EPAct/V2/E-89: Assessing the Effect of Five Gasoline Properties on Exhaust Emissions from Light-Duty Vehicles Certified to Tier 2 Standards

Final Report on Program Design and Data Collection

Appendix P
Derivation of FID Response Factors for Oxygenated Emission Species

Assessment and Standards Division
Office of Transportation and Air Quality
U.S. Environmental Protection Agency

National Renewable Energy Laboratory
U.S. Department of Energy

Coordinating Research Council

NOTICE

This technical report does not necessarily represent final EPA decisions or positions. It is intended to present technical analysis of issues using data that are currently available. The purpose in the release of such reports is to facilitate the exchange of technical information and to inform the public of technical developments.

EPA United States Environmental Protection Agency

EPA-420-R-13-004
April 2013

Exhaust hydrocarbons were measured in this program using a flame ionization detector (FID), which is calibrated to count carbon ions produced during complete combustion of propane. The FID has good linearity of response over a wide range of molecular sizes and concentrations of hydrocarbons, however, due to its principles of operation the instrument's response to some compounds can deviate significantly from unity. Methane and oxygenated species are examples of compounds that are known to have response factors different from 1.0. Since these responses are used in calculation of NMOG results, and the test fuels included several ethanol blends, it is important to account for these differences.

Typical response factors (RFs) are found in the literature, but can vary between labs depending on instrument models and calibrations. Therefore, prior to the start of Phase 3, SwRI performed measurements of RFs for methane, methanol, ethanol, and acetaldehyde (formaldehyde's RF was assumed to be zero). To ensure the results would be as accurate and relevant as possible for this dataset, RFs were measured on the same site where the emission tests would take place, and at concentrations as close as practical to the level occurring during the actual tests. The measurement process involved diluting known span bottle gases (concentrations between 49-200 ppm) using a calibrated Horiba 500-step divider.

After some initial trials using different gas divider ranges, the factors used for the program were derived by averaging several measurements made between approximately 1-10 ppm, as shown in the table on the next page. Final values used in the NMOG calculations and their sources are as follows:

r_{CH4} = 1.15 ppmC/ppmC (measured in this program)
r_{MeOH} = 0.63 ppmC/ppmC (measured in this program)
r_{EtOH} = 0.74 ppmC/ppmC (measured in this program)
r_{PrOH} = 0.85 ppmC/ppmC (taken from ARB documents)
r_{FormHO} = 0.00 ppmC/ppmC (multiple sources)
r_{AcetHO} = 0.51 ppmC/ppmC (measured in this program)

Mixture	Actual* (ppmC)	Measured (ppmC)	Response	Average
Methane / Air	13.56	15.49	1.14	
(90.4 ppm source)	4.52	5.21	1.15	
	1.81	2.09	1.16	
	0.90	1.04	1.15	1.15
Ethanol / N_2	9.80	7.19	0.73	
(98.0 ppm source)	4.90	3.61	0.74	
	0.98	0.73	0.75	0.74
Acetaldehyde / N_2	10.00	5.14	0.51	
(200.0 ppm source)	4.00	2.05	0.51	
	2.00	1.03	0.51	
	1.20	0.62	0.52	0.51
Methanol / N_2	9.97	6.06	0.61	
(49.9 ppm source)	4.99	3.15	0.63	
	2.49	1.60	0.64	0.63

*"Actual" refers to the concentration calculated by taking the source bottle concentration divided by the gas divider setting.