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Scaling of Infrared Remote Sensor Hydrocarbon Measurements for Motor Vehicle Emission Inventory Calculations

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Infrared (IR) remote sensors calibrated with propane understate volatile organic compound (VOC) concentrations in vehicle exhaust by 30−70% when compared to flame ionization detectors (FID). The difference depends on VOC composition and arises because many organic compounds in vehicle exhaust absorb less IR radiation than propane on a per-carbon basis. This study demonstrates an approach for scaling infrared measurements to reflect more accurately total exhaust VOC emissions from on-road motor vehicle fleets. Infrared versus flame ionization detector response to individual VOC was measured in the laboratory for methyl *tert*-butyl ether and a range of alkanes, alkenes, and aromatics that are prominent in vehicle exhaust. Overall IR/FID response to real exhaust mixtures was calculated by summing the response contributions of all individual VOC constituents. Average IR/FID response factors were calculated for typical on-road vehicle fleets based on VOC speciation profiles measured in several U.S. roadway tunnels. Results indicate that hydrocarbon concentrations measured by remote sensors with 3.4 μm filters should be multiplied by a factor of 2.0 ± 0.1 for light-duty vehicles using either California or federal reformulated gasoline blends and by 2.2 ± 0.1 when conventional gasoline is used.

Introduction

The study of on-road motor vehicle emissions has been enhanced in recent years by the development of roadside long-path infrared spectrometers, commonly referred to as remote sensors (*1−5*). Remote sensors measure the relative exhaust concentrations of carbon monoxide (CO), hydrocarbons (HC), and carbon dioxide (CO_2) as an infrared beam is projected across a roadway and through the tailpipe exhaust plume of each passing vehicle. By carbon balance, the CO/CO_2 and HC/CO_2 ratios measured by a remote sensor can be converted to fuel-normalized mass emission rates, e.g. gram

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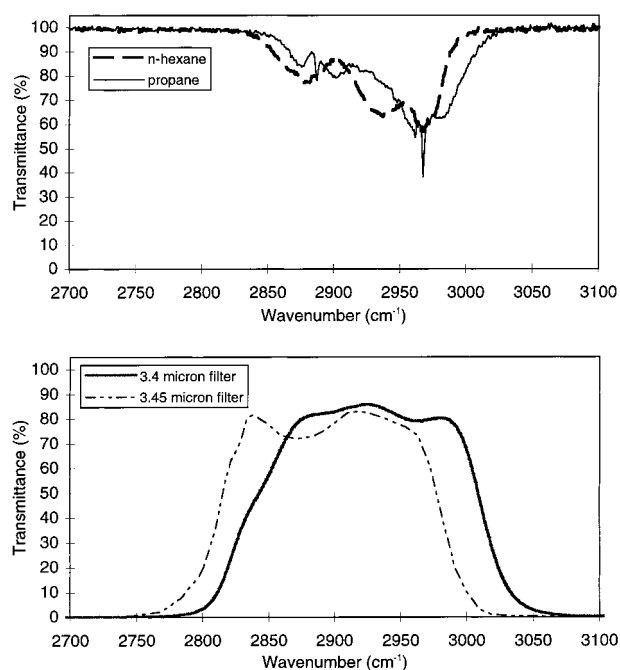
FIGURE 1. Infrared transmission profiles of propane, *n*-hexane, and filters used in infrared HC analyzers.

of pollutant emitted per liter of fuel burned. Singer and Harley (*6*) have demonstrated how the emission factors measured with remote sensors can be combined with fuel sales data to calculate CO emission inventories at the air-basin or regional level. In principle, fuel-based inventories may be calculated for pollutants other than CO if representative emissions data are available. The fuel-based inventory technique has not been applied to estimate HC emissions because of concerns that infrared sensors understate total HC concentrations in motor vehicle exhaust (*7*).

Remote sensors measure HC concentrations based on energy absorption within a narrow infrared band centered at 2940 cm^{-1}, or 3.4 μm (*8*). The absorption spectrum of an interference filter similar to those used in the University of Denver FEAT remote sensors is shown in Figure 1 (3.4 μm filter). Absorption in this region of the infrared is associated with vibrational frequencies, or stretching, of carbon−hydrogen bonds. The C−H bonds of paraffinic carbons absorb strongly within the range of wavelengths passing through the filter, whereas the C−H bonds of olefinic and aromatic carbons absorb at slightly higher energies: in the ranges of 3010−3040 cm^{-1} and 3075−3095 cm^{-1} for olefins and at 3030 cm^{-1} for aromatics (*9*). When calibrated with an alkane such as propane or hexane, an infrared detector with a 3.4 μm filter will therefore understate total HC concentrations relative to flame ionization detector (FID) measurements of mixtures containing alkenes and aromatics. In contrast, it has long been known that the response per carbon atom of a flame ionization detector is approximately the same for all hydrocarbons (*10*).

The response of a nondispersive infrared (NDIR) analyzer to individual organic compounds present in vehicle exhaust was first reported by Jackson (*11*). Using a hexane detector (i.e. a filter that passes infrared radiation between 3.3 and 3.5 μm, where hexane absorbs strongly), Jackson observed a measurement response close to 1.0 for several alkanes,

alkene responses ranging from 0.09 for ethene to 0.61 for 1-hexene, and near-zero response for benzene and toluene. Stephens and co-workers (7) measured concentrations of individual organic compounds using high- and low-range commercial NDIR analyzers mounted on-board a test vehicle, a General Motors (GM) remote sensor with a 3.4 μm filter, an older version of the Denver University remote sensor with a 3.3 μm filter, and an FID. The ratio of infrared sensor to FID reading was termed the response factor for each compound. Table 1 lists the individual organic compound response factors measured by Stephens et al. using a Horiba MEXA-324GE NDIR analyzer and the GM remote sensor. The relative responses of alkanes, alkenes, and aromatics measured by Stephens et al. were consistent with those measured by Jackson. Stephens et al. used the same suite of instruments to measure exhaust volatile organic compound (VOC) concentrations for two modern technology vehicles operated in a series of simulated failure modes. The authors noted that the exhaust VOC concentrations measured by NDIR would need to be scaled up by factors ranging from 1.5 to 4.4 to be consistent with FID measurements (7).

The objective of this study is to develop and demonstrate an approach for scaling infrared remote sensor measurements to represent total exhaust VOC emissions. Scaling factors presented in this study will support the use of on-road remote sensor HC measurements in motor vehicle emission inventory calculations.

Approach

Infrared response factors were measured for 31 individual organic compounds which together account for >60% of fleet-composite motor vehicle exhaust VOC emissions, as measured on-road (12). Special attention was given to branched alkanes, cycloalkanes, and C_9 aromatics whose response factors have not been reported previously. These measurements were used to calculate coefficients for a linear regression model which relates infrared absorption to the number and types of C—H bonds in a molecule. The regression model was used to predict response factors for additional exhaust VOC constituents. Since vehicle exhaust contains more than 150 identifiable, individual organic compounds—most of which are present at levels below 0.5% of total VOC mass—each individual compound was assigned to one of 20 response factor groups. Compounds were grouped by structural characteristics which affect infrared absorption and by their model-predicted response factors. Several important exhaust components, including methane, ethane, ethene, propene, isobutene, acetylene, benzene, toluene, and methyl *tert*-butyl ether (MTBE), were treated explicitly as individual species.

Group response factors (RF_g) were combined with speciated VOC measurements to predict response factors (RF_m) for vehicle exhaust mixtures as follows

$$RF_m = \sum_g (RF_g c_g) \approx \sum_g (RF_g w_g) \tag{1}$$

where c_g is the fraction of total organic carbon contributed by all of the organic compounds assigned to group g and w_g is the weight fraction of total VOC contributed by the organic compounds in group g. Use of w_g versus c_g in eq 1 gives similar results because weight fractions and carbon fractions are nearly identical for individual vehicle exhaust hydrocarbons. Strictly speaking, however, eq 1 should be applied using carbon fractions (c_g) since NDIR/FID response factors are based on carbon counts.

The accuracy of eq 1 was verified experimentally by collecting simultaneous IR and FID measurements of total VOC concentrations in real vehicle exhaust samples. Speciated VOC profiles measured from the same exhaust samples

TABLE 1. IR/FID Response Factors Measured by Stephens et al. (Ref 7)

compound	on-board NDIR analyzer	GM remote sensor (3.4 μm filter)	Denver University remote sensor (3.3 μm filter)
methane	0.15 ± 0.003	0.26 ± 0.043	0.35 ± 0.044
propane	1.01−1.09	0.94−1.08	0.91−1.02
n-butane	1.11 ± 0.015	0.99 ± 0.061	0.94 ± 0.033
isooctane	0.85 ± 0.022	0.76 ± 0.091	0.70 ± 0.060
MTBE	0.89 ± 0.016[a]	0.77 ± 0.137[a]	0.86 ± 0.033[a]
ethene	0.05 ± 0.001	0.08 ± 0.030	0.10 ± 0.008
propene	0.29 ± 0.004	0.29 ± 0.024	0.31 ± 0.037
isobutene	0.51 ± 0.007	0.46 ± 0.034	0.44 ± 0.039
toluene	0.08 ± 0.005	0.07 ± 0.047	0.11 ± 0.031
o-xylene	0.14 ± 0.002	0.21 ± 0.236	0.13 ± 0.057

[a] MTBE values reported by Stephens et al. do not account for partial response when MTBE is measured by FID.

were used to predict, with eq 1, the IR/FID ratio measured for each sample. VOC speciation profiles measured in recent tunnel studies were then used to calculate overall IR/FID response factors for on-road vehicle fleets using conventional and reformulated gasolines. Inverting these response factors yields FID/IR ratios which can be used to scale infrared HC remote sensor measurements to correspond to FID-based measurements. The approach is demonstrated for a "fleet" of 20 high-emitting vehicles recruited from an Orange County, CA, roadway (13).

Experimental Section

Measurement of Individual Compound Infrared Response Factors. Infrared response factors were determined by measuring with FID and an infrared spectrometer the concentrations of individual organic compounds in prepared air samples. Samples of HC-free air and a 167 ppmv (500 ppmC) propane standard were also measured to obtain baseline readings and a span calibration point for each instrument. Individual compounds chosen for testing include those that contribute significantly to motor vehicle exhaust VOC emissions and others that are structurally representative of major classes of VOC found in vehicle exhaust. A complete list of organic compounds tested is presented in Table 2.

Air samples containing single organic compounds were prepared by volatilizing ~5 μL of pure liquid, or by mixing 5−15 mL of pure gas, into 20 L Tedlar bags filled with 10−18 L of ultrapure hydrocarbon-free air (<0.01 ppmC, Scott-Marrin, Riverside, CA). Liquids were injected by syringe through a septum while the Tedlar bags were more than half full but still filling with ultrapure air. Gaseous species were injected by gastight syringe while the bags were filling with ultrapure air. Each bag was then kneaded for several minutes to promote mixing and set aside for ~1 h before being sampled. VOC concentrations were in the range of 350−650 ppmC for most samples. Compounds which were expected to show less infrared absorption were mixed to higher concentrations (in the ranges of 750−850 ppmC for toluene and xylene and 850−1200 ppmC for methane). These higher concentrations resulted in increased absolute infrared absorption, and more precise IR measurements for these weakly absorbing compounds. The actual concentration of VOC in each sample was determined by FID. The stability of organic compound concentrations in the bags was verified by repeating the measurements for several of the samples over a 4 h period.

The optics of an on-road remote sensor were simulated using a Nicolet Magna 760 FTIR spectrometer with the 3.4 μm filter shown in Figure 1. The infrared beam was reflected 8 times through a 530 cm^3 multiple path White cell for a total

TABLE 2. Measured IR/FID Response Factors for Individual Organic Compounds

compound	measured response 3.4 μm filter[a]	measured response 3.45 μm filter[b]
methane	0.21 ± 0.02	0.30
ethane	0.89 ± 0.03	0.81
propane	1.00	1.00
n-pentane	0.983 ± 0.002	
n-hexane		1.11
n-octane	0.91	
2-methylbutane	0.90	0.99
2-methylpentane	0.89 ± 0.02	0.99
2-methylhexane	0.89 ± 0.02	
2-methylheptane	0.88 ± 0.02	
2,3-dimethylbutane	0.858 ± 0.005	
2,4-dimethylpentane	0.811 ± 0.002	
2,4-dimethylhexane	0.82	
2,5-dimethylhexane		0.99
2,2,4-trimethylpentane	0.74 ± 0.04	0.90
cyclopentane	0.93	1.06
cyclohexane	0.95	1.15
methylcyclopentane	0.91	1.02
methylcyclohexane	0.94	1.13
ethene	0.085 ± 0.008	0.04
propene	0.37 ± 0.02	0.30
isobutene	0.53 ± 0.02	0.48
1-pentene	0.67	
1-hexene		0.70
benzene	0.01	
toluene	0.10 ± 0.02	0.15
p-xylene	0.20 ± 0.02	0.27
ethylbenzene	0.22	
1,2,4-trimethylbenzene	0.30	0.43
n-propylbenzene	0.27 ± 0.02	
MTBE[c]	0.69	0.72

[a] Filter similar to those used in Denver Univ remote sensors, shown in Figure 1. [b] Filter used in Horiba PIR-2000 NDIR analyzer, shown in Figure 1. [c] Measured IR/FID response of MTBE was multiplied by 0.86 (see text and ref 16).

path length of 240 cm. The 3.4 μm filter is centered at the same location, but has a slightly narrower band-pass than those used in the newer Denver University HC remote sensors (8, 14). To mimic a remote sensor detector which measures total transmitted energy, the FTIR transmittance versus wavenumber plot for each sample was integrated from 2700 to 3100 cm^{-1}. This range includes all energy transmitted by the 3.4 μm filter, as shown in Figure 1. Absorbance, $A = \log(I_o/I_s)$, was calculated as the ratio of energy transmitted when the cell was filled with hydrocarbon-free air (I_o) to the energy transmitted when the cell was filled with a sample (I_s). Since path length remained constant, the Beer−Lambert Law indicates that the measured absorbance should have been linearly proportional to the concentration of absorbing species in each sample.

For each sample, the White cell was evacuated to 0.03 atm pressure and then filled with sample air from the Tedlar bag three times before any measurements were made. On the fourth filling, the IR spectrum was recorded. The cell was then evacuated and filled and the spectra recorded, twice more for each sample. Each sample intensity I_s was calculated as the average of the three integrated intensities measured for each compound. The reference intensity I_o was obtained by performing the same procedure for a sample containing only ultrapure air. A calibration point was obtained by repeating the procedure with the propane-in-air standard. Following the IR measurement, the organic vapor concentration in each sample was measured by FID. Since each sample contained only a single compound of known identity, an external pump was used to bypass the column and introduce sample air directly to the flame

ionization detector of a Hewlett-Packard 5880A gas chromatograph. The sample flow rate to the FID was held constant and monitored continuously. The FID signal was zero-corrected using ultrapure air and calibrated using the propane standard. The linearity of both instruments over the range of experimental conditions described above was verified by measuring a series of n-pentane samples ranging in concentration from 296 to 1114 ppmC.

Measurement of VOC Exhaust Speciation for Individual Vehicles. In an ongoing surveillance program to measure in-use motor vehicle emissions, the California Air Resources Board (CARB) recruits and tests in-use vehicles on a series of prescribed dynamometer driving cycles (15). Nine high-emitting vehicles recruited to the program during the winter of 1996−97 were tested on the following four standard driving cycles: the urban dynamometer driving schedule, CARB's LA92 (Unified) cycle, the stop-and-go New York City cycle, and a high-speed highway driving cycle developed by CARB (SCF58). Collectively, these cycles span a wide range of driving conditions. The concentration of total VOC in the diluted exhaust from each vehicle test was measured by the dynamometer bench FID and a Horiba PIR2000 NDIR analyzer calibrated with n-hexane. On a per-carbon basis, the response of the NDIR analyzer to propane was measured to be 0.9 times the response to n-hexane. Since the HC channel of remote sensors is calibrated using propane, all of CARB's NDIR measurements were divided by 6 to convert from hexane equivalents to C_1 equivalents and then multiplied by 0.9 to be consistent with instruments calibrated with propane. A portion of each exhaust sample was collected in a 1 L Tedlar bag and analyzed by GC-FID to determine speciated VOC concentrations. All vehicle testing and speciated VOC analyses were performed at CARB facilities in El Monte, CA.

The interference filter used in the Horiba PIR2000 analyzer has a similar bandwidth but is centered at a slightly higher wavelength (3.45 μm) than the 3.4 μm filter for which response factors were measured; the absorption spectrum of each filter is shown in Figure 1. Using a slightly modified experimental procedure, IR/FID response factors appropriate to the 3.45 μm filter were measured for many of the organic compounds listed in Table 2. The operating software of the FTIR allowed for a digital representation of the 3.45 μm filter to be used in place of a physical filter. Absorption spectra of the filter and organic compound samples were combined by adding absorbance as a function of wavenumber. The result of this calculation is equivalent to the spectrum measured when a physical filter and organic compound air sample are measured in series. Other procedural differences included the use of nitrogen as dilution gas in place of ultrapure air, and FID measurement using a 0.32 mm × 20 m GasPro GSC column on the HP 5880A GC-FID. To verify the equivalence of this modified approach to the original test procedure, response factors were remeasured for selected compounds using the 3.4 μm filter and the modified approach described in this paragraph.

Results and Discussion

Individual Compound Response Factors. Measured IR/FID response factors for the individual organic compounds tested in this study are presented in Table 2. The IR/FID response of MTBE was multiplied by 0.86 to account for the partial response when MTBE is measured by a FID calibrated for propane (16). The response factor of acetylene was not measured in the current study because C−H absorption for this compound occurs at 3300 cm^{-1} (9), which is outside the band-pass region of the 3.4 μm filter shown in Figure 1. Accordingly, a response factor of zero was assumed for acetylene.

C−H bond type	coefficient[a]	value[b]
primary alkane	a_1	0.31 ± 0.01
secondary alkane	a_2	0.48 ± 0.01
tertiary alkane	a_3	0.49 ± 0.09
alkene	a_4	0.08 ± 0.04
aromatic	a_5	-0.04 ± 0.02

[a] Coefficients appearing in eq 2 used to predict individual compound response factors. [b] Coefficient estimate ± 1 standard error as determined by multiple linear regression using the measured IR/FID response factors for the 3.4 μm filter shown in Table 2.

Inspection of Table 2 shows that as alkanes become more highly branched, their response factors drop, while increasing the number of alkyl substituents on an aromatic ring increases the infrared response. Together, Tables 1 and 2 show that the individual compound response factors measured for the two filters in this study are generally consistent with each other and with those previously measured by Stephens et al. (7).

One notable difference is that, other than for ethane and the C_2-C_4 alkenes, response factors measured using the 3.45 μm filter were significantly higher than those measured for the same compounds using the 3.4 μm filter. This may be understood from Figure 1, which shows the absorption properties of propane, hexane, and the two interference filters. Some of the energy absorption by propane occurs at wavelengths which do not pass through the 3.45 μm filter, whereas most of the hexane absorption occurs within the range of this filter. As a result, more energy will be absorbed (per carbon atom) by hexane than by propane when a 3.45 μm filter is used. If an infrared spectrometer with a 3.45 μm filter is calibrated with a standard propane mixture, a sample containing n-hexane at the same carbon concentration (ppmC) will absorb more energy and a higher concentration will be reported. Since the other C_5+ alkanes listed in Table 2 absorb over a wavelength range similar to that of n-hexane, their 3.45 μm filter response factors are higher than those measured with the 3.4 μm filter. Ethane absorption occurs in a lower wavelength range relative to propane and hexane. The 3.45 μm filter thus captures less of ethane's absorption, and ethane's response factor drops relative to propane and hexane.

The measured 3.4 μm response factors listed in Table 2 were used to calculate coefficients for a linear regression model relating the number and types of C−H bonds to infrared absorption per carbon atom for each compound. Physically, this model is based on the understanding that each C−H bond is responsible for absorbing a portion of the total infrared energy absorbed by the molecule. Mathematically, the model is described by

$$RF_i = (a_1 n_1 + a_2 n_2 + a_3 n_3 + a_4 n_{olef} + a_5 n_{arom})/n_C \quad (2)$$

where RF_i is the response factor for compound i; n_1, n_2, and n_3 are the number of C−H bonds associated with primary, secondary, and tertiary paraffinic carbon atoms; n_{olef} and n_{arom} are the number of C−H bonds associated with olefinic and aromatic carbon atoms; n_C is the total number of carbon atoms per molecule; and the unknown coefficients a_i are determined by linear regression.

Results of the regression analysis shown in Table 3 indicate that each trio of primary C−H bonds and each pair of secondary C−H bonds absorbs an amount of infrared energy which indicates the presence of approximately one carbon atom. This is consistent with the observation that straight-chain alkanes have response factors close to 1. In contrast, each tertiary C−H bond indicates the presence of only about
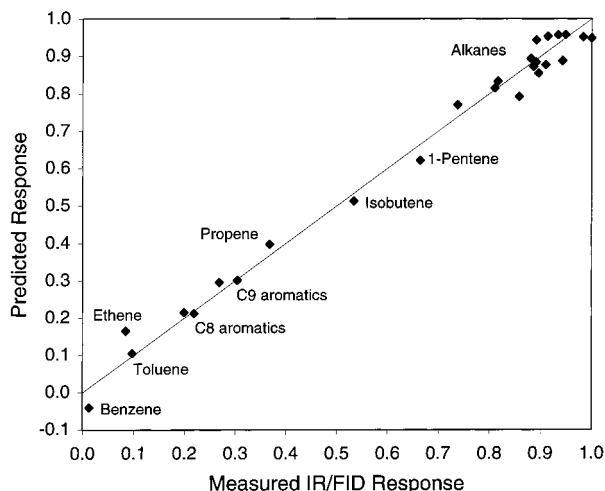

FIGURE 2. Predicted vs measured response factors at 3.4 μm for the individual organic compounds listed in Table 2. Predictions calculated using eq 2 and coefficients of Table 3.

one-half of a carbon atom; when combined with the fact that quaternary carbon atoms do not have C−H bonds and are thus not counted by the IR technique described, this explains the observed reduction in response factors for more highly branched alkanes. The small value of a_4 is expected because olefinic C−H bonds show little absorption in the wavelength range of the filter. The near-zero value of a_5 indicates that aromatic C−H bonds do not contribute to infrared absorption in the 3.4 μm filter window.

Equation 2 was used to predict response factors for all of the compounds listed in Table 2. As shown in Figure 2, these predictions correspond closely ($r^2 = 0.99$) to the individual compound response factors measured with the 3.4 μm filter. This is not surprising since the model coefficients were calculated from this experimental data. It is important to note, however, that the model accurately describes absorption at 3.4 μm for the full range of organic compounds listed in Table 2. Stephens et al. proposed a similar linear model which was not normalized to the total number of carbon atoms in a molecule (17). As a result, regression coefficients calculated by Stephens et al. do not have the same physical significance as those described above.

Response to Organic Compound Mixtures. Twenty lumped species groups were used to represent the absorption characteristics of all individual VOC found in vehicle exhaust; the corresponding group response factors for both the 3.4 and 3.45 μm filters are listed in Table 4. Uncertainty in the group response factors shown in Table 4 was estimated from uncertainty in the response factors measured for individual compounds and from variability among response factors for individual compounds assigned to each group. The regression model described above was used to predict the response of compounds whose response factors were not measured directly. These predictions were used to estimate the response factor for C_{10} or larger ($C_{10}+$) aromatics, to confirm that all C_5+ alkenes could be grouped together, and to assign to groups the minor exhaust constituents listed in the footnotes to Table 4. A response factor of 0.60 ± 0.15 (3.4 μm filter) was assigned to the unidentified fraction of total VOC because this group was expected to consist of branched $C_{10}+$ alkanes and/or $C_{10}+$ aromatics; the large uncertainty bounds on this response factor account for the possibility that the mass is composed entirely of alkanes or aromatics. Formaldehyde, which typically accounts for $\sim 1-2\%$ of exhaust VOC mass emissions (12, 16, 18), does not respond to FID measurement and was thus not included in the analysis.

TABLE 4. Organic Compound Grouping Scheme and Response Factors for Use with Eq 1

compound group	response for 3.4 μm filter	response for 3.45 μm filter
methane	0.21 ± 0.02	0.30
ethane	0.89 ± 0.03	0.81
C_3-C_5 n-alkanes	0.98 ± 0.01	1.00
C_6+ n-alkanes	0.91 ± 0.03	1.11
monosubstituted alkanes	0.89 ± 0.02	0.99
dimethylpropane/butanes	0.86 ± 0.02	0.99
other disubstituted alkanes	0.81 ± 0.02	0.99
trisubstituted alkanes	0.74 ± 0.04	0.90
cycloalkanes	0.93 ± 0.03	1.09
MTBE	0.69 ± 0.05	0.72
ethene[a]	0.09 ± 0.01	0.04
propene[b]	0.37 ± 0.02	0.30
isobutene[c]	0.54 ± 0.02	0.48
other alkenes	0.67 ± 0.05	0.70
acetylene	0	0
benzene[d]	0.01 ± 0.01	0.01
toluene	0.10 ± 0.02	0.15
C_8 aromatics	0.21 ± 0.02	0.27
C_9 aromatics	0.30 ± 0.03	0.43
$C_{10}+$ aromatics	0.37 ± 0.05	0.56
unidentified	0.60 ± 0.15	0.70

[a] Lumped group includes 1,3-butadiene, 1,2-propadiene, 1-buten-3-yne (see text). [b] Lumped group includes 1,2-butadiene, 1-propyne, 2-methyl-1,3-butadiene. [c] Lumped group includes 1-butyne, 2-butyne. [d] Lumped group includes styrene, naphthalene.
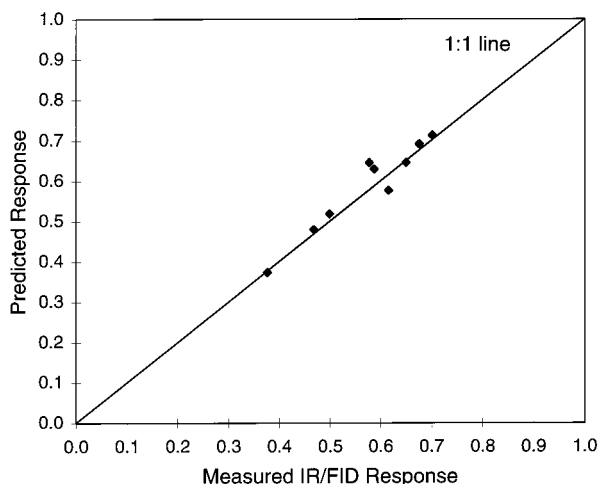

FIGURE 3. Comparison of exhaust mixture response factors (RF$_m$) predicted using eq 1 with NDIR/FID ratios measured from CARB surveillance program vehicles. Mixture response factors were calculated using the 3.45 μm group response factors listed in Table 4. NDIR/FID ratios were measured using an infrared analyzer with a 3.45 μm filter and a FID.

Using eq 1, the 3.45 μm group response factors shown in Table 4 were combined with measured VOC speciation profiles to predict exhaust mixture response factors for the CARB surveillance program vehicles. Predicted response factors are plotted in Figure 3 against corresponding measured values (i.e. the ratio of NDIR to FID measurements of exhaust VOC concentrations). Figure 3 shows that if the composition of VOC in vehicle exhaust is known, infrared response can be predicted accurately. Predicted exhaust response factors correlate 1:1 to measured NDIR/FID ratios with an r^2 of 0.93.

Figure 3 includes data from only 9 of the 36 dynamometer tests performed on CARB surveillance program vehicles. Despite a screening process which was intended to identify high-emitting vehicles, measured exhaust VOC concentra-

tions in all but 12 of the 36 tests were below 10% of the full scale NDIR setting of 3000 ppm. The ratio of predicted to measured IR response for these tests decreased and was much more variable as exhaust VOC concentration decreased. The bias was ~15−30% for measured VOC concentrations between 5 and 9% of full scale, but was much larger (~10−90%) for vehicles with exhaust VOC concentrations below 5% of full scale on the NDIR analyzer. Since there was no consistent change in exhaust VOC speciation that could be correlated to this trend, it was determined that infrared measurements below 10% of full scale were biased, and therefore were not used to calculate NDIR/FID ratios. Three additional tests were rejected because the total VOC identified and quantified during speciated analysis was less than 85% of the total measured by the dynamometer bench FID.

Fleet-Average Infrared Response Factors. The exact scaling of individual HC remote sensor measurements is infeasible in real-world sampling scenarios because the composition of VOC in each exhaust plume is unknown. It is often possible, however, to measure the composite VOC speciation profile for an on-road fleet similar to the fleet being measured by remote sensing. The measured VOC profile can be used to calculate a fleet-average IR/FID response factor; infrared remote sensor measurements can then be scaled by the inverse of this factor. Fleet-composite VOC speciation profiles are most readily measured in roadway tunnels. Speciated VOC profiles measured in roadway tunnels represent the average speciation, weighted by VOC mass emission rate, of all vehicles traveling through the tunnel during sampling. A tunnel-derived scaling factor will produce accurate estimates of total fleet VOC emissions if the composite VOC profile of the fleet being measured by remote sensing resembles the VOC profile measured in the tunnel, as demonstrated below.

As part of a separate study of on-road vehicle emissions (13), 20 in-use vehicles were recruited from an Orange County, CA, roadway based on high HC remote sensor readings. Total and speciated exhaust VOC emissions were measured for each vehicle by dynamometer testing. Table 5 includes a brief description of each vehicle along with the exhaust VOC concentration measured from the vehicle in an as-received state (i.e. without repairs). IR/FID response factors were calculated using eq 1, the 3.4 μm group response factors shown in Table 4, and the exhaust speciation profile measured for each vehicle (19). As shown in Table 5, 70% of the vehicles had response factors in the range of 0.45−0.55, and all but one of the response factors were between 0.40 and 0.60. The VOC concentration that would have been reported by infrared measurement of each exhaust sample was calculated as the product of the response factor and total VOC concentration for each vehicle. Since it has been shown experimentally that infrared response factors can be predicted accurately if VOC speciation is known (Figure 3), the calculated infrared readings will be discussed as if infrared measurements had actually been made. Assuming that emissions are proportional to exhaust VOC concentrations, the last row of Table 5 indicates that IR measurements would understate total VOC emissions by 48% for these 20 vehicles.

A composite VOC speciation profile for all 20 vehicles was calculated as the emissions-weighted average of the measured speciation profiles of the individual vehicles. Using this composite speciation profile together with eq 1 and the group response factors shown in Table 4, a fleet-average response factor of 0.52 was calculated. The inverse of this value (1.92) was used to scale up the calculated infrared measurement for each vehicle. Note that the same fleet response factor is calculated from the ratio of summed infrared to summed FID measurements shown at the bottom of Table 5. Table 5 shows two important results of this analysis: (1) the scaled emission estimate for each vehicle

TABLE 5. Comparison of IR and FID Estimates of Exhaust VOC Concentrations for 20 In-Use Orange County, CA, Vehicles

vehicle description	vehicle no.	exhaust VOC concn[a] (ppmC)	calcd IR/FID response[b]	estimated VOC by IR[c] (ppmC)	scaled IR estimate[d] (ppmC)
1985 Plymouth Voyager	134	28	0.50	14	26
1987 Volkswagen Jetta	136	58	0.46	27	51
1988 AMC Jeep Wrangler	9	75	0.48	36	69
1985 Toyota Corolla	13	117	0.43	51	97
1988 Nissan Sentra	68	118	0.52	62	118
1988 Suzuki Samurai	122	130	0.52	67	128
1983 Chevrolet Caprice	35	171	0.48	81	155
1976 Ford Pinto	6	211	0.43	91	173
1975 Mercedes 280C	16	262	0.40	104	199
1984 GMC S-15 Sierra	108	307	0.53	163	312
1987 Mercury Sable	127	420	0.45	189	360
1985 Oldsmobile Tornado	23	467	0.67	311	593
1987 Ford Taurus	89	504	0.51	258	493
1986 Chevrolet Blazer	59	519	0.53	277	529
1987 Ford Taurus	123	546	0.45	245	467
1985 Volkswagen Golf	138	701	0.46	321	612
1987 Chevrolet Blazer	97	987	0.58	574	1095
1975 Nissan 280Z	51	1610	0.47	758	1447
1985 Chevrolet S-10 Blazer	99	1706	0.59	1003	1914
1987 Dodge Dakota	91	3441	0.54	1856	3541
totals[e]		12379		6489	12379

[a] As measured by FID; does not include formaldehyde. [b] Calculated using eq 1, the measured exhaust VOC speciation for each vehicle, and the 3.4 μm filter response factors of Table 4. [c] Calculated as the product of response factor and exhaust VOC concentration measured by FID for each vehicle. [d] IR-based estimate of true VOC emissions: predicted infrared reading divided by fleet-average IR/FID response factor of 0.52 (see text). [e] Exhaust concentrations are assumed to be proportional to emission rates expressed as gram of HC emitted per unit volume of fuel burned. The total concentration is therefore assumed to be proportional to total emissions.

TABLE 6. IR/FID Response Factors Calculated Using VOC Speciation Profiles Measured in Roadway Tunnels

year	tunnel[a]	location	fleet[b]	fuel	RF$_m$[c] 3.4 μm filter	RF$_m$[c] 3.45 μm filter
1992	Ft. McHenry	Baltimore, MD	HD	>70% diesel	0.49 ± 0.04	0.58
1992	Tuscarora	PA Turnpike	LD	gasoline[d]	0.44 ± 0.02[e]	0.50[e]
1992	Ft. McHenry	Baltimore, MD	LD	gasoline[d]	0.45 ± 0.02[e]	0.52[e]
1994	Caldecott	Oakland, CA	LD	gasoline[f]	0.44 ± 0.03	0.50
1995	Caldecott	Oakland, CA	LD	gasoline[f]	0.47 ± 0.03	0.55
1995	Deck Park	Phoenix, AZ	LD	fed. RFG[g]	0.51 ± 0.03[e]	0.59[e]
1995	Van Nuys	Los Angeles, CA	LD	fed. RFG[g]	0.49 ± 0.03[e]	0.57[e]
1995	Callahan	Boston, MA	LD	fed. RFG[g]	0.53 ± 0.03[e]	0.60[e]
1996	Caldecott	Oakland, CA	LD	CA RFG[h]	0.51 ± 0.03	0.58
average scaling factor for vehicles using conventional gasoline					2.2 ± 0.1	1.9
average scaling factor for vehicles using reformulated gasolines					2.0 ± 0.1	1.7

[a] See refs 12, 18, 20–21. [b] Predominant vehicle type sampled: LD = light-duty; HD = heavy-duty. [c] RF$_m$ = mixture response factor calculated using measured exhaust VOC speciation profile, group response factors shown in Table 4, and eq 1. [d] Conventional gasoline. [e] Calculated response assumes 10% methane weight fraction (see text for details). [f] California phase 1 reformulated gasoline. Properties similar to conventional gasoline except for summer RVP limit of 7.8 psi, complete removal of lead, and requirement for detergent additives. [g] Federal reformulated gasoline. [h] California phase 2 reformulated gasoline.

is much more accurate than the unscaled infrared measurement and (2) the sum of the individual scaled estimates matches exactly the total measured VOC. This equality occurs because the fleet-average response factor was calculated from a composite VOC speciation profile which matches exactly the composite speciation of the vehicle sample.

Scaling Factors for Typical On-Road Fleets and Fuels. Typical fleet-average IR/FID response factors were calculated using VOC speciation profiles measured in roadway tunnel studies (12, 18, 20, 21). Table 6 lists the tunnel locations, the fuel in use at the time of study, and the calculated response factors. Methane emissions were reported for the Caldecott tunnel only, where methane accounted for about 10% of total VOC mass (12, 18). This same methane fraction was assumed when calculating IR/FID response factors for the other light-duty vehicle fleets. The heavy-duty vehicle fleet observed at the Fort McHenry tunnel (21) was comprised of >70% diesel-powered vehicles. As a result, VOC emissions from this fleet included significant contributions from high molecular weight alkanes that are not found in gasoline

engine exhaust. A response factor of 0.85 ± 0.05 (3.4 μm filter) was assigned to C_{11}+ n-alkanes based on the observation that n-alkane response decreases as carbon number increases (see Table 3 and the discussion of n-alkane absorption in ref 7). The unidentified branched alkanes measured from the heavy-duty fleet at the Fort McHenry tunnel were split equally and assigned to the di- and trisubstituted alkane groups shown in Table 4. Following the measurements of Clark et al. (22, 23) which show that diesel engines emit very low levels of methane, the nonmethane organic compound emissions profile reported from measurements in the Fort McHenry tunnel (21) was used without adjustment to estimate infrared response for heavy-duty vehicles.

Table 6 shows that for the 3.4 μm filter, light-duty fleet response factors range from 0.44 to 0.47 for vehicles using conventional gasoline, and from 0.49 to 0.53 for vehicles using either California or federal reformulated gasolines. Fleet response factors for the 3.45 μm filter are higher by about 15%. These results indicate that fleet-average infrared
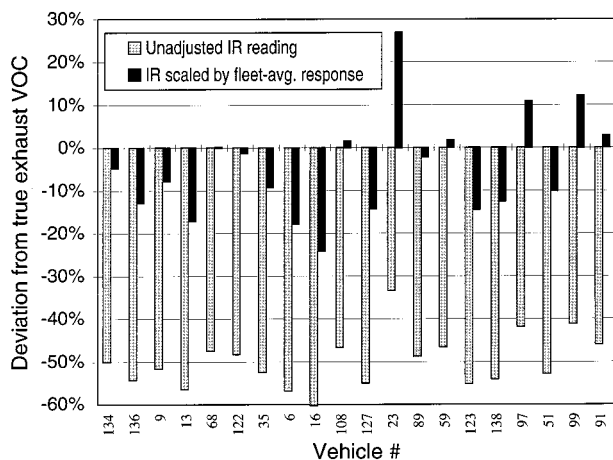
FIGURE 4. Results of using simulated IR readings to estimate true exhaust VOC concentrations for 20 in-use vehicles from Orange County, CA. Light bars show unadjusted IR readings consistently understating true VOC concentrations. Dark bars show that adjusted IR readings are within ±15% of true VOC for most vehicles.

response is most sensitive to filter band-pass and fuel composition, but varies less by geographic area or across the range of driving conditions in the tunnels studied. The higher response factors associated with reformulated gasolines may be explained by changes in the exhaust VOC emissions of vehicles burning these fuels. Specifically, reductions in the aromatic content of gasoline leads to exhaust mixtures that absorb more 3.4 μm infrared radiation per unit mass of VOC emitted. This result is expected given the low IR/FID response factors measured for individual aromatic hydrocarbons (see Table 2), compared to the higher response factors for branched alkanes, cycloalkanes, and MTBE that are blended into reformulated gasoline in increased amounts when aromatic levels are lowered.

Application of the fleet-average response factors presented in Table 6 is demonstrated using emissions data collected from the 20 Orange County, CA, vehicles discussed previously. This "fleet" includes a relatively small number of vehicles which have average VOC emissions comparable to those measured from much larger samples of on-road vehicles (*18*).

The scaling factor of 2.0 calculated from the VOC speciation profile measured in the Van Nuys tunnel was chosen as most appropriate because the tunnel is located in the same metropolitan area as the vehicles tested and because VOC sampling occurred at the tunnel during the same year as the individual vehicle testing. The average scaling factor for vehicle fleets using Federal reformulated gasoline also could have been used. When each of the infrared measurements listed in Table 5 is multiplied by the scaling factor of 2.0, the accuracy of individual vehicle VOC emissions estimates is improved substantially compared to the unscaled infrared data; this is shown in Figure 4. Unscaled infrared measurements understate tailpipe VOC concentrations by 33−60%, whereas most of the scaled infrared estimates fall within the range of ±15% of true VOC concentrations. Overall, the scaled infrared estimates overstate VOC emissions from this fleet by 4%; this small bias reflects the difference between the scaling factor derived from Van Nuys tunnel measurements (2.0) and the factor calculated explicitly for the Orange County vehicles (1.92).

Uncertainty. The reported uncertainty of each fleet-average response factor shown in Table 6 accounts only for the uncertainties in underlying group response factors for the 3.4 μm filter (shown in Table 4). The uncertainties in scaling factors for each fuel, shown at the bottom of Table 6, are also based on the group response factor uncertainties. The variability in response factors (RF_m) across the relevant

on-road studies for each fuel is less than the uncertainty resulting from the group response factors.

From the earlier discussion and results, it is clear that infrared response depends on the exact transmission range of the interference filter. The magnitude of this effect may be inferred from the ~15% difference between response factors calculated for 3.4 and 3.45 μm filters (last two columns of Table 6). This difference is consistent with the observation that exhaust mixture IR/FID response factors predicted with the 3.4 μm group response factors were 11% lower than those measured for CARB surveillance program vehicles with the 3.45 μm filter. Individual filters with the same nominal band center may in reality have slightly different band-pass ranges; however, the effect of these differences on mixture response should be smaller than the difference between the 3.4 and 3.45 μm filters. Whenever possible, the exact transmission range of an infrared filter should be determined before selecting an appropriate scaling factor. Band-pass range variability is bounded by the need to capture the large peak of most alkanes (similar to the absorption profile of hexane, as shown in Figure 1) while avoiding interference of water vapor below 3000 cm^{-1} (*8*).

Two other sources of uncertainty exist when using remote sensor measurements to quantify on-road vehicle emissions. First, and most important, is the accuracy of the remote sensor. Previous assessments show that HC remote sensors can accurately measure dry gas mixtures of propane (or hexane), CO, CO_2, and air (*24, 25*). This work thus assumes that remote sensors would yield accurate results if exhaust VOC emissions were composed entirely of propane. A second source of uncertainty—remote sensor measurement precision—would also have to be considered if in-use emissions levels of *individual* vehicles were to be estimated from single remote sensor measurements. Addressing this issue, Bishop et al. (*26*) have shown that emissions of high-emitting vehicles vary from test to test regardless of the analytical technique or test duration; the authors thus caution against using any single measurement to assess individual high-emitting vehicle performance. The individual vehicle test results of Figure 4 should be viewed in this light, with the additional understanding that infrared remote sensors provide the ability to obtain multiple test results for individual in-use vehicles. Most important to the objectives of this study, the precision of individual measurements is not an issue when remote sensors are used to estimate fleet-average emissions.

Motor Vehicle Emission Inventory Calculations. The objective of this work was to develop an approach for scaling infrared remote sensor measurements for quantitative fleet emissions assessment. Measurements of fleet-composite VOC speciation throughout the U.S. indicate that measurements from HC remote sensors equipped with 3.4 μm filters should be multiplied by a factor of about 2 when calculating fleet-average emission factors for motor vehicle emission inventory calculations. The exact scaling factor is slightly higher (2.2 ± 0.1) for vehicles using conventional gasoline, and slightly lower (2.0 ± 0.1) for vehicle fleets using either California or federal reformulated gasoline. Alternatively, a local fleet scaling factor can be calculated if on-road measurements of the composite exhaust VOC profile are available. The appropriate scaling factor can be applied to data sets containing tens of thousands of remote sensor measurements in the same manner that the scaling factor calculated from Van Nuys tunnel data was applied to the simulated infrared exhaust measurements of Orange County vehicles. The scaled remote sensor measurements can then be used to calculate fleet-average exhaust HC emission factors which can be used in fuel-based emission inventory calculations.

Literature Cited

(1) Bishop, G. A.; Starkey, J. R.; Ihlenfeldt, A.; Williams, W. J.; Stedman, D. H. *Anal. Chem.* **1989**, *61*, 671A–677A.

(2) Bishop, G. A.; Stedman, D. H. *Environ. Sci. Technol.* **1990**, *24*, 843–847.

(3) Lawson, D. R.; Groblicki, P. J.; Stedman, D. H.; Bishop, G. A.; Guenther, P. L. *J. Air Waste Manage. Assoc.* **1990**, *40*, 1096–1105.

(4) Stephens, R. D.; Cadle, S. H. *J. Air Waste Manage. Assoc.* **1991**, *41*, 39–46.

(5) Stephens, R. D. *J. Air Waste Manage. Assoc.* **1994**, *44*, 1284–1292.

(6) Singer, B. C.; Harley, R. A. *J. Air Waste Manage. Assoc.* **1996**, *46*, 581–593.

(7) Stephens, R. D.; Mulawa, P. A.; Giles, M. T.; Kennedy, K. G.; Groblicki, P. J.; Cadle, S. H.; Knapp, K. T. *J. Air Waste Manage. Assoc.* **1996**, *46*, 148–158.

(8) Guenther, P. L.; Stedman, D. H.; Bishop, G. A.; Beaton, S. P.; Bean, J. H.; Quine, R. W. *Rev. Sci. Instrum.* **1995**, *66*, 3024–3029.

(9) Bellamy, L. J. *The Infra-red spectra of Complex Molecules*, 2nd ed.; John Wiley & Sons: New York, 1958.

(10) Harris, D. C. *Quantitative Chemical Analysis*, 3rd ed.; W. H. Freeman and Company: New York, 1991.

(11) Jackson, M. W. *J. Air Pollut. Control Assoc.* **1966**, *11*, 697–702.

(12) Kirchstetter, T. W.; Harley, R. A.; Kendall, G. R.; Hesson, J. *Impact of California phase 2 reformulated gasoline on atmospheric reactivity of exhaust and evaporative emissions*. Presented at 90th Annual Meeting of the Air and Waste Management Association, Toronto, Ontario, Canada, June 8–13, 1997.

(13) Cadle, S. H.; Mulawa, P. A.; Ball, J.; Donase, C.; Weibel, A.; Sagebiel, J.; Knapp, K. T.; Snow, R. *Particulate and speciated HC emission rates from in-use vehicles recruited in Orange County, CA.* Presented at 6th CRC On-Road Vehicle Emissions Workshop, San Diego, CA, March 16–18, 1996.

(14) Bishop, G. A. Personal Communication. University of Denver, Denver, Colorado. Personal communication, 1997.

(15) Devesh, S. *Test Report of the Light-Duty Vehicle Surveillance Program, Series 12 (LDVSP 12).* Mobile Source Division, California Air Resources Board, El Monte, CA, 1994. MS-94–04.

(16) Hoekman, S. K. *Environ. Sci. Technol.* **1992**, *26*, 1206–1216.

(17) Stephens, R. D.; Mulawa, P. A.; Giles, M. T.; Kennedy, K. G.; Groblicki, P. J.; Cadle, S. H.; Duncan, J. W.; Knapp, K. T. *An experimental evaluation of remote sensing based hydrocarbon measurements: a comparison of FID measurements.* Coordinating Research Council, 1994. Contract VE-11-4.

(18) Kirchstetter, T. W.; Singer, B. C.; Harley, R. A.; Kendall, G. R.; Chan, W. *Environ. Sci. Technol.* **1996**, *30*, 661–670.

(19) Mulawa, P. A.; Cadle, S. H. Personal Communication. General Motors NAO Research and Development Center, Warren, MI, 1997.

(20) Gertler, A. W.; Sagebiel, J. C.; Wittorff, D. N.; Pierson, W. R.; Dippel, W. A.; Freeman, D.; Sheetz, L. *Vehicle Emissions in Five Urban Tunnels.* Desert Research Institute, Reno, NV; Report to the Coordinating Research Council, Project No. E-5, 1997.

(21) Sagebiel, J. C.; Zielinska, B.; Pierson, W. R.; Gertler, A. W. *Atmos. Environ.* **1995**, *30*, 2287–2296.

(22) Clark, N. N.; Atkinson, C. M.; McKain, D. L.; Nine, R. D.; El-Gazzar, L. *SAE Technol. Pap. Ser.* **1996**, No. 960322.

(23) Clark, N. N.; Gadapati, C. J.; Kelly, K.; White, C. L.; Lyons, D. W.; Wang, W.; Gautum, M.; Bata, R. *SAE Technol. Pap. Ser.* **1995**, No. 952746.

(24) Pedrosa, J.; Benjaminson, R.; Yang, M. *Technical Assessment of On-Road Emissions Measurement Systems.* California Bureau of Automotive Repair, Engineering & Technical Research Branch, Sacramento, CA, 1995.

(25) Stedman, D. H.; Bishop, G. A.; Beaton, S. P.; Peterson, J. E.; Guenther, P. L.; McVey, I. F.; Zhang, Y. *On-road remote sensing of CO and HC emissions in California.* University of Denver, Denver, CO, 1994. Final Report to the California Air Resources Board, Contract No. A032-093.

(26) Bishop, G. A.; Stedman, D. H.; Ashbaugh, L. *J. Air Waste Manage. Assoc.* **1996**, *46*, 667–675.