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Gas–solid chromatographic analysis of automobile tailpipe emissions as a function of different engine and exhaust system modifications

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Abstract

A single, relatively short gas–solid porous-layer open-tubular chromatographic column was used to separate aliphatic hydrocarbons, aromatic hydrocarbons and some inorganic gases (O_2, CO and CO_2) found in automobile exhaust. The column's performance and longevity did not appear to be affected by the presence of water or carbon dioxide in the samples. The concentrations of the emission gases varied considerably with changes in air/fuel ratio, coil voltage and use of catalytic converters. The results of the analyses were compared with those obtained using a commercial emission analyser ("sniffer").

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1. Introduction

Gas–solid chromatography (GSC) is a highly useful technique for separating gases and other volatile compounds. It is most often used for light hydrocarbons and a variety of inorganic gases. There are both packed and capillary GSC columns available. Useful GSC stationary phases are made from silica [1–4], aluminum oxide [5–14], porous polymers [15–18] zeolite-type molecular sieves [19–21] and most recently cyclodextrins [22–24]. Summaries of these approaches have been reported recently [22–24]. GSC alone or coupled with mass spectrometry may be the most viable analytical method to identify and determine a variety of individual components in automobile exhaust. The study of automobile tailpipe emissions is of increasing importance given social concerns about the environment and the resulting legislation and regulations [25–28].

Spark-ignition engines produce three general classes of tailpipe emissions that are unwanted and considered harmful: carbon monoxide (CO), hydrocarbons and nitrogen oxides (NO_x). Carbon monoxide results from the incomplete combustion (oxidation) of the fuel. Nitrogen oxides (largely NO and NO_2) form from the oxidation of N_2 in the air during high-temperature combustion. The hydrocarbons are a variety of organic compounds that come from uncombusted fuel. Vehicles produced for use in the USA after 1974 contain catalytic converters which, when functioning properly, decrease emissions of the aforementioned classes of compounds.

Currently, "tailpipe-sniffer" tests are used in cities that have air quality problems. Exhaust

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samples are taken and the amounts of carbon monoxide (CO), carbon dioxide (CO_2) and total hydrocarbons are measured. Infrared analysis (IR) is used for CO and CO_2 while flame ionization detection (FID) without separation gives an approximate total hydrocarbon number. While the "sniffer" tests are relatively fast and inexpensive, nothing is learned about the speciation of the hydrocarbons or about the other gaseous components.

The aim of this work was to determine if the majority of gaseous automobile tailpipe emissions can be separated and identified using a single new GSC column. This is a capillary column that evolved from earlier packed column work [22–24]. Measurements were also made with several different engine and exhaust system configurations and the results were compared with those from a standard "tailpipe-sniffer test". Specifically, the effects of catalytic converters, air/fuel ratio, ignition system and various combinations of these were examined.

2. Experimental

2.1. Analytical methodologies

A Hewlett-Packard (Avondale, PA, USA) 5890 Series II gas chromatograph equipped with a split–splitless injection port, flame ionization and thermal conductivity detectors and a liquid nitrogen cryogenic coolant system was used. The injector and detector ports were set at 150 and 200°C, respectively. The oven temperature programs were as follows (a) for hydrocarbons, 85°C for 3 min, then increased at 7.5°C/min to 250°C, which was held for 20 min; (b) for oxygen and nitrogen, −65°C isothermal; (c) for carbon monoxide, −55°C isothermal; and (d) for carbon dioxide, 25°C isothermal. Data collection was accomplished with a Hewlett-Packard 3396B Series II integrator. Helium was used as the carrier gas for all experiments with flow-rates of approximately 2 ml/min. The column used in this study was a 15 m × 0.32 mm I.D. GasPro column produced by Advanced Separation Technologies (Whippany, NJ, USA). This commercial column is not identical with those we made and discussed in previous reports, although some of the selectivities are similar [22–24]. Quantification of aliphatic hydrocarbons and inorganic gases was effected by making calibration graphs using gas mixtures of known concentrations. All gas standards including 1000 ppm C_1–C_6 *n*-alkanes (can mix 236), 1000 ppm C_2–C_6 alkenes (can mix 223), 15 ppm branched alkanes (can mix 2) and 5% inorganic gas mixtures (can mix 234) were purchased from Alltech (Scott Specialty Gases; Plumsteadville, PA, USA). An aromatic hydrocarbon standard mixture (benzene, toluene and xylenes) was prepared by weighing the pure liquids, 19.8 mg of benzene, 19.2 mg of toluene, 18.6 mg of *o*-xylene, 21.0 mg of *m*-xylene and 19.6 mg of *p*-xylene in 1.0 l of methylene chloride, resulting in a standard mixture containing 19.8 mg/l of benzene, 19.2 of toluene, 18.6 mg of *o*-xylene, 21.0 mg of *m*-xylene and 19.6 mg of *p*-xylene. Quantification of samples was effected via peak-area measurements through the calibration graphs for the standards. Most components from C_1 to C_8 appeared to be resolved. The major compounds were identified via retention comparison with authentic standards and by GC–MS analysis with a Hewlett-Packard Model 5970 instrument.

For comparative purposes the exhaust samples were also evaluated with a Model MCA-3000 modular computer analyzer (Sun Electric, Crystal Lake, IL, USA). This "sniffer" gives a number (in ppm, v/v) for total hydrocarbon emissions (using FID) and also concentrations of CO and CO_2 (using IR) and O_2 (via an oxygen sensor). It is calibrated periodically by the manufacturer. According to the instruction manual this is done with gas samples containing 600 ppm (v/v) of propane, 11.0% of carbon dioxide and 1.6% of carbon monoxide. This instrument also measures the exhaust temperature, engine rpm and the air/fuel ratio.

2.2. Engine and exhaust configuration

The engine used in this study was a 1969 Oldsmobile 7.4-l (455-in^3; 1 in = 2.54 cm) V-8 power plant with dual exhaust (5.72 cm diameter) and a two-barrel Rochester carburetor. The bore was 10.48 cm and the stroke was 10.80 cm. This engine produces 310 hp (1 hp = 745.7 W) at 4700 rpm and a torque of 68 kg m (490 ft. lb.) at

2400 rpm. A large number of variables affect automobile exhaust emissions including the type of fuel, air/fuel ratio, intake manifold, engine speed, exhaust gas recirculation (EGR), valve timing, head/piston/port/valve design, spark timing, spark quality, exhaust manifold design, use of air injection reactors (AIR), use of catalytic converters and exhaust pipe length. It was beyond the scope of this project to study all of these factors. However, a few representative factors that can be easily and reproducibly controlled were chosen: the air/fuel ratio (specifically the effect of a lean burn system), spark quality, the use of an AIR and the use of catalytic converters. Each of these modifications is summarized below [27–29].

(1) The air/fuel ratio is the mass of air divided by the mass of fuel delivered to the engine. The stoichiometric air/fuel ratio is considered to be 14.7 parts air to one part of gasoline fuel. The equivalence ratio (ϕ) is used to describe whether an engine is operating with an excess of air or fuel. The equivalence ratio is defined as the fuel/air ratio (note that this is the inverse of the aforementioned air/fuel ratio) delivered to the engine divided by the stoichiometric fuel/air ratio. Consequently, if $\phi < 1$ the engine is said to run lean (or with excess air), when $\phi > 1$ the engine is said to run rich (or with excess fuel) and if $\phi = 1$ the engine is said to operate at the stoichiometric condition. The equivalence ratio is an important variable for engine operation because it affects the exhaust composition in addition to the engine's efficiency, power and smoothness of operation. In general, it is known that as ϕ increases the concentrations of carbon monoxide and hydrocarbons in the exhaust also increase (because of a lack of O_2 to burn the fuel). As ϕ decreases there is usually a corresponding decrease in the exhaust levels of carbon monoxide and hydrocarbons until misfire occurs. Maximum engine power occurs when $\phi = 1.1$. In order to make the intake mixture leaner, a Lean Power digital carburetion system was installed. It consisted of an air-intake system with filter and valve which feeds air into a baseplate that fits between the intake manifold and carburetor. The amount of air fed into the intake was regulated by a computer which read a crank sensor mounted near the flywheel. When the engine was operating with the "lean system" the equivalence ratio (ϕ) was approximately 0.85.

(2) A Jacobs Electronics ignition system (Energy Pak) was used to improve the ignition of the fuel–air mixture. This system uses a computer to read impedance changes in the coil. This is done in order to compute the best spark intensity, duration and phase angle for each engine condition. The coil included with this system was capable of a higher output voltage (56 000 V) than was provided by the baseline system (40 000 V). In order to simplify the ignition comparison all factors were kept constant except for variations in the coil voltage.

(3) Fig. 1A shows the basic exhaust configuration for the test vehicle. The catalytic converters used were from a 1994 Chevrolet Caprice containing a 5.7-l (350-in.^{3}) V-8 LT1 engine (i.e., AC wide oval part No. 25152589). They were installed as shown in Fig. 1B. The original exhaust pipes can be closed so that all of the emissions go through the catalytic converter. Stainless-steel sample tubes were connected to the front and rear of the converter in order to take exhaust gas samples (Fig. 2). Thermocouples were mounted in the exhaust pipe, 6 in. in front of the converter monolith. These were used to monitor the exhaust temperature, as temperature has a great effect on conversion efficiency. The so-called "light-off temperature" is the temperature at which the catalyst in the catalytic converter operates at 50% conversion efficiency with an excess of oxygen (i.e., conversion of carbon monoxide and the hydrocarbons to CO_2

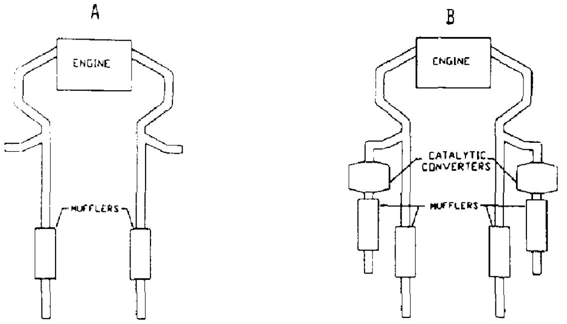

Fig. 1. (A) Unmodified exhaust system of original vehicle. (B) Modified exhaust systems showing the location of the two added catalytic converters (see Experimental for further details).

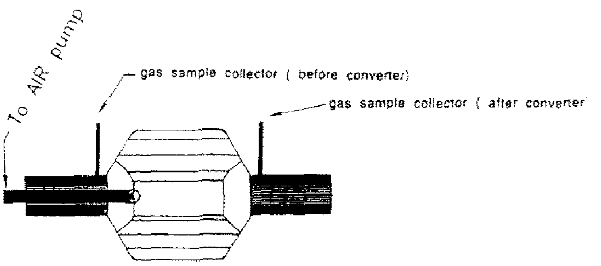

Fig. 2. Top view of an installed catalytic converter with "gas sample collection tubes" before and after the converter. Also shown is an additional AIR injection tube going directly into the catalytic converter (see Experimental for further details).

and water). The "light-off temperature" is in the range 250–300°C. Below this temperature the catalyst is considered ineffective for automotive purposes. There is also an upper temperature limit (ca. 500°C). This is the result of the sintering of the noble metal catalyst substrate at high temperatures, which lowers the surface area.

(4) The AIR pump was taken from a 1985 Oldsmobile Cutlass equipped with a 5-l (307-in.^{3}) V-8 engine. This is a rotary vane pump which forces additional O_2 (as air) into the catalytic converter in order to increase its effectiveness. The AIR pump was connected to brackets at the front of the engine in the same place where the air conditioning compressor is normally located. The supplemental air was injected into the front of the catalytic converter (see Fig. 2).

2.3. Sampling conditions

The following conditions were held constant for all samples. The engine was run on 87 octane unleaded gasoline. The engine was always run for 10 min at 1400 rpm allowing the exhaust gases to reach a steady-state temperature of 355 ± 20°C before any samples were taken.

All exhaust samples were taken with a 125-ml gas sampling bulb having PTFE stopcocks at both ends and a septum needle port on the side of the bulb (Supelco, Bellefonte, PA, USA). This bulb was attached to one or other of the previously described stainless-steel sample tubes. Approximately 30 "sample bulb volumes" of exhaust gas were passed through the sampling device before the stopcocks were closed (exit port first), thereby trapping the exhaust sample. Note that we did not dilute the samples ~14 to 1 with pure dry air as sometimes recommended by the EPA, in order to prevent condensation. This provided a more strenuous test of the column's relative inertness to injected water.

Samples were analyzed from seven different engine and/or exhaust configurations, as follows: (1) baseline engine (i.e., no catalytic converter, no AIR, no lean fuel mixture and the standard 40 000-V coil was used); (2) engine + coil (i.e., no catalytic converter, no AIR, no lean fuel mixture, but the special 56 000-V coil was used); (3) engine + lean + coil (i.e., no catalytic converter, no AIR, the lean carburetion system was used and the 56 000-V coil was used); (4) engine + converter (i.e., catalytic converter was used, no AIR, no lean fuel and the standard 40 000-V coil was used); (5) engine + converter + lean (i.e., the catalytic converter was used, the lean fuel carburetion system was used, no AIR and the standard 40 000-V coil was used); (6) engine + converter + lean + coil (i.e., the catalytic converter was used, the lean fuel carburetion system was used, the special 56 000-V coil was used, no AIR); (7) engine + converter + coil + AIR (i.e., the catalytic converter was used, the special 56 000-V coil was used, the AIR system was used, no lean fuel mixture).

3. Results and discussion

The ability to use a single, short (15 m) capillary column for the determination of aliphatic hydrocarbons, aromatic hydrocarbons and inorganic gases in automobile exhaust was convenient. However, because of different detection methods used [i.e., FID for the hydrocarbons and thermal conductivity (TCD) for the inorganic gases] and different column temperatures for the volatile analytes of interest, a minimum of two separate injections were required in order to determine all components. Fig. 3A shows the separation of the hydrocarbon components from the baseline engine exhaust (i.e., no catalytic converter or any other modifications; see Experimental). Note that most of the hydrocarbon

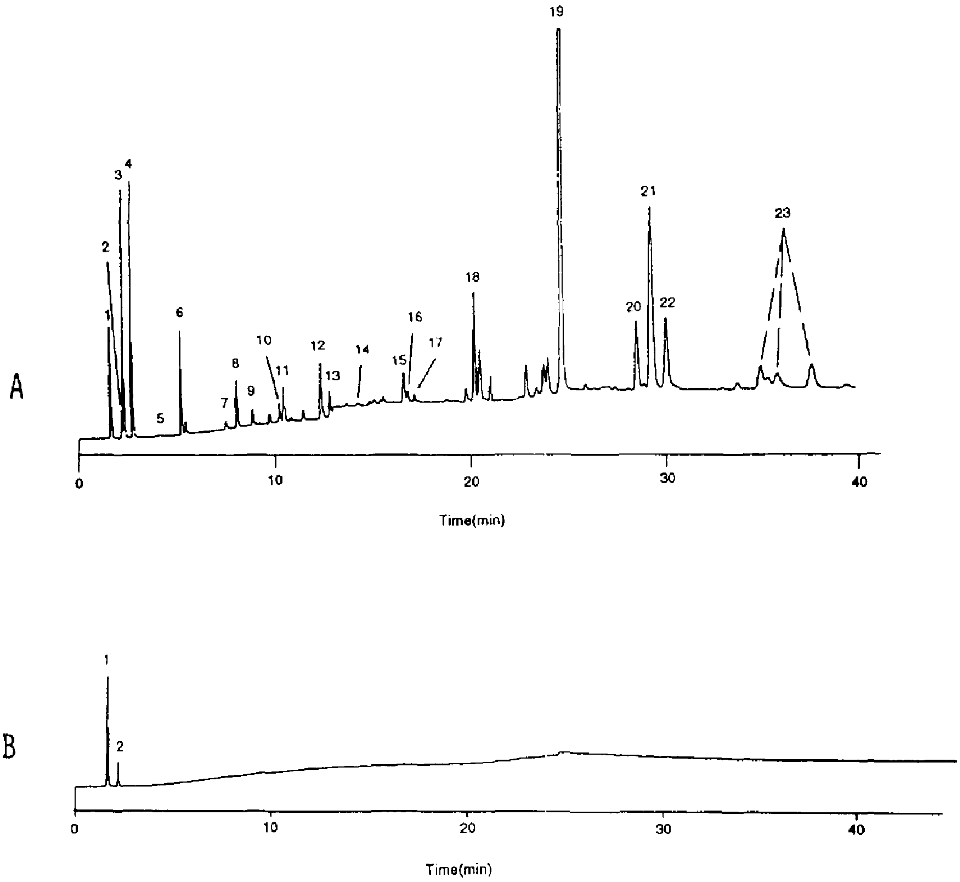

Fig. 3. (A) Gas–solid chromatogram showing the separation of a variety of aliphatic and aromatic hydrocarbon components in the exhaust of the baseline engine (i.e., an engine with no modifications to reduce unwanted emissions). This is characteristic for large pre-1975 engines in the USA. Peaks identified via GC–MS: 1 = methane; 2 = ethane; 3 = ethylene; 4 = acetylene; 5 = propane; 6 = propylene; 7 = isobutane; 8 = butane; 9 = propyne; 10 = butene; 11 = 1,3-butadiene; 12 = 2-methylbutane; 13 = pentane; 14 = pentene; 15 = 2-methylpentane; 16 = 3-methylpentane; 17 = hexane; 18 = benzene; 19 = toluene; 20 = ethylbenzene; 21 = *p*- and *m*-xylene; 22 = 0-xylene; 23 = alkylated benzenes. (B) Gas–solid chromatogram showing the effect of a catalytic converter in reducing hydrocarbon emissions in automobile exhaust (i.e., engine condition 5 in Table 1). The experimental conditions for (A) and (B) were identical (i.e., a 15 m × 0 32 mm I.D. GasPro column, flow-rate = 2.0 ml/min and a temperature program of 85°C for 3 min then ramped at 7.5°C/min to 250°C. See Experimental for further details.

species of interest appear to be easily resolved. An exception appears to be *m*- and *p*-xylene, which are co-eluted as peak 21. Fig. 3B is the analogous chromatogram generated under identical conditions except that the exhaust was run through a properly functioning catalytic converter (see Experimental). Fig. 4A shows the separation of oxygen, nitrogen and carbon monoxide on the same GSC column at subambient temperatures and Fig. 4B shows the separation of carbon dioxide at room temperature.

Table 1 lists the concentrations of many of the aliphatic hydrocarbons from the test automobile's exhaust under different conditions and Table 2 lists analogous data for the aromatic hydrocarbons. Table 3 gives the concentrations of several inorganic gases from the same samples. It was expected that the baseline engine emissions (with no control devices) would have the highest combustion product emissions. This was true except for case No. 3 (Tables 1–3), where the special carburetion system gave a lean air–fuel mixture to the engine. Ordinarily lean mixtures produce less hydrocarbon and carbon

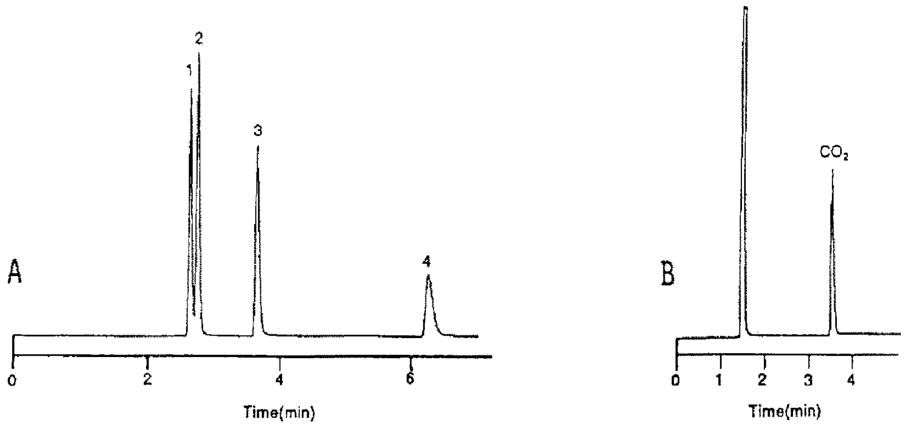

Fig. 4. GSC separation of (A) 1 = oxygen, 2 = nitrogen, 3 = carbon monoxide and 4 = methane on a 15 m × 0.32 mm I.D. GasPro capillary column at −65°C and (B) carbon dioxide on the same column at 25°C. When determining carbon monoxide (which is a very small peak in automobile exhaust) the separation is better at −55°C. The CO peak elutes faster and much sharper at this temperature (see Experimental).

monoxide emissions (owing to more complete oxidation processes). However, too lean a mixture will begin to cause engine misfire and an increase in uncombusted fuel products. That is what happened in this case. The chemical evidence for this is the increase in the exhaust concentrations of most hydrocarbons and oxygen (Tables 1–3). Clearly, when trying to improve fuel economy and emissions by having a lean air/fuel ratio, some caution must be exercised. An incorrect or inexpert modification that leads to misfires can make exhaust emissions worse rather than better. The two things in this study that seemed to give the greatest reductions in hydrocarbon and/or carbon monoxide emissions were the catalytic converter and the use of a higher coil voltage. In this test system the catalytic converter usually reduced the concentra-

Table 1
Concentrations of aliphatic hydrocarbons (ppm, v/v)[a] in the exhaust gas of the test vehicle

Engine conditions	Methane	Ethane	Ethylene	Propylene	Butane	Butene	2-Methylbutane	Pentane	2-Methylpentane	3-Methylpentane	Total[b]
(1) Baseline engine	49.3	7.3	69.7	21.1	6.6	0.5	6.4	1.0	6.2	NC[c]	369.2
(2) Engine + coil	15.0	3.4	40.4	14.1	3.0	0.1	2.4	ND	2.3	ND	183.1
(3) Engine + lean + coil	19.4	5.1	69.7	29.4	13.9	2.1	10.7	5.3	10.2	UD	462.4
(4) Engine + converter	18.3	3.0	ND	ND	ND	ND	ND	ND	ND	ND	24.3
(5) Engine + converter + lean	46.3	6.7	ND	ND	ND	ND	ND	ND	ND	ND	59.7
(6) Engine + converter + coil + lean	16.8	2.3	ND	ND	ND	ND	ND	ND	ND	ND	21.4
(7) Engine + converter + coil + AIR	10.8	2.3	0.9	ND	ND	ND	0.1	ND	0.1	ND	18.3

[a] These concentrations are given in ppm by volume of gas.

[b] in order to obtain this "sum" for the total hydrocarbon mixture, the measured concentration of each component was multiplied by the number of carbons in that component. These numbers were then added together.

[c] ND = Not detected. This means that the concentrations of these compounds were below the limit of detection (LOD) for this particular system (see Experimental). The LODs for the instrumental conditions of this study are as follows: (in ppm, v/v): methane = 1.2, ethane = 0.8, ethylene = 0.9, propylene = 0.6, butane = 0.2, butene = 0.2, 2-methylbutane = 0.3, pentene = 0.2, 2-methylpentane = 0.3, 3-methylpentane = 0.3.

Table 2
Concentrations of aromatic hydrocarbons (mg/l)[a] in the exhaust gas of the test vehicle

Engine conditions	Benzene	Toluene	*m*- +*p*-Xylene	*o*-Xylene
(1) Baseline engine	0.045	0.35	0.14	0.057
(2) Engine + coil	0.025	0.095	0.045	0.017
(3) Engine + lean + coil	0.032	0.14	0.048	0.019
(4) Engine + converter	0.0086	0.014	ND[b]	ND
(5) Engine + converter + lean	ND	ND	ND	ND
(6) Engine + converter + coil + lean	ND	0.049	0.041	0.016
(7) Engine + converter + coil + AIR	ND	0.023	0.020	0.0057

[a] Note that these concentrations are not directly comparable with those of the aliphatic hydrocarbons in Table 1 because their units of concentration are different. The standards used to obtain these concentrations were made up as liquid solutions. Hence these concentrations are given as mg of aromatic compound per liter of solution (see Experimental).

[b] ND = Not detected. This means that the concentration of these compounds were below the limit of detection (LOD) for this particular system (see Experimental). The LODs for the instrumental conditions of this study are as follows (in ppm, w/v): benzene = 0.002; toluene = 0.002; *o*-, *m*- and *p*-xylene = 0.002.

tions of most of the hydrocarbons by one to two orders of magnitude. Methane and ethane were also reduced but only by about 60%. The catalytic converter also effectively oxidized carbon monoxide in all cases (Table 3).

While the quantification of individual components in automobile tailpipe emissions provides useful research information, it will not be done routinely for all vehicles because of time and cost restraints. Instead, a more rapid analysis of a few representative components with a computer-monitored set of sensors is used. All samples analyzed by GSC in this study were also evaluated with such a commercial modular emissions analyzer or "sniffer" (see Experimental). A comparison of the results obtained by GSC analysis and with the commercial analyzer for oxygen, carbon dioxide, "total hydrocarbons" and carbon monoxide are shown in Figs. 5–8. Except for carbon monoxide it appeared that both methods give similar relative results but slightly different absolute concentrations. For example, GSC analysis consistently gave higher results for hydrocarbons and oxygen. Converse-

Table 3
Concentrations of some inorganic gases (%, v/v) in the exhaust gas of the test vehicle

Engine conditions	Oxygen	Carbon monoxide	Carbon dioxide
(1) Baseline engine	3.7	0.6	10.7
(2) Engine + coil	4.0	0.7	6.1
(3) Engine + lean + coil	6.2	0.7	6.1
(4) Engine + converter	4.3	ND[a]	9.2
(5) Engine + converter + lean	4.3	ND	9.0
(6) Engine + converter + coil + lean	4.9	ND	7.9
(7) Engine + converter + coil + AIR	9.0	ND	3.1

[a] ND = Not detected. This means that the concentrations of these compounds were below the limit of detection (LOD) for this particular system (see Experimental). The LODs for this instrument (%, v/v) are as follows: $O_2 = 0.06$, $CO = 0.07$, $CO_2 = 0.08$.

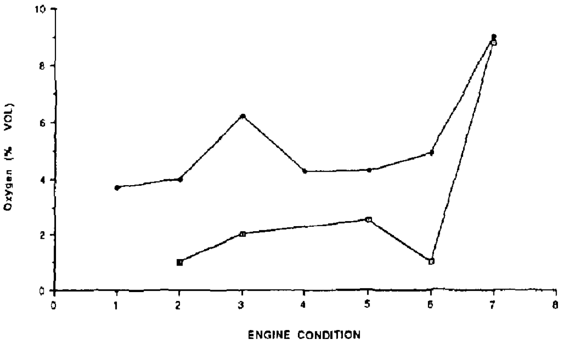

Fig. 5. Comparison of the oxygen levels measured in automobile tailpipe exhaust (◆) by GSC and (□) with the modular computer analyzer (see Experimental for details of the exact methodologies). The engine condition numbering convention is identical with that in Tables 1–3.

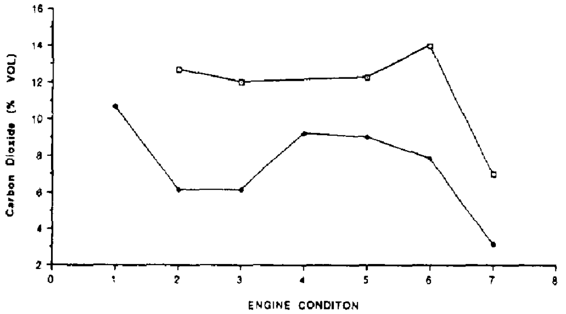

Fig. 6. Comparison of the carbon dioxide levels measured in automobile tailpipe exhaust (◆) by GSC and (☐) with the modular computer analyzer (see Experimental for details of the exact methodologies). The engine condition numbering convention is identical with that in Tables 1–3.

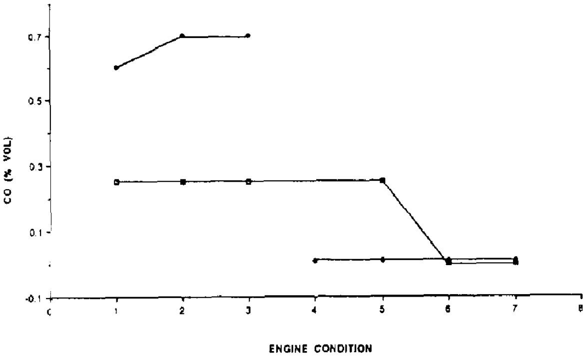

Fig. 8. Comparison of the carbon monoxide levels measured in automobile tailpipe exhauts (◆) by GSC and (☐) with the modular computer analyzer (see Experimental for details of the exact methodologies). The engine condition numbering convention is identical with that in Tables 1–3.

ly, it always gave lower results for carbon dioxide. The fact that the GSC results for hydrocarbons were slightly higher than those given by the commercial emissions (modular) analyzer was surprising (Fig. 7). This was because the GSC results included only the normalized sum of the amounts of the aliphatic and olefinic hydrocarbons listed in Table 1. Hence significant amounts of aromatic hydrocarbons and a few other components were not included in the GSC hydrocarbon total (Table 1 and Fig. 7). As noted in the Experimental section, the quantitative GSC results were obtained using a calibration graph for each component listed in Table 1. Conversely, the commercial analyzer was calibrated by the manufacturer every few months using a 600 ppm propane standard (i.e., a one-point calibration). The extent to which different hydrocarbon response factors and the matrix of the engine exhaust affect the modular emission analyzer's FID signal are not known to us. In view of these factors, it would be surprising not to find some differences in the two measurements of total hydrocarbons. Perhaps the worse correlation between the two methods was for carbon monoxide (Fig. 8). The modular emissions analyzer gave results over 50% lower in the first three tests, significantly higher for the fifth test and comparable results for the sixth and seventh tests (where the CO levels were lowest). This was the only case where there did not seem to be any correlation between the GSC results and the modular emissions analyzer results.

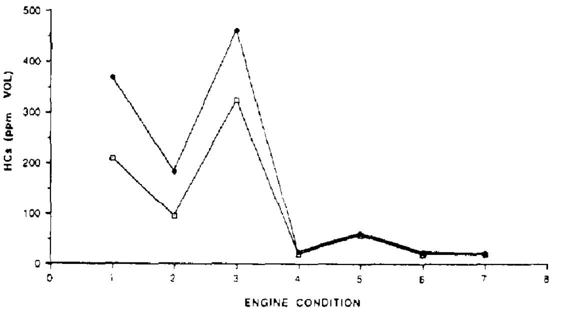

Fig. 7. Comparison of the total hydrocarbon levels measured in automobile tailpipe exhauts (◆) by GSC and (☐) with the modular computer analyzer (see Experimental for details of the exact methodologies). Note that the "total hydrocarbons" for GSC include only the results for the aliphatic hydrocarbons (Table 1). If the results for the aromatic hydrocarbons were converted into comparable units and added to this total, there would be a larger discrepancy between the two methods. The engine condition numbering convention is identical with that in Tables 1–3.

4. Conclusions

Both hydrocarbons and inorganic gases from automobile tailpipe emissions can be separated and determined on a single GSC capillary column. In the case of hydrocarbons, both aliphatic and aromatic components (up through alkylated benzenes) are measured in one run. Although subambient temperatures are needed for the oxygen–nitrogen separation, they were easily resolved from each other and the other compounds present. It was easy to see the effects of different engine and exhaust system modifications by monitoring the level of compounds in the exhaust. The use of catalytic converters and a higher voltage coil tended to produce the most pronounced decreases in emissions of hydrocarbons. The catalytic converter produces the most significant decrease in carbon monoxide concentrations. With the exception of carbon monoxide, the emissions measured by GSC and by commercial emission analyzers showed similar trends and relative concentrations but different absolute concentrations. Some of the variations may have been due to differences in the calibration of these methods.

Acknowledgement

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