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INVESTIGATION OF EMISSION RATES OF AMMONIA, NITROUS OXIDE AND OTHER EXHAUST COMPOUNDS FROM ALTERNATIVE-FUEL VEHICLES USING A CHASSIS DYNAMOMETER

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ABSTRACT–Exhaust emissions were characterized for a fleet of 10 alternative-fuel vehicles (AFVs) including 5 compressed natural gas (CNG) vehicles, 3 liquefied petroleum gas (LPG) vehicles and 2 85% methanol/15% California Phase 2 gasoline (M85) vehicles. In addition to the standard regulated emissions and detailed speciation of organic gas compounds, Fourier Transform Infrared Spectroscopy (FTIR) was used to measure ammonia (NH_3) and nitrous oxide (N_2O) emissions. NH_3 emissions averaged 0.124 g/mi for the vehicle fleet with a range from <0.004 to 0.540 g/mi. N_2O emissions averaged 0.022 g/mi over the vehicle fleet with range from <0.002 to 0.077 g/mi. Modal emissions showed that both NH_3 and N_2O emissions began during catalyst light-off and continued as the catalyst reached its operating temperature. N_2O emissions primarily were formed during the initial stages of catalyst light-off. Detailed speciation measurements showed that the principal component of the fuel was also the primary organic gas species found in the exhaust. In particular, methane, propane and methanol composed on average 93%, 79%, and 75% of the organic gas emissions, respectively, for the CNG, LPG, and M85 vehicles.

KEY WORDS : Alternative fuel vehicles (AFVs), Ammonia (NH_3), Nitrous oxide (N_2O), Fourier transform infrared spectroscopy (FTIR), Vehicle emissions

1. INTRODUCTION

As ambient air quality standards become increasingly stringent, the role of lower level and unregulated emissions is becoming more important. Ammonia (NH_3) and nitrous oxide (N_2O) from vehicles have received considerable attention recently. From an air quality standpoint, increased levels of NH_3 can play an important role in atmospheric chemistry leading to the formation of increased levels of secondary particulate matter (PM) in the ambient air. NH_3 has been measured from vehicle exhaust since the late 1970s (Bradow and Stump, 1977; Cadle *et al.*, 1979; Cadle and Mulawa, 1980; Pierson and Brachaczek, 1983; Smith and Carey, 1982; Urban and Garbe, 1979).

More recent studies have indicated that NH_3 emissions from vehicles may be greater than previously thought, including studies in tunnels (Fraser and Cass, 1998; Gertler *et al.*, 2001; Kean *et al.*, 2000; Moeckli *et al.*, 1996), remote sensing studies (Baum *et al.*, 2000, 2001), chassis dynamometer studies (Durbin *et al.*, 2001; Graham, 1999; Baronick *et al.*, 2000) and studies using dedicated vehicles (Shores *et al.*, 2000). Based on recent tunnel studies, mobile sources are estimated to represent about 18% of the NH_3 inventory in the South Coast Air Basin that surrounds Los Angeles (Chitjian *et al.*, 2000).

N_2O emissions from vehicle exhaust are a concern because N_2O is about 300 times more potent as a greenhouse gas than carbon dioxide. Studies have shown that N_2O concentrations in the atmosphere have increased since pre-industrial days (Sienfeld and Pandis, 1998). Early studies of N_2O emissions from vehicle exhaust also date back to the 1970s (Bradow and Stump, 1977; Cadle *et al.*, 1979; Smith and Carey, 1982; Urban and Garbe, 1979). More recent studies of N_2O emissions from vehicle exhaust have included chassis dynamometer testing (Michaels *et al.*, 1998; Ballantyne *et al.*, 1994; Laurikko and Aakko, 1995; Dasch, 1992; Jobson *et al.*, 1994; Odaka *et al.*, 1998; Barton and Simpson, 1994), engine testing (Pringent and De Soete, 1989), tunnel studies (Sjödin *et al.*, 1995; Berges *et al.*, 1993; Becker *et al.*, 1999, remote sensing studies (Jimenez *et al.*, 2000)) and studies using catalyst test beds (Odaka *et al.*, 1998;

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Table 1. Vehicle descriptions for test fleet.

#	Model Year	Make	Model	Fuel	Configura-tion	Conver-sion	Certifica-tion	Odometer (miles)	Engine Size (L)	Fuel, Air System	Catalyst
1	1999	Honda	Civic GX	CNG	Dedicated	OEM	ILEV	8,152	1.6	SFI	TWC
2	1995	GMC	Sonoma PU	CNG	Dedicated	OEM retrofit	Tier 1	32,419	4.3	TBI	TWC
3	1994	Dodge	Caravan	CNG	Dedicated	OEM	ULEV	23,265	3.3	SFI	TWC+OC
4	1994	Dodge	Ram 350 Van	CNG	Dedicated	OEM	LEV	87,535	5.2	SFI	TWC+OC
5	1994	Dodge	Ram 350 Van 2	CNG	Dedicated	OEM	LEV	6,569	5.2	SFI	TWC+OC
6	2000	Ford	F-150 XL	LPG Gasoline	Bi-fuel	Impco retrofit	ULEV	9,839	5.4	SFI	TWC
7	1999	Ford	F-250 PU	LPG Gasoline	Bi-fuel	GFI-retrofit	ULEV	44,907	5.4	SFI	TWC (2)
8	1992	Chevrolet	S10 PU	LPG	Dedicated	Impco retrofit	Tier 0	84,467	4.3	TBI	TWC
9	1994	Ford	Taurus GL	M85	Flex Fuel	OEM	TLEV	133,937	3.0	SFI	TWC
10	1992	Dodge	Spirit FFV	M85	Flex Fuel	OEM	Tier 0	15,551	2.5	TBI	TWC

CNG=Compressed natural gas, LPG=Liquefied petroleum gas, M85=Mixtures of gasoline with up to 85% methanol
ULEV=Ultra-Low-Emission Vehicle, LEV=Low-Emission Vehicle, ILEV=Inherently-Low-Emission Vehicle
TLEV=Transitional-Low-Emission Vehicle
TBI=Throttle body injection, SFI=Sequential fuel injection, TWC=Three-way catalyst, OC=Oxidation catalyst
PU=Pickup truck

Koike *et al.*, 1999). Based on literature data in conjunction with vehicle testing, Michaels *et al.* (1998) estimated that N_2O emissions from mobile sources represented about 1% of the U.S. greenhouse gas emissions inventory in 1996.

To date, studies of vehicle NH_3 and N_2O emissions have focused on more conventional gasoline vehicles. Data on advanced technology vehicles are limited, and almost no data exist on alternative-fuel vehicles (AFVs). Since N_2O and NH_3 emissions arise primarily from reactions that occur on the catalyst surface (Gandhi and Shelef, 1974; Pringent and De Soete, 1989; Jobson *et al.*, 1994; Odaka *et al.*, 1998; Koike *et al.*, 1999; Hirano *et al.*, 1992), it is expected that these emissions also could be found for AFVs. The objective of this study was to evaluate and characterize the exhaust emissions for a small fleet of 10 AFVs. For this test program, 5 compressed natural gas (CNG) vehicles, 3 liquefied petroleum gas (LPG) vehicles and 2 85% methanol/15% California Phase 2 gasoline (M85) vehicles were tested over the United States Federal Test Procedure (FTP). In addition to the standard measurements of regulated pollutants, NH_3 and N_2O emissions were measured by Fourier Transform Infrared Spectroscopy (FTIR). Additional measurements were conducted to obtain detailed speciation analyses of the hydrocarbons, carbonyls and alcohols. These results provide preliminary data on the relative NH_3 and N_2O emissions levels from different types of AFVs. The results of this study are summarized in the following paper and discussed in greater detail by Durbin *et al.* (2001).

2. EXPERIMENTAL PROCEDURES

2.1. Vehicle Recruitment

A total of 10 AFVs were recruited for this study. This included 5 CNG vehicles, 3 LPG vehicles, and 2 M85 vehicles. The vehicles ranged in model year from 1992 to 2000 with mileage accumulations of 6,000 to 134,000 miles (average ~45,000 miles). A description of each of the test vehicles is provided in Table 1.

All five of the CNG vehicles were dedicated for CNG use. The 1995 CNG GMC Sonoma was equipped with an original equipment manufacturer (OEM) certified retrofit kit from NGV Ecotrans in Los Angeles, CA. The other CNG vehicles were OEM production vehicles. The LPG vehicles were all equipped with retrofit kits. Two of the LPG vehicles were retrofitted using Impco conversion kits while the third was converted using a GFI Control Systems Inc. retrofit kit. The M85 vehicles were both OEM production flexible fuel vehicles (FFVs).

Vehicles 1-4 were obtained from the University of California (UC) at Riverside's campus fleet. Vehicles 5, 6, and 8 were obtained from the City of Moreno

Valley, CA, municipal fleet. Vehicle 7 was obtained from Mutual Propane for testing. Vehicle 10 was an in-house test vehicle, and vehicle 9 was obtained from a private party.

2.2. Test Fuels

The CNG and LPG vehicle were all tested with the fuel on board at the time of testing. An analysis of a CNG fuel sample from the UC Riverside campus fleet indicated that greater than 97% of the gas mixture was composed of methane. Ethane was the second most abundant component. The LPG vehicles were obtained from the City of Moreno Valley, CA, and from Mutual Propane. An analysis of LPG samples from each of these fleets indicated that propane represented between 93 and 97% of the gas mixture. Isobutane and ethane were other smaller components in the LPG.

The M85 fuel was splash blended using 15% California Phase 2 Certification fuel and 85% methanol. The methanol was obtained from Van Waters & Rogers Inc. in Commerce, CA. The California Phase 2 certification fuel was obtained from Chevron Phillips Chemical Co. in Borger, TX, and had a fuel sulfur content of 35 ppmw.

2.3. Protocol for Vehicle Testing

All vehicles were tested over one FTP to obtain mass emission rates for total hydrocarbons (THC), non-methane hydrocarbons (NMHC), carbon monoxide (CO), and nitrogen oxides (NO_x). In addition to the regulated emissions measurements, FTIR measurements, detailed hydrocarbon speciation measurements and carbonyl measurements were also collected for each vehicle, as discussed below. Alcohol measurements were also conducted on the M85 FFVs.

The CNG and LPG vehicles were preconditioned according to the typical protocols outlined in the Code of Federal Regulations for the FTP (CFR Part 86, Subpart B). The FFVs were each preconditioned and refueled on M85 using procedures from the Auto/Oil program (Burns *et al.*, 1991). Since ammonia is a relatively reactive compound, a heating pad maintained at a temperature of 110°C was wrapped around the transfer tube to minimize the loss of NH_3 through the sampling system.

2.3.1. Fourier transform infrared spectroscopy

NH_3 and N_2O emissions were measured by a Pierburg AMA/Mattson FTIR system. The FTIR samples from the dilution tunnel through a heated sampling line (110°C) with a PTFE core, and provides data once every 3 seconds. The minimum detection limits for NH_3 and N_2O are approximately 0.004 g/mi and 0.002 g/mi, respectively, for the FTIR over the FTP cycle. The FTIR was calibrated for NH_3 and N_2O with standard calibration gases from

Table 2. Summary of FTP emissions results for the test fleet.

Model Year	Make	Model	Fuel	NMOG (g/mi)	R-NMOG (g/mi)	CO (g/mi)	NO_x (g/mi)	NH_3 (g/mi)	N_2O (g/mi)
1999	Honda	Civic GX	CNG	0.005	0.002	0.252	0.026	0.021	<MDL
1995	GMC	Sonoma PU	CNG	0.045	0.025	1.604	**0.977**	<MDL	0.022
1994	Dodge	Caravan Minivan	CNG	0.015	0.007	0.464	0.200	0.005	0.008
1994	Dodge	Ram 350 Van	CNG	0.059	0.032	3.329	0.913	0.116	0.077
1994	Dodge	Ram 350 Van 2	CNG	0.028	0.015	1.698	0.217	0.127	0.016
2000	Ford	F-150 XL	LPG Gasoline	0.053	0.027	1.963	0.145	0.540	0.017
1999	Ford	F250 XLT	LPG Gasoline	0.037	0.019	0.355	0.420	0.078	0.012
1992	Chevrolet	S10 PU	LPG	0.756[a]	**0.679**[b]	0.086	0.492	<MDL	0.006
1994	Ford	Taurus FFV	M85	0.836	**0.343**	**9.074**	**1.108**	0.120	0.059
1992	Dodge	Spirit FFV	M85	0.130[c]	0.111[d]	4.001	0.209	0.235	0.004

Notes: R-NMOG=Reactivity-adjusted NMOG=(measured NMOG)*(reactivity adjustment factor) or for CNG vehicles=(measured NMOG)* (natural gas reactivity adjustment factor)+(measured methane)*(methane reactivity adjustment factor) (CARB, 1996)

a=total hydrocarbons as measured by FID

b=non-methane hydrocarbons as measured by FID

c=organic material hydrocarbon equivalent

d=organic material non-methane hydrocarbon equivalent

Bold Numbers=Emissions above the 50,000 miles in-use stanards for vehicles with $<$ 50,000 miles or above the 100,000 mile in-use standards for vehicles with $>$ 50,000 miles (Diamler Chrysler, 2001)

<MDL=below detection limits

Scott Specialty Gases at levels comparable to what is expected in the diluted exhaust gas (~10 ppm). It should be noted that the NH_3 was certified from the producer with an accuracy of ±5%, although others have suggested that it is difficult to achieve uncertainties of less than 10% for NH_3 calibration gases (Marrin, 2001). The N_2O gases were certified from the producer with an accuracy of ±2%. To adjust the modal emissions data to correct for the residence time in the FTIR cell, a well-mixed flow cell model was used. Specifically, the absorption cell for the FTIR has a volume of 5 liters, and the residence time in the cell is approximately 10 seconds. A 3-second average was applied to the data prior to using the well-mixed flow cell model. The data were also shifted to account for the delay between the time the exhaust gases were emitted from the tailpipe and when they were sampled by the FTIR. The use of a well-mixed flow cell model for analysis of modal emissions data is described in greater detail by Truex *et al.* (2000).

2.3.2. Detailed NMOG speciation sampling and analysis

Detailed non-methane organic gas (NMOG) speciation measurements were made for all tests. This included bag hydrocarbon (HC) speciation measurements for C_1-C_{12} and carbonyl measurements. Alcohol measurements were also obtained for the two M85 vehicles. Samples for the C_1-C_{12} HC speciation were collected in 8 liter black Tedlar bags. Hydrocarbon speciation analyses for C_1-C_{12} were conducted utilizing the protocols developed during Auto/Oil Phase 2 (Siegl *et al.*, 1993). Light hydrocarbons (C_1 through C_4) were measured using a Hewlett-Packard (HP) 5890 Series II gas chromatograph with a flame ionization detector (GC/FID) maintained at 250°C. A 15 m × 0.53 mm polyethylene glycol pre-column and a 50 m × 0.53 mm aluminum oxide "S" deactivation porous layer open tubular (PLOT) column were used. A second HP 5890 Series II GC with a FID maintained at 300°C was used to measure the C_4 to C_{12} hydrocarbons. A 2 m × 0.32 mm deactivated fused silica pre-column and a 60 m × 0.32 mm HP-1 column were used for this GC.

Dilute exhaust gas aldehydes and ketones were collected onto dinitrophenyl-hydrazine (DNPH)-coated silica gel cartridges. The DNPH cartridges were analyzed by high-performance liquid chromatography (HPLC). For the M85 vehicles, alcohol measurements were also collected using water impingers and analyzed with a GC/FID. Carbonyls and alcohols were all sampled through a heated line (~110°C).

3. EMISSIONS TEST RESULTS

3.1. Regulated Emissions Results

A summary of the FTP weighted mass emission rates is presented in Table 2 for standard organic gas emissions, CO, and NO_x. The NH_3 and N_2O results, as discussed below, are also included in Table 2 for comparison. The organic gas emissions are defined relative to the standard by which the vehicle was certified. For the vehicles certified to standards under the California Low-Emission Vehicle program, these results are presented as NMOG and reactivity-adjusted NMOG. Organic gas results for the 1995 GMC are also presented as NMOG since these levels are consistent with other CNG vehicles for a similar time period that are certified to LEV standards. For an earlier 1992 LPG vehicle, results are presented as THC and NMHC. The 1992 Dodge FFV results are presented as organic material hydrocarbon equivalent (OMHCE) and organic material non-methane hydrocarbon equivalent (OMNMHCE).

The results showed a range of emission levels over the test fleet, although the results were generally consistent with the respective vehicle in-use standards. The CNG vehicles all had relatively low NMOG emissions. The two newest LPG vehicles also had relatively low NMOG emissions. The older 1992 LPG retrofit and the 1994 Ford FFV, on the other hand, had organic gas emissions above their in-use standards. For LPG vehicles, previous studies have shown that earlier retrofitted LPG vehicles can have more variable emissions, and in some cases can be higher than comparable gasoline vehicles (Colorado Department of Health, 1993; Lyons and McCoy, 1993). The lower emissions for the new retrofitted LPG vehicles can be attributed to continuous improvements in retrofit technology as well as the implementation of regulations to control the emissions of retrofit vehicles (CARB, 2002). The higher NMOG emissions for the FFV can primarily be attributed to the methanol emissions, as discussed below. This vehicle was also the highest mileage vehicle in the fleet.

The lowest CO emissions were found for the gaseous-fueled CNG and LPG vehicles, with all of these vehicles meeting the in-use standards. About half of the gaseous-fueled vehicles had CO emissions below 0.500 g/mi. Interestingly, the 1992 Chevy S10 PU had the lowest CO emissions in the fleet, despite having relatively high hydrocarbon emissions. The 1999 CNG Honda Civic also had relatively low CO emissions. The two FFVs had the highest CO emissions in the fleet, with CO emissions for the 1994 Ford Taurus being above its certification level.

NO_x emissions for two vehicles were above their respective in-use standards. NO_x emissions for the 1999 CNG Honda Civic were considerably below those of the other vehicles in the fleet. This demonstrates, in part, the relatively low emissions levels that can be obtained using the most advanced production technologies. The 1994 FFV vehicle had the highest NO_x emissions, which exceeded its respective certification level.

3.2. NH_3 and N_2O Results

Included in Table 2 are the NH_3 and N_2O emissions results from the FTIR. NH_3 emissions averaged 0.124 g/mi for the vehicle fleet with a range from <0.004 to 0.540 g/mi. Excluding the highest NH_3 emitting vehicle drops the average for the 9 other vehicles to 0.078 g/mi. Interestingly, for a number of the vehicles, NH_3 emissions were comparable to or greater than some of the regulated emissions. The NH_3 emissions for 6 of the 10 vehicles were greater than those of NMOG emissions for the same vehicle, and NH_3 emissions for two vehicles exceeded those of NO_x for the same vehicles.

Overall, these NH_3 emission levels are comparable to those found in similar studies of conventional gasoline vehicles. Durbin *et al.* (2002) found NH_3 emissions ranged from <0.004 to 0.177 g/mi with an average of 0.054 g/mi for a fleet of 39 gasoline vehicles. A range of NH_3 emissions from <0.001 g/mi to nearly 0.300 g/mi was observed for a fleet of 75 in-use Canadian and United States (US) vehicles by researchers at Environment Canada (Graham, 1999). These results are also very comparable to results obtained in tunnel studies by Fraser and Cass (1998) [0.098 g/mi] and Kean *et al.* (2000) [0.079±0.0043 g/mi]. Other tunnel studies have measured lower rates including a 1999 study by Gertler *et al.* (2001) in the Tuscarora tunnel in Pennsylvania (0.015± 0.004 g/mi), a 1995 study by Moeckli *et al.* (1996) in Switzerland (0.024±0.006 g/mi), and a 1981 study by Pierson and Brachaczek (1983) in the Allegheny Tunnel in Pennsylvania (0.002±0.006 g/mi [for NH_3+NH_4^+]). Gertler *et al.* (2001) suggested their lower emission rates could be due to the newer, better maintained vehicles, higher average speeds, or lack of accelerations/decelerations observed in the Tuscarora tunnel. In this regard, it is important to note that vehicle measured in tunnels are generally operating under more steady state operating conditions than during the FTP and are typically not in a cold start condition. The studies by Moeckli *et al.* and Pierson and Brachaczek both included considerably higher percentages of non-catalyst vehicles, probably contributing the lower NH_3 emission rates.

N_2O emissions averaged 0.022 g/mi over the vehicle fleet with range from <0.002 to 0.077 g/mi. The N_2O emission rates were comparable to the reactivity-adjusted NMOG emission rates for some of the CNG and LPG vehicles, but were well below the CO and NO_x emissions for all vehicles. Again, these N_2O emission levels are comparable to those reported previously for conventional gasoline vehicles. Michaels *et al.* (1998) found N_2O emission rates of 0.028 g/mi for LEV-certified vehicles using a fuel with a 24 ppmw sulfur content. Higher emission rates were observed for these LEV vehicles (0.078 g/mi) and some Tier 1 vehicles (0.063 g/mi) when tested on a higher 285 ppmw sulfur fuel. Baronick *et al.* (2000) found N_2O emission rates of 0.005-0.015 mg/mi for two 2000 model year Volkswagen Golfs using a 1 ppmw sulfur fuel, although the emission rate for one of these vehicles increased to 0.086 g/mi when a 330 ppmw sulfur fuel was used. Somewhat higher N_2O emission rates were found by other researchers for older vehicles. This includes studies conducted by Ballantyne (1994) on 1986 to 1992 vehicles (0.074 g/mi for 5 vehicles with new catalysts and 0.126 g/mi for 9 vehicles with aged catalysts) and by Dasch (1992) on 1978 to 1990 vehicles (0.044±0.028 g/mi averaged over all catalyst types). A range of estimates for N_2O emission rates has also been found for tunnel studies, including an estimate of 0.170 g/mi by Berges *et al.* (1993), an estimate of 0.013-0.026 g/mi by Becker *et al.* (1999), and an estimate of 0.040 g/mi with a range from 0.011-0.090 g/mi by Sjödin *et al.* (1995). Again, a number of factors could contribute to differences between tunnel and dynamometer studies including the mode of operation, fleet make-up and size, fuel sulfur level, and/or lack of a cold start.

NH_3 and N_2O modal emissions are plotted against vehicle speed in Figures 1-3 for one CNG, one LPG, and one M85 vehicle, respectively. The vehicles selected for these Figures were ones with higher NH_3 and N_2O emission rates to better illustrate the modal trends in these emissions. The modal emissions show the transient nature of the NH_3 and N_2O emissions throughout the driving cycle. The onset of both NH_3 and N_2O emissions is observed during or after catalyst light-off, consistent with previous studies (Bradow and Stump, 1977; Cadle *et al.*, 1979; Smith and Carey, 1982; Shelef and Gandhi, 1972a/b). This shows the importance of the catalyst for NH_3 and N_2O formation. Although catalyst temperature was not measured as part of this study, the results are consistent with those of other studies where catalyst temperature was measured (Durbin *et al.*, 2002). The onset of N_2O emissions typically occurred before that of the NH_3 emissions during the initial stages of catalyst

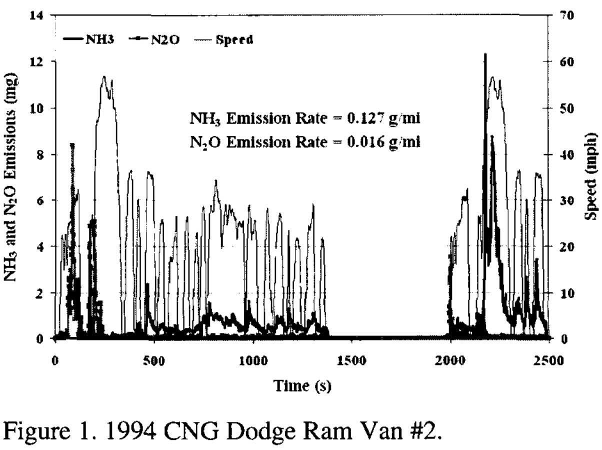

Figure 1. 1994 CNG Dodge Ram Van #2.

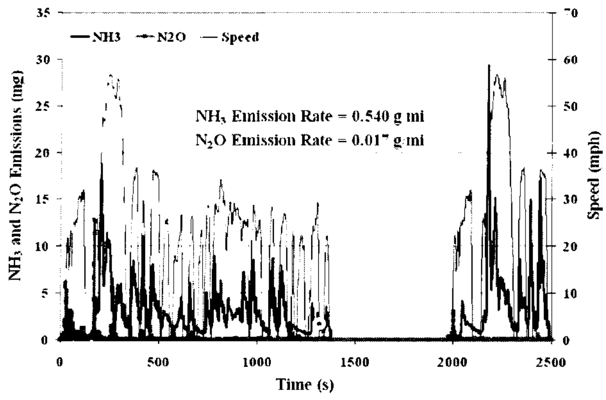

Figure 2. 2000 LPG Ford F150.

light-off. As the catalysts were lighting off and reaching their equilibrium temperatures, N_2O emissions usually declined, followed by an increase in NH_3 emissions. This is consistent with previous studies that have shown that N_2O emissions more readily form at intermediate temperatures (~250°C–450°C) as opposed to the higher temperatures near equilibrium operating ranges for the catalyst (Laurikko and Aakko, 1995; Pringent and De Soete, 1989; Jobson *et al.*, 1994; Odaka *et al.*, 1998; Koike *et al.*, 1999; Hirano *et al.*, 1992).

3.3. NMOG Speciation Results

A summary of the detailed speciation of the organic gas emissions is provided in Tables 3–5. These tables summarize the organic gas speciation results by compound class and the results for the individual organic gas species for the CNG, LPG, and M85 vehicles. More complete test results for each vehicle are provided in Durbin *et al.* (2001).

In general, the exhaust speciation profiles reflect the fuel on which each vehicle is operated, consistent with previous studies (CARB, 1991, 1993, 1994). For CNG vehicles, methane makes the largest contribution to the total organic gas (TOG) emissions, representing an average of about 93% of the total organic gas (TOG) emissions with a range from 81 to 96%. The remaining NMOG emissions were predominantly composed of alkanes, alkenes, and carbonyls, with alkanes generally making the largest contribution. Other species identified in the NMOG profiles for CNG include ethane, formaldehyde, and ethene.

The organic gas emissions for the LPG vehicles were dominated by propane. Propane composed between 76 and 82% of the total NMOG emissions for the three test vehicles. Correspondingly, alkanes composed 80 to 95% of the total NMOG. The majority of the remaining NMOG emissions were composed of alkenes, with one vehicle also having about a 7.4% contribution from carbonyls. Other species observed in the NMOG profiles for LPG include ethane, ethene, propene, and formaldehyde. The contribution of methane emissions varied from about 10% for two LPG vehicles up to 31% of the TOG emissions for the remaining LPG vehicle.

The organic gas profiles for the methanol vehicles were different from those for the CNG and LPG vehicles but were consistent with the M85 operating fuel. For these vehicles, methanol was the largest component, consisting of 74 to 77% of the total NMOG. The remaining species included alkanes, alkenes, aromatics, and carbonyls, although none of these represented more than 10% of the total NMOG emissions. Formaldehyde emissions were 9.0 and 30.6 mg/mi, respectively, for the 1992 Dodge Spirit and the 1994 Ford Taurus. For comparison, the certification value for California Tier 0 through LEV passenger cars at 50,000 miles is 15 mg/mi. It should be noted that the methanol and formaldehyde emissions measured by the impingers and DNPH cartridges compared well with those measured by the FTIR for the two M85 vehicles.

The specific reactivity of the NMOG emissions for each vehicle is also provided in Tables 3–5. Specific reactivity is a measure of the mass of ozone formed per mass of NMOG. The specific reactivity is calculated using the maximum incremental reactivity factors developed by Carter (1990) for the California Air Resources Board. The average specific reactivities, in grams of ozone per gram of NMOG mass, were 2.55 for CNG vehicles, 1.26 for LPG vehicles, and 1.32 for M85 vehicles. Although the specific reactivity for the NMOG for the CNG vehicles was higher than that for the LPG or M85 vehicles, it is important to note that TOG for CNG vehicles is primarily composed of methane. Since the reactivity factor for methane is very low, when the reactivity of the TOG, as opposed to the NMOG, is considered, the specific reactivity value drops to 0.22.

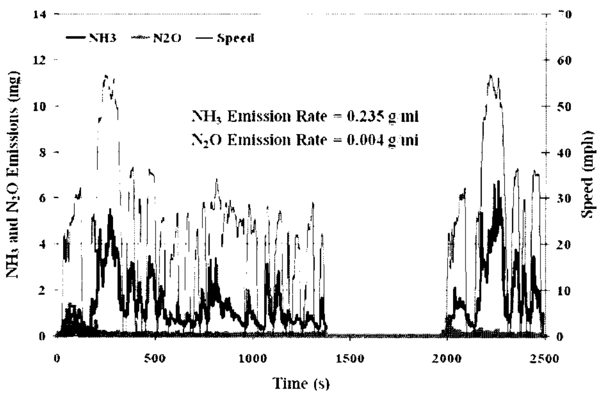

Figure 3. 1992 Dodge Spirit FFV on M85.

Table 3. Summary of organic gas emissions for compound classes and selected compounds for CNG vehicles.

	1999 Honda Civic GX	1995 GMC Sonoma	1994 Dodge Caravan	1994 Dodge Ram 350	1994 Dodge Ram 350 2
Total NMOG (mg/mi)	4.76	45.17	14.68	58.72	28.21
Reactivity Adjusted NMOG (mg/mi)	2.15	24.64	7.35	32.25	14.91
Specific Reactivity	3.691	1.481	2.336	2.560	2.658
Organic Gases by GC (mg/mi)					
Methane	20.63	1109.17	219.66	1490.01	591.38
Non-methane Alkanes	0.76	29.76	5.47	37.48	17.68
Alkenes	0.23	3.09	1.06	8.58	4.50
Alkynes	0.01	1.02	0.36	1.23	0.98
Aromatics	0.96	0.43	0.29	1.09	1.15
Ethers	0.00	0.00	0.00	0.00	0.00
Carbonyls	1.79	4.75	3.37	10.13	4.35
Unknowns	1.02	6.13	4.14	0.20	-0.45
Organic Gases by GC (% of GC TOG)					
Methane	81.2%	96.1%	93.7%	96.2%	95.4%
Organic Gases by GC (% of GC NMOG)					
Non-methane Alkanes	15.9%	65.9%	37.2%	63.8%	62.7%
Alkenes	4.8%	6.8%	7.2%	14.6%	16.0%
Alkynes	0.3%	2.2%	2.4%	2.1%	3.5%
Aromatics	20.1%	0.9%	2.0%	1.9%	4.1%
Ethers	0.0%	0.0%	0.0%	0.0%	0.0%
Carbonyls	37.6%	10.5%	23.0%	17.3%	15.4%
Unknowns	21.4%	13.6%	28.2%	0.3%	-1.6%
Selected Organic Gases by GC (mg/mi)					
Methane	20.63	1109.17	219.66	1490.01	591.38
Ethane	0.52	25.95	4.22	32.95	14.00
Formaldehyde	1.14	2.53	2.15	7.31	3.35
Ethene	0.17	2.92	0.80	6.54	3.88
Propane	0.06	2.16	0.43	2.56	1.82
Acrolein	-0.01	1.79	0.91	0.94	0.68
Ethyne	0.01	1.02	0.36	1.17	0.98
Acetaldehyde	0.17	0.24	0.23	1.70	0.20
Propene	0.04	0.17	0.07	0.92	0.43
Cyclopentane	0.00	0.67	0.00	0.11	0.62
Butane	0.02	0.34	0.09	0.57	0.36
Selected Organic Gases by GC (% of NMOG)					
Ethane	10.99%	57.45%	28.77%	56.11%	49.61%
Formaldehyde	23.90%	5.60%	14.65%	12.46%	11.89%
Ethene	3.61%	6.47%	5.46%	11.13%	13.76%
Propane	1.30%	4.78%	2.90%	4.36%	6.45%
Acrolein	-0.20%	3.96%	6.21%	1.60%	2.43%
Ethyne	0.27%	2.25%	2.44%	1.99%	3.47%
Acetaldehyde	3.49%	0.53%	1.59%	2.90%	0.69%
Propene	0.92%	0.39%	0.48%	1.57%	1.52%
Cyclopentane	0.00%	1.47%	0.00%	0.19%	2.20%
Butane	0.33%	0.76%	0.62%	0.98%	1.27%

Table 4. Summary of organic gas emissions for compound classes and selected compounds for LPG vehicles.

	2000 Ford F150	1999 Ford F250	1992 Chevy S10
Total NMOG (mg/mi)	53.43	37.32	699.04
Reactivity Adjusted NMOG (mg/mi)	26.71	18.66	349.52
Specific Reactivity	1.373	1.656	0.764
Organic Gases by GC (mg/mi)			
Methane	23.98	4.64	80.71
Non-methane Alkanes	45.23	29.79	664.67
Alkenes	4.88	3.53	21.12
Alkynes	0.12	0.05	0.61
Aromatics	0.22	0.01	0.84
Ethers	0.00	0.00	0.00
Carbonyls	1.68	2.75	9.08
Unknowns	1.30	1.19	2.71
Organic Gases by GC (% of GC TOG)			
Methane	31.0%	11.1%	10.4%
Organic gases by GC (% of GC NMOG)			
Non-methane Alkanes	84.7%	79.8%	95.1%
Alkenes	9.1%	9.5%	3.0%
Alkynes	0.2%	0.1%	0.1%
Aromatics	0.4%	0.0%	0.1%
Ethers	0.0%	0.0%	0.0%
Carbonyls	3.1%	7.4%	1.3%
Unknowns	2.4%	3.2%	0.4%
Selected Organic Gases by GC (mg/mi)			
Propane	41.76	28.32	575.83
Methane	23.98	4.64	80.71
Ethane	2.79	0.76	86.46
Ethene	3.33	2.43	11.07
Propene	1.45	0.99	6.97
Formaldehyde	1.37	1.98	5.90
Acetaldehyde	0.23	0.35	1.47
Acrolein	0.22	0.43	1.13
1,3-Butadiene	0.00	0.00	0.83
Butane	0.23	0.02	0.56
Ethyne	0.12	0.05	0.61
Organic gases by CG (% of GC NMOG)			
Propane	78.19%	75.91%	82.38%
Ethane	5.23%	2.05%	12.37%
Ethene	6.24%	6.51%	1.58%
Propene	2.71%	2.66%	1.00%
Formaldehyde	2.57%	5.31%	0.84%
Acetaldehyde	0.42%	0.93%	0.21%
Acrolein	0.41%	1.15%	0.16%
1,3-Butadiene	0.00%	0.00%	0.12%
Butane	0.44%	0.04%	0.08%
Ethyne	0.22%	0.14%	0.09%

Table 5. Summary of organic gas emissions for compound classes and selected compounds for M85 vehicles.

	1994 Ford Taurus	1992 Dodge Sprit
Total NMOG (mg/mi)	836.33	190.31
Reactivity Adjusted NMOG (mg/mi)	418.17	78.02
Specific Reactivity	1.246	1.402
Organic Gases by GC (mg/mi)		
Methane	50.47	24.16
Methanol	643.85	140.03
Non-methane Alkanes	64.93	14.52
Alkenes	25.49	5.89
Alkynes	1.88	1.81
Aromatics	41.82	12.05
Ethers	1.44	0.73
Carbonyls	34.25	10.32
Unknowns	22.66	4.95
Organic Gases by GC (% of GC TOG)		
Methane	5.7%	11.3%
Organic Gases by GC (% of GC NMOG)		
Methanol	77.0%	73.6%
Non-methane Alkanes	7.8%	7.6%
Alkenes	3.0%	3.1%
Alkynes	0.2%	1.0%
Aromatics	5.0%	6.3%
Ethers	0.2%	0.4%
Carbonyls	4.1%	5.4%
Unknowns	2.7%	2.6%
Organic Gases by GC (mg/mi)		
Methanol	643.85	140.03
Methane	50.47	24.16
Formaldehyde	30.62	8.98
Toluene	12.00	3.37
2-Methylbutane	11.32	2.47
Ethene	9.74	1.96
Benzene	10.03	1.64
2,2,4-Trimethylpentane (i-Octane)	8.39	3.02
m&p-Xylene	7.04	2.46
Propene	4.60	1.08
2,3-Dimethylpentane	3.72	1.22
Organic gases by CG (% of GC NMOG)		
Methanol	76.99%	73.58%
Formaldehyde	3.66%	4.72%
Toluene	1.44%	1.77%
2-Methylbutane	1.35%	1.30%
Ethene	1.16%	1.03%
Benzene	1.20%	0.86%
2,2,4-Trimethylpentane (i-Octane)	1.00%	1.59%
m&p-Xylene	0.84%	1.29%
Propene	0.55%	0.57%
2,3-Dimethylpentane	0.45%	0.64%

4. SUMMARY AND CONCLUSIONS

The objective of the present study was to characterize the emissions from 10 AFVs. In this project, 5 CNG vehicles, 3 LPG vehicles, and 2 M85 vehicles were tested over the US FTP. In addition to the standard regulated emissions, NH_3 and N_2O emissions were measured with an FTIR. Detailed NMOG speciation was also performed for each vehicle. The major results of this study are:

(1) Relatively low NMOG emissions were found for all the CNG vehicles and the two newest LPG vehicles. One LPG vehicle and one M85 vehicle had organic gas emissions above their respective certification levels. The two M85 FFVs had the highest CO emissions of the test vehicles;

(2) NH_3 emissions for the vehicle fleet averaged 0.124 g/mi for the vehicle fleet with a range from <0.004 to 0.540 g/mi. Excluding the highest emitting vehicle for NH_3 drops the average for the 9 other vehicles to 0.078 g/mi. N_2O emissions averaged 0.022 g/mi over the vehicle fleet with range from <0.002 to 0.077 g/mi. These emissions levels are comparable to those observed for more conventional gasoline vehicles;

(3) Modal emissions showed that the onset of NH_3 emissions typically occurred after catalyst light-off, near when the catalysts reached their respective equilibrium temperatures. The onset of N_2O emissions typically occurred before that of the NH_3 emissions during the initial stages of catalyst light-off. As the catalysts approached and reached their equilibrium temperatures, however, N_2O emissions generally decreased significantly;

(4) The speciation profiles were consistent with the fuels the vehicles were operated on. For CNG vehicles, methane made the largest contribution to the TOG emissions, representing an average of about 93% of the total organic gas emissions with a range from 81 to 96%. Other NMOG compounds that were observed for CNG vehicles include ethane, formaldehyde, and ethene;

(5) Propane was the largest NMOG component for the LPG vehicles, composing between 76 and 82% of the total NMOG emissions for the three test vehicles. Alkanes composed 80 to 95% of the total NMOG for the LPG vehicles;

(6) Methanol was the largest NMOG component for the M85 vehicles, composing 74 to 77% of the total NMOG. Formaldehyde emissions were 9.0 and 30.6 mg/mi, respectively, for the 1992 Dodge Spirit and the 1994 Ford Taurus.

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