Application Note: 50649

The Use of FT-IR to Analyze NO_x Gases in Automobile Exhaust

Key Words

- **Clean Air Act**
- **Exhaust Gas**
- **FT-IR**
- **Gas Analysis**
- **NO_x**

Introduction

The U.S. EPA Clean Air Act of 1990 set new standards for measurement of automotive exhaust emissions. The emission limits for regulated species such as CO, THC, and NO_x are being reduced, and new components such as methanol and formaldehyde are being added to the list of monitored species. These changes challenge engine manufacturers, fuel blenders, and catalytic converter designers to meet the new specifications. They also create the need for new measurement techniques to accurately monitor the concentrations of these emissions.

The standard on-line technologies for monitoring regulated emissions are effective at monitoring a few components, but are limited in their use for measuring other gases. Single-wavelength non-dispersive IR (NDIR) filters used for CO and CO_2 measurements cannot be used for most other species due to interferences from water and other compounds. Chemiluminescence analyzers (CLA) which measure NO_x compounds cannot differentiate NO from NO_2 in the same test, nor identify the other NO_x gases. Flame ionization detectors (FID) cannot differentiate individual hydrocarbons. To measure raw exhaust, each technique requires a cold trap for water vapor, which can affect the concentrations of other gases. In addition, time consuming calibrations are necessary for each analysis. These technologies are essentially unchanged from the original EPA emissions test procedures designed in 1970.

To sample other gases in the exhaust, bag samples must be collected and taken to a laboratory for further analysis. Expensive dilution equipment must be used to prevent water condensation in the bag. Each bag sample gathers exhaust for several minutes, therefore the final result of the test is an integrated average of the gas concentrations and all time resolution is lost. Methanol and formaldehyde samples are collected with impingers, which dissolve the gases by passing them through a water-based solution. The extract is then analyzed using high-performance liquid chromatography (HPLC). Gas chromatography (GC) can speciate many of the other hydrocarbons in a bag sample with high resolution and accuracy. While HPLC and GC are effective and widely used, they are unable to track transient concentration information.

The ideal analyzer for emissions testing would combine the advantages of on-line, real-time analysis with the accuracy and speciation of laboratory-based methods. Changes in emissions chemistry that occur with changes in engine speed and torque need to be measured every second. The analyzer must be able to identify the point at which exhaust levels are reduced by the catalyst as it heats up. Engineers require analyzers, which can accurately measure a wide variety of compounds during modal analysis. Reducing the costs of sample preparation equipment and frequent calibration of the analyzers would be an added benefit.

The performance of the Antaris™ IGS gas analyzer, a high performance system designed specifically for combustion gas analysis, addresses many of these issues. This analyzer uses Fourier transform infrared (FT-IR) spectroscopy to analyze exhaust gases. FT-IR measures the entire infrared spectrum to identify the unique chemical "fingerprint" of a wide variety of gases. Due to the fact that the whole spectrum is obtained at high resolution, the interferences from other gases, which would obstruct NDIR analyzers, are less important.

Raw or dilute exhaust can be measured directly from the source with no sample preparation. The Antaris IGS analyzer's high-speed spectral processing allows concentrations of up to 40 gases to be calculated simultaneously at one-second intervals. The flexible software allows new components to be added to custom methods, which can then be used to reanalyze stored data. The analyzer may be run independently or can be controlled by a host computer to integrate the results with other tests. Finally, this analyzer requires minimal maintenance and recalibration.

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 from the tailpipe with no pretreatment over the course of a complete US75 driving cycle. Using two Antaris IGS gas analyzers, the exhaust was sampled directly before and after the catalyst. Each analyzer used a method optimized for M85 fuel to monitor emissions levels at one-second time intervals. Other than passing the raw exhaust through a heated particulate filter, there was no sample pre-conditioning. It was not necessary to remove water from the exhaust.

Results and Discussion

NO_x gases are produced in the combustion chamber by chemical interactions between atmospheric nitrogen (N_2) and oxygen (O_2). Generally, NO_x gases are formed when the air/fuel ration is higher than stoichiometric or a “lean burn” condition. Nitric oxide (NO) is formed in the highest concentrations, but other NO_x compounds such as NO_2 are also formed in lower quantities. A complex equilibrium involving temperature, oxygen, and water vapor determines the concentrations of the various NO_x gases. For example, oxygen-rich bag samples will typically show higher relative NO_2 levels than samples from raw exhaust.

NO_x gases are measured using either the standard CLA analyzers or by FT-IR. CLA analyzers must be configured to detect either NO_2 alone or a combined NO_x total for each test cycle. Water must be removed from raw exhaust using a cold trap prior to the analysis. In contrast, the Antaris IGS gas analyzer can monitor NO and NO_2 individually without changing the chemistry of the exhaust with a cold trap. The analyzer can also speciate HNO_2 and HNO_3, but these are not typically found in raw exhaust and were not analyzed in the study.

Figure 1 shows the concentrations of NO when sampled before and after the catalyst during phase 1 of the US75 driving cycle. Initially, before the engine and catalyst warm, the NO concentrations are quite high. As the catalyst warms up, its efficiency in oxidizing NO to nitrogen improves to better than 90%.

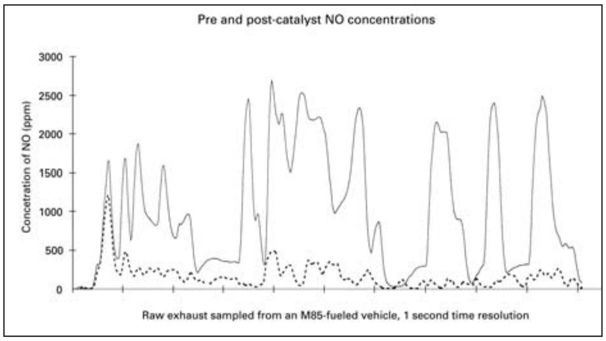

Figure 1: Raw exhaust sampled from an M85-fueled vehicle, 1 second time resolution

Figure 2 shows the concentrations of NO and NO_2 before the catalyst during phase 1 of the test cycle (note the difference in scale between the graphs). The cold engine produces a significant amount of NO_2, but the levels drop as the engine warms and runs more efficiently. There is virtually no NO_2 detected by the post-catalyst Antaris IGS spectrum after the initial 30 seconds.

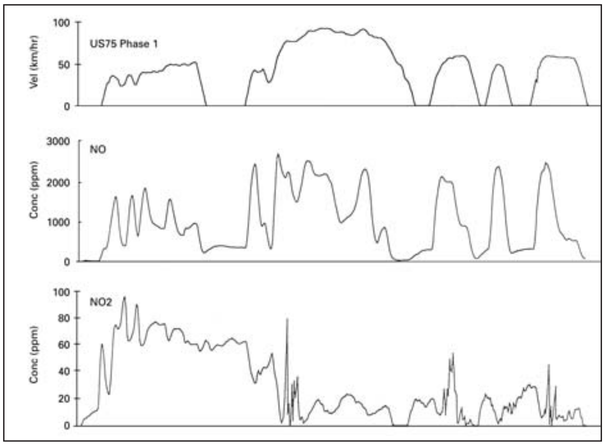

Figure 2: Raw exhaust sampled before catalyst, M85-fueled vehicle, 1 second time resolution

The analyzer may be used by designers of catalytic convertors to determine the mechanisms of catalysis. Figure 3 gives evidence of the reduction reactions occurring within the catalyst. It shows concentrations of nitrous oxide (N_2O) and ammonia (NH_3) monitored after the exhaust has passed through the catalytic convertor. When the catalyst is cold at the start of the test cycle, NO is partially reduced to N_2O. After 55 – 60 seconds, as the catalyst warms and becomes more effective, the production of N_2O declines, but another reaction produces NH_3. Neither N_2O nor NH_3 is found in the pre-catalyst exhaust.

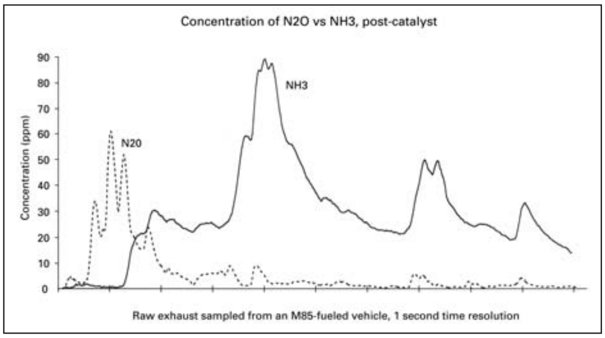

Figure 3: Raw exhaust sampled from an M85-fueled vehicle, 1 second time resolution

The Antaris IGS gas analyzer calculates the concentrations of the gases in Table 1 every second. Each concentration is shown with an error term, which is a scaled fit indicator for each component in the method. This allows the user to evaluate the accuracy of the measurement, to identify interferences, and to aid in diagnostics. The average error per measurement can be significantly improved if longer integration times are used. A standard spreadsheet format is used for the report, and concentrations can be transferred in real time to a host computer.

TABLE 1: Raw M85 Exhaust @ 100 seconds, Post-Cat

Component	Conc (ppm)	Error (±)
H_2O	143577.25	4476.26
CO	166.42	10.55
CO_2	122191.26	1803.23
NO	127.23	9.84
NO_2	1.59	8.68
N_2O	6.7	1.82
NH_3	25.39	0.54
CH_4	21.02	2.71
C_2H_2	0	4.08
C_2H_4	0.63	0.7
C_2H_6	0.64	3.05
C_3H_6	0	2.44
H_2CO	39.17	1.65
CH_3OH	138.88	2.79
13BUT	1.85	1.62
ISBUT	0	1.35
HCONT	1.18	1.74

Conclusions

The results of the NO_x studies demonstrate the capabilities of the Antaris IGS gas analyzer. The ability to measure each NO_x gas separately gives insight into transient combustion processes. It can also be used to monitor catalyst efficiencies and reaction mechanisms during different phases of the driving cycle. The raw infrared data can be saved permanently, therefore it is possible to reanalyze the test run later for compounds that were not calculated originally. Finally, analysis of raw exhaust by the Antaris IGS gas analyzer does not require sample pre-treatment. The ability to monitor a broad spectrum of emission gases in real time makes this analyzer an ideal research tool for emissions testing.

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