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HPLC Analysis of Aldehydes in Automobile Exhaust Gas: Comparison of Exhaust Odor and Irritation in Different Types of Gasoline and Diesel Engines

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Abstract – This study investigated high performance liquid chromatography (HPLC) to identify and measure aldehydes from automobile exhaust gas. Four aldehydes: formaldehyde (HCHO), acetaldehyde (CH₃CHO), acrolein (H₂C=CHCHO) and propionaldehyde (CH₃CH₂CHO), and one ketone, acetone (CH₃)₂CO are separated. The other aldehydes in exhaust gas are very small and cannot be separated. A new method of gas sampling, hereafter called bag-sampling in HPLC is introduced instead of trapping gas sampling method. The superiority of bag-sampling method is its transient gas checking capability.

In the second part of this study, HPLC results are applied to compare exhaust odor and irritation of exhaust gases in different types of gasoline and diesel engines. Exhaust odor, irritation and aldehydes are found worst in direct injection (DI) diesel engines and best in some good multi-point injection (MPI) gasoline and direct injection gasoline (DIG) engines. Indirect injection (IDI) diesel engines showed odor, irritation and aldehydes in between the level of MPI gasoline, DIG and DI diesel engines.

Keywords – Aldehydes, automobile exhaust gas, bag-sampling, exhaust odor and irritation, HPLC, gasoline and diesel engines.

1. INTRODUCTION

Partially burnt combustion products in automobile exhaust gas like aldehydes, organic acids and other oxygenated compounds are mainly responsible for exhaust odor [1]-[4]. Aldehydes as a single group has maximum share on exhaust odor [5]. Automobile exhaust is also irritating to nose, eyes and throats. Moreover, some aldehydes like HCHO, CH₃CHO and H₂C=CHCHO are placed to US environmental protection agency (EPA) probable carcinogens. Therefore, reduction of aldehydes from automobile exhaust gas is very important. However, before taking reduction measures, it is first necessary to identify and measure aldehydes in exhaust gases.

This study describes a method of analyzing automotive engine exhaust for aldehyde and ketone compounds (carbonyls) using acidified 2, 4-dinitrophenylhydrazine (DNPH)-absorbing solution. The absorbing solution (2, 4-DNPH) complexes the carbonyl compounds present in automobile exhaust into their diphenylhydrazone derivatives. Separation and analysis are performed using a HPLC with an ultraviolet detector, similar to that presented in references [6]-[7]. The only difference is that [6]-[7] used trapping method of gas sampling while this study used bag-sampling method. In trapping method, gas-sampling time is about 5-10 minutes; while in bag-sampling method time required is only about 5 seconds. Therefore, transient checking is possible by bag-sampling method. Moreover, bag-sampling method is less costly and less complex.

It is generally said that exhaust odor and irritation of gasoline engines are very low in comparison to that of diesel engines. HPLC results are applied to compare exhaust odor and irritation in different gasoline and diesel engines. Two types of gasoline engines (MPI and DIG) and two types of diesel engines (IDI and DI) are used. It is indicated earlier that partially burnt combustion products

are mainly responsible for exhaust odor. Unburnt fuel components also create odor and irritation. When the combustion temperature is low, maximum amount of unburnt fuel and partially burnt components is exhausted to the atmosphere. One such condition is cold start and idling under no load condition. Exhaust odor, irritation and aldehydes after one hour of idling from cold start (ambient temperature = -5°C) are investigated for various types of gasoline and diesel engines. Here three MPI gasoline, three DIG, two IDI diesel and two DI diesel engines were tested. Exhaust odor and irritation assessed by human assessment method were found highly correlated with aldehydes of exhaust gases.

Exhaust odor, irritation and aldehydes are found worst in DI diesel engines and best in some good MPI gasoline and DIG engines. However, some MPI gasoline and DIG engines showed very bad results even worse than DI diesel engines. IDI diesel engines showed odor, irritation and aldehydes in between the level of MPI gasoline, DIG and DI diesel engines. The level of odor and irritation in IDI and DI diesel engines is very consistent.

2. ALDEHYDE IDENTIFICATION AND MEASUREMENT BY HPLC

Identifying a compound by HPLC is crucial and challenging and is accomplished by researching the literature and by trial and error. A sample of a known compound must be utilized in order to assure identification of the unknown compound. The identifying peak should have a reasonable retention time and should be well separated from extraneous peaks. DNPH is a widely used derivatizing reagent for the determination of aldehydes and ketones. An absorbing solution is prepared by dissolving 0.11 - 0.13 grams of recrystallized DNPH in 1 L of HPLC grade acetonitrile. 10 mL of 3.8 M perchloric acid to 1 L of that solution is added (CARB procedure, [6]). This is the acidified DNPH-absorbing solution.

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The reaction between aldehyde and acidified absorbing solution of DNPH is presented below:

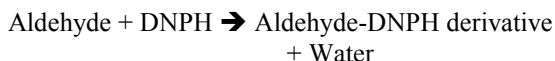


Figure 1 shows the schematic diagram of HPLC for the measurement of aldehydes from automobile exhaust gas. The exhaust gas of 10 L was collected in a sampling bag and acidified 2, 4-dinitrophenylhydrazine (DNPH)-absorbing solution of 20 mL was poured into the bag and was shaken well. Then the bag with DNPH-solution was cooled to -30°C for half an hour for the improvement of dissolution of aldehydes. This sample solution (aldehyde-DNPH derivative) is ready for HPLC checking. The sample solution of 10 μL was injected to the HPLC by a micro-syringe and gradient program was controlled by 50:50 mixtures of acetonitrile and water (HPLC grade) in one pump and 100% acetonitrile in the other pump. The sample was then taken to the checking column and an ultraviolet (UV) detector was used to detect the signal from aldehyde-DNPH derivatives. The outputs from the HPLC-UV detector were sent to a PC-controlled data acquisition system. The peak integrations were corrected as necessary in the data system. Any misplaced baseline segments were corrected in the reconstructed chromatogram. Samples containing compounds having concentrations above the documented range of instrument linearity were diluted and reanalyzed.

The conditions of HPLC are presented in Table 1. Five compounds: four aldehydes and one ketone were separated. They are HCHO, CH_3CHO , $\text{H}_2\text{C}=\text{CHCHO}$, $\text{CH}_3\text{CH}_2\text{CHO}$ and $(\text{CH}_3)_2\text{CO}$. The other higher aldehyde concentrations in exhaust gas are very small and cannot be separated.

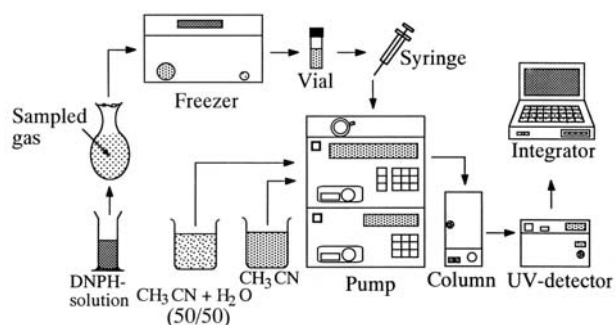


Fig. 1. Schematic diagram of HPLC

Calibration of Aldehydes

Quantification of compounds by HPLC is the process of determining the unknown concentration of a compound in a known solution. It involves injecting a series of known concentrations of the standard compound solution onto the HPLC for detection. The chromatograph of these known concentrations will give a series of peaks that correlate to the concentration of the compound injected. Using the area of a triangle equation ($A=1/2b \times h$) to calculate the area under each peak, a set of data is generated to develop a calibration curve. This is done by graphing peak area vs. the concentration of the sample solution.

Table 1. HPLC specifications and gradient program

Analysis method	HPLC-UV			
Main column	Zorbax ODS 4.0 mm $\Phi \times 15$ cm + Zorbax ODS 4.0 mm $\Phi \times 25$ cm			
Guard column	Inertsil ODS 1 cm			
Column temperature	50°C			
Gradient program	Mobile phase A- Water: Acetonitrile (50:50)			
	Mobile phase B- Acetonitrile			
	Time (min)	Flow (mL/min)	%A	%B
Initial	1.0	0	100	
30	1.0	60	40	
35	1.0	60	40	
Wavelength	365 nm			

Stock calibration standard was used for calibration. The stock calibration standard (aldehyde-DNPH derivative of known concentration) was purchased from Radian International in 1.2 mL ampules. A typical stock calibration standard contains 3.0 $\mu\text{g}/\text{mL}$ of each target carbonyl compound. Stock calibration standards of other concentrations may also be used. Stock calibration standard contains 13 aldehydes and ketones from formaldehyde to hexanaldehyde with known concentrations. Stock calibration standard was first investigated by HPLC with different concentrations. Figure 2 shows a typical liquid chromatogram of stock calibration standard. Different peaks of aldehydes and ketones are indicated by numbers from 1 to 13. Table 2 shows peak identification with different peaks and their retention times.

It is stated earlier that five aldehydes and ketones can be separated from automobile exhaust gas. Figure 3 shows the calibration of those five aldehydes and ketones. There is a linear correlation between the area counts (detector response) and the concentrations of aldehydes or ketones. Abscissa indicates the concentration of aldehydes or ketones in $\mu\text{g}/\text{mL}$ of acetonitrile. The relationship between area counts and aldehyde concentrations in exhaust gases is presented in Table 3 considering the gas volume of 10 L and 20 mL of DNPH-acetonitrile solution. Area counts for aldehydes or ketones of 1 mg/m^3 in exhaust gas and for 1 ppm in exhaust gas at 760 mm Hg, 25°C are presented.

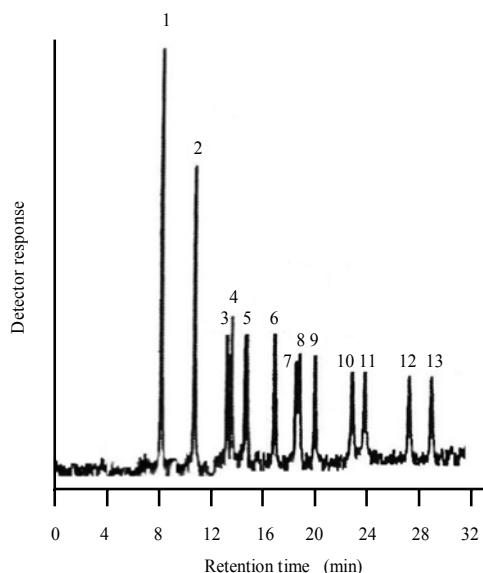


Fig. 2. Experimental liquid chromatogram of working standard-13

Table 2. Peak identification

Peak No.	Identification	Retention time (min)
1	Formaldehyde	8.10
2	Acetaldehyde	10.60
3	Acetone	13.30
4	Acrolein	13.60
5	Propionaldehyde	14.70
6	Crotonaldehyde	16.94
7	2-Butanone	18.54
8	Methacrolein	18.86
9	n-Butyraldehyde	20.00
10	Benzaldehyde	22.90
11	Valeraldehyde	23.74
12	m-Tolualdehyde	27.18
13	Hexanaldehyde	28.90

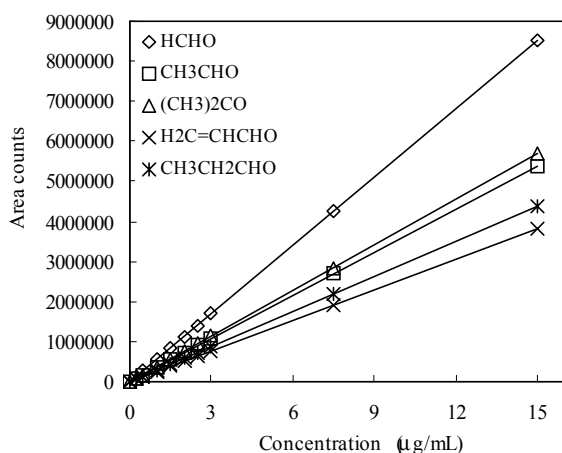


Fig. 3. Calibration curves between area counts of the detector and aldehyde concentrations of standard samples

Table 3. Relationship between area counts and aldehyde concentrations in exhaust gases

Components	Area counts (for 1 mg/m ³ in exhaust gas)	Area counts (for 1 ppm in exhaust gas 760 mm Hg, 25°C)
HCHO	557272	684609
CH ₃ CHO	359329	647439
(CH ₃) ₂ CO	376160	902784
H ₂ C=CHCHO	252585	578419
CH ₃ CH ₂ CHO	290362	688157

Figure 4 shows typical liquid chromatograms of different gasoline and diesel exhausts. Here, one best result from each group of engine is presented. Figures 4(a) and 4(b) show the results of a MPI gasoline and a DIG engine exhausts. The concentrations of various aldehydes are very similar in both engines. Figures 4(c) and 4(d) show the chromatograms of an IDI and a DI diesel engine exhausts. The concentrations of various aldehydes in IDI diesel engine are comparable with that of MPI gasoline and DIG engine exhausts except HCHO. HCHO in IDI diesel engine exhaust is more than double than in MPI gasoline and DIG engines. However, HCHO and CH₃CHO in DI diesel engine exhaust are much higher.

Gas Sampling for HPLC

It is expressed earlier that trapping method with proper solvent is usually used in HPLC for aldehyde measurement. A typical arrangement of trapping method is shown in Figure 5. Exhaust gas from engine is sucked by a pump at a constant flow rate, for example 1 L/min for about 5 to 10 minutes (1 L/min for 10 minutes in this study) depending on the concentrations of aldehydes in the exhaust gas and passed through DNPH-absorbing solution. When the concentration level is low, a longer time is required. The aldehyde and ketone compounds are trapped and dissolved in the solvent, and the solution is then used as HPLC sample. As the HCHO has very low boiling point of -21°C, this system needs some cooling arrangement below -21°C to collect maximum amount of HCHO in the solvent. Moreover, continuous use of bubbler gives poor repeatability of the results if cleaning of the bulb of the bubbler is insufficient. Further, this system takes at least some minutes for gas sampling. Therefore, no transient checking is possible by this method. All disadvantages were overcome by the use of bag-sampling method.

Figure 6 shows the schematic diagram of bag-sampling method. In bag-sampling method, exhaust gas of 10 L was taken in a bag and DNPH-absorbing solution was added to the exhaust gas and shaken well for about one minute. The bag was then cooled to -30°C for half an hour to make aldehydes and ketones to be better condensed and dissolved in the solution. This is the sample for HPLC, which contains aldehyde-DNPH derivative. The sample was then checked by HPLC (UV detection) in a detector column.

Figure 7 shows the comparison of aldehydes between bag-sampling and trapping methods. For better comparison of results, a controlled test environment in a laboratory engine was used. The engine room temperature was maintained at 20°C and the relative humidity was about 50%. The engine used was a 4-stroke, six cylinder,

DI diesel engine with a bore and stroke of 110 and 125 mm. The swept volume of the engine was 7127 cc and compression ratio 18.5. This was a constant injection pressure engine with injection pressure of 20 MPa. Injection timing was variable. For the comparison of aldehydes in bag-sampling and trapping methods, two injection timings: TDC and 10°BTDC were used. Test conditions were idling under no load and at an engine speed of 700 rpm. Data were taken after one hour of running idle when coolant temperatures become constant (at 83°C) and exhaust line temperature was unchanged.

This gave consistent data. It is found from Figure 7 that all aldehydes are very similar except HCHO in both bag-sampling and trapping methods for the injection timings of TDC and 10°BTDC. HCHO in trapping method is a little lower than in bag-sampling method, because the bubbler was cooled in an ice-water bath of temperature about 0°C. As the boiling point of HCHO is -21°C, some HCHO escaped rather than dissolving. The results suggest that the bag-sampling method can be used in HPLC with adequate accuracy.

Peaks: 1-HCHO, 2- CH₃CHO, 3-(CH₃)₂CO, 4- H₂C=CHCHO, 5- CH₃CH₂CHO

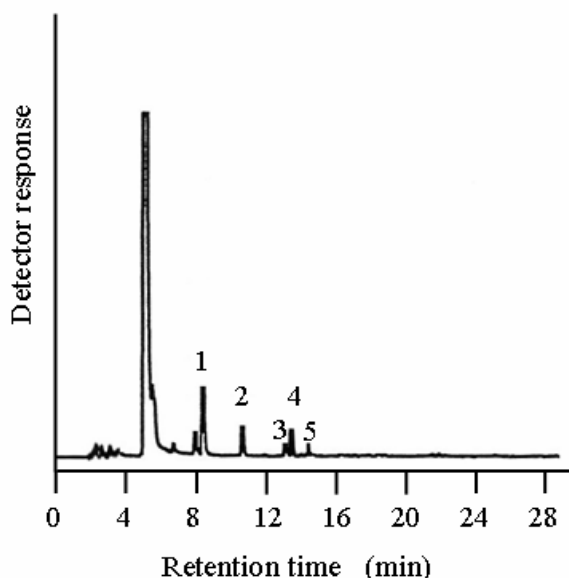


Fig. 4a. Liquid chromatogram of MPI exhaust

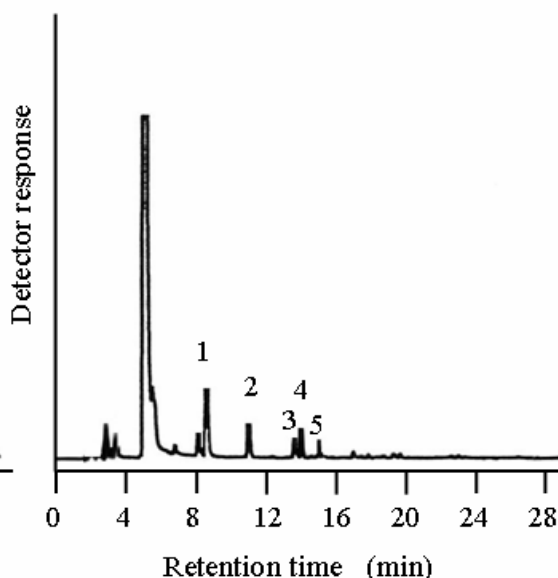


Fig. 4b. Liquid chromatogram of DIG exhaust

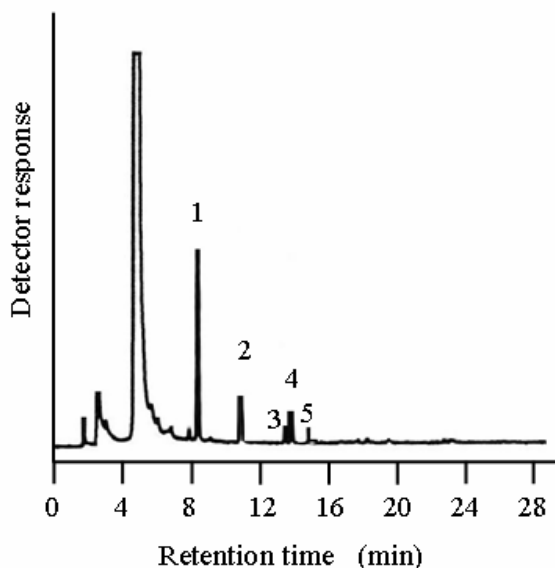


Fig. 4c. Liquid chromatogram of IDI exhaust

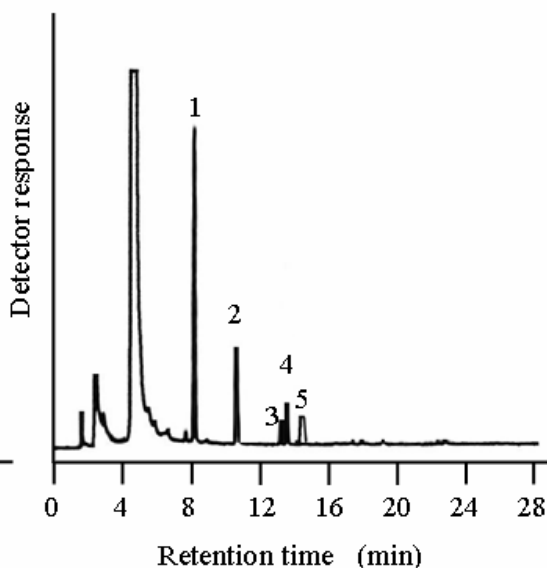


Fig. 4d. Liquid chromatogram of DI exhaust

3. ODOR AND IRRITATION COMPARISON

In general, gasoline engines odor and irritation are lower than that of diesel engines. This is true when both engines are fitted with catalyst. In most of engine running time for gasoline engines, exhaust temperatures are high enough to activate the catalyst. However, diesel exhaust temperatures at idling under no load condition with usual

idling speeds are only about 100-125°C [8]-[9]. At cold start and low temperature engine operations, catalyst does not work in any engine. Exhaust odor and irritation from different types of gasoline and diesel engines were investigated considering the cold start and idling condition of engines where there are no catalytic reactions. Even after one hour of idling from cold start for different engines with usual idling speeds of 700-900 rpm, exhaust temperatures at the exhaust manifold is only about 100-

125°C. Before showing the odor and irritation results of different engines, assessment method of exhaust odor and irritation needs to be clarified.

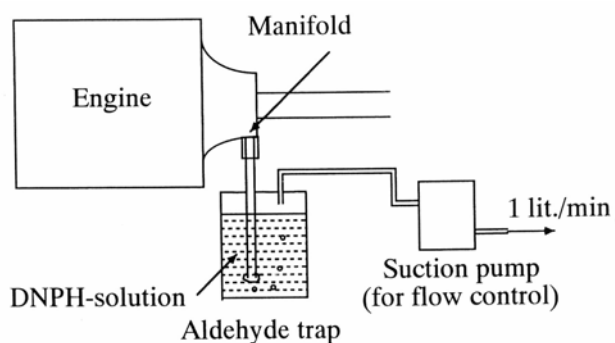


Fig. 5. Arrangement for trapping method in HPLC

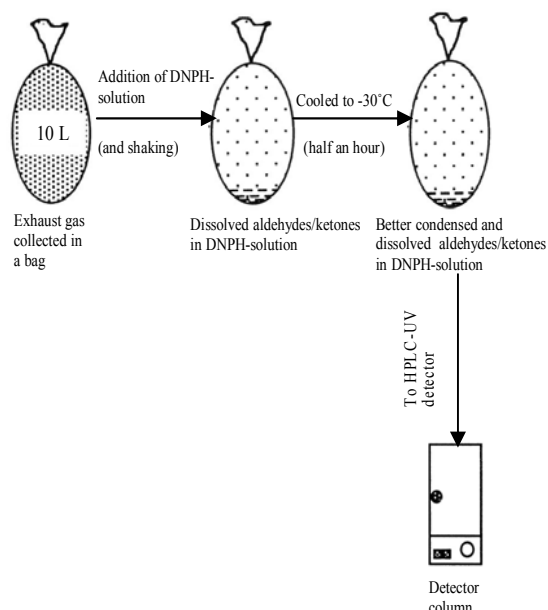


Fig. 6. Schematic diagram of bag-sampling method for aldehydes/ketones measurement by HPLC

Odor and Irritation Assessment by Human-Sensing

Human assessment is one technique used to check odor intensity of exhaust gases. In this method, the nose was used as a detector of smell and an odor intensity scale (Table 4) was used to evaluate the discomfort level of exhaust gases. A difference of one point is reported as being equivalent to a ten-fold change in the concentration of odorous gases [10]. Therefore, a one-point improvement in the odor scale is a significant improvement in exhaust odor. Odor level 2 or below is tolerable for all human beings.

There is a significant scatter in the results recorded by human assessors when the test personnel are inexperienced, but reliable results can be obtained with experienced test personnel [11]. In reference [11], a validation experiment has been reported to prove the reliability of the human assessors where ten assessors were used, of whom six were inexperienced and four were experienced. Although the results were very scattered in case of inexperienced assessors, very close results were obtained from the experienced assessors. This study used four experienced assessors, and the average value of odor ratings from these four assessors has been used throughout

the study. The range (maximum difference) of odor rating is about 0.25 points among the assessors for a data point or for replication of data and the standard deviation is about 0.2 points.

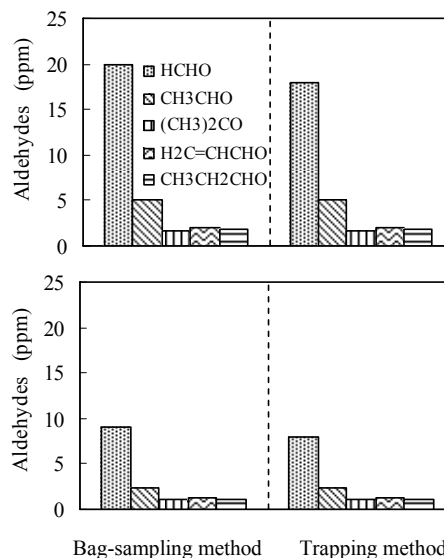


Fig. 7. Comparison between bag-sampling and trapping method

In human assessment, assessment is usually done at the exhaust manifold or at the tail pipe. In this study, the assessment was performed at the tail pipe (about 1 m from the tail pipe end). The assessors checked the odor rating directly by exposing their nose to the exhaust stream at the tail pipe. The assessed gas speed (exhaust gas speed at which the odor levels are examined) was about 2.5-3 m/s. Exposure time for odor assessment is about 2 to 3 seconds.

This investigation includes not only odor but also eye irritation of exhaust gases, because eye irritation is also a great concern in the areas like mines, tunnels, hospital or other public gatherings where diesel engines are used. Irritation was expressed by the term 'eye irritation time', which is measured by the time required to irritate the eyes when the eyes are exposed to the exhaust. The longer time required to irritate the eyes indicates that there are less irritants in the exhaust and vice-versa. The detail of the measurement of eye irritation time has been presented [11]-[12]. Figure 8 shows the inverse relationship between odor rating and eye irritation time. There is about one second improvement (longer) in eye irritation time when odor rating is one point decreased.

Table 4. Odor rating scale

Intensity rating	Verbal	Description
1	Not detectable	No odor
2	Slight	Odor but not uncomfortable
3	Moderate	Uncomfortable odor
4	Strong	Irritating odor, long time exposure not possible
5	Very strong	Very irritating odor, exposure even 1 or 2 s impossible

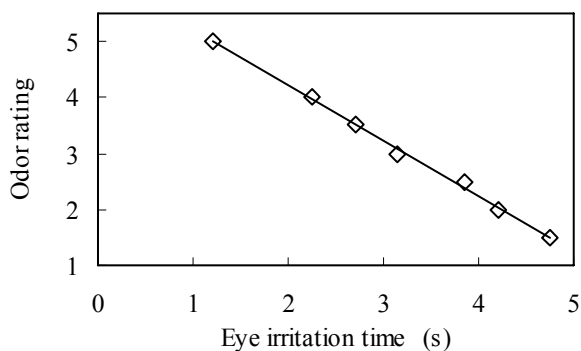


Fig. 8. Relationship between odor rating and eye irritation time

Odor and Irritation Results

Table 5 shows the outline of the tested vehicles. Here, ten cars of which six are gasoline and four diesels were tested. Figure 9 shows odor ratings of exhaust gases of different types of gasoline and diesel engines. Car ‘A’, with a MPI gasoline engine showed lowest odor, rating of about 1.5, which indicates that there is hardly any odor. The odor level is very low although there is no catalytic reactions at low exhaust temperatures. The odor reduction is believed to be because odorous gas components are adhered/adsorbed to the catalyst surfaces at low exhaust temperatures conditions. In addition the adsorption is higher for new or preconditioned catalyst rather than old or not preconditioned catalyst [8]. Car ‘D’, with a DIG engine has a similar level of exhaust odor to that of car ‘A’. These are the best gasoline engines. However, some MPI gasoline and DIG (car B, C, E, and F) engines emitted higher exhaust odor, even higher than diesel engines. Worse odor from some MPI gasoline and DIG engines maybe due to the deterioration of catalyst activity for long cruising length or improper setting of air-fuel ratio. In terms of average odor, MPI gasoline and IDI diesel showed similar results. However, DI diesel engine has the worst odor and the average rating is about one point higher than those of MPI gasoline and IDI diesel engines.

Figure 10 shows eye irritation time of exhaust gases for various engines. Here also car ‘A’, with a MPI gasoline engine and car ‘D’, with a DIG engine showed lowest and very similar level of eye irritation (eye irritation time about 5 seconds). However, some MPI gasoline and DIG (car B, C, E, F) engines’ eye irritation is very severe, even severer than diesel engines. In terms of average irritation trend, MPI gasoline and IDI diesel showed similar results. However, DI diesel engine has the shortest eye irritation time (i. e. highest irritation) about one second shorter than those of MPI gasoline and IDI diesel engines. Eye irritation results for different engines expressed the inverse relationship between exhaust odor and eye irritation time once again.

Figure 11 shows the concentrations of different aldehydes for different engines. Car ‘A’ and ‘D’ emitted lowest amount of aldehydes than other engines and the concentrations of aldehydes are less than 1 ppm except HCHO (2 ppm). IDI diesel engines (G and H) emitted HCHO from 5 to 6.5 ppm, while other aldehydes and ketone are as low as that of good MPI gasoline and DIG levels. However, DI diesel engines (I, J) showed the highest level of aldehydes. Here HCHO emission is from

9 to 12 ppm and CH₃CHO from 2.5 to 2.75 ppm. Other higher aldehydes are slightly higher than IDI diesel or good MPI gasoline and DIG engines. However, bad MPI gasoline and DIG engines (B, C, E, and F) emit very high levels of aldehydes. Here HCHO is emitted from 18 to 38 ppm. Higher aldehydes are not much higher in comparison to that of DI diesel engines. Car ‘F’, with a DIG engine showed the worst result. Aldehydes from different engines indicate that they have a very good correlation with exhaust odor and eye irritation. It has also to be noted that to get least odor and irritation from gasoline engine exhausts at cold start and at low temperature idling, good engine and catalyst condition is a prerequisite.

Table 5. Outline of the tested vehicles

Vehicle type*	Engine type**	Swept volume (L)	Cruising length (×10 ³ km)	With (w/) or without (w/o) Catalyst
A (P)	MPI	1.3	13	w/
B (S)	MPI	2.0	77	w/
C (W)	MPI	2.0	20	w/
D (P)	DIG	2.4	12	w/
E (W)	DIG	1.8	0.5	w/
F (P)	DIG	1.8	55	w/
G (P)	IDI	2.8	120	w/o
H (SUV)	IDI	3.0	70	w/o
I (SUV)	DDI	3.1	0.8	w/
J (SUV)	DDI	2.8	75	w/o

* P: Passenger car, S: Sports car, W: Wagon, SUV: Sports Utility Vehicle.

** MPI: Multi Point Injection (Gasoline), DIG: Direct Injection Gasoline, IDI: Indirect Diesel Injection, DDI: Direct Diesel Injection.

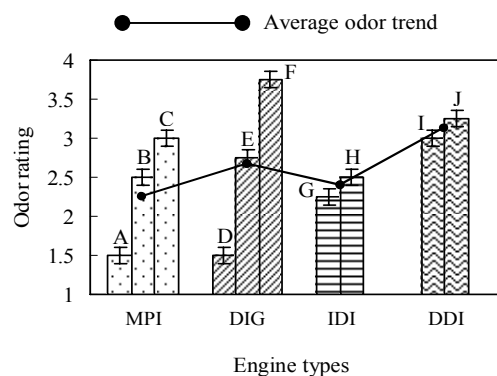


Fig. 9. Odor emissions in different types of engines

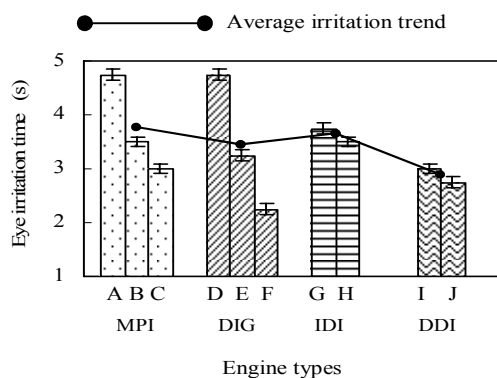


Fig. 10. Eye irritation in different types of engines

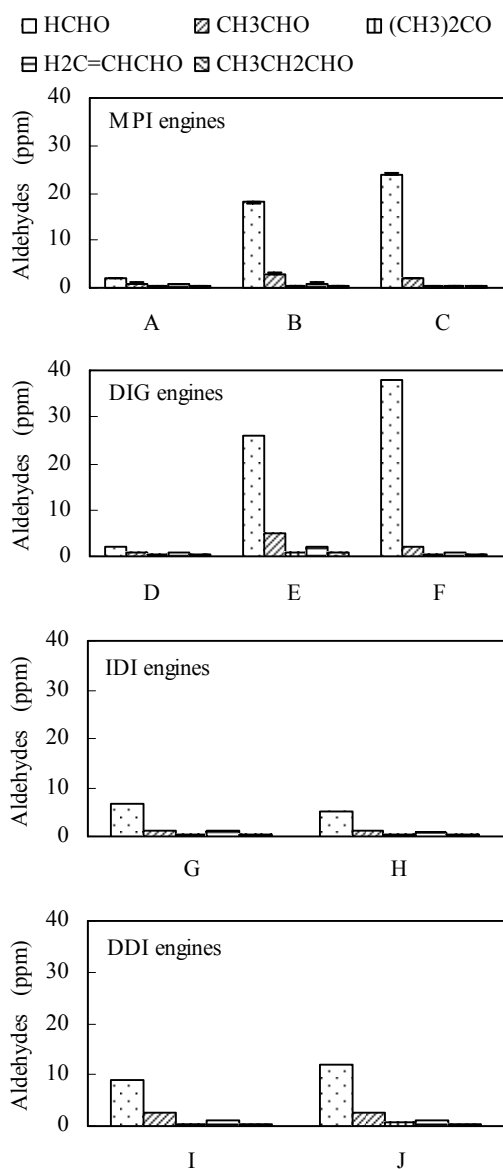


Fig. 11. Aldehydes in different types of engines

4. CONCLUSION

- HPLC with UV detection can be successfully used to identify and measure aldehydes in automobile exhaust gas. Presence of four aldehydes: HCHO, CH₃CHO, H₂C=CHCHO and CH₃CH₂CHO in automobile exhaust gas is significant.
- Bag-sampling method for gas-sampling in HPLC is found to show comparable results with trapping method. Moreover, bag-sampling method has the capability of transient gas checking.
- Aldehydes in automobile exhaust gas are highly correlated with exhaust odor and eye irritation. The higher the aldehydes in exhaust gas, the higher the odor and irritation and vice-versa.
- Good MPI gasoline and DIG engines emit lowest odor, irritation and aldehydes, while some others exhibit bad results due to catalyst deterioration or miss-match of fuel injection system.
- DI diesel engines produce highest amount of aldehydes as well as highest odor and irritation. IDI diesel engine emissions are in between the level of good MPI gasoline and DIG and DI diesel engines.

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