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Aldehyde, Ketone and Methane Emissions from Motor Vehicle Exhaust: A Critical Review

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Review Article

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ABSTRACT

Recent data indicate that, in many countries, mobile sources are responsible for the largest portion of emissions of aldehydes, ketones and certain other air toxic pollutants. These air toxic pollutants along with methane are either carcinogenic or pose significant human health threat. These pollutants also add to global warming in a substantial way. This paper gives an overview of their properties, basic chemistry and conditions of formation in internal combustion engines. Again worldwide many countries are promoting alternative fuels to tackle the crisis of traditional fuel. But the impact of this movement toward alternative fuels with respect to toxic emissions has not been well studied. Therefore, in this paper the analysis on the effects of engine operation and fuelling parameters is also reviewed with specific references in gasoline, diesel, natural gas, liquefied petroleum gas, ethanol blended petrol and Biodiesel fuelled engines. This is accompanied by the review of the studies of the performance of exhaust catalytic converters with respect to aldehydes, ketones and methane. Additionally, aldehydes, ketones and methane detection and measurement methods are summarized and analyzed from the view of their applicability to exhaust gas analysis.

Keywords: *Automobile; uncontrolled emission; aldehyde; ketone; methane; health problem; engine;*

1. INTRODUCTION

The mechanism of aldehyde, ketone and methane formation in engines and the effect on human health and environment are the subjects of this study. These pollutants also substantially add to global warming, which is a major concern worldwide (Mondal et al., 2011). This study reviews the aldehydes, ketones and methane emissions from engine exhaust using different fuels (gasoline, diesel, natural gas, liquefied petroleum gas, blended Biodiesel and ethanol). The presentation of this review study is in the order of aldehydes, ketones and methane properties, their environmental and health effects (section 2) followed by the chemistry of their formation (section 3). Section 4 discusses the effect of engine design, mode of operation and fuel formulation (gasoline, diesel, natural gas, liquefied petroleum gas, blended Biodiesel and ethanol) on aldehydes, ketones and methane emissions. The effect of catalytic converter is also discussed in the study. Finally the recent methods of aldehyde and methane sampling/ analysis are discussed.

1.1 Properties of Aldehydes, Ketones and Methane Emissions

Aldehydes and ketones are partially oxygenated organic compounds containing carbonyl group. An aldehyde functional group consists of a carbon atom bonded to a hydrogen atom and double-bonded to an oxygen atom ($\text{O}=\text{CH}-$). Whereas a ketone functional group contains a carbonyl group ($\text{C}=\text{O}$) bonded to two other carbon atoms in the form (Clark, 2003). The properties of the most common aldehyde and ketones in engine exhaust emissions are presented in Table 1.

2. HEALTH EFFECTS AND ENVIRONMENTAL EFFECTS

Aldehyde vapours effects on human health include irritation of eye, throat, nose, asthma, pulmonary function. Thresholds for sensory irritation determined by controlled exposure studies, are reported as $0.6\text{-}1.2\text{ mg/m}^3$ [$0.5\text{-}1.0\text{ ppm}$] (formaldehyde); $0.1\text{-}0.2\text{ mg/m}^3$ [$0.04\text{-}0.09\text{ ppm}$] (acrolein); and 90 mg/m^3 [50 ppm] (acetaldehyde) (Anonymous¹, 2000). These levels are substantially higher than the generally reported ambient air concentrations of these vapours. The California emission standard released current and future threshold limits for Formaldehyde and methane emissions in various category light duty vehicles which are presented in Table 2 (Anonymous², 2000).

Formaldehyde is classified as a probable human carcinogen by IARC (2006) and the US EPA. Epidemiological studies of occupationally-exposed subjects have suggested a causal association of high exposure levels with the development of nasopharyngeal cancers, whilst inhalation bioassays in rats showed significant incidence of tumours of the nasal respiratory epithelium at exposure levels $\geq 6.9\text{ mg/m}^3$ [5.6 ppm], with a disproportionately high tumour incidence at higher exposures ($\geq 12\text{ mg/m}^3$ [10 ppm]). According to a study by Winebrake et al. (2001), deaths related to Cancer Unit Risk Estimates of these emissions are quite considerable (Table 3).

The effect of these emissions on environmental ozone formation potential caused an increased attention on their regulation. Formaldehyde is a very reactive organic chemical with a high tendency to form ozone by photochemical oxidation. Lowi and Carter (1990) developed Maximum Incremental Reactivity (MIR) method to analyze and evaluate the potentiality of atmospheric ozone formation. Degobert and Marshall (1995) presented MIR values for methane and selected aldehydes/ketones to represent their ozone forming

potential compared with other non-methane organic gases (NMOG) which are shown in Table 4.

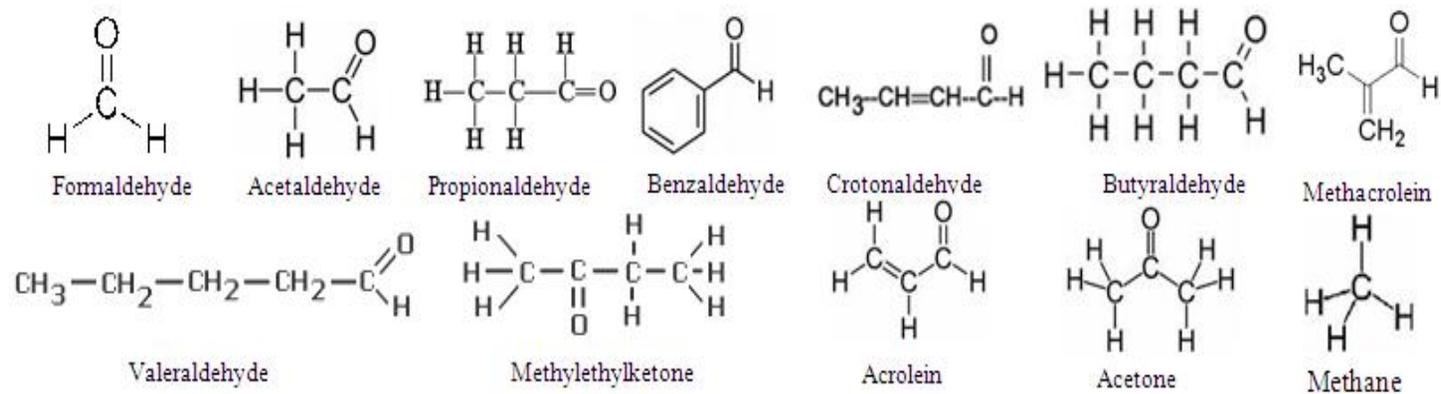


Fig.1. General Formula for Aldehydes, Ketones and Methane

(Source: commons.wikimedia.org: Accessed on 25th Feb 2009)

Table 1. Properties of methane and the some selected aldehydes and ketones

(Source: <http://en.wikipedia.org/wiki/>)

Sl. No.	Name of the Methane/ Aldehyde/ Ketone	IUPAC Name	CN umber	Chemical Formula	Molecular weight g/mol	Density kg/m ³	Melting point °C	Boiling point °C
1	Methane			CH ₄	16.04	422.62	-182.5	-161.6
2	Formaldehyde	Methanol	1	HCHO	30.03	815	-92	-21
3	Acetaldehyde	Ethanol	2	CH ₃ CHO	44.05	778	-123	20
4	Acetone	2-Propanone	3	CH ₃ COCH ₃	58.08	792	-95	57
5	Acrolein	Propanal	3	CH ₂ CHCHO	56.07	841	-86	53
6	Propionaldehyde	Propanal	3	CH ₃ CH ₂ CHO	58.08	797	-81	48
7	n-Butyraldehyde	Butanal	4	CH ₃ (CH ₂) ₂ CHO	72.11	803	-97	75
8	Methacrolein	2-Methyl- 2-Propanal	4	CH ₂ CCH ₃ CHO	70.09	843	-81	68
9	Crotonaldehyde	2-Butanal	4	CH ₃ CHCHCHO	70.09	852	-74	102
10	Methyl ethyl ketone	2-Butanone	4	CH ₃ COCH ₂ CH ₃	72.11	805	-86	80
11	n-Valeraldehyde	Pentanal	5	CH ₃ (CH ₂) ₃ CHO	86.13	808	-91	103
12	n-Capronaldehyde	Hexanal	6	CH ₃ (CH ₂) ₄ CHO	100.16	814	-56	128
13	Benzaldehyde	benzenecarbal aldehyde	7	C ₆ H ₅ CHO	106.13	1046	-26	179
14	m-tolualdehyde	MethylBenzene carbaldehyde	8	CH ₃ C ₆ H ₄ CHO	120.15	1030	-35	197-202

Methane is not toxic and the most significant hazard associated is that after inhalation it results in oxygen deficiency and respiratory difficulty causing headache, ringing in ears, dizziness, drowsiness, unconsciousness, nausea, vomiting, and depression of all the senses. At high concentrations, unconsciousness or death may occur (Anonymous², 2009).

Table 2. Summary of proposed emissions regulations of Californian standards for light-duty vehicles

Category	CO (g/mile)	NMHC/NMOG ¹⁾ (g/mile)	NOx (g/mile)	Formaldehyde ³⁾ (g/mile)	Particulates ⁴⁾ (g/mile)
Tier I gasoline	3.4	0.25 (0.31)	0.4 (0.6)	--- (---)	--- (---)
Tier I diesel	4.2	-0.31	-1	--- (---)	-0.08
TLEV	3.4 (4.2)	0.125 (0.156)	0.4 (0.6)	0.015 (0.018)	-0.08
LEV	3.4 (4.2)	0.075 (0.090)	0.2 (0.3)	0.015 (0.018)	-0.08
ULEV	1.7 (2.1)	0.04 (0.055)	0.2 (0.3)	0.008 (0.011)	-0.04
ZEV	0	0	0	0	0

1) NMOG= reactivity corrected values for alternative fuelled vehicles

2) Tier I gasoline & diesel regulations are in terms of Non methane hydrocarbons (NMHC)

3) flexible-fuel vehicles only

4) diesels only

Limits for 50,000 miles with 100,000 miles in parentheses

Table 3. Cancer Unit Risk Estimates and Annual Expected Cancer deaths Caused by Exposure to Mobile Source Air toxics (Winebrake et al., 2001)

Pollutant	CURE ^b ($\mu\text{g}/\text{m}^3$) ⁻¹	Annual Expected Cancer Deaths (U.S. Total)			
		1990	1995	2000	2010
Acetaldehyde	2.2×10^{-6}	5.3	3.6	2.8	3.0
Benzene ^c	8.3×10^{-6}	70	43	35	35
1,3-Butadiene ^d	2.8×10^{-4}	304	209	176	204
Formaldehyde	1.3×10^{-5}	44	28	21	22
Total: four air toxics		423	283	235	264
Diesel PM ^e	1.7×10^{-5}	109	66	39	27
Diesel PM ^f	3.0×10^{-4}	1923	1165	688	476

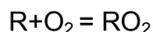
Table 4. Maximum Incremental Reactivity values of methane and selected aldehydes/ketones

Component	MIR (g O ₃ /g NMOG)
Methane	0.015
Formaldehyde	7.15
Acetaldehyde	5.52
Acrolein	6.77
Propionaldehyde	6
Acetone	0.56
n-Butyraldehyde	5.26
Crotonaldehyde	5.41
Methyl-ethyl-ketone	1.18

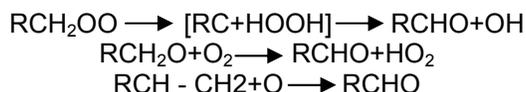
3. ALDEHYDE AND KETONE FORMATION

The ambient air contain aldehydes and ketones in significant concentrations compared to engine exhaust (Anonymous¹, 2009). Any aldehydes and ketones appearing in exhaust gases are formed from the engine and exhaust system. Wagner and Wyszynski (1996) reported that, in the basic aldehyde formation chain reactions, the important carriers are alkyl radicals (produced on combustion of hydrocarbons) which are formed by cleavages of C-C or C-H bonds of hydrocarbons. At high temperatures, dehydrogenation by oxygen and presence of other combustion related radicals influence the cleavages processes.

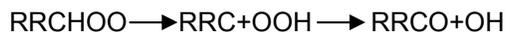
Regarding the higher aldehydes, the general mechanism is based on the formation of the alkyl radicals (RO₂).



This alkyl radical is the precursor for the further reactions, including intra-molecular hydrogen abstractions and decomposition. Finally leading to the following aldehyde formation reactions:



In the above three equations, first are based on the alkyl radicals and the third one is based on the alkenes. The ketone formation also starts from the alkyl-peroxy radicals RO₂. The ketone reaction equation is shown below:



More detailed information about combustion reactions is given in the literature by Miller et al, 1990.

Incomplete combustion due to partial oxidation of the un-burnt hydrocarbon fuels also produces aldehyde emission. Sources of un-burnt hydrocarbons are given by Raine et al. (1997). These are summarized below:

a) *Flame quenching:*

Flame quenching at the cool combustion chamber walls, which results in a thin layer of unburned fuel/air mixture close to the wall after flame passage.

b) *Crevices mechanism:*

Crevices in the combustion chamber wall which are too narrow for flame to enter leads to the fuel/air mixture escaping from the primary combustion processes.

c) *Absorption and desorption of fuel vapour in the oil layer and deposits:*

The oil layer presents on the combustion chamber wall and deposits formed on the combustion chamber absorb fuel vapour during intake and compression processes, and this fuel is desorbed during the expansion and exhaust processes.

d) *Gas-phase quenching:*

It has been created when the engine is operating under extreme conditions of equivalence ratio and spark timing.

e) *Leakage of unburnt mixture through the valve:*

Valve leakage can occur which leads to a small fraction of fuel/air mixture escaping the primary combustion processes.

f) *Unevaporated liquid fuel in the cylinder:*

For liquid fuels, an important process which could contribute to hydrocarbon emissions is the liquid fuel within the cylinder which fails to evaporate and mix with sufficient air to burn before the end of combustion, particularly during the engine starting and warm-up process.

In the following sections the oxidation of hydrocarbons is discussed. For this purpose the complex engine system can be divided into two parts: the combustion chamber and the exhaust system. Inside the cylinder, a fraction of hydrocarbons is oxidized during the expansion and exhaust process. The products are carbon dioxide, carbon monoxide and hydrocarbons containing oxygen like Aldehydes, ketones, ethers and alcohols.

Heywood, 1988 states that the oxidation of hydrocarbon is formed by 2 steps, namely,

Step 1: In-cylinder mixing and oxidation of hydrocarbon and

Step 2: Oxidation in the exhaust system.

Figure 2 denotes the major key factors and engine variables that influence the oxidation of hydrocarbon emissions. It is through each of these mechanisms that fuel or fuel-air mixture escapes the primary combustion process. That fuel must then survive the expansion and exhaust processes and pass through the exhaust system without oxidation if it is to end up in the atmosphere as HC emissions. The rate of unburned HC with the hot bulk cylinder gases, the temperature and the composition of the gases with the subsequent temperature –time and composition- time histories of the mixture will govern the amount of in-cylinder oxidation that occurs. The distribution of these HC around the combustion chamber is non-uniform (and changes with time); they are concentrated close to the walls of the chamber. The fraction of these HC that will exit the chamber during the exhaust process will depend on the details of the in-cylinder flow patterns that take them through the exhaust valve. Overall, the magnitude of the residual fraction will be one major factor; the residual gas is known to be much richer in HC than average exhaust. In particular, the flow patterns in the cylinder toward the exhaust valve will be important. Finally, a fraction of the unburned HC which

leave the cylinder through the exhaust valve will burn up within the exhaust system. Gas-phase oxidation in the exhaust ports and hotter parts of the exhaust manifold is significant. The amount depends on the gas temperature, composition, and residence time. If catalysts or a thermal reactor are included in the exhaust system, very substantial additional reduction in HC emission levels may occur. The ambient temperature might be sufficient for partial oxidation, but not high enough for a complete combustion.

Cylinder left out exhaust bulk gases are subjected to oxidation in the exhaust manifold (as shown in Fig 3). Regarding engine parameters which influence the oxidation are speed, spark timing, mixture composition, compression ratio, air /fuel ratio, load and heat losses.

Due to slow chemical reaction during delay period in the diesel engine, aldehydes are formed as intermediate products. In some parts of spray after the initial reaction aldehydes will be formed. These aldehydes may be oxidized in the later part of the cycle, if the mixture temperature is high, and if there is sufficient oxygen.

3.1 Aldehydes and Ketones in Engines

In the section, the effects of fuel compositions, engine design and selected engine parameters on aldehyde and ketone emissions are presented. The experiments referred in the literature differ in engine designs, test methods, test conditions and fuels. The comparison had been made with the absolute values. However, the measured results can illustrate trends in the aldehyde formation and its correlation with engine, fuel and environmental parameters.

In testing, DNPH and MBTH methods are used for aldehyde analysis and both are wet chemical analysis. The most significant difference is that DNPH gives more information on individual aldehydes where as MBTH is better suited for total aliphatic aldehydes.

3.1.1. Gasoline Engines

3.1.1.1. Aldehyde and ketone emission composition

Shore and Tonkin (1991) presented average values of proportion of individual aldehydes as a fraction of total aldehydes in gasoline fuelled engines. Those values are 44% Formaldehyde, 19% Acetaldehyde, 29% C₁ aldehyde with Acetone, and 5% Benzaldehyde. Characteristic values for current European vehicles tested over FTP and European drive cycle are given by them. For gasoline cars these characteristic values were producing approximately 0.032 – 0.080 g/mile Formaldehyde, 0.032 – 0.080 g/mile Benzaldehyde, 0.016 – 0.032 g/mile of total aldehydes. In India, typical values for current Indian vehicles tested over Indian driving cycle and Modified Indian driving cycle are given in Table 5 by ARAI (2007).

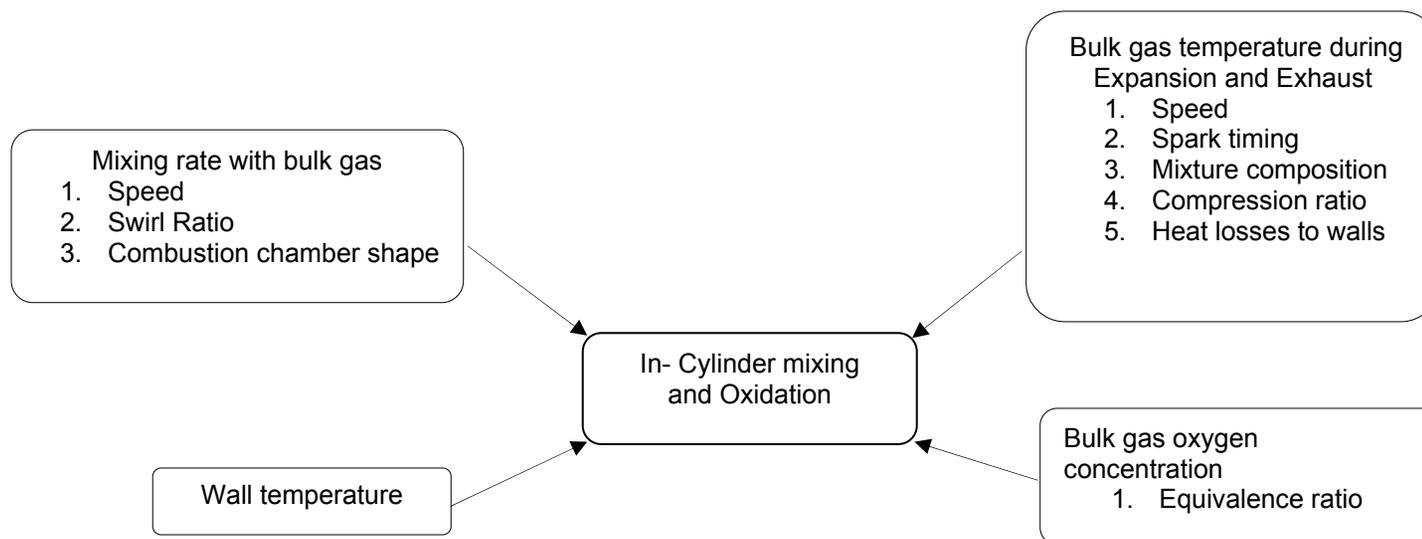


Fig. 2. In-cylinder mixing and oxidation of hydrocarbon

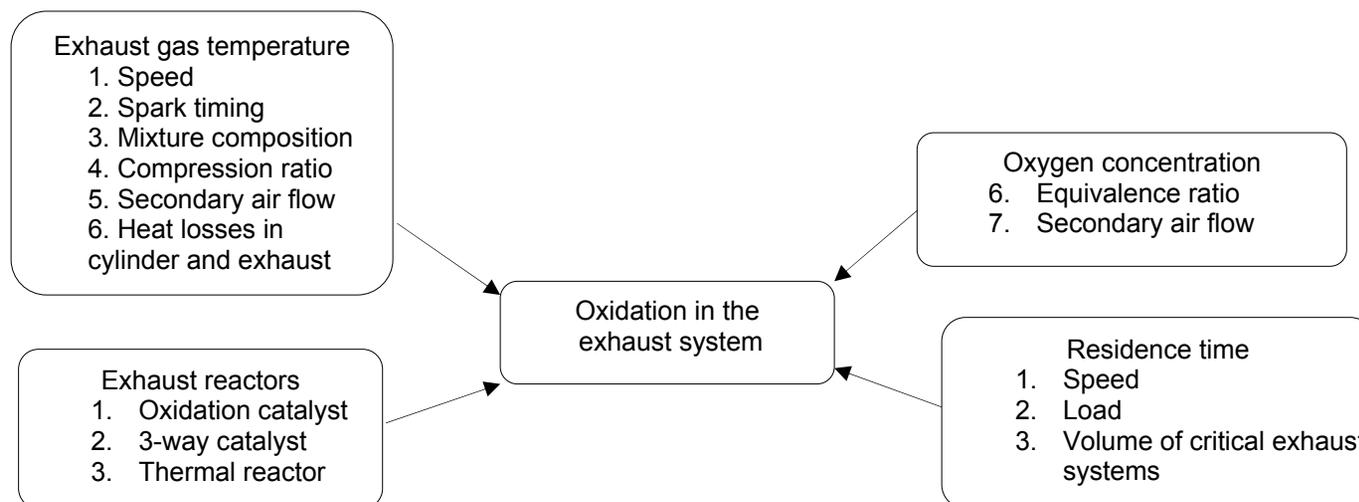


Fig. 3. Oxidation in the exhaust system

Table 5. Vehicle category Vs aldehyde emissions in Indian study

Sl. No.	Vehicle category	Formaldehyde (mg/km)	Acetaldehyde (mg/km)	Total aldehydes (mg/km)
01	Two wheeler (2 stroke)	0.002 - 0.1048	0.0001 – 0.0576	0.001 – 0.1716
02	Two wheeler (4 stroke)	0.001 - 0.0103	0.0015 – 0.0053	0.0022 – 0.0173
03	Three wheeler (petrol)	0.0062 – 0.0132	0.0012 – 0.0125	0.0224 – 0.609
04	Three wheeler (diesel)	0.0072 – 0.0261	0.0025 – 0.0125	0.0233 – 0.0609
05	Three wheeler (CNG)	0.0055 – 0.0072	0.0071 – 0.0072	0.0085 – 0.0149
06	Three wheeler (LPG)	0.0022 – 0.0075	0.004 – 0.0072	0.0097 – 0.0142
07	Four wheeler passenger cars (petrol)	0.0003 – 0.0181	0.0008 – 0.0109	0.0079 – 0.0453
08	Four wheeler passenger cars (diesel)	0.0108 – 0.0889	0.0003 – 0.003	0.0131 – 0.1244
09	Four wheeler passenger cars (CNG)	0.0007 – 0.0108	0.0011 – 0.0022	0.0018 – 0.0130
10	Four wheeler passenger cars (LPG)	0.0005 – 0.0145	0.0011 – 0.0101	0.0021 – 0.0245
11	LCV (diesel)	0.0028 – 0.1975	0.0059 – 0.0117	0.0222 – 0.2957
12	HCV (diesel)	0.0104 – 0.1015	0.0029 – 0.0197	0.0458 – 0.1458

Source: Air Quality Monitoring Project-Indian Clean Air Programme, ARAI, 2007

3.1.1.2 Effect of gasoline reformulation

Planned future changes, such as the CAA (Canadian Automobile Association), 1/1/1998 Complex Model specifications that are based on several major ongoing government/industry gasoline and emission research programmes, are more likely to provide unambiguous environmental improvements. One of the major problems is the nature of the ozone-forming reactions, which require several components (aldehydes and ketones) to be present. Reformulation does not always lower all emissions, as evidenced by the following aldehydes from an engine with an adaptive learning management system shown in Table 6, 7, 8.

The type of exhaust catalyst and management system can have significant effects on the emissions. With increase in the methyltertiarybutylether (MTBH) content of the fuel there will be an increase in formaldehyde emissions (Warner-Selph and Harvey, 1990). Acetaldehyde increases when ethanol or ethyltertiarybutylether (ETBH) are blended with gasoline (Reuter et al., 1992).

Wigg (1973) reported that increasing the aromatic content of the fuel decreased formaldehyde emissions. Rajan and Kappos (1986) reported that the use of a synthetic gasoline, made from oil shale and coal, in a normal gasoline engine (four-cylinder, 2.3 litre engine displacement, no catalyst) decreases the formaldehyde emissions and increases the acetaldehyde emissions slightly compared to normal gasoline. It was also stated that formaldehyde emissions for aliphatic fuels were five times higher than for the aromatic fuel. A study conducted by How-Ran Choa et al. (1998) in 1.5L Mazda engine fueled separately with a premium gasoline and a 95 unleaded gasoline, along with three popular additives, and was operated on four different speeds. The results show that, with increased engine speed, both concentrations and emission factor of aldehyde dropped, while the emission rate increased. The total emission rate of aldehydes from the premium gasoline was 14% higher than from the 95 unleaded gasoline. Additives increased the aldehyde emission by 5 to 55%, especially in formaldehyde, acrolein, and Crotonaldehyde. Pouloupoulos et al. (2001) studied that the order from the easiest to the most resistant to oxidation compound was: Alkene>Aromatic>Aldehyde>Ketone>Alkane.

Table 6. FTP-weighted emission rates (mg/mi)

Aldehydes	Gasoline	Reformulated
Formaldehyde	4.87	8.43
Acetaldehyde	3.07	4.71

Table 7. FTP-weighted emission rates (mg/mi) with effect of catalyst

Catalyst	Total Carbonyls	
	Gas	Reform
Non-Catalyst	174.50	198.73
Oxidation Catalyst	67.08	76.94
3-way Catalyst	23.93	23.07

Table 8. FTP-weighted emission rates (mg/mi) with noncatalyst and oxidation catalyst

Aldehydes	Formaldehyde		Acrolein		Acetaldehyde	
	Gas	Reform	Gas	Reform	Gas	Reform
Noncatalyst	73.25	85.24	11.62	13.20	19.74	21.72
Oxidation Cat.	28.50	35.83	3.74	3.75	11.15	11.76

(Source: rec. autos. tech, autos/gasoline-faq/part2, 17 November 1996, Version: 1.12)

3.1.1.3 Effect of engine design

A comparison of different gasoline engine designs is given by Gabele et al. (1977). The effect of Lean, Stratified, Wankled engines and an oxidation catalyst system on individual aldehyde emissions was tested with the DNPH method over different driving cycles. The stratified charge engine has nearly 50 percent lower aldehyde emissions (31.8 mg/miles) than Lean burn engine (75.5 mg/miles). The Wankled engine produces the largest amount of aldehyde emissions (131.7 mg/miles). The oxidation catalyst equipped engine has the lowest aldehyde emission value of 22.2 mg/miles. In those test the aldehyde emissions increases with increasing hydrocarbon emissions. The effect of increasing equivalence ratio ($\phi = 0.72$ to $\phi = 1.16$) the aldehyde concentration in the engine out emissions before catalyst decreased from 15 to 20 ppm.

3.1.2 Diesel engines

3.1.2.1 Aldehyde and Ketone emission composition

Standardized tests were performed in four diesel light duty commercial vehicles, using a frame dynamometer and test procedure FTP-75. The pollutants were analyzed by high performance liquid chromatography. Results have shown acetaldehyde emission ranged from 5.9 to 45.4 mg/km, and formaldehyde emission from 16.5 to 115.2 mg/km. The average emission for total aldehyde was 58.7 mg/km, ranging from 22.4 to 160.6 mg/km. The proportion between the two substances remained constant, close to 74% for formaldehydes and 26% for acetaldehydes.

The emission of diesel vehicle aldehydes was significant when compared with actual spark ignition vehicle emissions, or with the foresee limit for Otto cycle vehicles in Brazilian legislation. Establishing emission limits for these substances also in diesel vehicles is imperative in the light of the vehicle fleet growth, toxicity of these compounds, and their contribution as precursors in ozone gas formation reactions in low troposphere. (Rui de et al, 2005)

3.1.2.2 Effect of diesel fuel reformulation

Weitmann et al. (1988) investigated the effects of diesel fuel composition on aldehyde emissions from a VW 1.6 litre four cylinder engine in a naturally aspirated and a turbocharged version. The total aldehyde content was measured using the MBTH method in FTP driving cycles. With the increasing the cetane number, the aldehyde emissions were decreased from the both types of engine, as the cetane number correlates directly with the fuel density and aromatic content.

3.1.2.3 Effect of diesel engine design and operating parameters

Dietzmann and Lee, 1984 analyzed the effect of induced faults at diesel forklift engines with the DNPH method. Increasing the intake air restriction increases the aldehyde values dramatically from 0.167 g/kWh under standard conditions to 2.682 g/kWh. The same effect could be observed by adjusting the injection pump timing from 17 degree BTDC to 13 degree BTDC and by increasing the back pressure in the exhaust manifold. It was found that at low load conditions specific formaldehyde emissions is high.

3.1.3 Natural gas engines

Weaver, 1989 presents that the principal aldehyde in the exhaust of natural gas fuelled engine is formaldehyde and natural gas is mainly consists of Methane, C2 (ethane, ethene), C3 (propane, propene); no significant emissions of other hydrocarbons (except for carburetor-based technology). The carburetor-based technology vehicles gives high non-regulated hydrocarbons levels, with ethane (732mg/km), C3, C4, C5, C6, acetaldehyde (150mg/km) and acrolein (about 10 times higher than other CNG technologies). Comparing the aldehyde emissions from a natural gas engine with gasoline fuelled engines shows an increase of 20 percent in the formaldehyde value when the engine is fuelled with natural gas, while the catalyst conversion efficiency for formaldehyde is between 96 and 98 percent. Olsen and Mitchell (2000) observed that the ratio of formaldehyde to Total Hydro Carbon concentration is roughly 1.0–2.5 percent for a very wide range of large bore engines and operating conditions.

3.1.4 Liquefied petroleum gas engine

Improper design, blocking and clogging of the flue vent and insufficient combustion air result in improper combustion and the emission of aldehydes, hydrocarbons, and other organics. The exhaust gases of a LPG-fuelled engine contain formaldehyde, acetaldehyde, propionaldehyde, acrolein and acetone. The engine was run under stoichiometric, lean and rich air/fuel conditions. Table.9 shows concentration of aldehydes and ketones in exhaust gases of LPG-fuelled engines. Table 9 shows, Aldehyde and ketone levels are increasing when increasing the Air/fuel ratio (Rutten et al., 1988)

Table 9. Concentration (in ppmv) of aldehydes in exhaust gases of LPG fuelled engines

Parameters	Rich	Stoichiometric	Lean
Air/fuel ratio	14.6	15.6	16.6
Formaldehyde	2.8	4.5	17
Acetaldehyde	1.3	1.6	2.9
Propionaldehyde	0.06	0.1	0.13
Acrolein	0.03	0.035	0.07
Acetone	0.17	0.18	0.27
Sum of C1-C3 aldehydes	4.2	6.25	20.1

3.1.5 Ethanol blended gasoline engines

Antunes and Ricardo (2002) investigated an ethanol-fueled vehicle on a chassis dynamometer, following a standard urban cycle test procedure. The test simulated a medium-distance trip in an urban area, of approximately 5.8 km, with a warmed-up engine. The running parameters tested in the experiments were: the mixture equivalence ratio, the additional air flow used in decelerations (dash pot), the fuel interruption function in decelerations (cutoff), and gear-change speed. The results pointed to a reduction on aldehyde emissions for lower gear-change speeds and for richer fuel mixtures.

The results of this project for the 1999 fleet composition show that, when compared to use of neat petrol, use of 10% v/v ethanol/petrol blend has the emission of formaldehyde increases by approximately 25%; acetaldehyde increases by approximately 180% and acrolein by about 5% (ERDC, 2002).

Roger.magnusson (2002) investigated oliphatic gasoline and ethanol-blended gasoline which are intended for use in small utility engines (recently introduced on the Swedish market). The objective of this investigation was to study carbonyl emissions and regulated emissions from a two-stroke chain saw engine using ethanol, gasoline, and ethanol-blended gasoline as fuel (0%, 15%, 50%, 85%, and 100% ethanol). The effects of the ethanol-blending level and mechanical changes of the relative air/fuel ratio, lambda, on exhaust emissions were investigated, both for oliphatic and regular gasoline. Formaldehyde, acetaldehyde, and aromatic aldehydes were the most abundant carbonyls in the exhaust. Acetaldehyde dominated for all ethanol-blended fuels (1.2-12 g/kWh, depending on the fuel and lambda). Formaldehyde dominated for gasoline (0.74-2.3 g/kWh, depending on the type of gasoline and lambda). The main effects of ethanol blending were increased acetaldehyde emissions (30-44 times for pure ethanol), reduced emissions of all other carbonyls except formaldehyde and acrolein (which showed a more complex relation to the ethanol content), reduced carbon monoxide (CO) and nitrogen oxide (NO) emissions, and increased hydrocarbon (HC) and nitrogen dioxide (NO₂) emissions.

The main effects of increasing lambda were increased emissions of carbonyls. When the two types of gasoline were considered, benzaldehyde and tolualdehyde could be directly related to the aromatics or olefins content of gasoline. Acrolein, propanal, crotonaldehyde, and methyl ethyl ketone mainly originated from aromatics or olefins, while the main source for formaldehyde, acetaldehyde, acetone, methacrolein, and butanal was saturated oliphatic hydrocarbons.

3.1.6 Biodiesel blended diesel engines

Carbonyl emissions were evaluated on a heavy-duty diesel engine fueled with pure diesel (D) and biodiesel blends (v/v) of 2% (B2), 5% (B5), 10% (B10), and 20% (B20) (Sergio and Garcia, 2008). The tests were conducted using a six cylinder heavy-duty engine, typical of the Brazilian fleet of urban buses, in a steady-state condition under 1000, 1500, and 2000 rpm. Using average values for the three modes of operation benzaldehyde showed a reduction on the emission (-3.4% for B2, -5.3% for B5, -5.7% for B10, and -6.9% for B20) and all other carbonyls showed a significant increase: 2.6, 7.3, 17.6, and 35.5% for formaldehyde; 1.4, 2.5, 5.4, and 15.8% for acetaldehyde; 2.1, 5.4, 11.1, and 22.0% for acrolein+acetone; 0.8, 2.7, 4.6, and 10.0% for propionaldehyde; 3.3, 7.8, 16.0, and 26.0% for Butyraldehyde.

He et al, 2009 experimented in direct injection turbo charged diesel engine fueled with pure biodiesel and the results indicate that biodiesel-fueled engine almost has triple carbonyls emissions of diesel-fueled engine. The weighted carbonyls emission of 8-mode test cycle of biodiesel is $90.8 \text{ mg (kW h)}^{-1}$ and that of diesel is $30.7 \text{ mg (kW h)}^{-1}$. The formaldehyde is the most abundant compound of carbonyls for both biodiesel and diesel, taking part for 46.2% and 62.7% respectively. The next most significant compounds are acetaldehyde, acrolein and acetone for both fuels. The engine fueled with biodiesel emits a comparatively high content of propionaldehyde and methacrolein. Biodiesel, as an alternative fuel, has lower specific reactivity (SR) caused by carbonyls compared with diesel. Total carbonyls emissions from B20 and B100 are 8% and 32% higher respectively than those from diesel fuel. Formaldehyde is the most abundant carbonyl of the test fuels with 56.5%, 53.9%, and 52.7% contribution to total carbonyls in case of diesel, B20, and B100 respectively. Specific reactivity of carbonyls from the test fuels follow the order as $B20 < D < B100$. (Shah et al., 2009)

3.2 Methane in Engines

Methane is emitted from light duty vehicles due to the incomplete combustion of fuel in the vehicle engine and the incomplete oxidation of engine-out methane in current catalytic after-treatment systems. It is important to recognize, however, that current vehicles produce and emit substantially less methane than their older counterparts and, even in the absence of additional regulation, it is almost certain that future vehicles will exhibit even lower emission rates. Although there are currently no specific emission standards for methane, existing standards for non-methane organic compounds do effectively result in reduced methane emissions through the design and implementation of advanced combustion and catalyst technologies (Anonymous, 2004). Department of energy, Washington DC presented the values for methane from various fueled vehicles in Table 10.

Table 10. Fuel cycle methane emissions per vehicle mile travelled

Fuel cycle stage	Gasoline	Ethanol from corn	Compressed Natural Gas	LPG from oil and gas
	mg/VMT	mg/VMT	mg/VMT	mg/VMT
Vehicle emissions ^{b,c,d}	80	80	900	80

^b Decision Analysis Corporation, "Measurement of Emissions: Greenhouse Gas Estimates for Alternative Transportation Fuels," unpublished final report prepared for the Energy Information Administration (Vienna, VA, December 1995).

^c Greenhouse gas (GHG) emission values from vehicle end-use are revised.

^d The total GHG emission values are revised because vehicle end-use values are revised.

LPG = Liquefied petroleum gases; mg = Milligrams; mmol = Millimoles; VMT = Vehicle mile traveled

Poulopoulos et al. (2001) studied the effect of engine operating conditions on its exhaust emissions and on catalytic converter operation. A 4-cylinder OPEL 1.6 l internal combustion engine equipped with a typical three-way catalyst was used in the study. The highest hydrocarbon and carbon monoxide engine-out emissions were observed at engine power 2–4 HP. These emissions were decreased as the engine power was increased up to 20 HP. Methane exhaust emissions were monitored at engine and catalyst outlet. The concentration of each compound in the catalytic converter effluent was in the range 45–132 ppm. Methane was the most resistant compound to oxidation while ethylene was the most degradable compound over the catalyst.

4. EXHAUST CATALYTIC CONVERTER

Andrade and Antonio (1985) conducted a study, to determine the aldehyde composition of exhaust emissions from two typical Brazilian ethanol fueled vehicles, and to evaluate the effectiveness of three-way-catalytic converter in the reduction of aldehydes emissions. The weighted average emissions (in g/km) of formaldehyde and acetaldehyde by a GM Opal passenger car were 0.046 and 0.246 and for VW Golf vehicle are 0.019 and 0.143. Upon installation of catalysis, weighted reductions of over 70% were observed for both aldehydes.

Aldehydes are developed when primary alcohols (methanol and ethanol) with engine supplied with a high proportion of these alcohols. The methanol conversion rates are higher than ethanol. With platinum alumina, 95% conversion reached at 150°C for methanol and 240°C for ethanol. 95% reduction rate of aldehyde have been observed on thermal reactors and 50 to 80% rates on oxidation catalytic converters or oxidation reduction systems, with virtually total effectiveness on aromatic aldehydes (Degobert and Marshall, 1995).

Grimaldi et al. (1995) presented that formaldehyde was the major compound found most often in the exhaust gases, both with hot and cold engines, although sometimes acetaldehyde was the major compound in exhaust from cold engines. Concentrations of the other substances tested were considerably lower. With a cold engine, those vehicles with or without a catalytic converter and fuelled with 98-octane unleaded gasoline had the highest levels of carbonyl compounds in their emissions (converters do not work efficiently under these conditions). Vehicles without catalytic converters and using super leaded or gas oil (diesel) had lower levels of emissions. When the engine was warmed up and fuelled with 98-octane unleaded gasoline, formaldehyde concentrations in the exhaust gases increased in two types of cars. Concentrations of the other carbonyl compounds decreased when a catalytic converter was present. Using super leaded or gas oil in a warmed-up engine (without a catalytic converter), the amount of formaldehyde also increased, although that of the other compounds did not change much.

5. MEASURING & ANALYZING METHODS

5.1 Aldehyde and ketone analyzing methods

Air-quality standards and pollution-control legislation are generally based on the assumption that exceeding some concentration of any given pollutant will have harmful effects on human health that outweigh any economic disadvantage of imposing regulatory standards. Accurate determination of such "threshold concentrations" demands accurate methods of analysis.

The analytical methods are currently used for aldehydes, including techniques of sampling and calibration, and other available or potentially available methods. In general, the analytical methods for aldehydes are difficult, and much developmental work is needed in accuracy, precision, and applicability of the various measurement methods.

5.1.1 Wet-chemistry spectrophotometric analysis

Wet-chemistry spectrophotometric methods of analysis for aldehydes continue to be the most popular and widely used. The sensitivity associated with the formation of a dye chromophore and the ease of measurement with readily available spectrophotometers are not easily matched by other techniques. Field samples can usually be easily generated with simple equipment. However, spectrophotometric techniques are subject to error. The specificity and degree of completion of the chromophore-forming reaction must be

considered, as well as the stability and standardization of reagents. In many cases, spectrophotometric techniques are slower than more direct measurement methods. To sample air, wet-chemistry spectrophotometric methods are often applied to pre-concentrated samples that are generated with impingers. It is often overlooked that the detection limit for aldehydes in air depends on both the sensitivity of the analytical method and the degree of pre-concentration. If the time or flow rate is changed in sampling with impingers, the detection limit can be changed radically. Typically, aldehydes in air are sampled for 0.5-8 hrs at flow rates of 0.5-2.0 L/min.

Measurements of total aliphatic aldehydes are based on chemical reaction behavior imparted by the presence of the formyl group common to all aldehydes. As with formaldehyde, only wet-chemistry spectrophotometric techniques have been used for sampling total aliphatic aldehydes under field conditions. The application of more sophisticated instrumental techniques to the determination of total aliphatic aldehydes is inadvisable, because it is usually easier and more desirable to identify and measure each specific aldehyde separately (National Research Council, 1981).

5.1.2 3-Methyl-2-benzothiazolone Hydrazone (MBTH)

By far the most commonly used reagent for the determination of total aliphatic aldehydes is MBTH. First introduced by Sawicki et al. (1961), this reagent has been used for measuring lower-molecular-weight aliphatic aldehydes in auto exhaust and urban atmospheres. A tentative method using MBTH for determining aldehydes in ambient air was given by the Intersociety Committee. The method is as follows: Air to be sampled is bubbled through 0.05% aqueous MBTH contained in a midget impinger. After dilution to a known volume, an aliquot of an oxidizing reagent containing sulfamic acid and ferric chloride is added. After 12 min, the absorbance is read at 628 nm. At the recommended sampling rate of 0.5 slpm, assuming a minimal detectable absorbance change of 0.05 unit, a concentration of 0.03 ppm could be determined after sampling air for 1 hour.

The original method of Sawicki et al. (1961) used ferric chloride alone as the oxidizing reagent. Because of turbidity, acetone was incorporated into the dilution scheme. The turbidity can be effectively eliminated by adding sulfamic acid to the oxidizing reagent. The molar absorptivities of the aldehydic adducts formed vary between approximately 48,000 and 56,000. The formaldehyde adduct has a molar absorptivity of 65,000. Altshuller et al. (1967) recommended that concentrations of aldehydes determined by MBTH should be multiplied by a factor of 1.25 to account for the difference in response between formaldehyde and the remaining aliphatic aldehydes. The recommendation has not been followed in reported uses of MBTH.

5.1.3 2,4-Dinitrophenylhydrazine (DNPH)

2,4-Dinitrophenylhydrazine (DNPH) has received considerable attention as a reagent for determining aldehyde concentrations. The vast majority of DNPH techniques attempt to separate and identify the individual aldehydic adducts through the use of thin-layer chromatography, gas chromatography, or high-performance liquid chromatography. Wet-chemistry spectrophotometric procedures are based on the formation of a chromogen absorbing at 440 nm. These procedures have been hampered by the interference of ketones and problems with reagent stability. The minimal detectable concentration of aldehydes with these procedures is about 0.2 ppm (National Research Council, 1981). Common carbonyls that have been quantified using this method are shown in Table 11 (Yacoub, 1999). Principal

reaction of DNPH method is nicely described by Yacoub (1999). Aldehyde and ketone react with DNPH in the presence of an acid to form stable hydrazone derivatives. The 2,4-dinitrophenylhydrazones are frequently crystalline solids with characteristic sharp melting points and thus they are useful for isolation and identification of aldehyde and ketone. The reaction is given in figure 4.

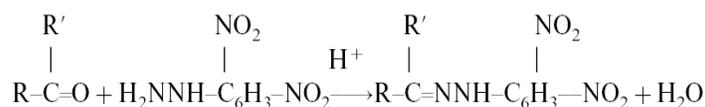


Fig. 4. Principal reaction of aldehyde and ketone with DNPH

Table 11. Carbonyls detected using DNPH method

Compound	Synonym	Structure
<i>Saturated aldehyde</i>		
Formaldehyde	Methanal	HCHO
Acetaldehyde	Ethanal	CH ₃ CHO
Propionaldehyde	Propanal	CH ₃ CH ₂ CHO
Butyraldehyde	Butanal	CH ₃ (CH ₂) ₂ CHO
Isobutyraldehyde	2-Methylpropanal	CH ₃ CHCH ₃ CHO
Valeraldehyde	Pentanal	CH ₃ (CH ₂) ₃ CHO
Isovaleraldehyde	3-Methylbutanal	(CH ₃) ₂ CH(CH ₂)CHO
Capronaldehyde	Hexanal	CH ₃ (CH ₂) ₄ CHO
Enanthaldehyde	Heptanal	CH ₃ (CH ₂) ₅ CHO
<i>Unsaturated aldehyde</i>		
Acrolein	Propenal	CH ₂ = CHCHO
Methacrolein	2-Methyl-2-propanal	CH ₂ = C(CH ₃)CHO
Crotonaldehyde	<i>trans</i> -2-Butanal	CH ₃ CH = CHCHO
<i>Aromatic aldehyde</i>		
Benzaldehyde	Benzenecarbonal	C ₆ H ₅ CHO
<i>o</i> -Tolualdehyde	2-Methylbenzenecarbonal	CH ₃ (C ₆ H ₄)CHO
<i>m</i> -Tolualdehyde	3-Methylbenzenecarbonal	CH ₃ (C ₆ H ₄)CHO
<i>p</i> -Tolualdehyde	4-Methylbenzenecarbonal	CH ₃ (C ₆ H ₄)CHO
	2,5-Dimethylbenzaldehyde	(CH ₃) ₂ (C ₆ H ₃)CHO
<i>Ketone</i>		
Acetone	2-Propanone	CH ₃ COCH ₃
Methyl ethyl ketone	2-Butanone	CH ₃ COCH ₂ CH ₃
<i>Bifunctional aldehyde</i>		
Glyoxal	Ethanedial	H(C = O)CHO
Methyl-glyoxal	2-Oxopropanal	CH ₃ (C = O)CHO

Where both R and R' are alkyl or aromatic groups (ketone), or both, or either R and R' is a hydrogen atom (aldehyde). An acid is necessary to catalyse the reaction. Most strong inorganic acids such as hydrochloric acid (HCl), sulphuric acid (H₂SO₄) or perchloric acid (HClO₄) are adequate. Perchloric acid is the preferred catalyst for impinger sampling when

using an acetonitrile (CH₃-CN) solution of DNPH as the absorbing solution. Very low HClO₄ concentrations are sufficient to obtain adequate recoveries. The DNPH derivatives do not precipitate from solution as readily as when hydrochloric acid is used as the catalyst. Several factors affect the derivatization rate, including the reaction pH, the reagent concentration and the temperature Yacoub (1999).

5.1.4 4-Hexylresorcinol

The most popular method for determining acrolein in air uses 4-hexylresorcinol (Cohen and Altshuller, 1961). Air is typically drawn through two midjet impingers at 1 slpm to collect the sample. The collecting solution can be either 1% sodium bisulfite or a reagent containing 4-hexylresorcinol, mercuric chloride, and trichloroacetic acid in ethanol. Samples collected in bisulfite are analyzed by adding 4-hexylresorcinol and mercuric chloride in ethanol and then a solution of trichloroacetic acid in ethanol. The solution is heated for 15 mm at 60C, and the resulting color is measured at 605 nm. Samples collected in 4-hexylresorcinol are analyzed simply by heating and measuring the color. For field sampling, the simplicity of the latter method is offset by the hazards of handling the toxic and corrosive reagent. In addition, the reagent and the samples collected are not very stable, and samples must be analyzed within a few hours. The bisulfite method is somewhat more complex, but it is safer to use. Besides using a less hazardous collecting solution, this method produces samples that are stable for up to 48 hrs if they are kept refrigerated, thus permitting later analysis at a central laboratory. A recent paper by Hemenway et al. (1980), pointed out a potential flaw in the 4-hexylresorcinol method given by NIOSH. Apparently, the order of addition of reagents for analysis differs between field samples and calibrating solutions, and this may lead to underestimation by as much as 35%. The validity of this objection still needs to be established.

5.1.5 Spectroscopic methods

Microwave, infrared, and laser-fluorescence spectroscopy have been used to measure aldehyde concentrations in ambient air. Each of the methods is prohibitively expensive for ordinary field sampling. The instrumentation required is often cumbersome and delicate, is seldom portable, and requires sophisticated maintenance and support facilities.

Microwave rotational spectroscopy can measure low concentrations of many compounds in gas-phase samples. Rotational resonances are very sharp at microwave frequencies and low partial pressures, so sample spectra can be easily resolved. Formaldehyde has been monitored continuously at concentrations as low as 10 ppb in air with a two-stage membrane separator for preconcentration (Hrubesh, 1973). Acetaldehyde has been detected directly at 15 ppm. Microwave spectroscopy has also been used to determine acrolein, acetaldehyde, and formaldehyde in tobacco smoke. The sensitivity of the technique was 2 ppm, but, again, this concentration is rather high and would not normally be encountered in ambient air. Furthermore, the response time of the instrument is long, rendering the technique insensitive to changes in concentrations.

Infrared spectroscopy is promising, owing to the sharpness of the rotational and vibrational peaks observed for gas-phase samples. Unfortunately, good spectral resolution (less than 0.1 cm⁻¹) and rapid measurements are hampered by the low power of infrared sources.

5.1.6 Fourier-transform infrared (FTIR) method

To overcome the above mentioned method difficulty, Fourier-transform infrared (FTIR) methods have been developed in which conventional Fourier-transform methods are used to derive the absorption bands. FTIR instruments are commercially available, but are exceedingly expensive. In one application, formaldehyde was continuously monitored at ambient concentrations of less than 10 ppb with an FTIR system. The system was used with a Michelson infrared interferometer with a sophisticated multiple-reflection optical cell whose path-length was 2 km. Longer path-lengths could not be obtained, because of image overlap. Other aldehydes were not measured.

A fluorescence procedure based on the direct excitation of formaldehyde by a dye laser has been reported. Formaldehyde is as low as 50 ppb in air could be detected and further refinements would increase the sensitivity. The application of this technique to other aldehydes is restricted by the weaker and less well-resolved absorption spectra in the accessible spectral region (Tuazon et al., 1978).

5.1.7 Chromatographic methods

Three chromatographic techniques have been applied to the analysis of aldehydes: gas chromatography, liquid chromatography, and ion chromatography. Gas-chromatographic analysis of aldehydes generally takes one of two forms: direct analysis by gas or solution injection and derivatization followed by analysis.

Formaldehyde presents special problems with respect to direct analysis by injection. In a flame ionization detector (FID), a universal detector widely used for quantitative work, formaldehyde decomposes and gives a very small response. Thermal conductivity detectors (TCDs) are less sensitive and respond only to very high concentrations of formaldehyde. An electron capture detector (ECD) has a limited linear response range and is sensitive only to conjugated carbonyl groups. The photoionization detector (PID) is reported to be sensitive to formaldehyde, but appears to have some drawbacks. Specifically, a high-energy lamp is required to detect formaldehyde; this drastically reduces both the selectivity and the lifetime of the detector.

In principle, it is possible to circumvent the insensitivity of the FID to formaldehyde by catalytically reducing formaldehyde to easily detectable methane. Because hydrogen is required for the operation of the FID, the reduction is easily achieved by passing a mixture of the column effluent and hydrogen gas over a short bed of catalyst before introduction into the FID. Deposits of nickel, thorium, and ruthenium on fine-mesh glass beads have all been used successfully to reduce formaldehyde to methane. The lack of success in applying the technique to routine analysis of formaldehyde can be attributed to problems in choosing proper gas-chromatographic conditions. Apparently, it is difficult to pass formaldehyde through any of a variety of column -packing materials quantitatively.

With the exception of formaldehyde, aldehydes may be analyzed by direct gas injection if concentrations are high enough. By using a six-port valve equipped with a 1-ml gas-sampling loop, aldehydes can be routinely detected with an FID at concentrations as low as 0.03 ppm without preconcentration. It is important to recall, however, that gas chromatography excels at separation, but provides minimal identification. Ambient-air samples often contain hydrocarbons, and their responses may overlap and obscure the aldehydic responses.

Bellar and Sigsby (1970) reported a complex automated gas chromatographic technique to analyze for C 2 -C 5 aldehydes that avoided this problem. Hydrocarbons and aldehydes from an air sample flowed onto polar cutter column, where the aldehydes were retained as the hydrocarbons were passed through and vented. The cutter column was then back flushed to a cryogenic trap, where the aldehydes were re-concentrated before introduction onto an analytic column. About an hour was required for a complete analysis. The method has not been used by other workers.

Derivatization is an alternative technique that has been extensively investigated. Levaggi and Feldstein (1970) introduced methods in which samples were collected with impingers containing 1% sodium bisulfite solution. Aldehydes react with the bisulfite to form adducts. Formaldehyde and acrolein are analyzed by chromatographic acid and 4-hexylresorcinol methods, respectively. To analyze the remaining aldehyde, the bisulfite solution is injected onto a packed column in a gas chromatograph. Samples must be kept cold to prevent deterioration. The Intersociety Committee-10 has adapted the technique as a tentative method for the 5 aldehydes, but there are no reported uses in the literature. A problem not explicitly discussed is the rapid degradation of column performance due to the in site production of sulfur dioxide and sodium hydroxide as the adduct thermally decomposes.

Much work has been aimed at using 2,4-dinitrophenylhydrazone (DNPH) derivatives of aldehydes, well known for many years for their use in the qualitative identification of aldehydes. DNPH reacts with aldehydes in aqueous solution to form precipitates. In most attempts, this precipitate is re-dissolved in an organic solvent, which is then injected into a gas chromatograph. The resulting chromatograms show double peaks for each derivative corresponding to the syn- and anti- isomers formed around the nitrogen-carbon double bond characteristic of the derivative. These peaks are not symmetrical, because of steric influences during formation of the derivative. The peaks observed for the derivatives of propionaldehyde, acrolein, and acetone overlap and are difficult to separate. The most consistent problem is the verification that quantitative derivatization of the available aldehydes has occurred.

DNPH was applied by Hoshika and Takata (1972) to the analysis of automobile exhaust and cigarette smoke. Papa and Turner¹ (1972) also applied it to automobile exhaust. In a two-step process, preliminary separation of DNPH aldehyde derivatives by preparative gas chromatography was followed by analytic gas chromatography.

5.1.8 High-performance liquid chromatography

In the direct analysis of aldehydes with high-performance liquid chromatography (HPLC) aldehydes can be made to react with DNPH to form a derivative with a strong ultraviolet-absorption spectrum. HPLC method is accurate, precise, reproducible, specific, and stability-indicating. The method has been found to be better than previously reported methods, because of its wide range of linearity, use of an economical and readily available mobile phase, UV detection, lack of extraction procedures, no internal standard, and use of the same mobile phase for washing of the column. All these factors make this method suitable for quantification of aldehydes. It can therefore be concluded that use of the method can save much time and money and it can be used in small laboratories with very high accuracy and a wide linear range. The method can be successfully used for routine analysis of aldehyde without interference (Papa and Turner², 1972).

5.1.9 Ion chromatography

Ion chromatography is a new technique, that has application to formaldehyde analysis, it combines liquid chromatography with an ion-exchange column to separate charged species. Low molecular weight aldehydes and acetone in aqueous samples are determined by single-column ion chromatography. The aldehydes and acetone are derivitized to alpha hydroxyalkanesulfonates using sodium bisulfate and the sulfonates that are formed then separated by ion chromatography and detected by using a conductivity detector. Ionic species that can interfere with chromatographing of the aldehydes and acetone are removed from the sample before the aldehydes and acetone are derivitized (Dean et al., 1985.)

5.1.10 Electrochemical methods

In addition to the usual techniques of analyzing organic materials, aldehydes can be analyzed by electrochemical methods. Both polarographic methods and amperometric titrations have been used.

Lupton and Lynch (1944) developed polarographic techniques for the analysis of aldehydes in a wide range of samples. McLean and Holland (1975) adapted their technique to a portable system for rapid analysis of aldehydes in automotive exhaust sampled by bubbling into water. The polarograph was rendered portable by replacing the dropping mercury electrode with a quiescent mercury pool a few millimeters in diameter. Analysis used the method of standard additions. The procedure is not specific, however, even for aldehydes.

5.2 Methane emission measurement methods

5.2.1 Optical Methane Detector

It is based on a highly sensitive open path infrared beam detector, located at the front of the leak survey vehicle. The infrared beam allows detection of methane down to 1ppm and because there is no pump, tubing or water filters, and the response is virtually instantaneous. It has been successfully utilized for finding low level gas leakage at speeds of up to 50 kph. As the system is specifically configured to react only to methane, the occurrence of "false positives" (indications due to other products, e.g. vehicle exhaust emissions) is eliminated.

5.2.2 Spectroscopic techniques

Spectroscopic techniques in the infrared and ultraviolet spectral regions may efficiently meet increasing measurement challenges in real-time detection of vehicle emissions in urban air quality studies. The results of a study are presented in which a Fourier transform infrared (FT-IR) spectrometer was used to continuously monitor motor vehicle exhaust emissions. The FT-IR identified several exhaust components, including ethylene, acetylene, propylene, isobutylene, the hydrocarbon continuum, carbon monoxide, carbon dioxide, methane, nitric oxide, and nitrous oxide. The emission of each species was shown to vary with vehicle type and the operating speed of the motor. Measurement results from this study support at least two commonly observed characteristics of motor vehicle exhaust. First, ethylene, propylene, and acetylene are common exhaust components. Ethylene was observed to be the most abundant and stable of the non-methane hydrocarbon emissions during idling for the three vehicles considered in this study. Second, the emission of NO as a function of time remains

high and fairly constant at high speeds. At high speeds the concentrations of CO, HC, and the non-methane hydrocarbons decrease sharply. The results of this study strongly suggest that the FT-IR can serve as a continuous, real-time monitor for measuring motor vehicle emissions. Because it can simultaneously detect multiple pollutants and can operate in an automated fashion, the FT-IR represents a cost-effective means of determining the effect of vehicle emissions on air quality (Gibbs et al., 1995).

6. CONCLUSION

- Aldehydes are formed by the incomplete combustion of hydrocarbons. They have a carcinogenic and ozone formulation potential.
- Aldehydes are beginning to be subject to emissions legislation.
- The most abundant aldehyde in engine exhaust emission is Formaldehyde.
- In gasoline and gasoline/ethanol blend engines lean combustion produces more aldehydes.
- Gasoline and natural gas engines equipped with catalytic converters have the lowest aldehyde emissions.
- Aldehyde measuring methods are based either wet chemical analysis or spectrometric detection. The most useful method is DNPH cartridge measurement method, as it allows the detection of individual aldehyde species.
- Methane is emitted from light duty vehicles due to the incomplete combustion of fuel in the vehicle engine and the incomplete oxidation of engine-out methane in current catalytic after treatment systems.

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