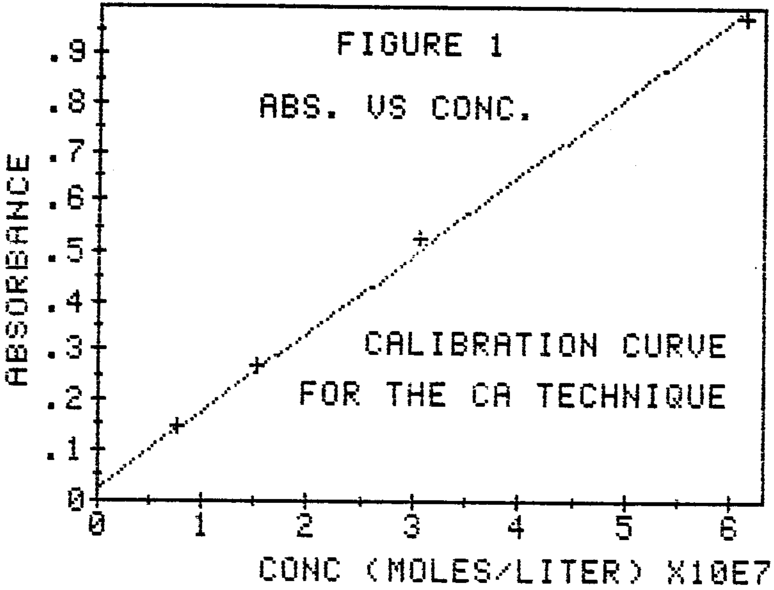


Figure 1. Calibration curve for the CA technique.

TABLE 1

RETENTION TIMES AND RESPONSE FACTORS FOR DNPH HYDRAZONES

Compound	Wavelength (nm)	Retention Time (min.)	Response Factor (molarity/mm^2) X10E7
DNPH	254	2.4	5.17
	360	2.4	2.57
Methanal	254	3.8	4.78
	360	3.8	2.30
Biacetyl	254	4.6	3.33
	360	4.6	1.05
Ethanal	254	4.8	4.95
	360	4.8	2.28
Acetone	254	6.0	4.46
	360	6.0	2.17

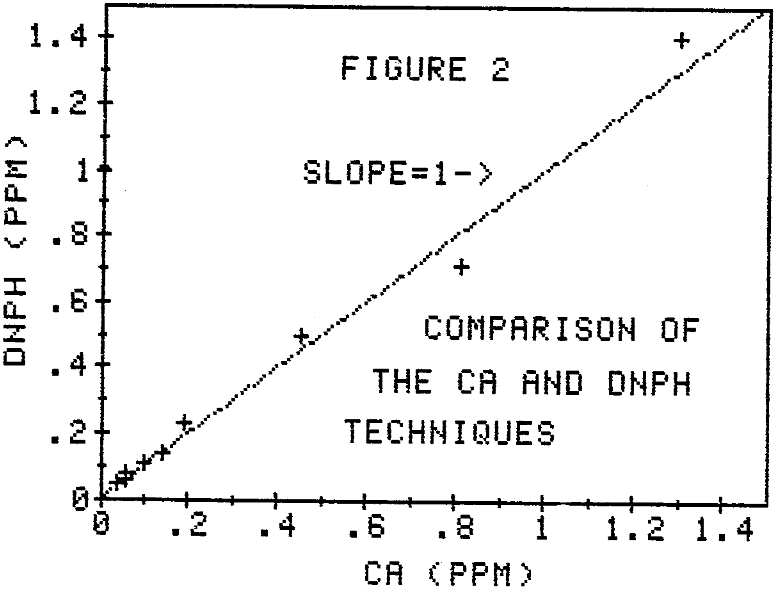


Figure 2. Comparison of the DNPH-acetonitrile and CA techniques in sampling formaldehyde produced by the permeation generator.

TABLE 2

THE AREA OF DNPH HYDRAZONES FOUND IN BLANKS

Blank #	Form.(mm^2)	Acetald.(mm^2)	Acetone(mm^2)
1	9.0	0.0	37.0
2	2.4	10.5	115.5
3	9.0	20.0	132.0
4	0.0	0.0	140.3
5	9.6	7.5	133.0
6	0.0	10.0	104.0
7	5.3	0.0	108.5
Std. Deviation	4.3	7.5	34.9
Adjusted Values*	2.7	0.5	2.2

* Values were standardized to an attenuation of 0.08 and a chart speed of 1 cm/min.

TABLE 3

FORMALDEHYDE AND ACETALDEHYDE LEVELS IN SCHENECTADY, N.Y.

Date	Formaldehyde (ppb)	Acetaldehyde (ppb)
6/23	30.5	1.2
6/27	16.1	0.75
6/29	7.1	2.2
6/29	8.1	0.77
6/30	14.3	2.0
6/30	9.6	1.1
7/11	12.2	0.34
7/14	1.9	0.41
7/19	8.4	1.6
7/21	4.7	0.34
8/10	3.7	0.17
8/16	9.5	0.85
8/16	8.2	0.75
8/17	8.0	0.60
8/18	4.9	0.36
8/18	6.5	0.41

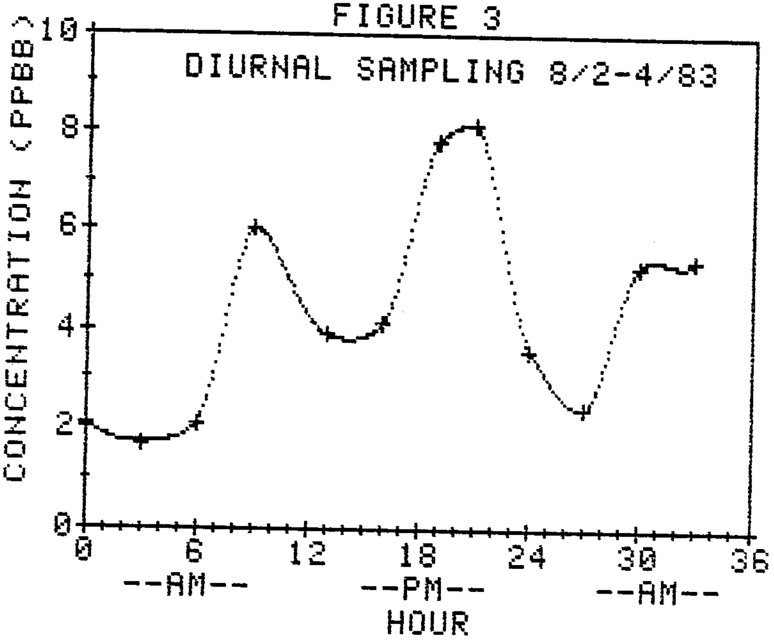


Figure 3. Formaldehyde concentrations at 3 hour intervals in Schenectady, N.Y. during August 2 through August 4, 1983.

TABLE 4

Formaldehyde, Acetaldehyde, And Ozone Concentrations In The Air On Whiteface Mtn., Wilmington, N.Y., August 14-19, 1983.

Sample #	Formald. (ppb)(1)	Acetald. (ppb)(2)	Ozone (ppb)	Time (hr)(3)
1	0.76	0.33	29	0
2	0.94	ND(4)	29	19.5
3	0.93	ND	29	22.5
4	0.61	ND	29	26
5	1.7	ND	30	29
6	1.2	0.35	37	32.5
7	1.3	ND	38	36
8	0.86	ND	35	39
9	1.0	0.32	38	42.5
10	0.64	ND	58	45.5
11	2.4	0.56	53	53.5
12	2.1	0.48	91	61
13	2.6	0.61	97	64.5
14	0.67	51	82	67.5
15	1.3	0.80	68	71
16	1.2	0.42	57	95
17	1.3	0.46	32	115.5
18	1.0	0.50	33	118.5

Notes:
1. Formaldehyde: >0.10 ppb is detectable
   >0.32 ppb is quantifiable
2. Acetaldehyde: >0.16 ppb is detectable
   >0.53 ppb is quantifiable
3. The first sample was taken at 2:30 PM, August 13, 1983
4. ND-Not Detected

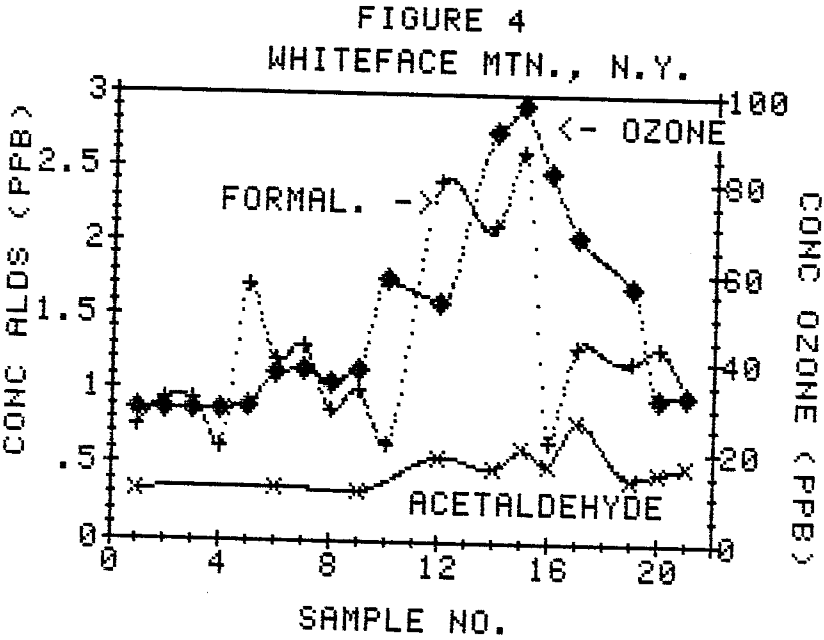


Figure 4. Formaldehyde, Acetaldehyde, and Ozone concentrations on Whiteface Mtn. during August 14 through August 19, 1983.

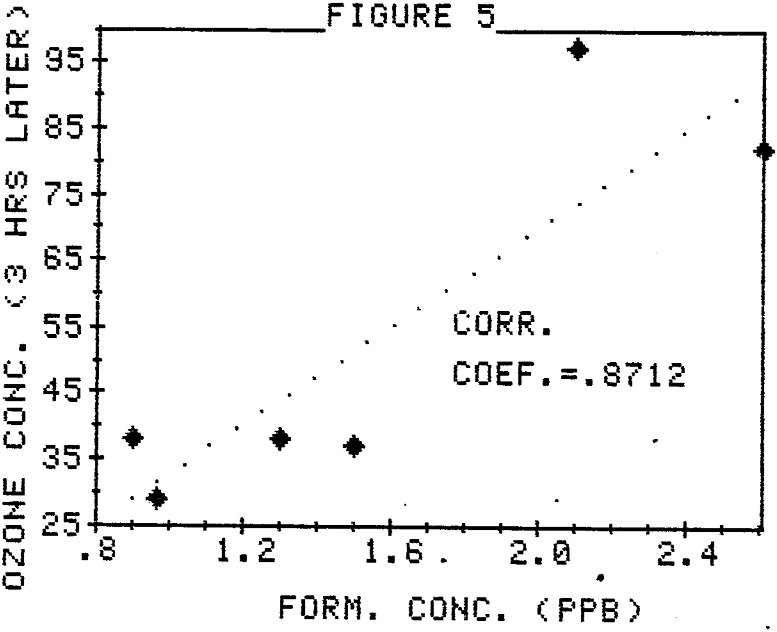


Figure 5. Ozone (delayed by 3 hours) vs. Formaldehyde concentrations on Whiteface Mtn.

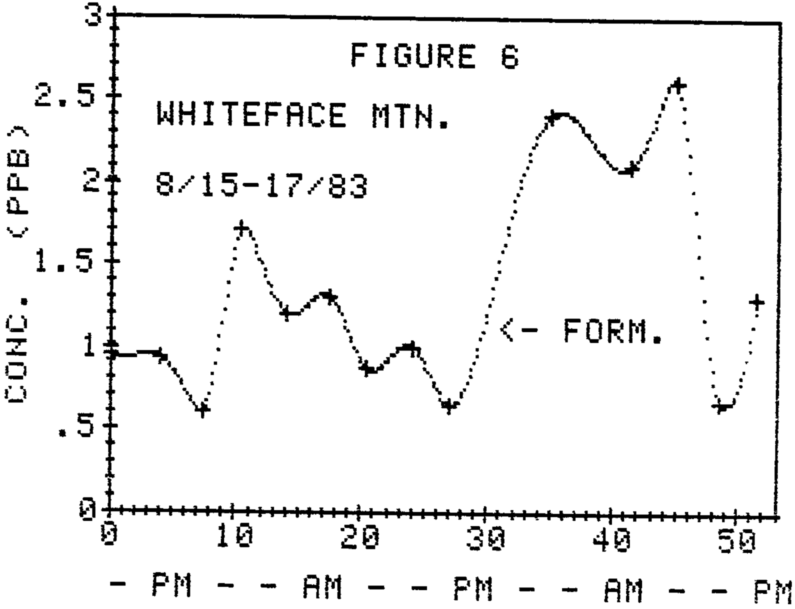


Figure 6. Formaldehyde concentrations at 3 hour intervals on Whiteface Mtn. from August 15 through August 17, 1983.

TABLE 5

Comparison Between The Impinger And Cartridge Techniques In Sampling A Series Of Concentrations Emitted By The Permeation Generator.

Dilution Flow (1/min)	Cartridge (ppb)	Impinger (ppb)	% Difference
1	1.55	1.50	3
2	.83	.78	6
6	.23	.26	10
10	.15	.16	6
13	.13	.12	8

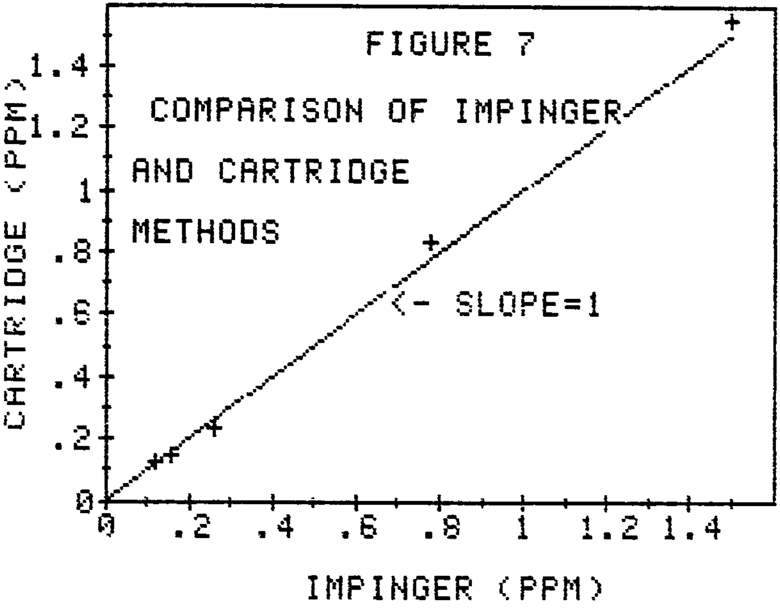


Figure 7. Comparison of the impinger and cartridge techniques in sampling formaldehyde produced by the permeation generator.

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APPENDIX

PERMEATION RATES FOR DYNACAL PERMEATION TUBES

Gas	Permeation Rate ng/min-cm	T(°C)
Acetone	330	50
Acetaldehyde	360	30
Benzaldehyde	125	70
Formaldehyde	240	90
Propionaldehyde	455	50

THE DILUTION FLOW RATES OF THE DYNACALIBRATOR PERMEATION GENERATOR AT SPECIFIED METER READINGS

Dilution Flow (l/min)	Meter Reading
1	2.5*
2	4.0*
6	10.2*
10	8.1**
13	10.4**
16	12.7**

Note:
* Center of steel ball
** Center of red ball