Specac

Application Note

UK: +44 (0) 1689 892902 US: +1 866 726 1126

Analyzing Car Exhaust Fumes with the Atmos Gas Cell

WWW.SPECAC.COM
Contact us for more information

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London,
England
+44 (0)1689 892902

Beijing,
China
frank.li@specac.com

Fort Washington,
America
+1 866 726 1126

Singapore,
Asia
kamhar.woo@specac.com

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Atmos: Your final destination for high spectral throughput low spectral noise analysis of trace gases.

Car exhaust emissions contain many harmful pollutants. The majority of these are IR active and can be monitored by FTIR spectroscopy: hydrocarbons, carbon monoxide and NO_x gases are all detectable and quantifiable. This application note examines the data that can be extracted when the exhaust gases are collected and analysed.

The intensity of the peaks in an infrared spectrum are proportional to a species concentration and the pathlength of the gas cell. For very concentrated gases short pathlengths in the cm range are sufficient. For trace gases at the ppm or ppb level significantly greater pathlengths are required. The Atmos gas cell range is designed for trace gas analysis with pathlengths ranging from 2.5 to 20 m. It has been designed to maximise spectral throughput to reduce spectral noise and greatly improve the limits of detection.

Specac Atmos Gas Cell™

Experimental

An Atmos 2.5M gas cell was placed under vacuum and sealed. A background spectrum was obtained and then samples of exhaust gas were collected by inserting the inlet pipe of the cell into the car exhaust pipe and opening the cell for 10 s. Car exhaust samples were collected under cold start conditions by running the car for 60 s prior to opening the cell. A hot engine sample was collected by driving the car for 6 miles prior to sample collection. Between each sample the Atmos cell was purged by cycling vacuum-atmosphere three times. The exhaust gasses could also be plumed directly into the gas cell which would enable real time monitoring of the car emissions.

Spectra were recorded on a commercially available spectrometer at high spectral resolution (0.8 cm^{-1}) with a box-car apodization function. Low spectral resolution would result in the loss of the rotational fine structure and is therefore not normally advised for gas phase analysis. In order to convert the spectra into ppm values the following reference absorbance values (Abs_{Ref}) were used for concentration-pathlength products (CPP) of 100 ppm meters: CO Abs_{Ref}: 0.041 at 2172 cm^{-1}; NO Abs_{Ref}: 0.015 at 1900 cm^{-1}; C_2H_4 Abs_{Ref}: 0.147 at 950 cm^{-1}. The gas concentration in ppm can be calculated from the following formula where Abs_{Meas} is the measured absorbance at the specified wavenumber value and PL is the pathlength of the cell in meters:

$$\frac{Abs_{Meas} \times CPP}{PL \times Abs_{Ref}}$$

Results and Discussions

Figure 1 shows the spectrum of an exhaust sample with the relevant gas components highlighted. The major products of combustion, CO_2 and H_2O, totally absorb at their central positions, whilst pollutant gases are clearly resolved. Overlapping broad features are observed in the alkane C-H stretching region, 3000-2800 cm^{-1}; broad peaks with no fine structure are observed when the rotational fine structure spacing is less than the peak widths and is indicative of larger molecules, hence these are assigned to alkanes with a chain length greater than 4 carbon units. A peak at 950 cm^{-1} is highly indicative of the Q branch of C_2H_4, whilst the P and R branches of CO are observed centered at 2142 cm^{-1}. A comparison of the pollutant gases from several different cars is shown in figure 2. Also shown is a comparison of the worst car (petrol, 2002) under cold start and under normal operating conditions. Direct comparisons are limited as the age of the car and engine size will both impact on the emissions. In agreement with the emission control regulations, petrol cars emit significantly more hydrocarbon and CO than diesel cars [1]. In order to further analyze the data a gas phase H_2O spectrum was subtracted, and the residual analyzed for gases hidden in the water region.

Figure 3 shows a reference spectrum of NO, along with the water subtracted spectrum from the 2002 petrol car. Negative peaks are due to an imperfect subtraction of the H_2O features due to gas phase peak broadening however NO is clearly present.

Table 1 summarizes the different cars analyzed, along with the ppm values for various pollutant gases calculated from the FTIR spectra. A comparison of the 2002 petrol car under cold start and standard operating (hot) conditions show a clear decrease in the pollutant gases as the catalytic converter becomes more efficient.

Conclusions

A number of pollutant gases were successfully identified from their spectral fingerprints. The Atmos gas cell offered superb levels of signal-to-noise and is ideally suited to the analysis of trace pollutant gases.

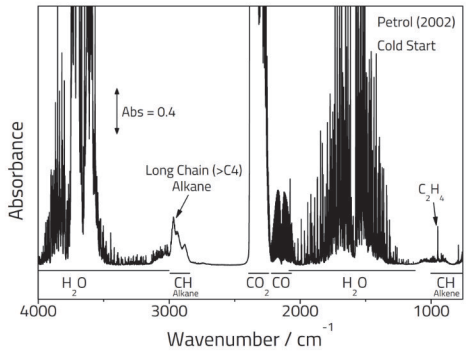

Figure 1: Spectrum of car exhaust gas highlighting the major gas components.

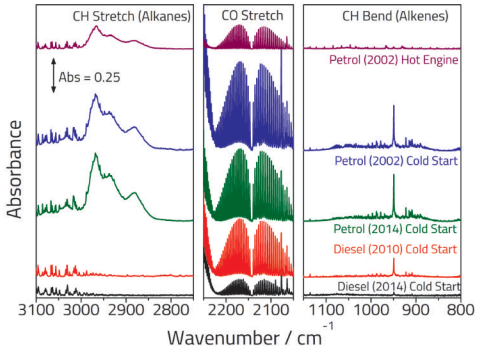

Figure 2: Comparison of exhaust emissions from several cars showing selected pollutant spectral windows. Also shown is a comparison between a car operating under cold start conditions and under normal operating conditions (blue vs. purple)

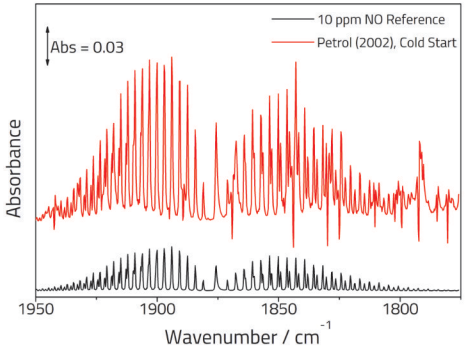

Figure 3: Water subtracted spectra showing the NO region. Also shown is a 10 ppm NO reference spectrum.

References

[1] COMMISSION REGULATION (EU) No 459/2012 amending Regulation (EC) No 715/2007 of the European Parliament and of the Council and Commission Regulation (EC) No 692/2008 as regards emissions from light passenger and commercial vehicles (Euro 6), [2012] OJ L 142, 1.6.2012, p. 16–24

Fuel Type	Engine Size	Car Age	Engine Temperature	CO/ppm	NO/ppm	C_2H_4/ppm
Diesel	1968CC	2014	Cold	121	42	2
Diesel	3500CC	2010	Cold	257	49	14
Petrol	1242CC	2014	Cold	358	35	33
Petrol	1299CC	2002	Cold	479	217	32
			Hot	89	<3	2
		Limit of detection (ATMOS 2.5M)		1	3	0.3

Table 1: Summary of cars and testing parameters along with concentrations of selected pollutant gases. Also shown are the limits of detection for these gases in the ATMOS 2.5M cell. Lower limits are achieved with longer pathlength cells.