

# The Measurement of Methanol and Formaldehyde in Automobile Exhaust Using Fourier Transform Infrared (FT-IR) Spectroscopy

## Key Words

- Alternative Fuels
- Clean Air Act
- Exhaust Gas Analysis
- FT-IR
- Spectroscopy

## Introduction

Improving air quality through reduction of elevated smog levels is the focus of ongoing U.S. federal and state regulations relative to automobile exhaust emissions. The U.S. EPA Clean Air Act (CAA) of 1990 was a defining moment for tough new regulations on CO, NO<sub>x</sub> and hydrocarbon (HC) emissions. Led by California's requirement that new cars meet Low Emission Vehicle (LEV, ULEV, ZLEV) standards, several states are expanding upon the legislative precedents set forth in the CAA. These changes put high demands on the automotive industry to develop improved technologies to meet the new standards.

One facet of the new legislation is the regulation of fuel composition. There is now greater incentive to develop cleaner burning fuels without compromising benefits such as fuel economy, performance or price. Reformulated gasoline blends, which decrease emissions of volatile organic compounds (VOCs), are already mandated in cities which most often exceed ozone air quality standards. The blends use oxygenated additives such as MTBE and alcohols to reduce significantly emissions from incomplete combustion. The combustion of fuels such as compressed natural gas (CNG) and liquid petroleum gas (LPG) emit considerably fewer ozone-forming hydrocarbons when compared to conventional fuels. As such, these fuels are considered viable alternatives to gasoline blends, particularly for fleet vehicles.

Methanol fuel blends have received much attention in the development of cleaner fuels. Methanol, or wood alcohol, is derived from natural gas, coal and renewable biomass sources. The combustion of methanol blends is characterized by lower HC levels, particularly for highly reactive species such as benzene and 1, 3-butadiene<sup>1</sup>. Further advantages include reduced CO production and a lower fuel vapor pressure resulting in reduced evaporative emissions. In return for these advantages, price and fuel economy suffer, and methanol and formaldehyde emissions rise significantly over those of conventional fuels<sup>2</sup>.

Determining the relative costs and benefits of the different fuel choices requires accurate measurement of their emissions. These data are needed to optimize the parameters of different fuel blends, engine control systems and the design of catalytic converters. New analytical techniques are needed to provide the information required to implement the new mandates. For methanol blends in particular, the measurement of methanol and formaldehyde levels are of the highest concern.

The conventional measurement technique for methanol involves bubbling a diluted exhaust stream through water in an impinger. The dissolved methanol is then measured by gas chromatography using a flame ionization detector (GC-FID). A separate set of impingers are chemically treated to react with formaldehyde in the diluted exhaust and is then analyzed by HPLC. The impinger techniques produce a total methanol or formaldehyde level integrated over each phase of the driving cycle, or a total of six bag measurements for the standard US-75 driving cycle.

Fourier transform infrared (FT-IR) technology has significant advantages in the measurements of methanol, formaldehyde and other NMHC gases. The Antaris™ IGS gas analyzer, a high performance system designed specifically for combustion gas analysis, determines the concentrations of exhaust gases either directly from the tailpipe or diluted from a constant volume sampler (CVS). The measurements are modal, in one second intervals, enabling concentration data to be directly correlated with such driving cycle events as cold starts, acceleration, coast and deceleration. When used for catalyst studies, the real-time data facilitate the calculation of oxidation efficiencies, light-off timing and catalysis mechanisms. This system minimizes sample preparation and eliminates time consuming laboratory analyses.

## Experimental

A study of exhaust gases from a methanol-fueled (M85) car was conducted in an automotive emissions lab using a chassis dynamometer. Raw exhaust was sampled directly before and after the catalytic converter with no pretreatment over the course of a complete US75 driving cycle. Two Antaris IGS analyzers were used simultaneously to monitor the catalyst efficiency in real time. Each analyzer was optimized to measure the emissions from M85 fuel at two-second time intervals. There was no sample pre-conditioning other than passing the raw exhaust through a heated particulate filter. It was not necessary to remove moisture from the exhaust.

The data were collected from the optical bench, using RESULT™ software. The calculated values for each measurement were stored in RESULT report format as well as exported to text file where they could be used for further analysis, such as mass flow calculations. The infrared spectra were stored to the hard drive for archival and use in further research studies.

## Results and Discussion

Figure 1 shows the concentration levels of methanol during Phase 1 of the US75 driving cycle, or cold start 505 test. The pre-catalyst concentration immediately rises to almost 1% (10,000 ppm) as the engine emits unburned methanol during the cold start. The levels drop over the first 120 seconds as the engine warms up and starts burning more efficiently. The concentration of unburned methanol eventually falls to a level of about 600 ppm, with variations due to the driving cycle.

The post-catalyst methanol concentration is also shown in Figure 1. An anomaly appears when the post-catalyst concentration exceeds the pre-catalyst levels during part of the cold start. Comparison of the infrared spectra from the two samples, however, shows that there are indeed higher levels of post-catalyst methanol than the pre-catalyst levels for samples taken 30 seconds into the test (Figure 2).

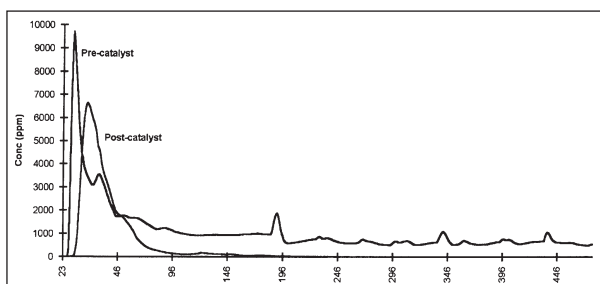


Figure 1: Pre and Post-Catalyst Integrated Methanol Concentration

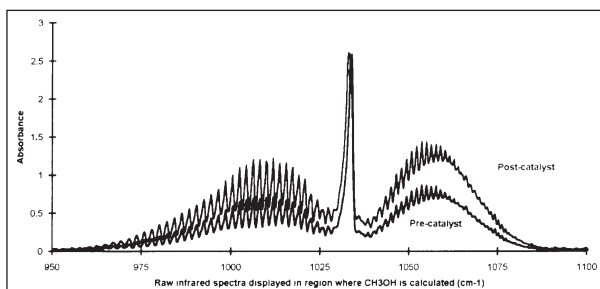


Figure 2: Methanol Levels in Pre-and Post-Catalyst Exhaust. Both samples collected 30 seconds after starting.

An explanation for these results is the trapping of methanol in the cold exhaust system. The condensed methanol then re-vaporizes in a highly concentrated slug as the catalyst system heats up. Although the peak concentration appears much higher in the post-catalyst exhaust, the total integrated level of post-catalyst methanol never exceeds the pre-catalyst totals. The data in Figure 3 show that nearly all the methanol emissions in Phase 1 come out during the cold start. Eighty-eight percent of the total methanol emissions evolve during the first 60 seconds of the 505 test.

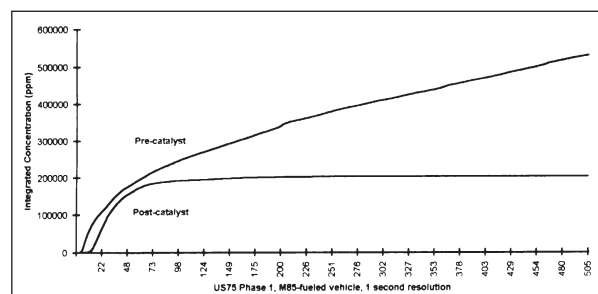


Figure 3: Pre and Post-Catalyst Integrated Methanol Concentration

A similar effect is seen in the formaldehyde plot shown in Figure 4. Again, the post-catalyst formaldehyde levels start out at zero, then rise above the pre-catalyst concentrations for about 30 seconds. The pre-catalyst levels remain at 150 ppm ( $\pm 50$  ppm) for the duration of the test, whereas the post-catalyst levels gradually decrease. Formaldehyde is a highly polar compound which readily adsorbs to metal and glass surfaces. The gradual decrease of the post-catalyst level is most likely due to desorption of condensed formaldehyde from the exhaust system.

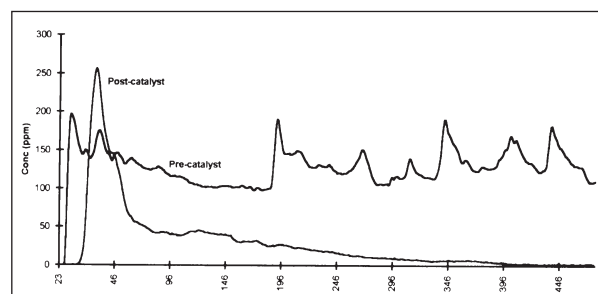


Figure 4: Pre and Post-Catalyst Formaldehyde Concentrations

Table 1 shows a spreadsheet containing calculated values of the pre-catalyst exhaust concentrations at different times during the driving cycle. The quantitative method used by the Antaris IGS in this test calculated 18 different components, including the regulated species CO and CO<sub>2</sub>, and the NO<sub>x</sub> gases NO and NO<sub>2</sub>. The C2-C4 olefins were also calculated individually, including the air toxic 1, 3 butadiene. A statistical confidence term was calculated for each component's concentration value to evaluate the precision of the measurement, identify interferences and aid in diagnostics.

| COMPONENT<br>SECONDS                | CONCENTRATION AT TIME = |            |             | 505       |
|-------------------------------------|-------------------------|------------|-------------|-----------|
|                                     | 0 SECONDS               | 30 SECONDS | 300 SECONDS |           |
| Methanol                            | 2.97                    | 4733.25    | 2.47        | 0.00      |
| Formaldehyde                        | 0.00                    | 252.97     | 10.46       | 2.23      |
| Water                               | 20396.10                | 45747.16   | 269576.21   | 224388.22 |
| Carbon Monoxide                     | 64.28                   | 8157.65    | 13.20       | 43.84     |
| Carbon Dioxide                      | 826.16                  | 127502.63  | 2064.88     | 114055.85 |
| Nitric Oxide (NO)                   | 1.07                    | 1212.82    | 76.70       | 8.04      |
| Nitrogen Dioxide (N <sub>2</sub> O) | 6.24                    | 8.50       | 0.00        | 0.00      |
| NO <sub>x</sub>                     | 7.31                    | 1221.32    | 76.70       | 8.04      |
| THC                                 | 5.15                    | 140.72     | 0.00        | 0.00      |
| Nitrous Oxide (N <sub>2</sub> O)    | 0.26                    | 28.69      | 1.22        | 1.06      |
| Ammonia                             | 0.18                    | 0.63       | 26.26       | 14.76     |
| Methane                             | 3.11                    | 100.69     | 12.10       | 1.88      |
| Acetylene                           | 2.17                    | 18.94      | 0.00        | 0.00      |
| Ethene                              | 0.15                    | 33.50      | 0.26        | 0.58      |
| Ethane                              | 0.00                    | 0.00       | 1.16        | 0.49      |
| Propene                             | 1.38                    | 18.72      | 3.75        | 0.00      |
| 1,3-Butadiene                       | 0.00                    | 3.34       | 3.70        | 2.27      |
| 2-Methyl-Propene                    | 0.00                    | 6.65       | 1.74        | 1.44      |

Table 1

## Conclusions

The results of this study demonstrate the advantages of the Antaris IGS gas analyzer over impinger techniques for methanol and formaldehyde measurements. Real time analysis of concentration levels gives insight into emissions system parameters that static bag samples cannot supply. By measuring the raw exhaust directly, expensive CVS equipment and time-consuming LC/GC lab analysis can be eliminated. The infrared spectra may be stored for archival and further analysis. The ability to speciate individual hydrocarbons in real time is a capability unique to this analyzer.

RESULT software, which includes OPC server output, integrates easily into dynamometer control systems. Exhaust concentration levels are communicated in real-time in industry standard formats. Data can also be reviewed and post-processed for calculating total emissions when combined with mass flow measurements.

The ability to monitor a broad spectrum of emission gases in real time makes the Antaris IGS gas analyzer an ideal research tool for emissions testing.

## References

1. Auto/Oil Air Quality Improvement Research Program, Phase I Final Report, May 1993.
2. P.A. Gabele, K.T. Knapp, "A Characterization of Emissions from an Early Model Flexible-Fuel Vehicle", J. Air Waste Manage. Assoc. 43:851-858.

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