

LEV レベルの排気成分分析手法の開発

Development of Analytical Technology for Measuring Exhaust Species at Low Emission Levels

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要 旨

カリフォルニア州大気資源局による Low Emission Vehicle (LEV) 規制の導入により、自動車各社は、排気中の炭化水素 (HC) 成分分析技術の開発が必要となった。これまで、HC はトータルエミッションで測定評価されてきたが、LEV 規制により、個々の HC 成分について、オゾン生成能力に基づいて評価することが必要となった。

この規制に対応するため、ホンダのカリフォルニア・エミッション・ラボでは、排気中の個々の HC 成分を分離、同定、そして定量する計測設備や手法を開発した。研究の目的とするところは、LEV レベルでの HC 成分を種類ごとに分離、測定する技術の開発であり、言い換えると、ppb レベルの成分を測定する設備と手法を実現化することであった。

この設備として、特別なサンプリングシステムを具備したガスクロマトグラフ、高感度ガスクロマトマススペクトルメータ、液体クロマトグラフ、そしてカルボニルサンプル設備を用いた。

本報告では、これらシステムにより、排気中の各種 HC を LEV レベルで精度良く測定することが可能になったことを述べるとともに、LEV エミッションでの測定例について示す。

ABSTRACT

The chemical reactivity of vehicle exhaust has been addressed by recent California Air Resources Board (CARB) regulations. Previously, only the total non-methane hydrocarbon (NMHC) emissions were considered. However, now each hydrocarbon is evaluated separately in terms of its chemical potential to form ozone. In order to assess a vehicle's environmental impact from this new perspective, Honda's California emission laboratory has developed instrumentation and methods to separate, identify, and quantify the individual components of vehicle exhaust.

This project required instrumentation and methods that could measure exhaust components in the low part-per-billion (ppb) range. The instrumentation used for this purpose included two gas chromatographs with custom sample inlet systems, one high-sensitivity gas chromatograph - mass spectrometer, one liquid chromatograph, and one carbonyl sampling device.

This paper demonstrates that the laboratory's goals have been met; exhaust species can now be accurately measured at very low concentration levels with high precision. Examples of analyses performed on a low emission vehicle and on reference standards are given as evidence of the laboratory's performance.

1. INTRODUCTION

1.1. Background

The recent LEV/CF (Low Emission Vehicle and Clean Fuel) regulations¹⁾ from the California Air Resources Board will precipitate many changes in

future automobiles and their fuels. The regulations call for strict reductions in pollutants from automobile exhaust. CARB believes that improvements in vehicle technology coupled with changes in fuel chemistry will lead to these reductions.

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Table 1 Common Problems Encountered with Early HC Speciation Methods

Problem	Symptoms	Cause
Poor Precision	Bad peak area reproducibility. Retention time drift.	Irreproducible operation of GC. Inadequate sample concentration/injection technique.
Poor Separation	Unresolved peaks. Broad peaks.	Non-optimal column conditions, (i.e., chemistry, temperature, and/or pressure). Inadequate sample injection technique.
Inadequate Detection Limits	Detection Limits >50 ppbC.	Insufficient amount of sample. Any item also responsible for poor precision or separation, (as above).

The LEV/CF regulations address the fact that some hydrocarbons produce more ozone than others when released to the atmosphere. Emission standards are relaxed for vehicle/fuel combinations found to create relatively less ozone. In order to take advantage of the new regulations, a manufacturer must have the capability to accurately assess the reactivity of a vehicle's exhaust. To perform the measurement of this "specific reactivity" (SR), the exhaust hydrocarbons must first be separated ("speciated"), and then accurately measured. Honda's California emission laboratory* has developed techniques to accomplish this task at low emission levels.

1.2. Concept of Exhaust Speciation

The separation of hydrocarbons (HCs) is usually accomplished by the technique of gas chromatography (GC). A sample of the exhaust is directed into a long glass tube ("column"), typically at least 30 meters long, with an inside diameter of about 0.2 to 0.5 millimeters. The inside walls of the column are coated with a thin film of a polymeric chemical. As the exhaust sample is carried through the column by an inert gas, the hydrocarbons interact with the polymer through chemical or physical mechanisms. Separation occurs because some hydrocarbons interact more strongly than others, causing them to be retained longer in the column. The separation depends on the chemistry of the polymer, and the temperature of the column. When the separated hydrocarbons emerge from the end of the column, they are ionized and detected electronically, producing a series of peaks called a chromatogram

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(Fig. 5). The area of the peaks is proportional to the concentration of the hydrocarbon. The amount of time a given HC remains in the column is theoretically constant, and this "retention time" is used to help identify a peak.

Oxygen-containing hydrocarbons called carbonyls are also components of automobile exhaust. These compounds tend to decompose during gas chromatography. For this reason, the carbonyls are captured in an organic liquid matrix by bubbling the exhaust through glass "impingers". The impinger liquid contains DNPH (dinitrophenylhydrazine), which attaches itself to the carbonyl in a derivatization reaction. This reaction helps trap the carbonyl, and also makes it more visible to the detector. The liquid sample is then analyzed using liquid chromatography (LC). This technique is similar in principal to GC, but in this case the sample is carried through the column by a solvent mixture under high pressure, and detected by ultra-violet (UV) light. The separation depends on the column chemistry and the composition of the solvent mixture.

1.3. Problems with Previous Methods

The three most common problems associated with early work in hydrocarbon speciation were poor precision, poor separation, and inadequate detection limits. Table 1 lists these difficulties together with their symptoms and probable causes.

2. OBJECTIVE

The following objectives were defined at the start of this project.

2.1. Hydrocarbon Analysis

Accuracy. There were two major criteria for the determination of accuracy. First, the summation of all non-methane hydrocarbons measured by the gas chromatograph should be $\pm 10\%$ of the total measured by the dynamometer analyzer. (Results from the dynamometer analyzer are considered the industry standard for total hydrocarbon measurement.) Second, an analysis of a multi-component "standard" gas should produce results that agree with the published concentrations. In addition, all hydrocarbons must be identified as accurately as possible.

Precision. The target for repeatability was set at $\pm 5\%$ for hydrocarbons having a major influence on the SR calculation. To ensure accurate identifications, the retention times should also remain stable.

Limit of Detection (LOD). The LOD target was set at 20 ppbC (parts-per-billion, carbon equivalent). This value was specified by CARB. The LOD equation used by CARB also included a linearity term; therefore, the linearity of the detector response was also important.

Separation Efficiency. The objective for speciation ability was to separate the hydrocarbons as completely as possible, while keeping the total analysis time at one hour or less.

Automation. The final objective was to perform the analyses with minimal operator intervention; the instrument must be able to analyze a series of samples unattended. This feature would free the operator to perform other tasks, and also help establish accuracy and precision.

2.2. Carbonyls

A carbonyl sampling system would consist of two components: an impinger system to collect the sample, and a liquid chromatograph to perform the analysis. While most of the objectives for this combined system were similar to those listed for hydrocarbon analysis, the issue of accuracy was somewhat more complex. The quality of the

Table 2 GC Column Suitability for Hydrocarbons $< C_6$

Column	Item	Unresolved Peaks	Retention Time Stability	Sensitive to H ₂ O ?
DB-1		C2 species	good	no
Al ₂ O ₃ /KCl PLOT		ethyne/2M-propane	fair	yes
Al ₂ O ₃ /Na ₂ SO ₄ PLOT		none	fair	yes
Al ₂ O ₃ /Na ₂ SO ₄ PLOT + CP-Wax		none	very good	no

final result would be contingent upon LC system performance and exhaust sampling accuracy. It was therefore considered important to construct an accurate and reliable impinger system

3. NEW INSTRUMENTATION AND METHODS

3.1. Hydrocarbon Analysis (Gas Chromatography)

(1) **Column Chemistry.** It was determined that adequate hydrocarbon separation could not be obtained using a single column. Therefore, two gas chromatographs were used; one was optimized for C₂ to C₅ compounds ("lightend"), and the other for C₅ to C₁₂ ("midrange"). For the lightend system, an Al₂O₃ PLOT column deactivated with Na₂SO₄ provided the best separation. (PLOT = Porous Layer Open Tubular.) However, this column required protection

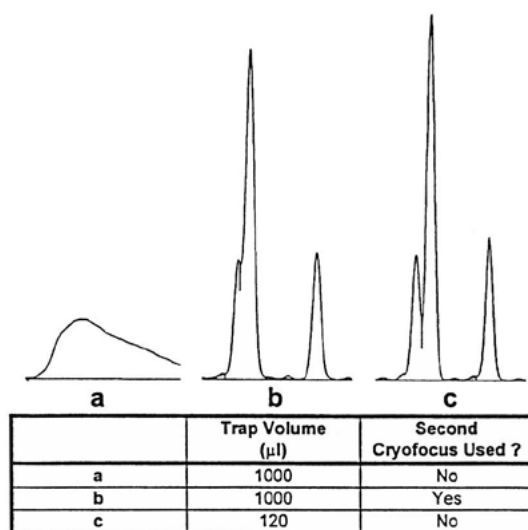


Fig. 1 Comparison of Same C₇ Region of Chromatogram Using Three Different Injection Conditions.

Table 3 Sequence of Events...Hydrocarbon Analysis Gas Chromatography
(Items in Shaded Areas Apply to Lightend GC Only)

Step	Event	Automated?	Importance / Effect on Result
1	GC sampling bags heated and flushed with nitrogen.	Yes	Purges volatile chemicals from bag material that would interfere with analysis.
2	Samples collected.	Yes	
3	Bags attached to GC sampling manifold.	No	
4	Fixed volume of sample delivered to both GCs.	Yes	Ensures that amount of sample analyzed is constant; precision is optimized.
5	Sample allowed to reach constant pressure and temperature.	Yes	
6	Sample passed through cryogenic traps.	Yes	Constant, controlled sample flow into trap minimizes risk of losing hydrocarbons.
7	Traps isolated and heated.	Yes	Precise control of trap temperature also minimizes HC loss, and optimizes precision.
8	Trap opened, sample injected into DB-1 column.	Yes	
9a	Trap opened, sample injected into Wax column.	Yes	Wax column protects PLOT column from H ₂ O and heavy HCs. In PLOT column, water causes selectivity changes (peak movement), and heavy HCs interfere with subsequent analyses.
9b	Hydrocarbons < C ₆ pass into PLOT column.	Yes	
9c	HCs >C ₅ and H ₂ O back-flushed out of Wax column.	Yes	
10	Hydrocarbons separate within column.	Yes	
11	HCs measured by PID and FID detectors.	Yes	Dual detectors help identify hydrocarbons.

from water and heavy hydrocarbons. This problem was addressed by adding a polar column (CP-Wax) upstream to trap the unwanted compounds (Table 2). A common non-polar column (DB-1) was used for the midrange system.

(2) Sample Handling. To maintain accuracy and precision, it was important to optimize the sample's introduction into the column, while preventing the loss of any hydrocarbons. To eliminate problems associated with the injection of large volumes of gas into the column, a cryogenic concentrator trap was used.

A large volume trap (1000 µl) was found to cause "band broadening" effects; i.e., the chromatographic peaks became wider, compromising both detection limit and resolution. Samples injected from this trap required a second cryofocus at the column head in order to achieve adequate performance, which increased liquid nitrogen consumption and lengthened analysis time. However, a small volume trap (120 µl) produced sharp peaks without the use of a second cryofocus (Fig. 1). The trap assembly consisted of an empty 1/16 inch nickel line coiled around a small steel cylinder. In order to permit optimum thermal

contact, the line was soldered to the cylinder. Unlike typical designs, the trap was cooled by passing liquid nitrogen inside the cylinder, and out through holes surrounding the nickel line. A separate pocket within the cylinder accommodated a heating element and thermocouple. This design permitted precise control of the actual temperature experienced by the sample, ensuring optimum trapping conditions. After ballistically heating the trap, the sample was introduced into the column via a short (25 cm) transfer line, thereby injecting the concentrated sample as a narrow band.

To prevent hydrocarbon condensation within the sampling system, all valves and sample lines were heated. Even with heating, however, it was found that stainless-steel sample lines caused the loss of some hydrocarbons heavier than C₆, perhaps through adsorption. This problem disappeared when the lines were changed to nickel.

(3) Detection. The standard .02 inch flame tips on the flame ionization detectors (FIDs) were replaced with .01 inch tips, enhancing the sensitivity by a factor of two. This effect presumably results from the tighter flame shape permitting better combustion

(ionization) of the sample. Thus, lower detection limits were achieved without compromising the FID's operation.

A photoionization detector (PID) was also installed in each system. The radiation from a PID detector selectively ionizes hydrocarbons that have low ionization potentials, such as unsaturates, (i.e., compounds with double carbon bonds). This feature helped differentiate compound classes, such as alkanes and aromatics.

(4) System Operation and Automation. The steps required for our hydrocarbon analysis have been summarized in Table 3. It was found that two events related to the cryogenic trap were critical in terms of maintaining high precision and accuracy: precise temperature control, and careful optimization of the sample flow rate through the trap. A setting of 12 ml/min proved to be ideal; hydrocarbon discrimination was experienced at other flow rates.

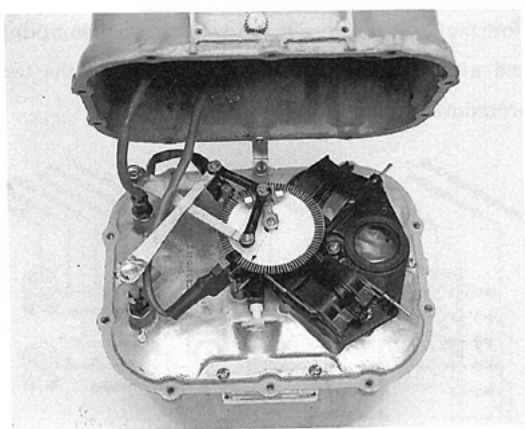
The exact timing of events was also very important. For this reason, the GC systems were automated as much as possible. This also minimized

operator intervention; after calibration, the systems could analyze up to 16 samples unattended. The entire operation was controlled by a single personal computer system, which also served as the data acquisition/calculation system.

3.2. Hydrocarbon Identification (Gas Chromatography/Mass Spectrometry)

An instrument often used to identify the peaks in an exhaust chromatogram is the gas chromatograph/mass spectrometer (GC/MS). In this instrument, the hydrocarbons are fragmented by a beam of electrons as they leave the column. Each hydrocarbon has its own distinct pattern of fragmentation ("mass spectrum"), permitting identification without the use of reference compounds. (Examples of mass spectra can be seen on the right side of Fig. 9.) Unfortunately, the concentration of many exhaust hydrocarbons is too low to acquire a complete mass spectrum. It was therefore a common practice to analyze gasoline samples on this instrument, and apply the resulting identifications to exhaust samples. This is a problematic approach, since gasoline and exhaust do

a



b

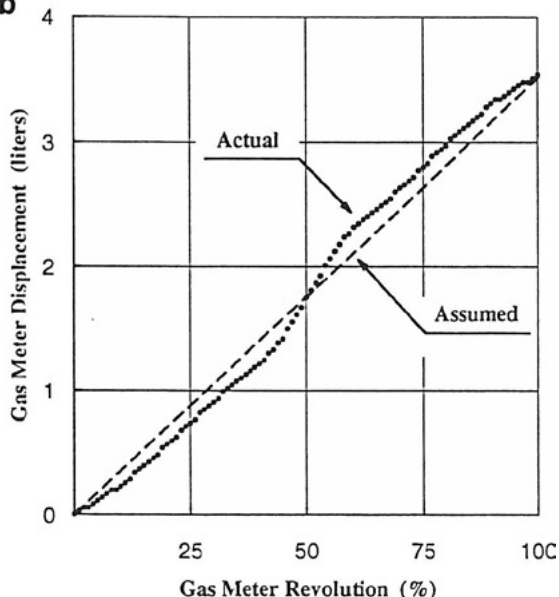


Fig. 2 a) Inside View of Gas Meter, Showing Asymmetric Mechanism and Modifications to Permit Electronic Determination of Volume. (Optical Sensor Disk Colored White for Photo)
b) Deviations from Linear Response During one Complete Cycle of Meter's Mechanism.

not contain exactly the same hydrocarbons.

At our laboratory, a new type of mass spectrometer utilizing “ion-trap” technology was evaluated. This instrument was capable of producing complete, good quality spectra from samples as small as 10 picograms; it was approximately ten times more sensitive than conventional mass spectrometers. The GC was modified in a manner similar to the other instruments, and a special interface was installed which allowed the column flow rate to be varied without disturbing the vacuum inside the MS. These modifications allowed the GC/MS to use exactly the same methods as the other GCs. It was thus possible to analyze exhaust samples directly on this instrument, and obtain hydrocarbon identifications at concentrations as low as 20 ppbC.

3.3. Carbonyl Sampling - Impinger System

The purpose of a carbonyl system is to divert an accurately measured volume of diluted tailpipe exhaust through a series of glass impingers. The carbonyls are retained in the impinger liquid for subsequent analysis on the liquid chromatograph. Although there were commercial systems available, they were deemed too expensive and too difficult to customize. A sampling system was developed and constructed in our laboratory at a reasonable cost, with the following features:

Simple, Accurate Volume Measurement. Many commercial systems use electronic mass-flow controllers (MFCs) to measure the volume of the sampled exhaust gas. Unfortunately, these devices can be prone to clogging. Also, the MFC's response changes with variations in the composition of the measured gas. Therefore, our laboratory decided to use simple mechanical gas meter technology. Special test meters were chosen because of their high accuracy and small displacement. Although the meters were accurate at full and half revolutions, the authors discovered that the mechanism's asymmetry caused a non-linear response at partial revolutions; (see Fig. 2). This presented a problem when small volumes

were measured. This was remedied by installing two optical sensors in each meter. One sensor determined the mechanism's position at the start of sampling, and the other detected revolution intervals with high precision. A computerized table of correction factors was then used to accurately determine the measured volume.

Automatic Impinger Switching. The system received signals directly from the main exhaust sampling controller (i.e., the CVS system). This allowed the sample flow to be switched to the next set of impingers in exact sequence with the other sampling systems. A solid-phase cartridge could be substituted for the impingers with minor modifications.

Temperature Control. All lines and manifolds carrying the exhaust sample from the tailpipe to the impingers were heated to 115°C. This prevented the condensation of water from the exhaust. This was important because carbonyls are easily trapped in water. The impingers themselves were cooled to about 5°C by a water chiller/ circulator, preventing excessive vaporization of the trapping solution. All important temperatures could be monitored by a digital display on the system's control panel.

A schematic of our system can be seen in Fig. 3. Note that provisions were made for alcohol sampling and also for adding additional phases to the test procedure.

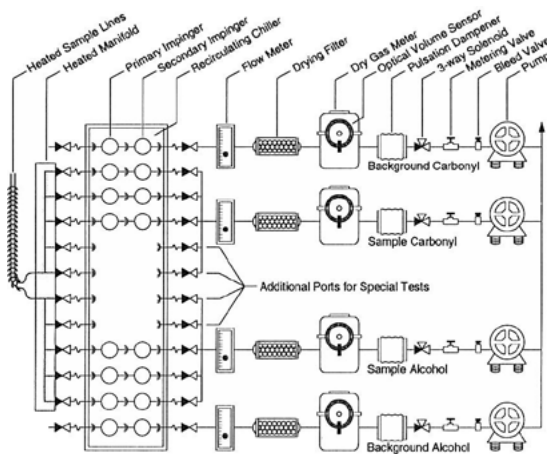


Fig.3 Impinger System Schematic

Table 4 Comparison of Total Hydrocarbon (NMHC) Analyses: Dynamometer Analyzer Versus Gsa Chromatographs

Test Date	Dynamo-meter Result (mg/mi)	GC Result	
		(mg/mi)	(% of Dyna. Result)
Nov. 23, '93	42.8	41.5	97
Nov. 24, '93	40.9	40.2	98
Nov. 30, '93	39.2	38.8	99
Dec. 1, '93	39.2	39.3	100
Dec. 2, '93	42.1	42.0	100

3.4. Carbonyl Analysis

(Liquid Chromatography)

A standard liquid chromatograph equipped with a ternary pump and variable wavelength UV detector was sufficient for carbonyl analysis. The exhaust samples are transferred from the impingers to small vials, which were placed in the LC's autosampler for injection. Separation was accomplished with a $3.9 \times 150\text{mm}$ C_{18} -based column with a $4\mu\text{m}$ particle size. A mixture of water, acetonitrile, and ethyl acetate were used as the solvents ("eluent"). This combination of column and eluents was chosen because it produced a good separation in less than 15 minutes. This method also avoided the use of tetrahydrofuran (THF), which is difficult to store and dispose of. The use of a guard column was rejected in favor of an in line filter; guard columns are expensive and not necessary for this analysis. As with the GC system, all operations were computer controlled.

Fig. 4 gives an overview of the equipment used to characterize dilute vehicle exhaust.

4. RESULTS

4.1. Accuracy and Precision

(1) NMHC Results from a Prototype LEV. A series of five complete dynamometer tests (FTP-75) were performed on a prototype low-emission vehicle, over a ten day period. The concentrations of the individual hydrocarbons measured by the gas chromatograph systems were added together for each test. The resulting values were compared to the non-methane hydrocarbon results produced by the dynamometer analyzer. As seen in Table 4, the GC results compared very well with those from the dynamometer, easily meeting the objective of $\pm 10\%$. One set of chromatograms obtained during this study are displayed in Fig. 5.

(2) Analysis of a Reference Standard Gas with Known Concentrations. In order to determine the quality of the speciated results from the gas chromatograph systems, a reference gas was analyzed. This gas was purchased from Takachiho Chemical in Japan, and contained 20 non-methane hydrocarbons. Table 5 summarizes the results from 14 analyses of this gas performed over a two day period, (i.e., 2 sets of 7 consecutive analyses).

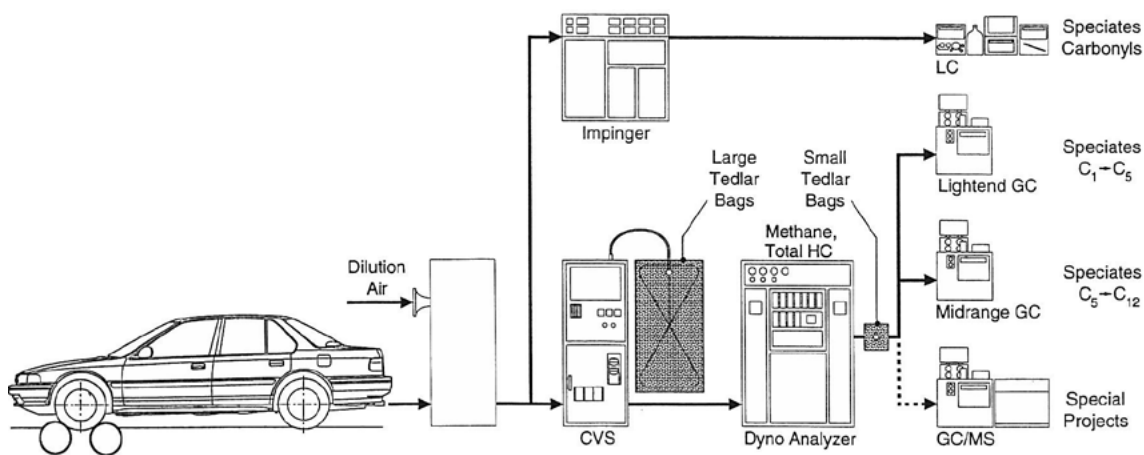


Fig. 4 Overview of Equipment Used to Characterize Dilute Vehicle Exhaust.

Table 5 Analysis of Reference Standard by Gas Chromatography:
Comparison with Reference Concentrations, and Precision of Results
(Based on 14 Analyses over a Two Day Period)

Hydrocarbon	Formula	Takachiho Concentration (ppmC)	Measured Concentration			Retention Time	
			Mean (ppmC)	% Diff from Takachiho	Rel Std Dev $s_{(n-1)}/\bar{x} \times 100\%$	Mean (min)	Rel Std Dev $s_{(n-1)}/\bar{x} \times 100\%$
Ethane	C ₂ H ₆	2.10	2.17	+3.4	.7	8.42	.15
Ethene	C ₂ H ₄	.97	.914	-5.8	.7	10.47	.40
Propane	C ₃ H ₈	2.20	2.07	-5.7	.6	13.42	.35
Propene	C ₃ H ₆	.94	.919	-2.2	.6	18.20	.32
Butane	C ₄ H ₁₀	2.13	2.08	-2.4	.7	21.04	.31
Butene	C ₄ H ₈	1.02	.932	-8.6	.7	25.04	.27
Pentane	C ₅ H ₁₂	.50	.482	-3.6	.7	28.42	.26
Cyclohexane	C ₆ H ₁₂	.50	.483	-3.4	.9	33.85	.23
Hexane	C ₆ H ₁₄	.50	.512	+2.4	.5	15.10	.08
Benzene	C ₆ H ₆	.51	.509	-.1	1.0	17.10	.07
Heptane	C ₇ H ₁₆	.52	.508	-2.2	.9	19.23	.06
Toluene	C ₇ H ₈	.49	.476	-2.9	1.8	21.49	.04
Octane	C ₈ H ₁₈	.50	.495	-.9	.8	23.31	.04
Xylene	C ₈ H ₁₀	.50	.512	+2.4	2.4	25.61	.03
Nonane	C ₉ H ₂₀	.49	.517	+5.5	.7	27.16	.03
Trimethylbenzene	C ₉ H ₁₂	.50	.490	-2.0	3.3	29.33	.02
Decane	C ₁₀ H ₂₂	.53	.532	+4	1.0	30.74	.02
Dimethylethylbenzene	C ₁₀ H ₁₄	.53	.529	-.1	7.2	33.07	.02
Undecane	C ₁₁ H ₂₄	.62	.646	+4.1	1.8	34.06	.02
Dodecane	C ₁₂ H ₂₆	.57	.563	-1.2	2.5	37.17	.02

The hydrocarbons in the shaded areas are important because of their large contribution to the specific reactivity of exhaust from a typical vehicle. Both GCs were calibrated using only an NIST-traceable propane standard, as required by CARB. Hydrocarbons from ethane to cyclohexane were measured on the lightend GC.

The concentration results from the gas

chromatograph systems agreed well with Takachiho's results; most results differed by less than 5%. The precision of the concentration values was also very good, with an average RSD (relative standard deviation) of 1.5%. The retention times remained very stable; the average RSD was 0.14%.

(3) Analysis of Carbonyl Control Standard. Table 6

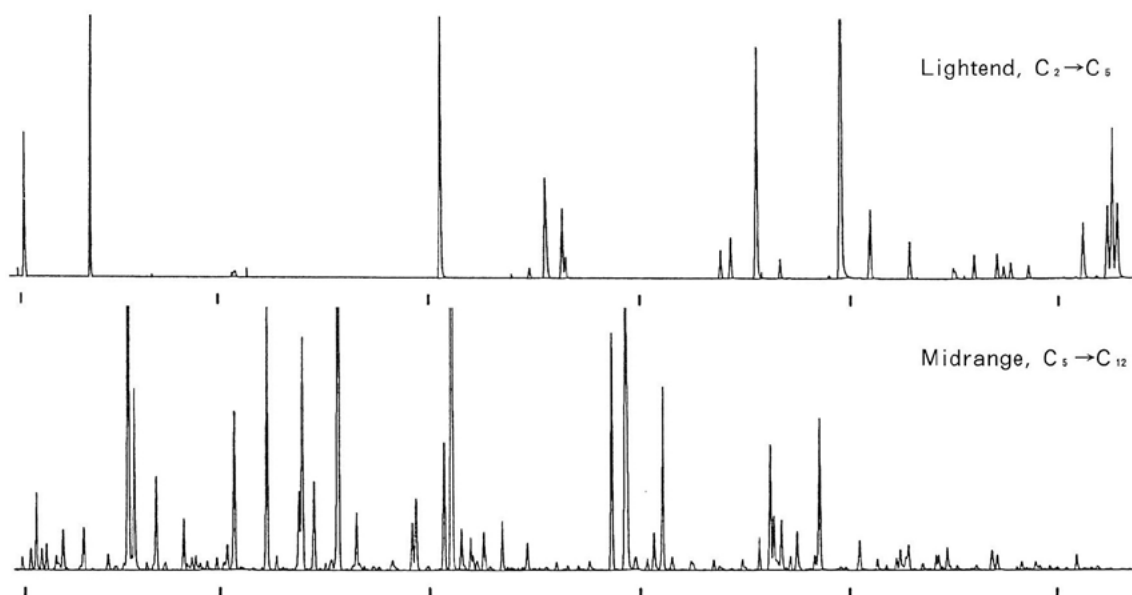


Fig.5 Gas Chromatograms Obtained from Low-emission Vehicle. (Interval between Marks = 5 min. Chromatograms have been Expanded off Scale for Illustrative Purposes.)

Table 6 Analysis of Control Standard by Liquid Chromatography: Precision of Results
(Based on 9 Consecutive Analysis)

Carbonyl	Formula	Measured Concentration		Retention Time	
		Mean $\mu\text{g/ml}$	% Rel Std Dev	Mean (min)	% Rel Std Dev
Formaldehyde	CH_2O	.575	1.4	4.02	.2
Acetaldehyde	$\text{C}_2\text{H}_4\text{O}$	.454	3.0	5.58	.2
Acetone	$\text{C}_3\text{H}_6\text{O}$	.231	2.6	7.13	.2
Acrolein	$\text{C}_3\text{H}_4\text{O}$	.226	1.8	7.58	.2
Propionaldehyde	$\text{C}_3\text{H}_6\text{O}$	.227	4.3	8.07	.2
Crotonaldehyde	$\text{C}_4\text{H}_6\text{O}$	.226	2.3	9.37	.2
Methyl Ethyl Ketone	$\text{C}_4\text{H}_8\text{O}$	.227	2.3	9.71	.2
Butyraldehyde	$\text{C}_4\text{H}_8\text{O}$	.242	2.3	10.13	.1
Benzaldehyde	$\text{C}_7\text{H}_6\text{O}$	.220	3.4	10.97	.1
Valeraldehyde	$\text{C}_5\text{H}_{10}\text{O}$	.223	2.9	12.01	.1
Tolualdehyde	$\text{C}_8\text{H}_8\text{O}$	.212	3.7	12.58	.1
Hexanal	$\text{C}_6\text{H}_{12}\text{O}$	.218	7.4	14.01	.1

summarizes the results from 9 consecutive analyses of a carbonyl “control” standard. This standard contained 12 carbonyls in concentrations similar to those encountered during a typical vehicle test, and was run on a daily basis to check the operation of the instrument. The precision of the concentration values was acceptable; the average RSD was 3.1%. The retention times were very constant, with an average RSD of 0.16%. A chromatogram from this study is shown in Fig. 6.

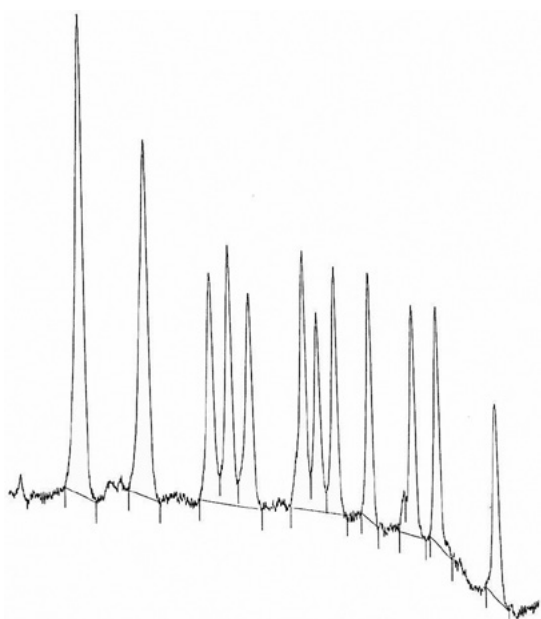


Fig. 6 Liquid Chromatogram of Control Standard. (Carbonyl Concentrations Range from .05ppm to .09ppm.)

(4) Accuracy of Carbonyl Analysis. The determination of accuracy for a carbonyl analysis procedure is somewhat difficult. It is easy to check the liquid chromatograph results by analyzing reference materials, but a check of the impinger sampling system is problematic. Our laboratory performed the acetone recovery method commonly used to check the operation of such systems. A known weight of liquid acetone was vaporized into the system, at the point where a vehicle's tailpipe would normally be connected. A series of these tests was run. Typically 90% to 99% of the expected acetone weight was recovered in the impingers.

Although this technique was apparently successful, it is not an entirely accurate method for determining actual carbonyl recovery during an emissions test. Carbonyls are sensitive to heat and moisture, but these parameters are absent from the acetone recovery test. Our laboratory will investigate the possibility of performing a carbonyl recovery experiment with the vehicle connected to the system.

4.2. Linearity and Limit of Detection

(1) Hydrocarbons. A preferred method for LOD determination has been specified by CARB in their “California Non-Methane Organic Gas Test Procedures” document²⁾. This method is somewhat unusual in that it requires analytical data at multiple concentration levels. Thus, a linearity determination

is performed concurrently with the LOD method. The LOD equation is given as:

$$\text{LOD} = |A| + 3.3(s)$$

where “A” is the x-intercept of a least squares regression of the multipoint concentration data, and “s” is the standard deviation of replicate analyses of the lowest standard. In order to obtain the multiple data points required for this determination, a reference gas containing the requested target hydrocarbons was diluted to four different concentration levels. The gas was diluted in six-liter, deactivated metal canisters fitted with electronic pressure gauges. Dilutions of high accuracy were obtained with this system.

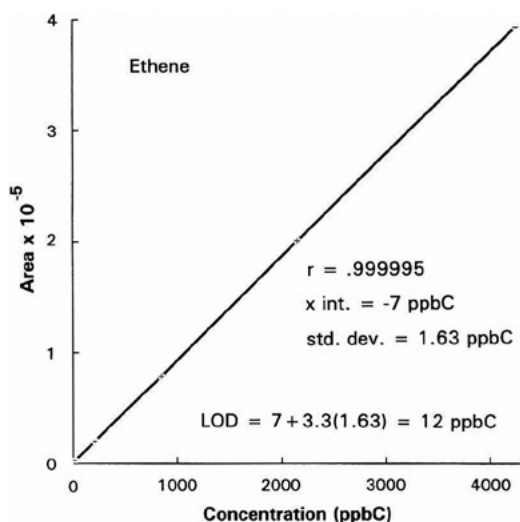


Fig. 7 LOD Determination for the Hydrocarbon Ethene.

CARB specified a maximum detection limit of 20 ppbC, and a minimum correlation coefficient, “r” of 0.995 (where $r = 1$ indicates perfect linearity). The average detection limit obtained in our laboratory (using the rigorous CARB method) was 12 ppbC, with no LOD exceeding 17 ppbC. Correlation coefficients were 0.9998 or better. An example of a hydrocarbon LOD determination can be seen in Fig. 7.

(2) Carbonyls. The CARB-specified method for carbonyl LOD determination was exactly the same as that for hydrocarbon LOD. However, obtaining the multiple data points was much easier for the

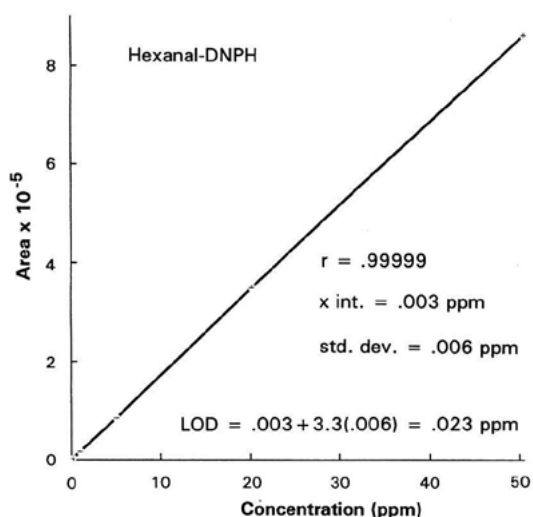


Fig. 8 LOD Determination for the Derivatized Carbonyl Hexanal-DNPH.

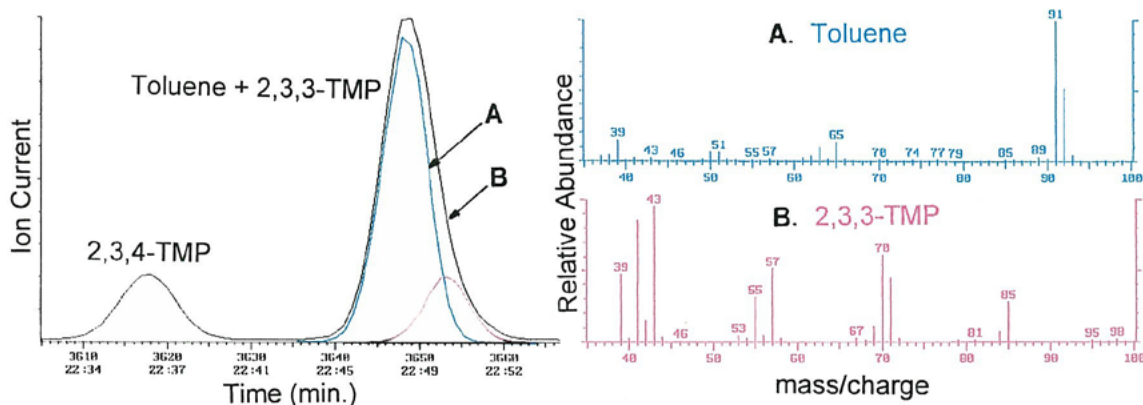


Fig. 9 GC-MS Chromatogram Revealing Contribution of Toluene (Blue) and 2,3,3-TMP (Red) to Total Peak Area (Black). Mass Spectra Extracted from This Peak are Shown on Right.

carbonyls, since the liquid standard could simply be diluted by volume. The maximum LOD specified by CARB was 0.06 ppm derivatized carbonyl, and the minimum value of “r” was 0.995. All detection limits in our laboratory were less than 0.06 ppm, and all correlation coefficients were greater than 0.9999. Fig. 8 shows an example of a carbonyl LOD determination.

4.3. Separation

(1) Hydrocarbons. Peak separation in the chromatograms was sufficient to provide accurate quantitative data for most of the detected hydrocarbons. Since the two GC methods were run simultaneously, this separation could be accomplished in less than 40 minutes. Major compounds that did not separate well required special attention:

Toluene and 2,3,3-trimethylpentane. These hydrocarbons had virtually identical retention times, which caused them to appear as a single peak in the chromatogram. By mathematically extracting characteristic mass fragments, the GC/MS was used to determine the contribution of each compound to the total peak area (Fig. 9). For tests performed using Phase II certification fuel, 2,3,3-trimethylpentane was typically found to account for about 14% of the combined peak area. (This value was somewhat dependent on vehicle type.)

Methyl t-butyl ether. The oxygenate MTBE was sensitive to slight changes in column conditions, which resulted in somewhat unstable retention times. The MTBE peak would often obscure the 2,3-dimethylbutane peak. Fortunately, 2,3-dimethylbutane could be measured on the lightend GC, permitting the determination of MTBE by subtraction.

Benzene and methylcyclopentene. Data from the GC/MS revealed that this combined peak typically consisted of less than 2% methylcyclopentene, for vehicles tested using Phase II fuel. The concentration calculated from this value was near the detection limit of the instrument. Therefore, no data

manipulation was performed; the entire peak area was assigned to benzene.

Meta- and para-xylenes. It was not possible to separate these isomers without increasing analysis time and/or changing column chemistry. Since they are chemically very similar, they were simply treated as a single peak, and reported as m+p xylene. For the purpose of calculating specific reactivity, the combined peak was assigned an averaged reactivity value.

(2) Carbonyls. The carbonyl analysis was also optimized for separation and speed. This method required more than twice as many samples per test as the hydrocarbon method; therefore, the run time was kept below 15 minutes. A secondary advantage of short analysis times was the conservation of the LO solvents.

4.4. Identification

Four methods were used in the identification of hydrocarbons. The primary method was direct identification with the GC/MS, as described previously. The PID detectors aided in the identification of hydrocarbons with similar mass spectra, such as alkenes and cyclo-alkanes. When available, standard reference gasses were used to confirm identifications. Finally, scientific literature was consulted^{3) 4)} in order to compare identifications obtained at other laboratories.

Reference materials made from pure carbonyl derivatives were used to identify peaks in the carbonyl chromatogram.

5. CONCLUSION

In response to the recent LEV/CF regulations, Honda's California emission laboratory has developed the capability to assess the reactivity of a vehicle's exhaust. Hydrocarbons and carbonyls were speciated using chromatographic methods. Efficient cryogenic pre-concentration and precise

instrument control were important for the accurate determination of hydrocarbons. The measurement of carbonyls required reliable sample collection and accurate volume measurement. Analyses performed on a low emission vehicle and on reference standards revealed the high accuracy and precision of these new techniques. Good compound separation and low detection limits were also achieved.

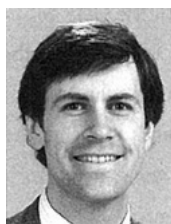
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