

Aircraft Engine Speciated Organic Gases: Speciation of Unburned Organic Gases in Aircraft Exhaust



Aircraft Engine Speciated Organic Gases: Speciation of Unburned Organic Gases in Aircraft Exhaust

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

and

AEE-300 - Emissions Division
Office of Environment and Energy
Federal Aviation Administration

Technical Support Document

1 than 99% of the fuel through complete combustion to carbon dioxide (CO₂) and water
2 (H₂O). At idle conditions, much less fuel is consumed and, in the interest of maintaining
3 stable combustion at lower power conditions, some sacrifice in combustion efficiency
4 occurs even though this inefficiency is still only a percent or so. Any combustion
5 inefficiency of HC fuel will result in emissions of some combination of CO and
6 incompletely oxidized HCs, as well as some carbonaceous particles.

7
8 From the point of view of understanding the combustion process, knowing the
9 combustion efficiency is important since any HC emission represents an inefficiency in
10 converting fuel to CO₂ and H₂O. In order to understand the environmental impact of the
11 emissions, it is important to quantify the amounts of the emitted species, especially those
12 that are deemed highly toxic or carcinogenic. The US EPA considers a number of HCs
13 (among other pollutants) as HAPs, and quantification of levels of these species takes on a
14 special importance. This report will discuss the emissions of HAPs from aircraft engines
15 and how the speciation of the HC emissions relates to levels of the various HAPs present
16 in aircraft exhaust.² Since the concentrations of HCs and HAPs are highest in the exhaust
17 at low power conditions, the emphasis will be on measurements under such conditions.

18
19 Components of PM emissions from aviation engines may also be classified as Hazardous
20 Air Pollutants, but PM emissions are measured and analyzed very differently than
21 gaseous emissions, and are not discussed in this document. Much work is currently being
22 directed at identifying measurement approaches and resolving sampling issues for
23 aviation gas turbine engine PM emissions (e.g. the APEX and related campaigns), and
24 data characterizing PM emissions from a variety of commercial aircraft gas turbine
25 engines is being accumulated.

26
27 **Background:** Several studies have attempted to document the speciation of the HCs
28 emitted from aircraft engines. Most notably, in the 1980s Spicer et al. (Spicer, Holdren et
29 al. 1994) performed a series of studies on a set of military engines using a variety of
30 analytical techniques to quantify a wide range of HCs. Subsequently Gerstle et al.
31 (Gerstle, Virag et al. 1999) examined another set of military aircraft, with a similar set of
32 analytical techniques. Most recently, a set of studies initiated by NASA called Aircraft
33 Particle Emissions eXperiment (APEX), and supported by a wide range of sponsors
34 (NASA, FAA, CARB, EPA, DoD ...) has focused attention on commercial aircraft
35 Particulate Matter (PM) emissions (Wey 2004; Onasch, Jayne et al. 2006; Wey,
36 Anderson et al. 2006; Lobo, Hagen et al. 2007), using a wide range of analytical
37 techniques. These studies also included HC gaseous emissions analysis. Some of the
38 techniques employed in APEX1-3 overlap with the earlier tests, but also some more
39 advanced (faster time response/higher sensitivity) techniques were used during APEX.³

² It should be noted that because a compound is considered hazardous it does not imply health or welfare effects at current levels, or that it is appropriate to adopt controls to limit the emissions of such a compound from turbine engine aircraft or their fuels.

³ APEX was the collaborative research effort of NASA, EPA, DoD, and the FAA. The main objective of the APEX research was to characterize both gaseous and particulate emissions to advance the understanding of emissions from commercial aircraft engines. APEX1 was conducted in April of 2004 with a NASA-owned DC-8 aircraft equipped with CFM-56-2C1 engines. APEX2 was conducted in August 2005 for typical in-use aircraft engines (CFM56 engines on B737 aircraft), APEX3 testing was conducted

Technical Support Document

1 The range of experiments and the variety of techniques employed can be used to provide
2 greater confidence in the HAPs emissions measurement data, and to allow assessment of
3 which results can be verified by multiple techniques. In addition, one engine type, a
4 CFM56 (a high bypass turbofan engine), was part of both the Spicer and APEX studies,
5 so that a most direct cross comparison can be made.⁴
6

7 The comprehensive measurements of Spicer et al. (Spicer, Holdren et al. 1994) have
8 provided valuable data for the CFM56-3 and the TF-39 (forerunner to the General
9 Electric CF6 class of high bypass turbofan engines).⁵ These measurements were
10 conducted using a mixture of on-line instrumentation and canister sampling with off-line
11 analysis developed from a prolific program of military engine emissions characterization.
12 This work chose to report values as ppmC present in the exhaust. The data labeled 'idle'
13 in this work was conducted at nominal 'ground idle' and does not reflect the ICAO
14 definition of idle, also called 7% of rated thrust. The Spicer et al. work finds that 40% of
15 the organic gas mass is accounted for by the compounds, ethene, formaldehyde, propene,
16 ethyne and methane.
17

18 In a report to the US Air Force, Gerstle and co-workers (Gerstle, Virag et al. 1999)
19 reported HC emission rates for several engines not included in the ICAO databank, as
20 well as some emissions from auxiliary power units. Some of the military engines
21 addressed in this study represent older engine technologies that are no longer represented
22 in the commercial fleet and, as such, there may be issues regarding combustion
23 efficiencies at low power conditions that may cause significant differences in emissions
24 due to raw fuel contributions to the HCs emissions at low power (personal
25 communication Will Dodds, GE, and KBE, February 2007 et seq.).
26

27 A more recent series of measurements have focused on commercial engines. NASA's
28 interest in charactering the emissions from commercial engines in dedicated engine tests
29 was demonstrated during the EXCAVATE campaign. Anderson et al. (Anderson, Chen
30 et al. 2006) measured the speciated organic gas emissions from a Rolls-Royce RB211-
31 535-E4 engine (another high bypass turbofan engine) for two different fuel sulfur levels.
32 A very comprehensive program continued with the APEX-1 campaign (Wey, Anderson
33 et al. 2006) within which HAPs characterization was conducted with high time response
34 on-line organic gas speciation using infrared fingerprint absorption spectroscopy and
35 chemical ionization mass spectrometry for a CFM56-2C1 (Knighton, Rogers et al. 2007;

in October and November of 2005 spanning a range of engines from a small business jet, through a modern regional turbofan, a single-aisle transport turbofan, to a large high bypass ratio turbo fan, representing five different engine types, some measuring more than one example. In all studies, exhaust plumes were sampled at the engine exit plane and several downstream measurement locations.

⁴ CFM56 and the CFM logo are for CFM International, which is a joint company of Snecma and General Electric. Snecma is a French manufacturer of engines for commercial and military aircraft, and space vehicles.

⁵ The General Electric TF-39 was the first high bypass turbofan engine, and it was developed for the Air Force back in 1965 for a new transport aircraft. Turbofan engines with a bypass ratio of 5 or greater are considered to be high bypass turbofan engines (Cumpsty, N., Jet Propulsion, Cambridge University Press, 2002, p. 46.). Bypass ratio is the ratio between the mass flow rate of the air drawn in by the fan, but bypassing the engine core, to the mass flow rate passing through the engine core (Cumpsty, loc. cit.).

Technical Support Document

1 Yelvington, Herndon et al. 2007). Time integrated LTO cycle data were also collected at
2 the same time (Kinsey et al, document in preparation). An analysis of the JETS/APEX-2
3 (Lobo et al., 2007)⁶ and APEX-3 datasets is forthcoming (Timko et al., in preparation).
4

5 In all of the APEX dedicated engine tests, measurements were made at both the engine
6 exit plane and in the plume at a downstream location (nominally 30 m for an intermediate
7 engine size such as a CFM56). It is important to note that the measured HC profile is
8 relatively consistent regardless of measurement location. In the ensembles of data
9 presented below, all of the various distances, fuels, and power conditions below 30% of
10 rated thrust are combined in demonstrating the tight correlations among HC emissions.
11 Further, in the airport studies discussed next, much further downwind measurements also
12 indicated no change in the relative concentrations of species, although as the exhaust
13 continues to dilute, the species present as very small fractions of the total profile begin to
14 fall below detection limits as distances increase further from the emission source.
15

16 In addition to dedicated engine tests, sampling from airports during routing operation
17 have also provided useful data for HAPs emissions. Using analysis of wind-advected
18 plumes sampled at Boston Logan International Airport, selected speciated organic gas
19 emissions were characterized from in-use aircraft (Herndon, Rogers et al. 2006).
20 Schürmann et al. (Schürmann, Schäfer et al. 2007) also measured volatile organic
21 compounds using canister sampling of diluted exhaust in an operational taxiway area.
22 They found that refueling activity altered the profile of hydrocarbons considerably. An
23 analysis of the wind advected data collected at the Oakland GRE and taxiway/runway
24 sampling is forthcoming (Herndon et al., in preparation).
25

26 All of the studies indicate that a wide range of combustion-related emissions are present
27 in aircraft exhaust. Despite the long list of species present, a ranking of the species by
28 concentration indicates that 15-20 species represent most (95% or more) of the emissions
29 on the basis of concentration. A greater number of species are present at a fraction of a
30 percent or smaller of the total concentration. Of the overall speciated mixture, a number
31 of species can be considered HAPs, while another set may be significant to the overall
32 level of VOC emissions but data indicating toxicity are lacking.
33

34 An important point to note is that no instrument measures all of the HC emissions. The
35 fast time response instrument (Proton Transfer Reaction Mass Spectrometer: PTR-MS)
36 used for HC measurements in APEX was focused on measuring relevant HAPs, and as
37 such was not capable of measuring alkanes or acetylene. Since the PTR-MS is capable of
38 measuring a wide range of HCs other than alkanes and acetylene, the measurement focus
39 was on a list of species that were measurable by the PTR-MS, identified EPA HAPs
40 species, and present in aircraft exhaust. Formaldehyde and ethylene were also not
41 measurable with the PTR-MS, but were measured separately in APEX using IR
42 techniques (Tunable Infrared Laser Absorption Spectroscopy: TILDAS). In the Spicer

⁶ Additional data reported from JETS/APEX2, taken by the UC Riverside team, was not used to develop the jet aircraft speciation profile, because the compromised sampling system for that data source prevented a complete and high-confidence organic compound data set from being assembled from the UC Riverside data.

Technical Support Document

1 studies, a wide range of techniques was used, but no measurement of methanol was
2 attempted, and none of the trimethylbenzenes nor several of C9-C11 aromatic species
3 were identified with the techniques employed therein. In many of the studies, a Flame
4 Ionization Detector (FID) was used to quantify the total “unburned hydrocarbons”
5 (UHCs), but this is an imperfect estimation of the total emissions due to the FID’s non-
6 uniform response to different carbon-containing compounds. All this is to note that,
7 while these several data sets provide very useful data on many individual compounds and
8 their relationship to one another, arriving at an estimate of a total quantity by mass or by
9 concentration is dependent on which species are included in the total. And, the measured
10 species are determined by what measurement techniques have been employed.

11
12 **Data Comparison:** The most direct intercomparison between the earlier studies and the
13 recent APEX mission is accomplished through the overlap with the CFM56 engine.
14 Table 1 reproduces Spicer’s speciation data for this engine (Spicer, Holdren et al. 1994)
15 ranked in order of decreasing concentration. The first column lists the species present in
16 the highest concentration, which represent about 95% of the total speciated non methane
17 hydrocarbon (NMHC) emissions on a concentration basis as measured by Spicer. The
18 highlighted species indicate those species measured by Spicer that were also quantified in
19 APEX by PTR-MS (yellow) or TILDAS (green). In the first column, only acetylene and
20 ethane are not highlighted. In subsequent columns, the sum of which represents 5% of
21 the Spicer emissions concentration, a number of other alkanes also are not highlighted.
22 These species, not measured by PTR-MS or TILDAS, represent about 1.4% of Spicer’s
23 total, and are not typically considered HAPs. It is worth noting that, of the species noted
24 in the “EPA 14” and “FAA 10” HAPs lists that were developed based on relevant HC
25 emissions from aviation engines (URS and FAA 2003), all of those species are in the
26 highlighted (measured in both studies) elements of Table 1.

Technical Support Document

1 Table 1. NMHC emission ratios for the CFM56-3 engine reported by Spicer et al. listed
 2 in decreasing magnitude. The first column represents 95% of the emissions on a molar
 3 basis. Green highlighted cells indicate compounds that are measured by TILDAS. Yellow
 4 highlighted cells indicate compounds that are quantified by the PTR-MS.
 5

Compound	ER (mmole/mole)	Compound	ER (mmole/mole)	Compound	ER (mmole/mole)
ethylene	0.77	acetone	0.0089	1-nonene	0.0027
formaldehyde	0.572	C5-ene	0.0072	propane	0.0025
acetylene	0.211	2-methylpentane	0.0066	1-CH ₃ -naphthalene	0.0024
propene	0.151	benzaldehyde	0.0062	hexanal	0.0023
acetaldehyde	0.135	1-heptene	0.0061	C5-cyclohexane	0.0023
acrolein	0.061	naphthalene	0.0059	ethylbenzene	0.0023
1-butene	0.044	C5-ene	0.0055	C4-benzene	0.0023
glyoxal	0.044	cis-2-butene	0.0052	o-xylene	0.0022
1,3-butadiene	0.044	styrene	0.0041	2-CH ₃ -naphthalene	0.0020
benzene	0.03	n-undecane	0.0040	C5-benzene	0.0020
methylglyoxal	0.029	n-pentane	0.0038	1-decene	0.0018
ethane	0.024	n-dodecane	0.0038	C13-alkane	0.0014
butanal/crotonaldehyde	0.019	m,p-xylene	0.0037	C14-alkane	0.0013
propanal	0.017	2-methyl-2-butene	0.0037	n-heptane	0.0009
1-pentene	0.015	1-octene	0.0034	n-octane	0.0008
1-hexene	0.012	n-decane	0.0031	n-nonane	0.0007
toluene	0.0097	phenol	0.0029	C12-C18 alkanes	0.0045

6
 7 The highlighted sections in Table 1 indicate that comparisons can be made for the
 8 measurements of those species measured for Spicer's CFM56 and the several CFM56
 9 engines measured in APEX. Those comparisons are listed in Table 2 as mass ratios,
 10 expressed as ratios of Emission Indices (EIs). The EI of a species is the mass of that
 11 species emitted in grams, divided by the mass of fuel consumed in kilograms (species
 12 g/kg fuel). The unhighlighted elements in Table 1 indicate that the APEX PTR-
 13 MS/TILDAS data set is missing those elements and no direct comparison can be made
 14 and are thus not included as rows in Table 2. The unhighlighted elements in Table 1
 15 represent approximately 12% of the concentration in Spicer's list.

16
 17

Technical Support Document

1 Table 2. Compound EIs normalized to formaldehyde (EI_x/EI_{HCHO}) for low engine powers
 2 (4-15% rated thrust) evaluated as the slopes of plots of $EI(x)$ vs $EI(HCHO)$

Compound	APEX 1 EI_x/EI_{HCHO}	APEX 2 EI_x/EI_{HCHO}	APEX 3 EI_x/EI_{HCHO}	Spicer et al. EI_x/EI_{HCHO}
Methanol	0.18	0.14	0.12	--
Propene	0.36	0.39	0.38	0.37
Acetaldehyde	0.32	0.36	0.36	0.35
Butene + Acrolein	0.30	0.45	0.48	0.36
Acetone + Propanal + Glyoxal	0.18	0.16	0.20	0.24
Benzene	0.15	0.17	0.16	0.14
Toluene	0.056	0.082	0.073	0.052
mass 107	0.088	0.138	0.103	0.089
mass 121	0.074	0.119	0.085	--
mass 135	0.035	0.074	0.051	--
mass 149	0.014	0.038	0.027	--
Naphthalene	0.018	0.034	0.020	0.044
Methylnaphthalenes	0.009	0.023	0.016	0.037
Dimethylnaphthalenes	0.0026	0.011	0.0083	--
Phenol	0.063	0.064	0.050	0.016
Styrene	0.020	0.035	0.023	0.025
Acetic acid	0.16	0.057	0.084	--

3 **propene** – quantified assuming that 68% all of the ion intensity measured at m/z 43 originated originates
 4 from propene.

5 **butene + acrolein** – quantified assuming the m/z 57 signal is distributed as reported by Spicer et al. 45%
 6 butenes and 55% acrolein.

7 **acetone + propanal + glyoxal** – quantified assuming the m/z 59 signal is distributed as reported by Spicer
 8 et al. 12% acetone, 25% propanal and 63% glyoxal.

9 **Mass 107** – quantified as p-xylene and represents the sum of o,m,p-xylene, ethyl benzene & benzaldehyde

10 **Mass 121** – quantified as 1,2,4-trimethylbenzene and represents the sum of C_9H_{12} and C_8H_8O

11 **Mass 135** – quantified using a single rate constant and represents the sum of $C_{10}H_{14}$ and $C_9H_{10}O$

12 **Mass 149** – quantified using a single rate constant and represents the sum of $C_{11}H_{16}$ and $C_{10}H_{12}O$

13
 14 However, as is noted by the first row of Table 2, Spicer did not measure methanol, which
 15 is approximately 5% of Spicer’s total concentration, which would increase the HC total
 16 by that amount. There are also several other aromatic species listed in Table 2, which
 17 were not identified in the Spicer analysis. While these compounds would fall into the
 18 second two columns of Table 1 if they were included, and thus represent only a percent
 19 or so of the total concentration profile, they do represent a significant number of aromatic
 20 compounds. These several differences in the lists of species measured in these
 21 measurement studies highlight the uncertainty in working with any “total” emissions
 22 level: the “total” is only a sum of whatever species are included in the “total”.

23
 24 A longer list of species measured in the APEX campaigns but not measured by Spicer is
 25 included in the accompanying spreadsheet. In that spreadsheet, the additional species are
 26 color coded by blue (from PTR-MS) and yellow (from EPA’s set of integrating
 27 measurements, Kinsey et al, manuscript in preparation).

28

Technical Support Document

1 This spreadsheet also provides a normalized emission profile. This profile was
2 developed based on Spicer's original speciation and carbon balance. Adjustments and
3 additions were made, based on the new data available (all APEX1-3 data discussed in this
4 report), but the measured species continue to make use of the original carbon balance.
5 Thus, because of the longer list of species now quantified, these refinements to the
6 speciation profile result in a decrease of the unidentified emitted mass from about 35% in
7 the original Spicer work (34% if methane were included, but as discussed below, Spicer
8 has shown elsewhere that the methane measurement was due to background methane and
9 should not be included in the sum) to about 29% due to the additionally identified species
10 and refinements to phenol and butyraldehyde/crotonaldehyde. Separate analysis of the
11 total HC emissions by independent measurements during the APEX1-3 campaigns (J.
12 Kinsey, personal communication) used time-integrated sampling over a range of power
13 conditions. Because that approach is distinguished from the single power points
14 measured by Spicer and the data presented here, precise agreement would not be
15 expected due to different dependence on background levels and related data analysis
16 issues. However, despite these potential differences, similar ratios of the sum of
17 identified to the total HC mass were calculated using the time integrated measurements in
18 APEX1-3 as compared to those of this revised profile, giving increased confidence in the
19 overall HC mass balance presented with these data.
20

21 While the unidentified species mass has been reduced through this process, the
22 composition of that unidentified mass remains an uncertainty. In the original Spicer
23 profile, which used gas chromatography and various HC capture techniques, the
24 unidentified mass could possibly include contributions from some of the species that
25 were specifically identified. In other words, based on the original Spicer work, one could
26 argue that some of the identified species may have been present in larger amounts than
27 were reported because they may have also been contributing to the unidentified mass.
28 That would be a result of some mass "sticking" to a GC column or a HC capture medium.
29 The new additional data reduces that uncertainty considerably, since independent real-
30 time data were collected which largely corroborated the Spicer profile. The combination
31 of the original and new data provide good evidence that the identified species contribute
32 to the profile at the levels measured and have little or no contribution to the unidentified
33 HC mass fraction.
34

35 Table 2 compares the concentration of the particular species of interest to that of
36 formaldehyde, which is one of the most prevalent emissions and serves as a useful
37 reference species. This is done, rather than directly compare concentrations, since the
38 combustion efficiency is highly dependent on precise fuel flow and power settings at low
39 engine powers, with ambient temperature also having a significant impact on emission
40 levels (Yelvington, et al.). Since engine operating point, ambient temperature, and
41 related details are all slightly different from test to test, the combustion efficiency is also
42 likely to vary from data set to data set. However, the relationship of the various
43 emissions to each other is quite constant even though their levels may go up and down
44 together.
45

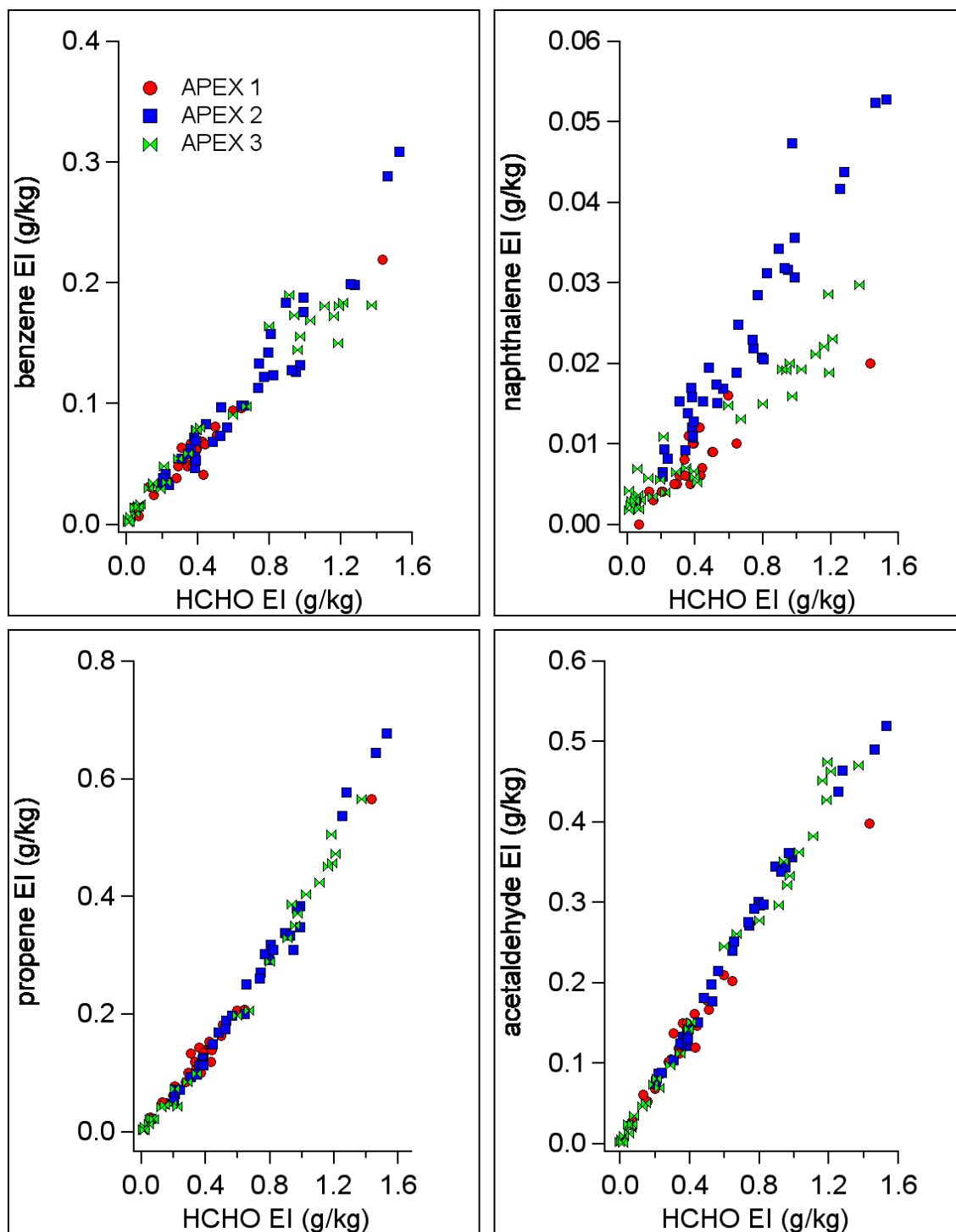
Technical Support Document

1 Figure 1 shows that this is true not only for the CFM56 measured in APEX1 and
2 discussed by Yelvington et al. but it is also true for the several CFM56 engines measured
3 in JETS/APEX2 and, indeed, is equally true for the wider range of different commercial
4 engine types measured in APEX3. In fact, not only is it true that the speciation is
5 invariant as a specific engine varies power and combustion efficiency, but for the range
6 of commercial engines measured in APEX1-3 and the range of standard jet fuels used
7 through those tests, the relationship between the various HC emissions, (i.e. the
8 *speciation profile* shown here as individual species plotted versus formaldehyde, HCHO),
9 is also invariant across these different commercial engine types: all of the curves lie
10 essentially on top of one another. ***The invariance of the speciation profile across power***
11 ***settings, ambient temperature, and engine types for commercial engines is very useful***
12 ***for interpreting HAPs emissions from commercial engines.***

13
14 The range of fuels used in the diverse set of tests presented in Figure 1 suggests that fuel
15 also has a minimal impact on the speciation profile. Fuel sulfur and aromatic content
16 spanned a range of values across these tests, particularly when the APEX1 fuel sulfur
17 additions are included. However dramatic changes in the hydrocarbon composition of
18 the fuel, as might be encountered using alternative fuels like Fischer-Tropsch or bio-
19 fuels, have not been explored in the set of data presented here.

20
21 The correlation of each of the individual species versus formaldehyde plotted in Figure 1
22 show that, for the three APEX campaigns, there are very tight correlations for the several
23 species plotted. Species present in greater concentration (propene and acetaldehyde)
24 have a tighter correlation than species at lower concentrations (benzene and, especially,
25 naphthalene, which is a PAH and may begin condensing on PM emissions soon after
26 leaving the engine, which might affect its gas phase concentration).

Technical Support Document



1
2
3
4
5
6
7
8

Figure 1. Correlation scatter plots of selected HC vs. HCHO emission indices measured on the 1-meter probe under low power, 4-15% rated thrust.

Table 2 provides the comparison between the speciation profile measured by Spicer and that from PTR-MS/TILDAS from APEX. The three data columns from APEX cover the CFM56-2C1 measured in APEX1, the several CFM56-3 and -7 engines measured in

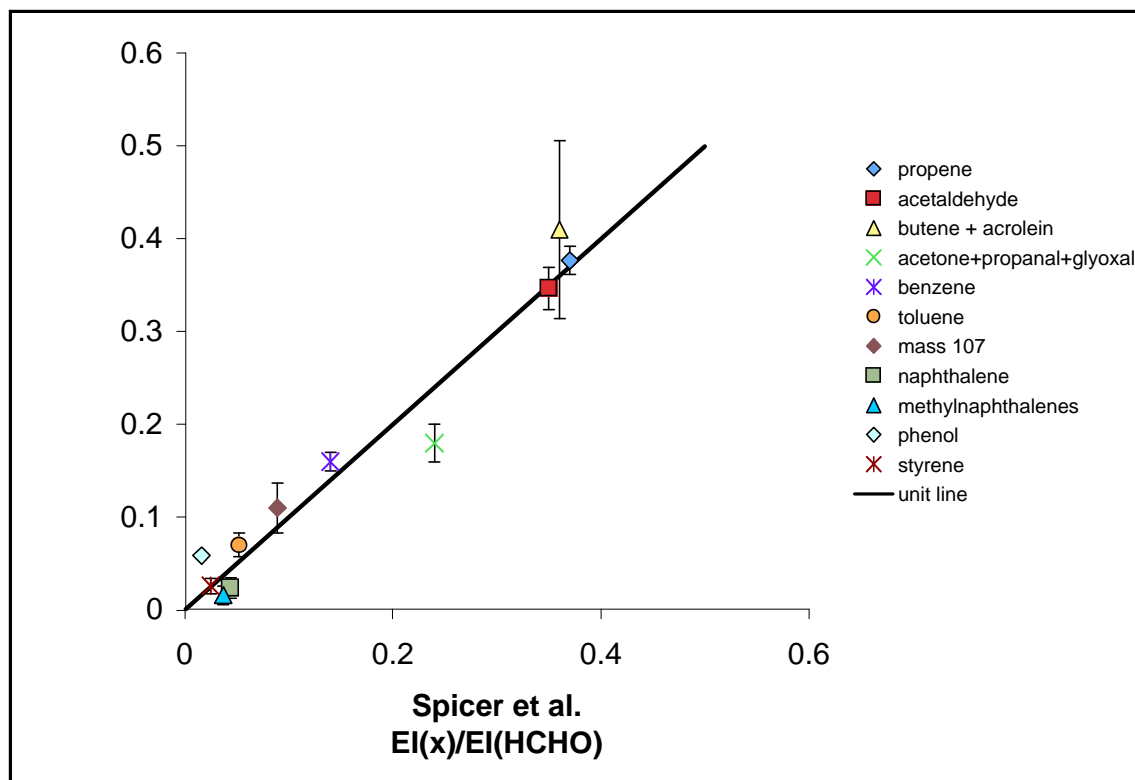
Technical Support Document

1 APEX2, and an average over the set of engines (excluding the AE3007 for this analysis)
2 measured in APEX3. For many species, especially those at larger concentration ratios,
3 the variation among the various tests is no greater than the variation between APEX and
4 Spicer. The speciation for these species appears to be very robust. Some of the more
5 minor species show more significant variation, which may be partly due to measurement
6 uncertainty and may be partly due to sensitivity to other variables such as minor fuel
7 composition variations and so forth. It is worth noting that many of these smaller
8 contributors represent less than 1% of the speciated concentration mixture.

9
10 One species of particular note is phenol. The APEX series of measurements indicate a
11 concentration ratio three times higher than that of Spicer. That is the largest
12 disagreement in Table 2 (excluding cases where a Spicer measurement is not available),
13 and deserves further comment. While phenol represents only about 0.1% of the
14 speciation concentration profile, it does represent a test of the ability to measure a minor
15 species accurately. While further analysis might be warranted, phenol was measured by
16 Spicer using canister capture to deliver the sample to the gas chromatographic
17 measurement system. Given the significant differences indicated for this compound, wall
18 losses might be suggested as a possible explanation for this unique discrepancy in the HC
19 speciation.

20
21 The overall agreement between the Spicer and the APEX speciation profiles is shown in
22 Figure 2. This is a direct comparison of the overall APEX speciation profile to that of
23 Spicer for those species where the measurements are available in both studies. Except for
24 phenol and the combination of acetone, propanal, and glyoxal (which, unlike phenol, is
25 still within 2 sigma), all of the data are within the standard deviation of the measurements
26 themselves to the unit line (the unity line represents perfect agreement).

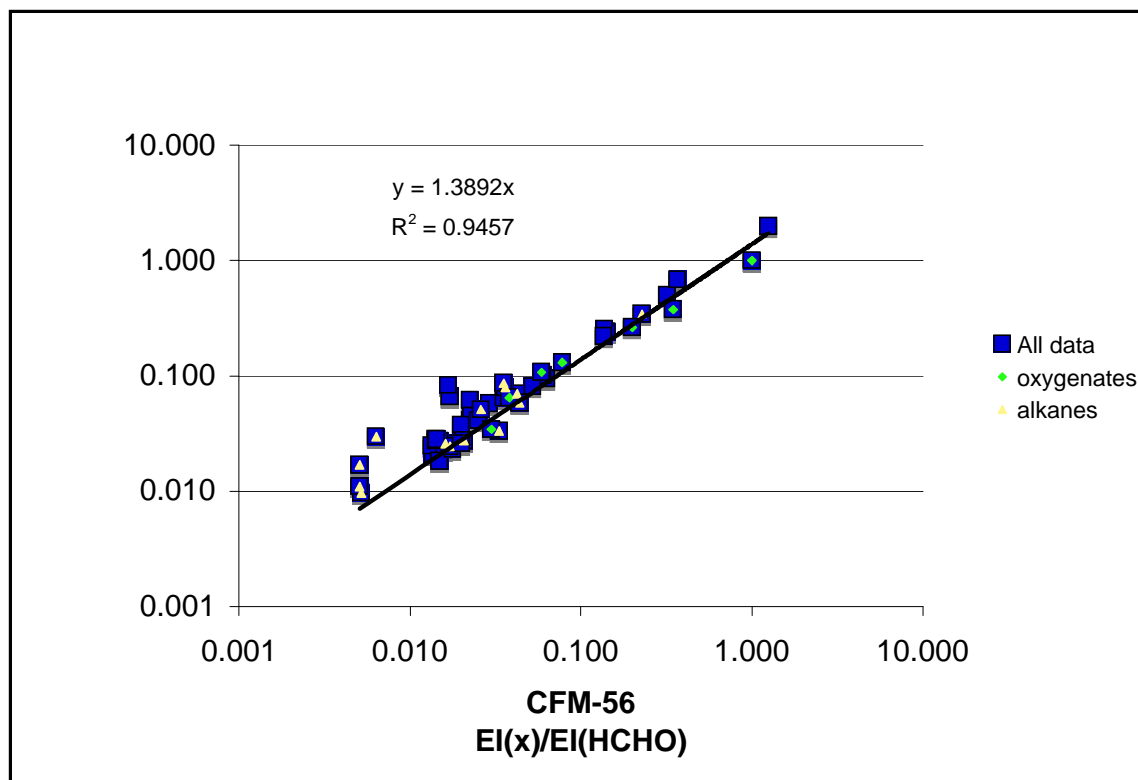
Technical Support Document



1
2 *Figure 2. Correlation plot of normalized compound EIs derived from the APEX*
3 *experiments versus that reported by Spicer et al. APEX data is derived from the slopes of*
4 *the plots of EI(x) versus EI(HCHO) for data obtained at low power 4% - 15% rated*
5 *thrust on the 1-meter probe. Error bars reflect the standard deviation of the three*
6 *measurements.*

7
8 The comparison of the various PTR-MS/TILDAS measurements across different engines
9 in APEX3 provides strong support that the speciation profile is invariant across engine
10 technologies for commercial engines. A similar question could be posed for the various
11 military engines measured by Spicer and Gerstle. Initial analysis (data not shown here:
12 KBE) indicates that there is much agreement between some of the relative amounts of
13 relevant HAPs. Detailed analysis of the TF39 (a forerunner to the GE CF-6 engine)
14 measured by Spicer is shown in Figure 3 comparing the speciation profiles for the TF39
15 with that of the CFM56 measured by Spicer, in analogy to what was shown in Figure 2
16 between the many engines of APEX1-3 and the Spicer CFM56-3. The speciation profiles
17 for these two engines measured by Spicer, which received the careful analysis required
18 for archival publication (Spicer et al. 1994), also support the contention that the
19 speciation profile from aviation gas turbine engines is invariant across engine types.
20

Technical Support Document



1
2 Figure 3. Correlation plot of normalized compound EIs for the TF39 vs. CFM56 engines
3 at ground idle derived from the measurements reported by Spicer et al.
4

5 **Discussion:** The emissions of organic gases are controlled by combustion efficiency.
6 The ICAO datasheets show a very clear trend of decreasing UHC emission indices from
7 idle and approach to climb-out and take-off. There are strong dependences of the
8 magnitude of UHC emissions between different engine models in the ICAO databank.
9 The Yelvington et al. result from APEX-1 (Yelvington, Herndon et al. 2007) shows there
10 is a strong dependence of the emissions of HCHO on temperature; that emissions
11 increase at colder ambient temperatures, particularly for ground idle. This dependence is
12 greater than estimated in the Boeing Fuel Flow Method-2⁷ correction (DuBois and
13 Paynter 2006).
14

15 Despite these strong dependences of the magnitude of UHC emissions on various factors,
16 a remarkable and simplifying result is that the relative profile of organic gas emissions
17 near idle does not have any such significant dependence, as presented in Figure 1. This
18 has been demonstrated for various engines to be valid for conditions from ground idle up
19 to ~15% of rated thrust. This invariant speciation profile demonstrates that despite large
20 variations in the total amount of emissions, the ratio of benzene to ethylene, for example,
21 is a relatively constant value among different conditions and engines.
22

⁷ The Boeing Fuel Flow Method is a theory-based means of obtaining estimated emissions data at power conditions other than the ICAO specified power points by interpolating ICAO certification data.

Technical Support Document

1 One HC emission of particular note is methane (CH₄). This compound was measured by
2 Spicer, but not in more recent studies. While methane is present in the exhaust of aircraft
3 engines, it is present at levels below ambient levels for most power conditions (Spicer,
4 Holdren et al. 1992, Wiesen et al, 1994, Vay et al., 1998). Indeed, in that reference
5 Spicer notes “At power levels above idle, the exhaust is depleted in methane compared
6 with the incoming air used for combustion. The methane concentrations observed in the
7 engine exhaust are consistent with partial combustion of the atmospheric methane present
8 in the inlet air, although some methane production during combustion cannot be ruled
9 out.” At idle the methane values in the exhaust during the Spicer were consistent with
10 ambient levels, so any methane production must have been small enough to be within the
11 experimental uncertainty or was balanced by methane consumption. Methane is not
12 considered to be a significant emission from aircraft gas turbine engines burning Jet A,
13 and is not included in the profile information provided here.⁸

14
15 At engine power conditions significantly higher than ~15% rated thrust, the engine
16 combustion efficiency is so close to 100% that measurement of many HCs becomes
17 difficult or impossible due to instrument detection levels for diluted exhaust gases (either
18 with 1 m dilution probes or downwind sampling): the HC concentrations are too small to
19 measure. Thus, when considering the total emissions contribution from a given aircraft
20 operation, the amount of HCs is dominated by the low power conditions. Since the total
21 emissions burden is the product of an emission index (g pollutant/kg fuel) times the fuel
22 flow rate (kg fuel/sec) times the time in mode for that power condition, even the high fuel
23 flow rates of take-off and climb-out cannot compensate for the very small emission
24 indices for HCs and the short times in the take-off and climb-out power conditions.

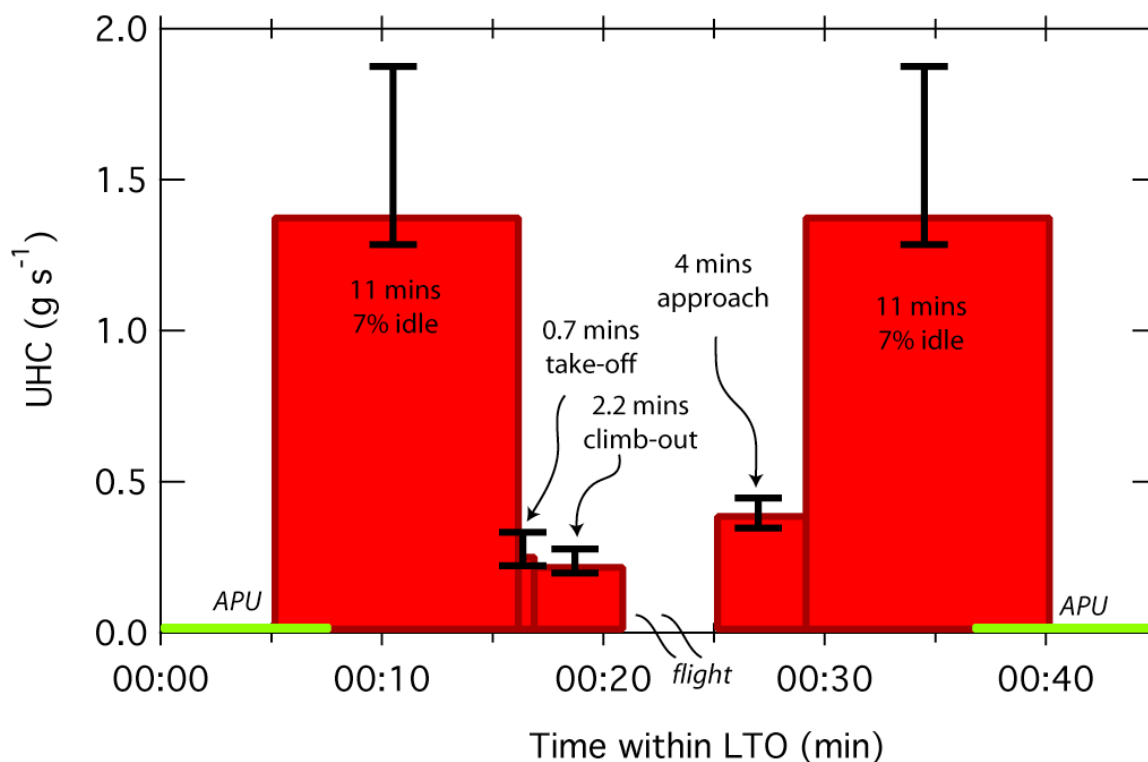
25
26 The dominance of the low power conditions in determining the overall HC emission
27 loading suggests that any changes to the HAPs profile above 15% power will have
28 limited impact on the net HAPs loading. Since the emissions levels become too small to
29 measure for many of the smallest percentage HAPs in the profile, a bound can be placed
30 on how much their fractional contribution to the HAPs profile might be increasing as
31 power increases. In lieu of specific data for these very small levels, a default of retaining
32 the same profile as power increases beyond 15% could be suggested, which would be
33 used for those powers above which the smallest contributors can be measured. An
34 analysis of the potential errors introduced in using this default could be performed,
35 however Figure 4 suggests that the limits of detection of the instruments, in combination
36 with the rapidly decreasing overall HC emissions, will limit the overall uncertainties in
37 the overall HC loading when using a low power HAPs profile.

38
39 Figure 4 demonstrates the relative importance of the elements of an LTO cycle by
40 accounting for times in mode and emission indices for UHCs from the ICAO databank
41 for a CFM56-3C1 engine (two engines for a 737-300). The LTO cycle in the figure
42 reflects times in mode reported in the Boston Logan Airport 2005 Environmental Data

⁸ When using this speciation profile in concert with reported certification HC emission indices, it is worth noting that ICAO CAEP Annex 16 Vol II makes no account for corrections to measured HCs due to ambient methane concentrations when reporting FID measurements for certification. Presumably ambient methane levels may be included in the certification FID measurements of EI HC unless otherwise noted.

Technical Support Document

1 Report (Wilkins 2007). Essentially, it is a modestly adjusted set of times but the same
2 power conditions as a standard ICAO LTO cycle. Whatever the variation in the
3 speciation profile at the higher powers, the lower EIs at the high powers preclude a
4 significant impact on the total emissions burden from the complete LTO cycle, at least in
5 this first attempt to assess the speciated emissions. Variation in the HC speciation profile
6 at higher powers are unlikely to have a significant impact on airport air-quality modeling
7 or to risk assessment from the compounds that are HAPs.
8
9



10
11 *Figure 4. Emission Rate vs. Time in Mode. The estimated emission rate, coupling fuel*
12 *flow and emission index for UHC for a CFM56-3C1. The LTO profile begins and ends*
13 *with a 7.5 minute APU interval. In this figure the apparent area of the 'boxes' reflect the*
14 *total emissions magnitude for the defined modes.*

15
16 **Relationship of Dedicated Engine Tests to Airport Measurements:** Dedicated engine
17 tests allow control of the engine operation. However emissions at airports are due to
18 airplanes being operated as required to satisfy airline requirements. Table 3 compares
19 normalized emission ratios (Species concentration/Formaldehyde concentration) for
20 several APEX measurements and for advected plumes measured at Boston Logan,
21 Zurich, and Oakland airports. While greater uncertainties might be expected in the
22 advected plumes measured in a non-interference basis at airports, there is very good
23 agreement between the emissions ratios measured in these disparate studies. In the
24 advected plumes (last column) the error bars represent the width of the distribution of
25 results. This uncertainty can be taken as an upper limit on the real variability in these
26 ratios. When the detailed analysis of the instrumental contribution to this noise is
27 complete, it will likely narrow the range of species variability, as opposed to instrument

Technical Support Document

1 noise. This is possible because the observed distribution in this sample is nearly
2 Gaussian.

3
4 *Table 3. Speciated VOC Index Ratio (HCHO relative)*

Compound	Spicer et al.	APEX-1	Logan	EXC	Zurich	APEX-2	OAK
						Staged	Advetced
HCHO	1	1	1			*1	1
Acetaldehyde	0.35	0.24	0.26			0.37	0.31±0.09
C ₂ H ₄	1.26	0.78		1*	1*	0.76	0.85±0.3
Propene	0.36	0.31		0.32	0.32	0.45	0.42±0.2
Butenes+Acrolein	0.36	0.45	0.25	0.45	0.26 ^{&}	0.49	
Pentenes	0.11	0.31			0.11		
Benzene	0.14	0.14	0.11	0.08	0.11	0.18	0.15±0.08
Toluene	0.05	0.06	0.06	0.01	0.13	0.09	
1-ring Aromatics	0.28	0.48	0.3	-	0.39	0.73	
Styrene	0.03	0.03			0.04	0.04	
Naphthalene	0.04	0.01				0.04	

5 Table Notes:

6 All values are in units of grams of VOC per gram of HCHO, except for the EXCAVATE
7 column, which is grams of VOC per gram of C₂H₄.

8 *The EXCAVATE and Zurich datasets have been normalized by the emission index for ethene
9 in lieu of formaldehyde.

10 [&]The Zurich tabulation for Butenes+Acrolein assumes the ratio of Acrolein to the sum of the
11 butene isomers is that found in Spicer et al.

12 The APEX-2, Staged aircraft column represents the average result for 'ground-idle' including
13 the following engines; 3 CFM56-7B22, 1 CFM56-3B1, 2 CFM56-3B2.

14 Tabulated values in the OAK Advected column represent Gaussian fits to the distribution of
15 measured compound to HCHO ratios. The error bar is one Gaussian width.

16
17 **Next Step Recommendations:** First, recent work has reinforced the overall speciation for
18 commercial engine as measured by Spicer for the CFM56-3 engine. Both in comparison
19 to the TF39 measured by Spicer and the wider range of commercial engines in APEX1-3,
20 this speciation profile is insensitive to engine type, engine power condition, and ambient
21 conditions, even though those parameters significantly impact the *total* amount of UHCs
22 (or VOCs or total HCs, however one wants to add up a total). Other measurements
23 (Gerstle and airport advected plume studies) are also consistent with the general
24 invariance, *near idle*, of this speciation.

25
26 Several modest uncertainties are present, particularly for species that are present in small
27 quantities. These may be due to measurement uncertainties, or due to actual variations in
28 emissions numbers themselves. Modest dependences on fuel composition or other
29 unknown parameters may cause some of this variation. Most of these variations are
30 within the uncertainties between studies or engines. One notable exception is the
31 significant variation associated with phenol. The APEX studies all agree with one
32 another for phenol, while Spicer is significantly lower. Wall losses in the canister

Technical Support Document

1 sampling done by Spicer are a possible explanation for such a loss, but additional studies
2 may be warranted to resolve this discrepancy.

3
4 For future work, two remaining questions should be kept in mind.

- 5 1. On which set of species do we need to focus to further refine the HAPs profile?
6 (E.g.: [1] phenol discrepancy, [2] methanol and the several aromatics and long list
7 of species present at a fraction of a percent of total mass not measured by Spicer
8 et al., [3] questions regarding acrolein/butene etc.)
- 9 2. What is our approach to evaluating (and possibly revising) the UHC-to-VOC-to-
10 TOG conversions?

11
12 With the completion of this analysis of Spicer and APEX data, we can offer the
13 speciation profile provided in the accompanying spreadsheet for inclusion into the EPA's
14 SPECIATE database.

15 16 *Cited References:*

17
18 Anderson, B. E., G. Chen and D. R. Blake (2006). "Hydrocarbon emissions from a
19 modern commercial airliner." Atmospheric Environ. **40**(19): 3601-3612.

20
21 DuBois, D. and G. C. Paynter (2006). "'Fuel Flow Method2" for Estimating Aircraft
22 Emissions." SAE Technical Paper Series **2006-01-1987**.

23
24 Gerstle, T., P. Virag and M. Wade (1999). "Aircraft Engine and Auxiliary Power Unit
25 Emission Testing: Vol. 1." United States Air Force: IERA **RS-BR-TR-1999-0006**.

26
27 Herndon, S. C., T. Rogers, E. J. Dunlea, R. C. Miake-Lye and B. Knighton (2006).
28 "Hydrocarbon emissions from in-use commercial aircraft during airport operations."
29 Environmental Science and Technology **40**(14): 4406 - 4413.

30
31 Kinsey, J. S., Y. Dong, and D. C. Williams (in preparation 2008). "Characterization of
32 Emissions from Commercial Aircraft Engines during the Aircraft Particle Emissions
33 eXperiment (APEX)", U. S. Environmental Protection Agency, Office of Research and
34 Development, National Risk Management Research Laboratory, Research Triangle Park,
35 NC.

36
37 Knighton, W. B., T. Rogers, C. C. Wey, B. E. Anderson, S. C. Herndon, P. E. Yelvington
38 and R. C. Miake-Lye (2007). "Application of Proton Transfer Reaction Mass
39 Spectrometry (PTR-MS) for Measurement of Volatile Organic Trace Gas Emissions
40 From Aircraft." Journal of Propulsion and Power **23**: 949-958.

41
42 Lobo, P., P. D. Whitefield, D. E. Hagen, S. C. Herndon, J. T. Jayne, E. C. Wood, W. B.
43 Knighton, M. J. Northway, R. C. Miake-Lye, D. Cocker, A. Sawant, H. Agrawal and J.
44 Wayne Miller (2007). "The development of exhaust speciation profiles for commercial
45 jet engines." Final Report, Contract No. 04-344, California Air Resources Board,
46 Sacramento, CA, October 31, 2007.

Technical Support Document

- 1
2 Lobo, P., D. E. Hagen, P. D. Whitefield and D. J. Alofs (2007). "Physical
3 characterization of aerosol emissions from a Commercial Gas Turbine Engine." Journal
4 of Propulsion and Power **23**: 919-929.
- 5
6 Onasch, T. B., J. T. Jayne, S. C. Herndon, P. Mortimer, D. R. Worsnop and R. C. Miake-
7 Lye (2006). "Chemical Properties of Aircraft Engine Exhaust Aerosols Sampled During
8 APEX." NASA/TM-2006-214382 ARL_TR_3903: Appendix J.
- 9
10 Schürmann, G., K. Schäfer, C. Jahn, H. Hoffmann, M. Bauerfeind, E. Fleuti and B.
11 Rappenglück (2007). "The impact of NO_x, CO and VOC emissions in the air quality of
12 Zurich Airport." Atmospheric Environ. **41**: 103-118.
- 13
14 Spicer, C. W., M. W. Holdren, R. M. Riggan and T. F. Lyon (1994). "Chemical
15 composition and photochemical reactivity of exhaust from aircraft turbine engines." Ann.
16 Geophysicae **12**: 944-955.
- 17
18 Spicer, C. W., M. W. Holdren, D. L. Smith, D. P. Hughes and M. D. Smith (1992).
19 "Chemical composition of exhaust from aircraft turbine engines." Journal of Engineering
20 for Gas Turbines and Power **114**(1): 111-117.
- 21
22 Timko, M. T., S. C. Herndon, E. Wood, T. B. Onasch, M. J. Northway, J. T. Jayne, M. R.
23 Canagaratna, R. C. Miake-Lye and W. Berk Knighton (manuscript in preparation, 2008).
24 "Gas Turbine Engine Emissions Part 1. Hydrocarbons and Nitrogen Oxides" Aerodyne
25 Research, Inc., Billerica, MA.
- 26
27 Timko, M. T., T. B. Onasch, M. J. Northway, J. T. Jayne, M. R. Canagaratna, S. C.
28 Herndon, E. Wood and R. C. Miake-Lye (manuscript in preparation, 2008). "Gas Turbine
29 Engine Emissions Part 2. Chemical Properties of Particulate Matter" Aerodyne Research,
30 Inc., Billerica, MA.
- 31
32 URS and FAA (2003). Select resource materials and annotated bibliography on the topic
33 of hazardous air pollutants (HAPs) associated with aircraft, airports and aviation.
34 Technical Directive Memorandum: D01-010, CSSI Contract: DTFA 01-99-Y-01002.
- 35
36 Wey, C. C. (2004). Overview of the Aircraft Particle Emissions eXperiment (APEX)
37 Program. Aircraft Particle Emissions Workshop, Cleveland, OH.
- 38
39 Vay, S.A., B.E. Anderson, G. W. Sachse, J. E. Collins, Jr., J. R. Podolske, C. H. Twohy,
40 B. Gandrud, K. R. Chan, S. L. Baughcum, H. A. Wallio. (1998) DC-8-based
41 observations of aircraft CO, CH₄, N₂O, and H₂O_(g) emission indices during SUCCESS.
42 Geophysical Research Letters **25** 1717-1720.
- 43
44 Wey, C. C., B. E. Anderson, et al. (2006). "Aircraft Particle Emissions eXperiment
45 (APEX)." NASA/TM-2006-214382 ARL-TR-3903.
- 46

Technical Support Document

- 1 Wiesen, P. J., J. Kleffmann, R. Kurtenbach, K.H. Becker. (1994) Nitrous Oxide and
2 Methane Emissions form Aero Engines. *Geophysical Research Letters* 21 2027-2030.
3
4 Wilkins, J. (2007). Description of the 2005 Boston Logan Airport Environmental Data
5 Report. S. Herndon. Boston: LTO times compiled from actual data collected at the airport
6 during 2005.
7
8 Yelvington, P. E., S. C. Herndon, J. C. Wormhoudt, J. T. Jayne, R. C. Miake-Lye, W. B.
9 Knighton and C. C. Wey (2007). "Chemical Speciation of Hydrocarbon Emissions from a
10 Commercial Aircraft Engine." *Journal of Propulsion and Power* **23**: 912-918.
11
12
13
14

Technical Support Document

Aircraft Engine Speciated Organic Gases: Speciation Profile Spreadsheet

R.C. Miake-Lye

Introduction: A numerical spreadsheet⁹ was developed that used both the Spicer data and APEX data to formulate a speciated profile of HC emissions, as discussed in the main body of this report. These several pages that follow are a description of the process used to develop that spreadsheet and an explanation of how the equations are used to provide the resulting calculated quantities. The spreadsheet (in Microsoft Excel format) is intended to accompany this documentation, with its data and imbedded equations.

The initial formulation of the spreadsheet was based on the several data sources (Spicer, and APEX, including both ARI/MSU and EPA contributions). These data sources are listed in columns, with the rows representing the numerous species measured by the several investigators. These data are combined to provide a single profile, as described more fully in the main body of the report. Below, the approach for that combination will be described.

After the profile was finalized, with many new species added and a few adjustments of specific species values from the original Spicer speciation, several additional quantities were calculated. The calculations are all imbedded in the spreadsheet, via the equations used to generate the quantities in the labeled cells, and the rationale behind the calculations will be presented below. The types of calculations are primarily directed at understanding how the speciated profile relates to the total amount of HCs emitted, which requires some assumptions since no measurement can quantify with complete certainty all of the HC emissions. As part of developing that understanding, calculations were also made to address questions of 1) how the limited measurements (such as that from a Flame Ionization Detector or FID, as used in certification testing) can be corrected to approximate the full HC complement and 2) how to convert HC emissions expressed in terms of methane mass equivalents, the reporting convention for HC EIs measured with a FID, into an estimate of the actual total mass of the full speciation profile, including unmeasured species. These calculations are all described below, as well.

An abbreviated version of the speciation spreadsheet is reproduced in Table 4 below. Species that have no mass fraction that are included in the spreadsheet for completeness are not included in Table 4. Also, the only columns from the spreadsheet that are shown in Table 4 are the profile species with non-zero mass fractions, their molecular mass and formula numbers, and the profile mass fraction. In the last two rows of Table 4, the fractions of the total profile mass represented by the identified species (71%) and that represented by the unidentified mass (29%) are listed, based on the total mass estimates given by Spicer and refined with the new measurements, and supported by the EPA

⁹ The accompanying Microsoft Excel filename is **FAA-EPA_TSD_Speciated_HC_Aircraft_04AUG08.xls** and all references to columns, rows, or cells can be found in the worksheet titled **"Data Summary"**.

Technical Support Document

1 APEX data as discussed in the main report. The approach for calculating these quantities
 2 is discussed below.

3
 4
 5
 6

Table 4. Aircraft Profile Speciation

Species	Molecular Weight	Formula			Mass Fraction
		C	H	O	
Ethylene	28	2	4		0.15459
Acetylene	26	2	2		0.03939
Ethane	30	2	6		0.00521
Propylene	42	3	6		0.04534
Propane	44	3	8		0.00078
Isobutene/1-Butene	56	4	8		0.01754
1,3-Butadiene	54	4	6		0.01687
cis-2-Butene	56	4	8		0.00210
3-Methyl-1-butene	70	5	10		0.00112
1-Pentene	70	5	10		0.00776
2-Methyl-1-butene	70	5	10		0.00140
n-Pentane	72	5	12		0.00198
trans-2-Pentene	70	5	10		0.00359
cis-2-Pentene	70	5	10		0.00276
2-Methyl-2-butene	70	5	10		0.00185
4-Methyl-1-pentene	84	6	12		0.00069
2-Methylpentane	86	6	14		0.00408
2-Methyl-1-pentene	84	6	12		0.00034
1-Hexene	84	6	12		0.00736
trans-2-Hexene	84	6	12		0.00030
Benzene	78	6	6		0.01681
1-Heptene	98	7	14		0.00438
n-Heptane	100	7	16		0.00064
Toluene	92	7	8		0.00642
1-Octene	112	8	16		0.00276
n-Octane	114	8	18		0.00062
Ethylbenzene	106	8	10		0.00174
m-Xylene/p-Xylene	106	8	10		0.00282
Styrene	104	8	8		0.00309
o-Xylene	106	8	10		0.00166
1-Nonene	126	9	18		0.00246
n-Nonane	128	9	20		0.00062
Isopropylbenzene	120	9	12		0.00003
n-Propylbenzene	120	9	12		0.00053
m-Ethyltoluene	120	9	12		0.00154
p-Ethyltoluene	120	9	12		0.00064
1,3,5-Trimethylbenzene	120	9	12		0.00054
o-Ethyltoluene	120	9	12		0.00065
1,2,4-Trimethylbenzene	120	9	12		0.00350
1-Decene	140	10	20		0.00185
n-Decane	142	10	22		0.00320
1,2,3-Trimethylbenzene	120	9	12		0.00106
n-Undecane	156	11	24		0.00444
n-Dodecane	170	12	26		0.00462
n-Tridecane	184	13	28		0.00535

Technical Support Document

C14-alkane	198	14	30		0.00186
C15-alkane	212	15	32		0.00177
n-tetradecane	198	14	30		0.00416
C16-alkane	226	16	34		0.00146
n-pentadecane	212	15	32		0.00173
n-hexadecane	226	16	34		0.00049
C18-alkane	254	18	38		0.00002
n-heptadecane	240	17	36		0.00009
phenol	94	6	6	1	0.00726
naphthalene	128	10	8		0.00541
2-methyl naphthalene	142	11	10		0.00206
1-methyl naphthalene	142	11	10		0.00247
dimethylnaphthalenes	156	12	12		0.00090
C4-Benzene + C3-aroald	134	10	14		0.00656
C5-Benzene+C4-aroald	148	11	16		0.00324
Methanol	32	1	4	1	0.01805
Formaldehyde (FAD)	30	1	2	1	0.12308
Acetaldehyde (AAD)	44	2	4	1	0.04272
Acetone	58	3	6	1	0.00369
Propionaldehyde	58	3	6	1	0.00727
Crotonaldehyde	70	4	6	1	0.01033
Butyraldehyde	72	4	8	1	0.00119
Benzaldehyde	106	7	6	1	0.00470
Isovaleraldehyde	86	5	10	1	0.00032
Valeraldehyde	86	5	10	1	0.00245
o-Tolualdehyde	120	8	8	1	0.00230
m-Tolualdehyde	120	8	8	1	0.00278
p-Tolualdehyde	120	8	8	1	0.00048
Methacrolein	70	4	6	1	0.00429
Glyoxal	58	2	2	2	0.01816
Methylglyoxal	72	3	4	2	0.01503
acrolein	56	3	4	1	0.02449
Sum of all identified species					0.70787
Unidentified mass					0.29213

1
2 **Development of the Profile:** As described in the main report, most of the species
3 contributions measured by Spicer were supported by the APEX measurements. So, the
4 data columns in the spreadsheet (not included in Table 4 above) show values for each
5 measured species, in separate columns for each data source. If the data from APEX were
6 not significantly different from Spicer's, the value from Spicer's column was used. This
7 was true for almost all of the species measured by Spicer. The two exceptions were
8 phenol and butyraldehyde (also called butanal). In these two cases, the more recent
9 APEX data were used to update the values for those species. Then, additional species
10 from either the ARI/MSU team (color coded blue in the spreadsheet) or from EPA
11 (yellow) were also added to the species list and their contributions quantified. All of
12 these quantifications are first entered into the spreadsheet as column L as ratios of
13 emission indices of the species in question to the emission index of formaldehyde.
14 Column L is titled "Revised Ratios" since these are the EI ratios of the individual species
15 to formaldehyde accounting for both Spicer and the more recent APEX data.
16

Technical Support Document

1 **Mass Fractions of Identified and Unidentified Species:** Since the ratios of EIs are really
2 mass ratios (EIs are mass ratios of the species to mass fuel burn, so ratioing EIs divides
3 one EI by another and the fuel burn divides out), this column is a set of
4 species:formaldehyde mass ratios. This is not useful for general application, since
5 formaldehyde emissions are not generally measured or known. To be most generally
6 useful, a profile for the full complement of species was desired. This could be done for
7 the identified species, but there may be some HC species which contribute to the mass
8 but which could not be identified.

9
10
11 In order to attempt to account for all of the HC species, including those not identified,
12 Spicer's data was reviewed. Spicer attempted to do a complete carbon balance, based on
13 the suite of instruments employed and accounting for corrections for sensitivities. With
14 the set of species measured by Spicer, an estimate was made for the mass of the identified
15 species and for those that were not identified. For the present purposes, we have taken
16 Spicer's values to be correct for the unidentified species based on his measurements. We
17 have also compared to the time-integrated LTO cycle HC data taken by EPA, which were
18 taken under a different set of measurement protocols (integrating over power settings,
19 including engine start, and the corresponding different effects of backgrounds) and have
20 determined that the APEX EPA data is largely consistent with the Spicer data set (see
21 main report).

22
23 So Spicer's unidentified mass fraction was taken as a starting point. However, the
24 additional species included in APEX actually reduced this unidentified list and
25 unidentified mass. And the adjustments of phenol and butyraldehyde must also be
26 accounted for. So, in calculating column K of the spreadsheet (reproduced for non-zero
27 mass fraction species in Table 4 above), the original species in Spicer's profile were
28 summed (see cell K7 in the spreadsheet). In the equation in cell K7, the phenol and
29 butyraldehyde values were individually reset to Spicer's original values rather than use
30 the new "Revised Ratio" values in column L, and the sum was set to Spicer's original
31 identified mass fraction so that Spicer's carbon balance could be used, albeit with the
32 unidentified mass reduced due to the newly added species. (Note that Spicer quotes his
33 numbers in terms of parts per million carbon (ppmC) concentrations. However, within
34 the limits of accuracy of these calculations, the fractions of ppmC reported for identified
35 and unidentified are equivalent to the masses identified and unidentified in that the
36 mass/carbon for the two fractions, identified and unidentified, is not significantly
37 different for these two fractions.)

38
39 With the sum calculated and set equal to the Spicer's identified mass fraction, the
40 individual mass ratios in column L can be scaled such that they can be referenced to a
41 total given by Spicer's carbon balance. Cell K7 of the spreadsheet takes the sum and
42 uses Spicer's identified mass fraction, to give a scaling factor for each identified species
43 in the "Revised Ratios" column (L) to give the resulting profile in column K. Because
44 more species are now identified, the sum of the identified profile now comes to 70.8% of
45 the total HC mass (cell K119). The new additions to the list represent 6.4 of the total HC
46 mass (cell K120), while phenol and butyraldehyde adjust things a little as well from

Technical Support Document

1 Spicer's original identified mass. The unidentified mass represents 29.2% of the total
2 mass in this new profile (K126).

3
4 ***Determining Effective Mass of Total Profile and Corrections for FID response:*** Since
5 certification data from commercial engines are available, such data are often used for
6 estimating HC emissions. Unfortunately, there are two problems with that certification
7 data. The measurement device prescribed for this measurement uses a FID, which
8 essentially "counts carbon atoms". This raises two problems. One is that the FID does
9 not count carbon atoms that have an oxygen atom attached, and so is not equally sensitive
10 to all HC species. Second, since the measurement is "counting carbons", it keeps track of
11 a concentration and there is no direct indication of the mass of the species in question.
12 (Mass is determined by the amount of hydrogen and oxygen in the molecule in addition
13 to the number of carbons.) For the certification numbers, a mass/carbon based on the
14 methane molecule (molecular mass 16.04) is used by convention. This is purely an
15 assumption and has not been based on measurements to date, as far as the authors know.
16

17 These two problems can be addressed with the detailed profile provided in column K.
18 For the known species, the mass/carbon can be calculated, since both the number of
19 carbons and the molecular mass are known (given in Table 4 above and in spreadsheet
20 columns D and H, as well as hydrogen and oxygen numbers provided in columns I and J).
21 From the individual mass/carbon numbers and the mass fractions in column K, the mass-
22 weighted mass/carbon can be calculated for the identified profile. In order to correct the
23 mass for the total profile, one would need to have the mass-weighted mass/carbon for the
24 complete profile. Since we do not have the molecular masses and formulas for the
25 unidentified species (because they are unidentified), that calculation cannot be done
26 rigorously. Thus, an estimate of the mass/carbon for the full profile is required.
27

28 In order to estimate the mass/carbon for the full profile, the mass/carbon was examined
29 for two classes of species in the identified species. The first class represents those
30 species present at greater than 1% of the total HC mass in column K. This includes many
31 light oxygenated HCs, which have a large oxygen contribution to their total mass. The
32 mass/carbon for these light species is not likely to be similar to those larger HC in the
33 unidentified mass contributions. These light species have a mass/carbon of 17.6 (cell
34 C130). The remaining species in the identified list have a mass/carbon of 14.4 (cell
35 C132), which is likely closer to what might be expected for the larger, partially oxidized
36 species in the unidentified component. Any deviation from 14.4 for the unidentified,
37 while not expected to be large, is also devalued by the modest (29%) contribution of the
38 unidentified to the total. This argument indicates that a good estimate for the
39 mass/carbon for the full profile can be calculated using this approach. Thus, assigning
40 14.4 to the unidentified and combining with the identified, gives a total mass/carbon for
41 the full profile of 15.97 (cell C137). (This is surprisingly close to the original convention
42 of using methane's molecular mass of 16.04.)
43

44 The problem of the FID's lack of sensitivity to carbons bound to oxygen can also be
45 rectified by the profile information. By a similar approach to calculating the mass-
46 weighted mass/carbon, the mass-weighted C/H/O ratios for the various profile

Technical Support Document

1 components discussed above can be calculated. These are included in cells EFG130,
2 EFG132, and EFG137. By ratioing to carbon, in cells EFG131, EFG133, and EFG138,
3 the number of oxygens/carbon can be determined. Since each carbon effectively cancels
4 out the measurement of one carbon by the FID, the FID response for the full profile can
5 be estimated by subtracting cell G138 from cell E138 (or $1.00 - 0.1365$). The FID
6 response is then 0.8635 of the total carbon number, or the correction for the FID's lack of
7 sensitivity due to oxygen containing molecules is 1.16 times the FID output.

8
9 To summarize:

10
11 To correct for the FID response to account for the oxygen content, multiply the FID
12 measurement by 1.16.

13
14 To make use of the best estimate of the actual molecular masses of the HC species
15 instead of using the equivalent methane convention, multiply the FID measurement by
16 $15.97/16.04 = 0.996$.

17
18 The net total correction is $1.16 \text{ times } 0.996 = 1.16$.

19
20