SAMPLING AND ANALYSIS OF CARBONYL IN LABORATORY ATMOSPHERES.

J. T. AYODELE and Y. MOHAMMED

ABSTRACT

A sampling and analytical method has been developed for carbonyl concentrations in different laboratory atmospheres at the Faculty of Science Bayero University; Kano, Nigeria using cold oximation followed by titrimetric finish. The analysis was carried out between 008 and 1800 hrs from October 2002 to June 2003. Samples of air were collected from each laboratory by bubbling through 6% hydroxylamine hydrochloride releasing hydrochloric acid equivalent to the carbonyl in the air. The collection was 100 percent in the range 2-50 ppb carbonyl and the trapping solution was stable for over 30days both before and after carbonyl collection. The carbonyl concentrations in each laboratory are functions of the activities and type of chemicals stored or used in them. The mean carbonyl level in these laboratories was 14.63ppb with a coefficient of variation of 11.25%.

KEYWORDS: Carbonyl, determination, laboratories Bayero University, Kano, Nigeria.

INTRODUCTION

Air pollution kills as has been demonstrated in London, New York and Donora (Heiman, 1961; Altshuller, 1963). Air pollution impairs health by choking the individual with emphysema, bronchitis and asthma and may lead to lung cancer, stings the throat, makes eyes water, causes headache, reduces visibility, spoils scenic areas, makes driving hazardous, rots and soils clothing, deteriorates house paints and metals, dirties monuments and public buildings (Wolff et al., 1975; Frank, 1964; Ayodele and Mohammed, 2001; Ayodele and Mohammed, 2003).

Hazardous air pollutants may come from mobile and stationary sources such as cars, trucks, buses, motorcycles, boats and planes, iron and steel, oil refineries, dry cleaners and gas stations. More than half of city air pollution comes from mobile sources, the exhausts of which contain carbonyl, volatile organic compounds, nitrogen oxides, particulates and lead (Holbrow, 1962; Yocom and McCaldin, 1968; Anderson, 1970).

Stationary sources generate air pollutants usually by burning fuel for energy and as a byproduct of industrial processes (Ajax et al., 1967; Altshuller, 1983; Koren, 1991; Piccot et al., 1992). The electric utilities, factories and commercial buildings burn coal, oil, natural gas, wood and other fuels and therefore is the principal sources of sulphur dioxide, nitrogen oxides, carbon monoxide, particulates, volatile organic compounds and lead (Tice, 1962; Salvin, 1963).

Fuel oils contaminated with toxic chemicals, hazardous waste disposal facilities, municipal incinerators, landfills and electric utilities are some of the sources of toxic air pollutants. The majority of organic discharges into the air occur from natural sources, transportation and stationary sources. These organic sources consist of the oxygenated hydrocarbons, the homogenate hydrocarbons, the olefins and the aromatics. The oxygenated hydrocarbons include aldehydes, ketones, alcohols and acids .In quantity they produce eye irritation, reduce visibility in the atmosphere along with other components in the atmosphere. Formaldehyde found in industrial discharges causes eye irritation even at low concentrations (Huess and Glasson, 1968). Simple carbonyl compounds, α β-unsaturated aldehydes and dicarbonyl compounds are reported to be direct–acting mutagens in which atmospheric relevance include formaldehyde, acrolein, methyl-glyoxal and glyoxal respectively (Marnett et al., 1985) The literature on carbonyl is extensive because of its reactivity and distribution of its compounds in natural and manufactured materials (Hanna, 1966).

Different methods have been reported for its determination (Ioddles et al., 1939; Mitchell et al., 1941; Duke, 1944; Rees and Anderson, 1949; Goldman and Yagoda, 1943; Goddu, 1958; Tenney, 1958; Sensabough et al., 1958; Wilson, 1958; Bartkiewicz and Kenyon, 1963; Cowell and Selby, 1963; Jungnickel and Forbes, 1963; Ayodele et al., 1987). This paper reports the carbonyl concentration in different laboratory

J. T. AYODELE, Chemistry Department Bayero University, Kano - Nigeria
Y. MOHAMMED, Chemistry Department Bayero University, Kano - Nigeria

atmospheres at the Faculty of Science Bayero University, Kano, Nigeria.

MATERIALS AND METHODS.

All chemicals were of analytical reagent grade unless stated otherwise. All experiments were carried out at room temperature using water or non-aqueous solvents. 6% hydroxylamine hydrochloride solution was prepared by dissolving 60g of it in 250cm^3 water in a litre volumetric flask containing methanol and 6cm^3 of 0.04% bromo phenol blue (BPB) .The mixture was stirred and brought to the mark with methanol (ICI, 1969).

Flow rate and sampling Time
The carbonyl in the sampled air was absorbed in 200 cm^3 hydroxylamine hydrochloride using variable flow rates and times. The carbonyl absorbed in the impinger was a function of the flow rate. An increase in the flow rate caused a resultant increase in the carbonyl in the first impinger while for all the flow rates tested; the second impinger gave a negative test for carbonyl. The results were quantitative with the least co-efficient of variation at 45l/min. Thus a flow rate of 45l/min. was selected for subsequent experiments (Ayodele and Mohammed, 2001)
For the internal quality control of the time required for sampling and in monitoring the constancy of performance of the analytical method, varying time intervals were chosen. The results obtained did not show significant departures from the normal standards of performance of the method during this study.

Absorption Efficiency
The absorption efficiency of carbonyl in 200 cm^3 hydroxylamine hydrochloride solution was evaluated for various concentrations of carbonyl gas and formaline solutions. A 4,500 litres of air containing fixed amount of the gas was passed through the impinger at 45l/min. Aliquots of the resulting solutions were analyzed. The recovery from the first impinger was 100 per cent whereas no carbonyl was detected in the second (Ayodele and Mohammed, 2001; Ayodele and Mohammed, 2003).

Sampling and Analysis

Carbonyl gas samples were collected using Drechsel bottles containing hydroxylamine

hydrochloride solution at a rate of 2.8 m^3/hr for 30 minutes attached to Edward vacuum pump (Model E$_2$M$_2$). The carbonyl in the air reacted with the hydroxylamine hydrochloride liberating hydrochloric acid and water. The resultant acid was titrated against standardized sodium carbonate/sodium hydroxide solution.
The vacuum pump air outlet was connected to the air inlet of the sample bottle containing 200 cm^3 hydroxylamine hydrochloride. Another bottle was stoppered and was set aside as the blank. They were both sealed with grease to prevent diffusion of air from the external source into the bottles. The pump was operated for 30 minutes after which the bottle was detached and its content was determined. The content of the comparison bottle was treated in a similar manner. From the titre data, the concentration of carbonyl in the sampled volume of air corrected for the blank was calculated.
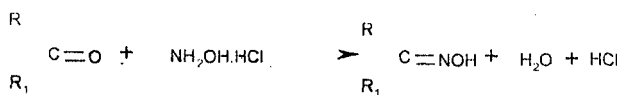
Procedure
A known volume of air was passed through 200 cm^3 of 6-% hydroxylamine hydrochloride solution in a 500cm^3 Drechsel bottle at a rate of 45l/min. The machine was stopped at the end of the prescribed period and the sample bottle inlet was shut off and the content of the bottle agitated. The solution was transferred into a 250cm^3 volumetric flask and was titrated against 0.01M sodium hydroxide. The concentration of carbonyl in the various air samples was determined.
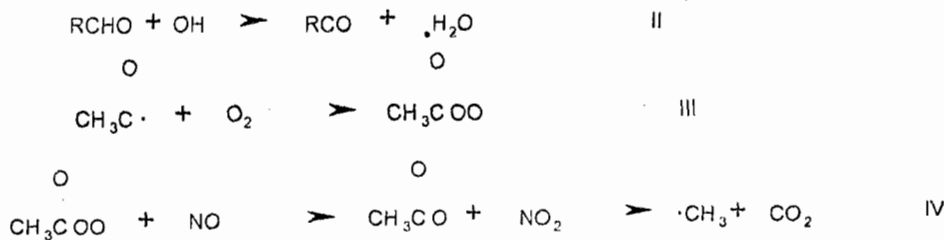
RESULTS AND DISCUSSION

The chemistry of the reaction.
The oximation reactions between carbonyl compounds and hydroxylamine or its salts are used for its determinations Hydroxylamine hydrochloride reacts with carbonyls to liberate water and hydrochloric acid (equation I). The liberated acid may be titrated either by manual, potentiometry or spectrophotometric methods to determine its carbonyl contents in water, methanol, dioxane or benzene (Ayodele et al., 1987).

The amount of carbonyl present can be determined by measuring the amount of oxime consumed or the water or acid, set free. The reaction is quantitative as most carbonyl compounds react with hydroxylamine hydrochloride quantitatively (Duke, 1944).

$$\begin{array}{c} R \\ \diagdown \\ C = O \\ \diagup \\ R_1 \end{array} + NH_2OH.HCl \longrightarrow \begin{array}{c} R \\ \diagdown \\ C = NOH \\ \diagup \\ R_1 \end{array} + H_2O + HCl$$

$$RCHO + OH \longrightarrow RCO + H_2O \qquad\qquad II$$

$$\overset{O}{CH_3C\cdot} + O_2 \longrightarrow \overset{O}{CH_3COO} \qquad\qquad III$$

$$\overset{O}{CH_3COO} + NO \longrightarrow \overset{O}{CH_3CO} + NO_2 \longrightarrow \cdot CH_3 + CO_2 \qquad IV$$

In a spectrophotometric titration, a suitable indicator is added and the absorbance as known titrant volume increments added are recorded .It may be necessary to force the reaction to completion by using nearly non-aqueous solvent systems (Ayodele et.al, 1987).

The possible fates of carbonyl in a laboratory atmosphere are reactions with OH, HO₂, NO₃ and

photolysis. Since formaldehyde is the major carbonyl components of solutions used as preservatives in the laboratories and the most typically found in the highest concentrations in the ambient air (Horowitz and Calvert, 1982) hence the major components of the laboratory ambient air. During the daylight hours, photolysis predominates in its loss in a relatively clean laboratory atmosphere while the reactions with HO_2, NO_3 and OH will be considerably less. At night when the concentrations of OH and HO_2 are low and no Photolysis occurring the recorded concentrations in the early morning hours are observed. (Lloyd, 1979; Grosjean, 1982).

Carbonyl is oxidized by the suggested mechanisms shown in equations I-IV which involve its oxidation by the hydroxyl radicals, HO_2, NO_3 and photolysis. It is itself an important pollutant with biocidal properties. The mean carbonyl in the laboratories
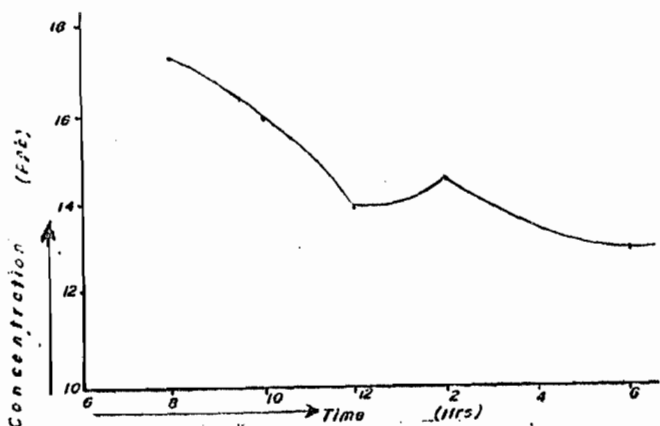

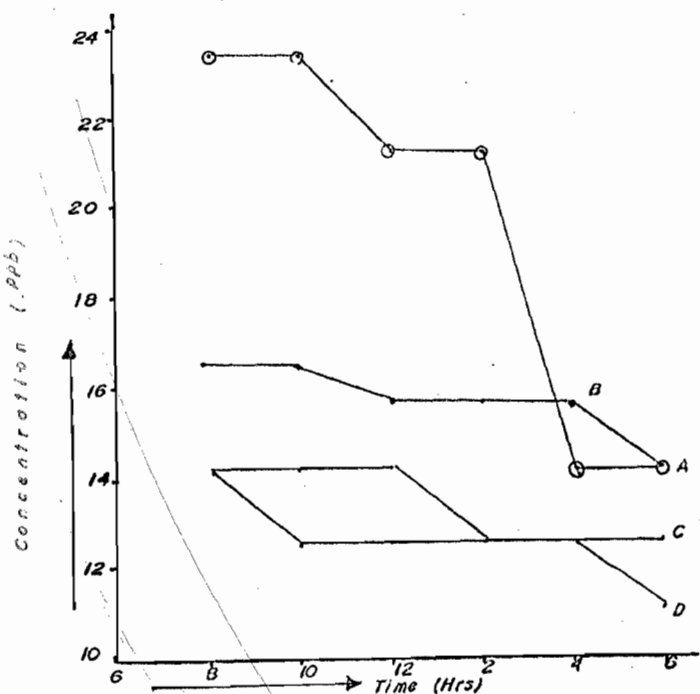Fig 1: Mean Carbonyl Concentration in all the laboratories.

Fig 2: Mean Carbonyl Concentration in (A) Organic, (B) Museum, (C) Inorganic and (D) Physical laboratories.
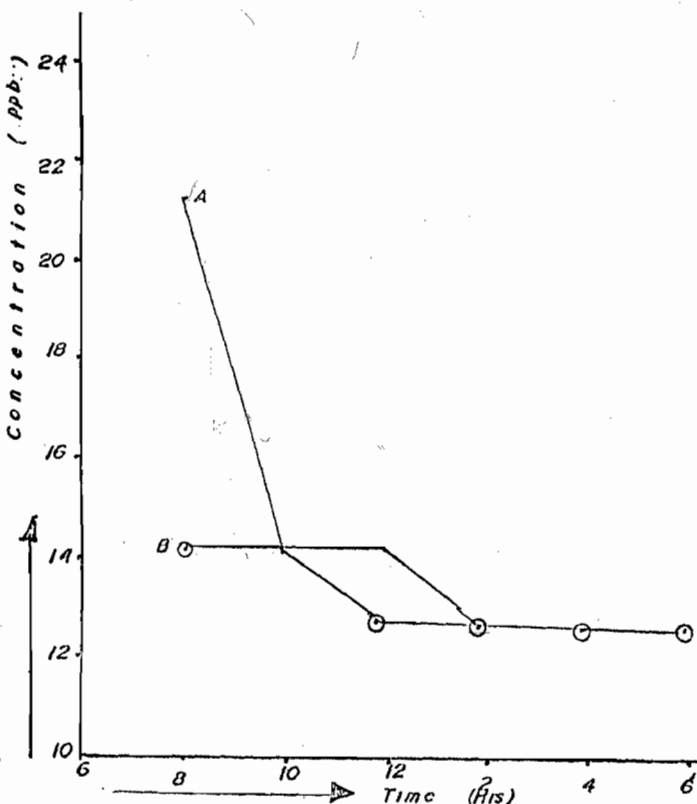

Fig 3: Mean Carbonyl Concentration in (A) Research and (B) Biology, Laboratories.

Table1: Levels of Carbonyl (ppb) in Different Laboratories.

	Physical	Organic	Research Lab	Inorganic	Biology	Museum
Maximum	14.16	23.35	21.23	14.16	14.64	16.52
Minimum	11.09	14.16	12.59	12.64	12.64	14.16
Mean ( )	13.13	19.58	14.55	12.89	13.17	15.73
Std. Dev.	1.26	4.30	3.36	0.62	0.79	0.86
CoV (%)	9.59	21.98	23.1	4.80	5.97	5.48
No.	6	6	6	6	6	6

atmospheres follows the observed patterns for each of the laboratories with a mean of 14.63ppb and a coefficient of variation of 11.25%. The highest carbonyl concentrations were observed in the early hours with a gradual decrease in its levels in the afternoon.

In order to obtain the background information for the carbonyl levels for all the laboratories its mean concentration at hourly intervals and its distribution is as shown in Fig 1 with a gradual decrease in its value at 008hrs to a mean value of 14ppb. Figs2 &3 show the hourly mean carbonyl concentrations in each of the six laboratories the determinations were carried out. Distinct periods of high carbonyl concentrations corresponding to low or no reactions with OH, HO_2, NO_3 and Photolysis at night time preceding the early hours when the reactions of OH, HO_2, NO_3 and Photolysis were low. However during daylight hours, all these factors come into play, hence the observed low carbonyl concentration.

The organic and the organic research laboratories showed mean carbonyl levels in excess of 19 and 17ppb respectively with their means and standard deviations as shown in Table1. The museum laboratory where most of the biological specimens preserved in formaline solutions are stored also recorded a high level of carbonyl in its atmosphere. Comparing the carbonyl levels in organic laboratory with others, except for the research laboratory there appeared some levels of significance ($P \leq 0.05$). The same observation holds for the research and the remaining laboratories. Organic compounds may have impacts on human health through direct mechanisms in addition to their indirect impacts through photochemical formations (Derwent, 1995). Some organic compounds affect the human senses through their odour, some others exert a narcotic effect, and certain species are toxic (WHO, 1987) and some concern should be expressed about organic compounds, which could induce cancer in the human population (Fuhrer and Acherman, 1994).

The control of air toxics is a national and an international activity that should involve international forums as some of the commonly used important chemicals (benzene, formaldehyde, poly-nuclear aromatic hydrocarbons, polychlorinated biphenyl compounds and dioxins) are air toxics that are widely distributed in the ambient laboratory atmosphere.

CONCLUSION

Thus as expected the carbonyl level in the physical laboratory appeared the least .The results from the organic and museum laboratories suggest that the carbonyl levels in these locations lie close to the value expected in equilibrium with atmospheric carbonyl. These values could be higher by the presence of carbonyl of anthropogenic origin. The amounts of carbonyl in the samples collected from these laboratories were less than expected but it is anticipated that the influence of OH, HO_2, NO_3 and Photolysis could have drastically reduce their carbonyl levels. It would seem therefore that despite the magnitude of the carbonyl released in these laboratories they may not be large enough to effect significantly their carbonyl levels.

REFERENCES

Ajax, R. L., Combe, C. J and Upham, J. B., 1967. The Effects of Air Pollution on the Fading of Dyed Fabrics. J Air Pollution Assoc.17: 220-224.

Altschuller, A. P., 1983. Review: Natural Volatile Organic Substances and Their Effects on Air Quality in the United States.Atmos.Environ.17: 2131-

Anderson, 1970. Europe's Crumbling Cathedrals and the 20th Century. The Sunday Home News New Brunswick, NJ. P, D5.

Ayodele; J.T., Cooksey, B. G., Ottaway, J. M. and Campbell, W.C., 1987. Automatic spectrophotometric Titration: Determination of carbonyl in some industrial samples Nig Journal of Scientific Research 1 35-40.

Ayodele, J. T and Mohammed, M. I., 2001. Sampling and analysis of sulphur dioxide in the Kano municipality atmosphere. Tropical Journal of Environmental Reasearch.3: 209-216.

Ayodele, J. T. and Mohammed. M. I., 2003. Determination of ozone in Kano municipality air. Journal of Environmental Sciences. In press.

Bartkiwicz, S. A. and Kenyon, L.C., 1963. Automated Determination of Trace Carbonyls Anal Chem 35: 422-423

Cowell, D. B. and Selby, B. D., 1963. Titration of weak Bases in Acetic-anhydride Analyst 88:974-976.

Derwent, R.G., 1995. Sources, Distribution and Fates of VOCs in the Atmosphere .In Hester, R.E and Harrison, R.M, Eds Issues in Environmental Science and Technology. "Volatile Organic Compounds in the Atmosphere" The Royal Society of Chemistry, Cambridge, UK. PP1-15.

Duke, F. R., 1944. Colour test for Carbonyl Group. Ind Eng.Chem.Anal.Ed 16:110.

Frank, N. R, 1964. Studies on the effect of acute exposure to sulphur –dioxide in human subjects. Proc.Roy.Soc.Med. 57: 1029-33.

Fuhrer, J and Acherman, B., 1994. Critical Levels for Ozone, Schriftenreihe der FAC Liebefeld Number16, Swiss Federal Research Station for Agricultural Chemistry and Environmental Hygiene, Liebefeld-Ben, Switzerland.

Goddu, R. F., 1958. Near-infrared Data on oximes at 2.78 microns. Anal.Chem 30:1707-1708

Goldman, F. H. and Yagoda, H., 1943. Ind.Eng.Chem.Anal. Ed 15: 377-378.

Grosjean, D., 1982. Formaldehyde and Other Carbonyls in Los Angeles Ambient Air.*Environ*.Sci.Tech.16: 254.

Hanna, J. G., 1966. Carbonyl-Chemical and Physical methods of Analysis in Saul Patai Ed The chemistry of carbonyl group. Interscience, London.

Heiman, H., 1961. Effects of Air Pollution on Human Health. WHO air pollution monograph series.46: 159-220.

Holbrow, G. L., 1962. Atmospheric Pollution: its measurement and some effects on paint. J. Oil Colour Chem. Assoc.45:701-718.

Horowitz, A and Calvert, J. G., 1982. Wavelength Dependence of the Quantum Efficiencies of the primary Processes in Acetaldehyde Photolysis .J .Phy. Chem.86: 3105

Huess, J.M and Glasson, W.A (Hydrocarbon reactivity and eye irritation.Environ.Sci.Technol. 2:1109.

ICI Imperial Chemical Industries, 1969. Procedures for the determination of carbonyl by Hot Oximation: HOC/AR/5A/2.

Iddles. H. A., Low, H. W., Rosen, B. D and Hart, R.T., 1939. Determination of Carbonyl Compounds. Ind. Eng.Chem.Anal.Ed.11: 102.

Jungnickel, J. L and Forbes, J. W., 1963. Quantitative measurement of hydrogen types by integrated nuclear magnetic resonance intensities. Anal.Chem.35: 938-942.

Koren, H., 1991. Air Quality Management in Handbook of Environmental Health and Safety Principles and Practices Vol II 2nd Edition. Lewis Publishers CRC Press Inc. Florida U.S.A Chpt I.

Lloyd, A. C., 1979. Tropospheric Chemistry of Aldehydes, in Chemical Kinetic Data Needs for Modeling the Lower Troposphere J.T. Herron, R.E, Huie and J.A Hodgeson Eds; National Bureau of Standards Spec. Pub 557pp27-48.

Marnett, L. J., Hurd, H. K., Hollstein, M. C., Levin, D. E., Esterbauer, H. and Ames, B. N., 1985. Naturally occurring carbonyl compounds are mutagens in Salmonella Tester Strain TA104. Mutat.Res.148: 25.

Mitchell, J. M., Smith, D. M and Bryant, W. M. D., 1941. Journ. Amer Chem. Soc.63: 573

Rees, H. L and Anderson, D. H., 1949. Determination of Benzaldehyde in Benzyl Alcohol. Anal.Chem. 21:989-991.

Piccot, S. D., Watson, J. J and Jones, J. W., 1992. Journ. Geophys Res. 97: 9897.

Sensabough, A. J., Cundiff, R. H. and Markunas, P.C., 1958. Non-aqueous Titration of 2 4-Dinitrophenylhydrazones. Anal.Chem.30: 1445-1447.

Salvin, V. S., 1963. Effect of air pollutant on Dyed fabrics. J. Air Pollution Control Assoc 13:416-422

Tenney, H. M., 1958. Selectivity of various liquid substrates used in gas chromatography. Anal.Chem.30: 2-8.

Tice, E. A., 1962. Effects of air pollution on the atmospheric Corrosion Behaviour of Some Metals and Alloys. J. Air Pollution Control Assoc.12: 553-559.

WHO, 1987. World Health Organization, Air quality guidelines for Europe. European Series no 23 WHO Regional Publications, Copenhagen.

Wilson, K. W., 1958. Fixation of Atmospheric Carbonyl Compounds by Sodium Bisulphite. Anal.Chem. 30: 1127-1129.

Wolff, R.K; Dolovich, M; Rossman, C.M and Newhouse, M.T., 1975. Sulphur dioxide and tracheobronchial clearance in man. Arch Environ.Health.30: 521-7.

Yocom, J. E. and McCaldin, R. O., 1968. Effects of air Pollution on materials and the Economy in Stern, A.C. (Ed) Air Pollution. Academic Press NY Vol I P617