JOURNAL OF PROPULSION AND POWER
Vol. 23, No. 5, September–October 2007

Quantification of Aircraft Engine Hydrocarbon Emissions Using Proton Transfer Reaction Mass Spectrometry

Walter B. Knighton* and Todd M. Rogers†
Montana State University, Bozeman, Montana 59717
Bruce E. Anderson‡
NASA Langley Research Center, Hampton, Virginia 22681
and
Scott C. Herndon,§ Paul E. Yelvington,‖ and Richard C. Miake-Lye¶
Aerodyne Research Inc., Billerica, Massachusetts 01821

DOI: 10.2514/1.22965

A proton transfer reaction mass spectrometer was used to measure the concentrations of selected volatile organic compounds in the exhaust of a commercial turbofan aircraft engine. Nine different compounds including methanol, acetaldehyde, acetic acid, benzene, toluene, phenol, styrene, naphthalene, and the methylnaphthalenes were identified as engine exhaust components that are free of spectral interferences and quantifiable by the proton transfer reaction mass spectrometer. The emission characteristics of the engine were examined as a function of engine power, fuel composition, and downstream distance from the engine. The hydrocarbon emission indices were found to be highly variable, upwards to a factor of 10 for the same nominal engine power setting. Although the magnitude of the HC emissions exhibited large variation, we observed that plots of the HC emission indices versus that of the emission index determined for formaldehyde (normalized plots) were linear and essentially independent of power setting and fuel composition, which suggests that the HC emissions scale together. The results of this study are critically examined and are shown to compare favorably with those of previous studies and serve to validate the proton transfer reaction mass spectrometer method as a reliable quantitative technique for online monitoring of selected hydrocarbon emissions within the engine exhaust matrix.

I. Introduction

THE impact of commercial aircraft operations on local air quality is coming under increasing scrutiny. To accurately assess the effect of aircraft emissions on the health of workers, patrons, and residents in and around airport terminal areas, detailed information on the concentrations and chemical speciation of aircraft-generated pollutants is needed. Although commercial aircraft engines are emission-certified to meet standards set by the International Civil Aviation Organization (ICAO), this process only documents the levels of CO, NOx, total hydrocarbons, and smoke number in engine exhaust. The certification process fails to adequately address the air toxic component of the HC emissions, and smoke number is a poor indicator of fine particle emissions. Both the fine particle emissions and the air toxic component of the HC emissions are of particular importance in relationship to human health.

Incomplete combustion of fuel in aircraft gas turbine engines results in the emission of unburned, cracked, and partially oxidized HC products; fine particles composed of solid carbonaceous material; and nonvolatile compounds as well as contributions from volatile organics that condense as the exhaust cools [1–4]. The emission indices, grams of pollutant per kilogram of fuel burned, for the HC emission components are highly power-dependent [2–5] and may also depend on fuel composition [5]. Total HC emissions from gas turbine engines are the highest at low engine power settings (idle) even compared with takeoff conditions, which have the highest fuel consumption [2]. Depending on the nature of the chemical composition of the HC emission products, this may be of concern, because operating commercial aircraft spend the bulk of their time at airports under low engine power conditions like taxiing or at idle. Only a limited number of studies have addressed the chemical speciation of the HC emissions at relevant airport operating conditions [2,5]. One of these studies has raised concern, because it suggests that at engine idle, the air toxics formaldehyde, acetaldehyde, acrolein, 1,3-butadiene, and benzene comprise a significant fraction (~26%) of the total nonmethane HC emissions [2].

All of the previous studies that provided chemical speciation of the nonmethane HC emissions from aircraft have relied on a limited number of samples. Although these studies have provided considerable insight into the nonmethane HC emissions from aircraft, these contributions point to the need for more measurements in order to further understand the power and fuel dependencies. In this paper, we describe the first use of the proton transfer reaction mass spectrometer (PTR-MS) technique for the examination of the HC emissions from a gas turbine engine under well-defined operating conditions. The PTR-MS has sufficient sensitivity and selectivity to quantify selected HC exhaust components in a diluted exhaust sample in real time (~8 s). Ambient air samples can be directly analyzed, because only those components in the sample having proton affinities greater than that of water react with the H_3O^+ reagent ions. The permanent gases and small alkanes all have proton affinities less than that of water, whereas the olefins, aromatics, and most oxygenated hydrocarbons have proton affinities greater than water and can be detected using the PTR-MS. The capability to directly analyze a diluted exhaust stream is important, because it allows the PTR-MS to continuously monitor the exhaust products emitted under stable operating conditions as well as during the

---

Received 3 February 2006; revision received 5 June 2006; accepted for publication 10 July 2006.

*Research Associate Professor, Department of Chemistry and Biochemistry, P.O. Box 173400.

†Graduate Student, Department of Chemistry and Biochemistry, P.O. Box 173400.

‡Senior Research Scientist, Chemistry and Dynamics Branch/Science Directorate, Mail Stop 483.

§Principal Scientist, Centers for Atmospheric and Environmental Chemistry and Aero-Thermodynamics, 45 Manning Road.

‖Senior Engineer, Center for Aero-Thermodynamics, 45 Manning Road.

¶Principal Scientist and Director, Center for Aero-Thermodynamics, 45 Manning Road. Member AIAA.

transitions between these conditions. The limitation of the PTR-MS method is that the ion signals provide only mass-to-charge information that is often insufficient for complete compound identification. A major focus of this paper is to critically evaluate the observed PTR-MS ion signature and to examine which aircraft exhaust HC components can be accurately quantified using the PTR-MS technique. We will show that the PTR-MS is a reliable high temporal-response technique for monitoring numerous HC emission components in jet turbine engine exhaust, which is capable of addressing the impact of fuel composition and engine power on the chemical speciation of the exhaust emissions.

II. Experimental

The emission measurements discussed in this section were recorded during the NASA-sponsored, aircraft particle emission experiment (APEX), which was conducted at NASA's Dryden Flight Research Center during April 2004. The focus of APEX was to characterize the aerosol and trace-gas emissions from a large, commercial-class airliner as a function of engine power, plume age, and fuel composition and is more fully described in the overview paper in this issue by Wey [6]. The NASA DC-8 was selected as the source platform for APEX, because its CFM56-2-C1 engines are operationally representative of many of the modern turbofan engines used in the current commercial fleet. Three different fuels were used: a baseline JP-8 containing 17.5% aromatics, a high aromatic fuel containing 21.8% aromatics, and a high sulfur fuel doped with tertiary butyl disulfide to increase the sulfur content to about 1600 ppmm sulfur. For the tests, the aircraft was chocked in a run-up area and sample extraction probes were positioned at 1, 10, and 30 m downstream of its right inboard engine (Fig. 1). A detailed description of the sampling system is provided in [7] and so only a brief description is provided here. The 1- and 10-m probes contained multiple gas and aerosol sampling tips to facilitate mapping pollution concentration fields across the engine exhaust plane. Dry N_2 dilution gas was provided to the 1- and 10-m aerosol inlet tips to reduce water and aerosol precursor concentrations to prevent condensation and formation of secondary aerosols within the sample transport lines. Dilution ratios were varied from 3 to 100 to examine the impact of concentration on aerosol microphysical properties, but were nominally held near 10:1 for routine sampling. Sample streams from the gas inlet tips were undiluted, but heated according to ICAO Annex 16 regulations. Air collected at 30 m was typically diluted by factors of 40 or more by entrainment of ambient air into the high-velocity exhaust plume. From the probes, aerosol sample air was drawn though unheated stainless steel tubing to analytical instruments housed in trailers positioned just off the aircraft's right wingtip, a distance that ranged from 25 to 35 m, depending on probe selection (Fig. 1). Sample residence times within the tubing varied from about 5 to 10 s and depended on sample dilution ratio, probe selection, sample pressure, the number of analytical instruments drawing flow, and the position of the instrument along the sampling train. Although we occasionally analyzed samples from the gas-probe stream, the PTR-MS and other trace-gas instruments housed in the ARI trailer were set up to draw samples from the APEX aerosol sample distribution manifold. Within the ARI trailer, the sample flow was isokinetically split to provide flows to aerosol and gas phase instruments. The sample inlet lines to the individual gas phase instruments were fitted with Teflon filters (20-μm pore diameter) to eliminate particles from the sample line.

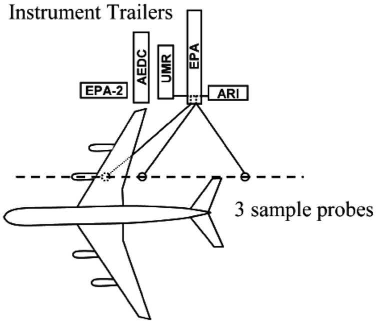

Fig. 1 Schematic of the experimental setup for the emission measurement performed on NASA's DC-8 aircraft equipped with CFM56-2-C1 engines. Trailer designations: Environmental Protection Agency (EPA), Arnold Engine Development Center (AEDC), University of Missouri—Rolla (UMR), and Aerodyne Research, Inc. (ARI).

Formaldehyde (HCHO) was measured by tunable infrared laser differential absorption spectroscopy (TILDAS). The TILDAS instrument directs an IR laser beam through a multipass cell and onto a detector. The light source was a tunable lead-salt diode laser (TDL). The frequency of the laser was swept over a narrow region of the spectrum (<1 cm^{-1}) at a high repetition rate (>3 kHz). The spectral feature used to measure HCHO was located at 1725.8 cm^{-1} and concentrations were determined by fitting the measured rotational-vibrational transmission spectra to a Voigt line shape model using line strength and other line parameters from Herndon et al. [8]. The 1 s root mean square (rms) precision for these HCHO measurements was typically less than 700 pptv and the absolute uncertainty is estimated at 7% [9]. The response time of this instrument is determined by the flow rate through the sample cell under the conditions of this experiment and is estimated to be approximately 1 s.

Two nondispersive infrared absorption instruments were used to detect CO_2: a Licor-6262 for concentrations up to 4000 ppmv and a Licor-820 for values up to 20,000 ppmv. Both instruments were calibrated with NIST traceable standards. The time response for these instruments is approximately 1 s.

The PTR-MS (Ionicon Analytik GmbH) is a chemical-ionization-based mass spectrometry method that uses H_3O^+ as a reagent ion. This instrument has been described in considerable detail by a number of authors [10–13], and so only a brief description of the relevant details is provided here. The instrument consists of an ion source, a drift tube reaction region, and a quadrupole mass spectrometer. H_3O^+ reagent ions formed in the hollow cathode discharge ion source are electrostatically injected into the drift tube through which the sampled airstream is continuously passed at reduced pressure, 1.9 mbar. These H_3O^+ reagent ions are pulled through the air sample by an electric field, where they can react via proton transfer reactions with those components in the sample having proton affinities greater than that of water. The reagent ions and the resulting proton transfer reaction products are mass-selected and detected using the mass spectrometer.

The PTR-MS sampled the exhaust stream from the main sample inlet through a short length of 0.3175 cm o.d. Teflon tubing via a high temporal-response pressure-controlled inlet [11]. The volumetric flow through the inlet system is approximately 500 sccm, under normal sampling conditions. About 15 sccm of the sampled exhaust enters the drift tube reaction region, where those components of the sample having proton affinities greater than that of water undergo proton transfer reactions with H_3O^+ reagent ions. The sample inlet and the drift tube are not temperature-controlled and were operated at ambient temperature. The mass spectrometer monitored a selected set of 32 ions at 0.2 s per mass, along with the drift tube pressure and temperature, which yielded a cycle measurement time of approximately 8 s. The ions monitored included the reagent ions H_3O^+ (m/z 21 O-18 isotope) and $H_3O^+(H_2O)$ (m/z 39 O-18 isotope), the diagnostic ions NO^+ (m/z 30) and O_2^+ (m/z 32), and 28 sample ions. In normal environmental applications, the sampled flow stream would be periodically diverted through a heated Pt catalyst (400°C) to provide a volatile organic compound (VOC)-free gas stream for determining the instrumental background. In this study, the Pt catalyst typically did not efficiently remove the VOCs from the engine exhaust sample stream and this reduced efficiency has been attributed to poisoning of the catalyst due to the high sulfur content of the fuel. Under circumstances where the catalyst appeared to be compromised, instrumental background measurements were determined when the main inlet was purged with N_2 blowoff from a liquid N_2 Dewar. The instrumental background is nonzero for most masses, and the reported concentrations reflect the difference between the sample and background signals.

The concentration of a HC emission component R can be deduced from the measured ion signals using relationships derived either from simple reaction kinetics or from calibrated response factors. For a limited number of components, calibrated response factors have been determined and the relationship between the response factors and the volumetric mixing ratio (VMR) is given by Eq. (1).

$$\mathrm{VMR}_R = \left(\frac{1}{S_R}\right)\left(\frac{I_{RH^+}}{I_{H_3O^+} + X_R \cdot I_{H_3O^+(H_2O)}}\right)\left(\frac{T^2}{P^2}\right) \qquad (1)$$

where I_{RH+}, I_{H_3O+}, and $I_{H_3O+(H_2O)}$ represent the raw measured ion intensities, T is the drift tube temperature, and P is the drift tube pressure. S_R represents the overall sensitivity and X_R compensates for the reaction efficiency of $H_3O^+(H_2O)$ reagent ion. Sensitivity factors S_R are determined from the slopes of calibration curves [12] created through dilution of a certified high-pressure multicomponent gas mixture (Apel-Riemer Environmental, Inc.) and were checked periodically throughout the measurement period. The calibration factors employed in this study are reported in Table 1.

For compounds where calibration gas standards were not available, the concentrations were calculated assuming simple reaction kinetics apply [13] and the following relationship was used.

$$\mathrm{VMR}_R = \left(\frac{I_{RH^+}/BF}{I_{H_3O^+} k_c t}\right)\left(\frac{1}{N_{\mathrm{tot}}}\right) \qquad (2)$$

where I_{RH+} and I_{H_3O+} are the respective transmission corrected ion intensities, BF is the product ion branching fraction, t is the drift time of the reagent ions, k_c is the reaction rate constant, and N_{tot} is the total number density (molecules/ml). For polar compounds capable of reacting with the $H_3O^+(H_2O)$ ion via a ligand switching reaction [17], I_{H_3O+} represents the sum of H_3O^+ and $H_3O^+(H_2O)$. Reaction rate constants k_c used in this study were taken from the compilation of Zhao and Zhang [14] and are reported in Table 1. The branching fractions, included in Table 1, account for the loss of signal intensity to the ion of interest due to fragmentation of the pseudomolecular ion. Inherently, there are greater uncertainties associated with the concentrations derived using Eq. (2), stemming from uncertainties in the value of the reaction rate constant [18], correction factors for the ion detection, and transmission characteristics of the instrument [19,20]. Table 2 compares the concentrations determined by the two methods for the components present in the calibration gas mixture, where the ratio represents the concentration calculated assuming simple reaction kinetics [Eq. (2)] relative to that determined using calibrated response factors [Eq. (1)]. With the exception of benzene, the variation from the calibrated value is within ±25%, which is considered to be good agreement. Benzene appears to be lower than the other compounds for several reasons. Benzene is the only compound that does not react with the $H_3O^+(H_2O)$ reagent ion [21,22]. Also, the distribution of H_3O^+ and $H_3O^+(H_2O)$ exiting the drift tube is altered by collision-induced dissociation reactions occurring between the drift tube and the quadrupole mass spectrometer [20,23]. Similar results can be expected for nonpolar hydrocarbon components having proton affinities less than or equal to that of benzene, because these compounds also do not react with $H_3O^+(H_2O)$, which includes propene and the 2-butenes [24]. On the

Table 1 Compounds monitored within the exhaust emission matrix and their respective calibration factors, reaction rate coefficients, and branching fractions used for quantification

Compound	Ions formed (abundance)	Ion quantified (branching fraction)	S_R	X_R	k[a] ml/s $\times 10^9$
Methanol	[b] 33 (100%)	33 (methanol)	0.3	0.38	2.33
Propene	[b] 41 (31%), 43 (69%)	43 (0.69)	-	-	1.58
Acetaldehyde	[b] 45 (100%)	45 (acetaldehyde)	0.73	0.6	3.36
Butenes	[c] 57 (100%)	57 (1.0)	-	-	1.73
Acrolein	[d] 57 (100%)	57 (1.0)	-	-	3.35
Acetone	[b] 43 (3%) 59 (97%)	59 (acetone)	1.05	0.7	3.00
Propanal	[c] 59 (100%)	59 (acetone cal)	1.15	0.7	3.44
Glyoxal	[d] 59 (100%)	59 (acetone cal)	0.47	0.7	1.34
Acetic acid	[b] 43 (48%), 61(52%)	61 (0.52)	-	-	2.27
1-pentene	[b] 41 (13%), 43 (53%), 71 (34%)	71 (0.34)	-	-	1.87
Butanal	[c] 55 (57%), 73 (43%)	73 (1.0)	-	-	3.49
Methylglyoxal	[d] 73 (100%)	73 (1.0)	-	-	-
Benzene	[b] 79 (100%)	79 (benzene)	0.51	−0.4	1.97
1-hexene	[b] 41 (13%), 43 (50%), 57 (13%), 85 (24%)	85 (0.24)	-	-	2.02
Toluene	[b] 93 (100%)	93 (toluene)	0.70	−0.1	2.12
Phenol	[e] 95 (100%)	95 (1.0)	-	-	2.52
1-heptene	[b] 41 (6%), 57 (92%), 99 (2%)	99 (0.02)	-	-	2.14
Styrene	[b] 105 (100%)	105 (1.0)	-	-	2.33
o,m,p-xylene	[b] 107 (100%)	107 (p-xylene cal)	0.75	0.15	2.27
Ethylbenzene	[b] 79 (30%) 107 (70%)	107 (p-xylene cal)	-	-	2.25
Benzaldehyde	[c] 107 (100%)	107 (p-xylene cal)	-	-	4.12
C3-benzenes	[b] 121 (100%) propylbenzene 79 (70%) 121 (30%)	121 (1,2,4 $(CH_3)_3$-C_6H_6)	0.70	0.25	2.4
Naphthalene	[d] 129 (100%)	129 (1.0)	-	-	2.59
C4-benzenes	[c,d] 135 (isomer-dependent) 79 (isomer-dependent)	135 (1.0)	-	-	2.5
Methylnaphthalenes	[d] 143 (100%)	143 (1.0)	-	-	2.71
C5-benzenes	[d] 135(isomer-dependent) 79 (isomer-dependent)	149 (1.0)	-	-	2.6[f]
Dimethylnaphthalenes	[d] 157 (100%)	157 (1.0)	-	-	2.9[f]

[a] Reaction rate coefficients are taken from Zhao and Zhang [14]

[b] This study, ambient temperature, and drift tube pressure of 1.93 mbar.

[c] Drift tube pressure of 2.4 mbar (Warneke et al. [15]).

[d] Anticipated product distribution.

[e] Christian et al. [16]

[f] Estimated reaction rate coefficient.

Table 2 Ratio of calculated to measured concentrations for the components contained within the calibration gas standard.

Compound	Ratio	Compound	Ratio
Methanol	0.81 ± 0.04	Benzene	0.65 ± 0.02
Acetaldehyde	0.92 ± 0.04	Toluene	0.84 ± 0.03
Acetone	1.08 ± 0.05	p-xylene	0.87 ± 0.03
Isoprene	0.78 ± 0.06	1,2,4-trimethylbenzene	0.77 ± 0.03
Methacrolein	0.83 ± 0.06	Alpha-pinene	0.80 ± 0.03

basis of the benzene result and the additional uncertainty associated with correcting for fragmentation, the concentrations calculated using Eq. (2) are considered to be accurate within ±40%.

Limits of detection (LD) for most of the compounds in this study are on the order of 0.3–1.2 ppbv for the 0.2-s ion integration times. These LD are defined as three times the signal-to-noise ratio (S/N), where the S/N is taken as the 1σ scatter in the measured background signals. Compounds detected at ion masses having higher persistent instrumental backgrounds have proportionately higher LD, shown in parentheses, and include methanol (2.8 ppbv), propene (3.4 ppbv), acetaldehyde (2.7 ppbv), and acetic acid (3.4 ppbv).

III. Results

Figure 2 shows a time series of the emission profiles of CO_2, formaldehyde, and benzene observed from the 1-m particle probe as the engine power is stepped down from 100% rated thrust to 4% rated thrust. The sampled gas stream is only diluted by the amount of dry N_2 added within the sample probe tip and the extent of this dilution is reflected by the CO_2 level shown in the top part of the trace. The shaded zones represent the times over which the engine operating condition was considered to be stable. The concentration traces of benzene and formaldehyde both show low, nearly zero, values from high power until the engine reaches 15% rated thrust, at which point the concentrations increase very rapidly as the engine power is further reduced to 4%. The large increase in the hydrocarbon emissions at reduced engines powers is consistent with that observed in previous studies [2,5].

Engine emissions are typically reported in terms of an emission index (EI), which reflects the mass of pollutant emitted per mass of fuel consumed. In the current study, emission indices were computed from emission ratios (ER) determined from data like that shown in Fig. 2. It is noted that, with the 1-m particle probe, both the HC analyte and CO_2 concentrations are diluted by the same amount so that the extent of dilution does not alter the computed ER.

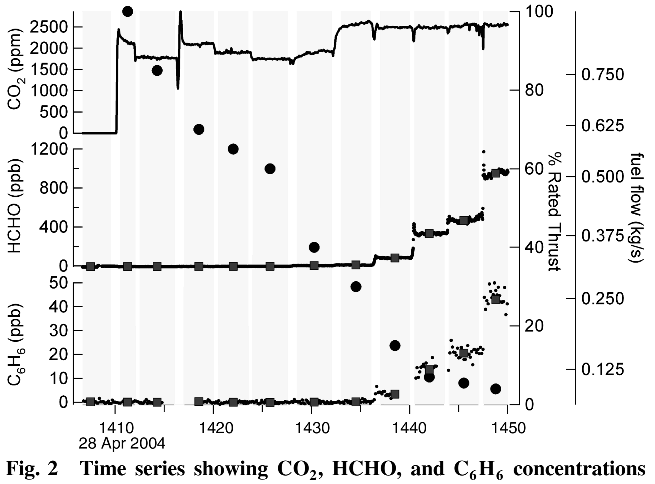

Fig. 2 Time series showing CO_2, HCHO, and C_6H_6 concentrations measured using the 1-m particle probe as a function of engine power setting. The extent of dilution occurring in the probe tip is reflected by the CO2 concentration. Black dots indicate the engine power setting as a percentage of the rated thrust or fuel flow and the shaded regions indicate the time periods of stable engine operation. The gray squares represent the averaged analyte concentration for each time period

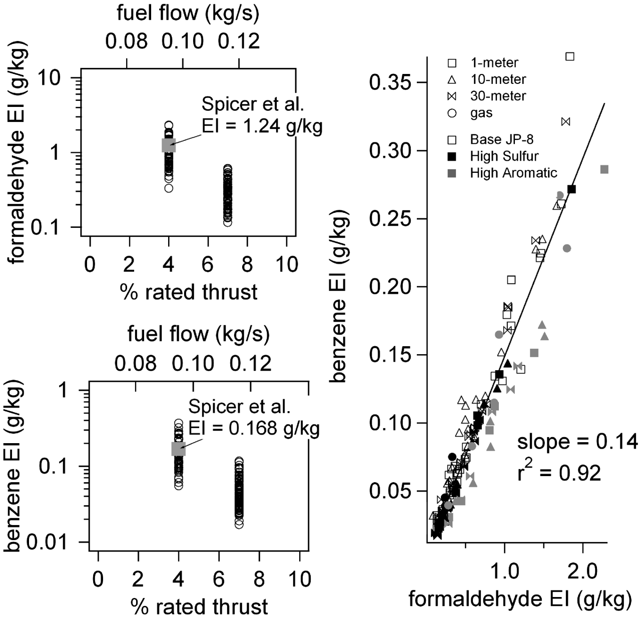

Fig. 3 Benzene and formaldehyde emission indices determined under low engine power conditions. The scatter plot of the benzene emission indices vs the formaldehyde emission indices is highly correlated, which indicates that the variability in the individual emission indices reflects real compositional changes in exhaust. Note that the slope of the plot is equal to the ratio of the benzene and formaldehyde emission indices reported by Spicer et al. [2].

Determination of the amount of CO_2 originating from the engine for the 10- and 30-m probes must account for dilution of the plume by ambient air, and this procedure is discussed in the article by Yelvington et al. [25] within this special issue. Values were derived for the different engine power settings using concentrations of the individual components and CO_2 averaged over the stable operating times. These ratios, in turn, were converted into equivalent emission indices using Eq. (3) [5,26].

$$\mathrm{EI}\left(\frac{\mathrm{g}_x}{\mathrm{kg}_{\mathrm{fuel}}}\right) = \mathrm{ER}\left(\frac{\mathrm{mole}_x}{\mathrm{mole}_{\mathrm{CO}_2}}\right)\left(\frac{MW_x}{MW_{\mathrm{CO}_2}}\right)\left(\frac{3160\ \mathrm{g}_{\mathrm{CO}_2}}{\mathrm{kg}_{\mathrm{fuel}}}\right) \quad (3)$$

where MW_x and MW_{CO_2} are the molecular weights of component X and CO_2, respectively, and (3160 $g\,CO_2/kg\,fuel$) is the average emission index of CO_2, assuming 100% efficient combustion of JP-8 fuel. Figure 3 exhibits emission index values at power settings of 4 and 7% rated engine thrust derived from all formaldehyde and benzene measurements recorded during the campaign. Both low power settings refer to "idle" conditions, with 4% rated thrust being ground idle and 7% rated thrust being the defined idle condition for ICAO engine certification tests. For comparison, the reported emission indices for formaldehyde and benzene measured at 4% rated thrust reported by Spicer et al. [2] have been included in Fig. 3. Although the emission indices for both benzene and formaldehyde reported by Spicer et al. fall within the range of the values determined here, it is difficult to make any meaningful comparison between the different data sets due to the large variability in the present measurements. The large variability in the emission indices for both benzene and formaldehyde is surprising, because under these conditions neither of the measurements is sensitivity limited, which implies that the observed variability reflects real changes in HC emissions from the engine. In a companion article [25], we show that this emission variability is primarily caused by changes in ambient temperature. While examining the variability in the respective benzene and formaldehyde measurements, we found that a plot of the benzene emission indices vs the formaldehyde emission indices (Fig. 3) showed a strong linear relationship and that the slope of this plot is the same as the ratio of the benzene and formaldehyde

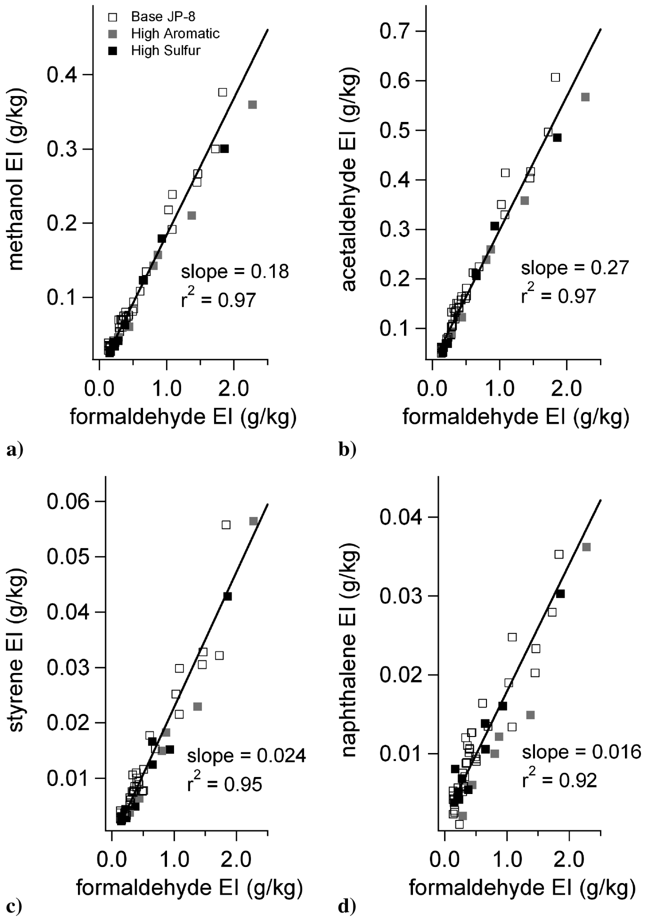

Fig. 4 Representative plots of selected HC emission indices vs the formaldehyde emission indices at low power (4 and 7% rated thrust) measured on the 1-m particle probe. The slopes of the lines and the correlation coefficients r^2 are determined using linear least-squares analysis.

emission indices reported by Spicer et al. The data points shown in the scatter plot of Fig. 3 have been modified to indicate the sampling probe and fuel type used, and we note that the EI values of formaldehyde and benzene scale similarly for the different fuels, power settings (4% and 7% rated thrust), and probe locations. Plots of the emission indices of the other hydrocarbon components relative to that of formaldehyde revealed similar linear relationships, as is demonstrated in Fig. 4, in which selected HCs having different functional groups including an alcohol (methanol), an aldehyde (acetaldehyde), an aromatic alkene (styrene), and a polynuclear aromatic (naphthalene) have been plotted. This common behavior suggests that all of the hydrocarbons emissions scale together and that the HC speciation is not significantly altered as a function of fuel composition or power setting. Normalizing the emission data relative to that of formaldehyde provides a convenient means by which to remove the effect of ambient temperature from the data and allows us to examine the relative distribution of the different hydrocarbon emission products present in the exhaust. The PTR-MS data (ratio of the HC emission ratio to formaldehyde emission ratio) reported in Table 3 were determined from the slopes of plots similar to that illustrated in Fig. 4 and was restricted to the measurements collected from the 1-m particle probe at 4 and 7% rated thrust for three different fuels. We have not included the measurements from the downstream probes, because they were occasionally perturbed by crosswinds that caused the exhaust plume to be swept away from the probe. The PTR-MS measurement resolution of only 8 s was insufficient to reliably measure these perturbations, and it is for this reason that the downstream probe data have been excluded from this analysis. The correlation coefficient r^2 from the plots has also been included in Table 3 to reflect the degree of correlation of the two measurements.

Aircraft turbine engine exhaust contains a complex mixture of hydrocarbons. Spicer et al. [2] identified 57 different organic compounds in their study of the exhaust of a CFM-56 engine, of which 45 are expected to be ionized and detected by the PTR-MS. Many of these components do not provide unique ion signatures in the PTR-MS and thus are not distinguishable or identifiable on the basis of ion mass alone. Interpretation of the PTR-MS analysis of aircraft turbine engine exhaust is aided considerably and shaped heavily by detailed chemical composition information taken from studies like that of Spicer et al. By knowing what compounds are present along with the ionization dynamics for those compounds, it is possible to interpret the mass spectrum and reasonable decisions can be made regarding which exhaust compounds can be accurately quantified using the PTR-MS. Table 3 provides a compilation of the compounds and their emission data, which were examined by the PTR-MS technique during the APEX campaign. In the section that follows, each of the compounds in Table 3 is critically evaluated in terms of which neutral components contribute to the intensity of that ion signal. Where possible, an estimate of the fraction of the signal attributable to the different components is also provided. Chemical composition information is taken from the studies of Spicer et al., Slemr et al. [3,4] and Anderson et al. [5]. Proton transfer reaction product branching fractions are taken primarily from independent laboratory studies performed under experimental conditions similar to those experienced during the APEX measurement campaign. However, in some cases, the branching fractions and ionization efficiencies are taken from other studies determined under different experimental conditions and are not necessarily totally reflective of the measurements of this study.

A. Methanol

Proton transfer to methanol results only in the formation of the pseudomolecular ion (m/z 33) and is the only VOC known to react in the PTR-MS to form an ion at m/z 33, and so its presence in aircraft exhaust can be deduced directly from the presence of this ion in the mass spectrum. This ion does not suffer from any hydrocarbon interferences and only the oxygen-17 isotope of O_2^+ provides any interference to the measurement. The contribution of this ion interference is evaluated during the instrumental background measurement and leads to an elevated detection limit for this compound. This is the first report that identifies methanol as a component of aircraft exhaust.

B. Propene

Proton transfer to propene produces two product ions, the pseudomolecular ion m/z 43 that constitutes approximately 69% of the ion signal and a fragment ion m/z 41. It is not possible to confirm the presence of propene in the exhaust stream solely on the presence of ion intensity at m/z 43, as other exhaust components such as acetic acid, pentenes, hexenes, and the larger alkanes (>C7) are also known to contribute intensity to this ion. The total intensity measured at m/z 43 (I^{tot}) reflects the sum of the contributions from each of the different compounds. The relative contribution from each component can be expressed as the normalized emission ratio weighted by the reaction rate constant and the branching fraction, Eq. (4)

$$I_{43}^{\mathrm{tot}} \propto \sum (\mathrm{ER}_x/\mathrm{ER}_{\mathrm{HCHO}}) BF_{43}^{x} k_c^{x} \tag{4}$$

where ER_X and $\mathrm{ER}_{\mathrm{HCHO}}$ represent the respective emission ratios of component X and HCHO, BF represents the fraction of the ion signal detected at m/z 43 that comes from component X, and k_c is the reaction rate constant for component X. The fraction of the signal attributable to propene is then equal to $I^{\mathrm{propene}}/I^{\mathrm{tot}}$ and can be evaluated using the normalized emission ratios reported for the alkenes by Spicer et al. [2] and for acetic acid by the PTR-MS in Table 3, along with the branching fractions and reaction rate constants in Table 1. The alkane (>C7) contribution can only be approximated, but is expected to be small, because the molar

Table 3 Comparison of PTR-MS measurements with that of Spicer et al. [2] for CFM-56 engine at idle.

Neutrals	ER_x/ER_{HCHO} PTR-MS slope, r^2	ER_x/ER_{HCHO} Spicer et al.	% deviation	EI_x[a], g/kg	*LD*[b], g/kg
Methanol	0.17 (0.97)	NA	NA	0.22	0.003
Propene (estimated, see text)	0.31 (0.97)	0.26	19	0.53	0.01
Acetaldehyde	0.18 (0.97)	0.24	−22	0.33	0.01
Butenes + acrolein	0.18 (0.98)	0.19	−7	0.41	0.002
Acetone + propanal + glyoxal	0.076 (0.94)	0.122	−26	0.18	0.004
Acetic acid	0.038 (0.64)	NA	NA	0.09	0.01
Pentenes	0.28 (0.98)	0.056	401	NR[d]	-
Butanal + methylglyoxal	0.032 (0.95)	0.065	−51	0.093	0.004
Benzene	0.060 (0.94)	0.053	15	0.19	0.004
Hexenes	0.13 (0.98)	0.021	527	NR	-
Toluene	0.023 (0.93)	0.017	34	0.086	0.002
Phenol	0.024 (0.88)	0.005	374	0.093	0.003
Heptenes	0.62 (0.89)	0.011	5540	NR	-
Styrene	0.0070 (0.95)	0.0073	−3	0.030	0.001
C2-benzenes + benzaldehyde	0.027 (0.95)	0.025	7	0.12	0.002
C3-benzenes	0.022 (0.92)	NA	NA	0.11	0.002
Naphthalene	0.0038 (0.92)	0.01	−63	0.020	0.001
C4-benzenes	0.010 (0.95)	0.0038	162	0.055	0.001
Methylnaphthalenes	0.0019 (0.88)	0.0078	−76	0.011	0.001
C5-benzenes	0.0041 (0.86)	0.0035	17	0.025	0.002
Dimethylnaphthalenes	0.0007 (0.81)	NA	NA	0.004	0.001

[a] Based on ER of formaldehyde of 5.72×10^{-4} (mole HCHO/mole CO_2) from Spicer et al. [2].
[b] Calculated based on the PTR-MS detection limit and a $CO_2 = 2000$ ppmv.
[c] NA: no data available.
[d] NR: not reported.

concentrations of these species are low [2]. This alkane contribution can be estimated from Spicer et al., where the sum of the alkanes >C7 yields a normalized emission ratio of 0.037 and from Jobson et al. [19], who provide a reaction rate constant of 1×10^{-9} mL/s and an approximate branching fraction (0.23). The relative contributions from each of the components are then as follows: propene 68%, acetic acid 10%, pentenes 14%, hexenes 6%, and the alkanes 2%. If all of the intensity at m/z 43 was quantified as if it came from propene, a normalized emission ratio measurement of 0.45 is obtained, which is 72% higher than that reported by Spicer et al. We note that only 68% of the total is attributable to propene and the reported propene emission ratio is 0.31, which is 19% higher than the result reported by Spicer et al.. Quantification of propene using the PTR-MS technique has a number of caveats, as discussed previously, and this measurement has greater uncertainty associated with its determination, arising from the need to estimate and adjust for the spectral contributions from other species.

C. Acetaldehyde

Proton transfer to acetaldehyde produces only protonated acetaldehyde (m/z 45). Acetaldehyde is known to be a significant aircraft emission product and the majority of the measured ion intensity is attributed to this compound. There are no known hydrocarbon constituents of aircraft exhaust that are expected to interfere with the measurement of acetaldehyde, but CO_2 does produce a weak response in the PTR-MS [15]. Because the CO_2 concentration varies greatly in these experiments and the instrument background measurements could not be made reliably using the Pt catalyst, the acetaldehyde measurements have been corrected for the CO_2 interference. The magnitude of the CO_2 interference has been determined to be 1 pptv acetaldehyde equivalent per ppmv of CO_2, and this factor was used to compensate for the CO_2 interference. The acetaldehyde concentrations were derived from calibrated response factors. The acetaldehyde measurements made in this study are in reasonable agreement with those reported by Spicer et al. [2].

D. Butenes and Acrolein

The isomeric butenes and acrolein are both expected to form pseudomolecular ions and be detected at m/z 57 and thus cannot be separately quantified. This is unfortunate, because acrolein is an important air toxic and its potential presence in commercial aircraft exhaust raises considerable concern. Because the relative molar contributions of these two substances in the exhaust are thought to be similar, butenes (45%), acrolein (55%), and a weighted average rate constant of 2.6×10^{-9} ml/s, that is,

$$0.45 * 1.75 \times 10^{-9}\ \mathrm{ml/s} + 0.55 * 3.35 \times 10^{-9}\ \mathrm{ml/s}$$

were used to quantify the sum of these two components. Because there are also a number of higher molecular weight alkenes and alkanes that produce fragment ions at m/z 57, the potential contributions from these components and their relative importance should be addressed. Using Eq. (4) as discussed previously, the relative contributions from the different components to the intensity measured at m/z 57 are estimated as follows: butenes 24%, acrolein 65%, hexene 1%, heptene 4%, >C7 alkenes 3%, and >C7 alkanes 3%. The contributions from the larger alkenes and alkanes were estimated using normalized emission ratios of >C7 alkanes (0.037), >C7 alkenes (0.014), m/z 57 branching fractions for the >C7 alkenes and >C7 alkanes of 0.5 [19], and reaction rate constants of 2.5×10^{-9} ml/s and 1×10^{-9} ml/s, respectively. The normalized emission ratio measurement determined here is very similar to the result predicted from the work of Spicer et al. [2]. As noted previously, there are a variety of compounds that can interfere with this measurement and one should not make any strong conclusions regarding the amount of acrolein present in the exhaust stream on the basis of these PTR-MS alone.

E. Acetone, Propanal, and Glyoxal

Three known aircraft emission components contribute to the ion intensity monitored at m/z 59. There are no known mass spectral interferences from other substances, and the greatest error in quantifying the concentration sum should be related to the uncertainty in the value of the response factor. The signal at m/z 59 was quantified using a weighted average response factor of 0.71. The calibration factors reported in Table 1 for propanal and glyoxal were estimated by scaling the calibrated acetone response factor by the ratio of the reaction rate constants, for example, the response factor for glyoxal

$$(1.34 \times 10^{-9}/3.00 \times 10^{-9}) * 1.05 = 0.47$$

The relative proportions of acetone (0.125), propanal (0.25), and glyoxal (0.625) were taken from Spicer et al. [2]. The normalized emission ratio reported here is low (−38%) with respect to derived from Spicer et al. for these compounds. Glyoxal is considered to be a sticky compound and sampling glyoxal through unheated lines may be problematic. The fact that the present result is low is consistent with the premise that glyoxal is being lost to the surfaces of the sampling lines.

F. Acetic Acid

The ion detected at m/z 61 has been attributed to protonated acetic acid. This assertion is based on molecular weight and a persistent ion signal that was slow to clean up when the instrument was purged with clean nitrogen. The sluggish time response is indicative of a highly-polar compound, which allows us to eliminate less-polar species having the same molecular weight, such as methylformate and methoxyethane. Glycolaldehyde cannot be eliminated and may be a constituent of aircraft exhaust. The signal at m/z 61 was quantified assuming 52% of acetic acid is detected as the pseudomolecular ion. The correlation between the acetic acid signal and that of formaldehyde is not as high as it is for the other compounds studied. The apparent nonlinear behavior at low concentrations is currently attributed to sampling problems associated with this compound. Acetic acid has not been previously detected in aircraft exhaust and this study indicates that it is present in significant amounts.

G. Pentenes

Proton transfer to 1-pentene results in a significant amount of fragmentation at 1.9 mbar, with only 34% of the product being detected at the pseudomolecular ion m/z 71. Based on the work of Warneke et al. [15], we assume that the other pentene isomers fragment to a similar extent. The ion at m/z 71 is not a unique indicator of the presence of pentene in the exhaust, as higher molecular weight alkanes and alkenes will also contribute some ion intensity at this mass. Proton transfer to >C7 alkenes [19,27] and >C7 alkanes [19] reportedly produce fragment ions at m/z 71. Spanel and Smith [28] indicate that O_2^+ reactions with large alkanes yields fragment ions at m/z 71. However, O_2^+ levels in the PTR-MS are generally small (a few percent of the total ion intensity) so that these reactions can be ignored. The contributions from the larger alkenes and alkanes were estimated using normalized emission ratios of >C7 alkanes (0.037), >C7 alkenes (0.014), m/z 71 branching fractions for the >C7 alkenes and >C7 alkanes of 0.20 [19], and reaction rate constants of 2.5×10^{-9} ml/s and 1×10^{-9} ml/s, respectively. The estimated contributions from the different components to the intensity measured at m/z 71 are as follows: pentenes (70%), >C7 alkenes (16%), and >C7 alkanes (14%). Ignoring the contributions from these higher molecular weight components and quantifying the signal at m/z 71 as if all of the ion intensity arises from proton transfer reactions to the various pentenes leads to a normalized emission ratio for the pentenes that is almost a factor four larger than that derived from Spicer et al. [2] Although the low branching fraction magnifies small errors, this large discrepancy indicates that some unknown component(s) contribute additional ion intensity to this mass. We note that Spicer et al. were only able to identify about 70% of the total hydrocarbon emissions in their exhaust study. Unsaturated 4-carbon aldehydes and ketones are potential candidates for compounds that might be present in the exhaust matrix that would also be detected at m/z 71. Because of these uncertainties, deriving the pentene concentration from the ion intensity at m/z 71 is not considered to be reliable in the present study, and no value is reported for the emission index of this compound in Table 3.

H. Butanal and Methylglyoxal

There are two previously reported emission components that are expected to react via proton transfer to form ions at m/z 73. Methylglyoxal is expected to only form the pseudomolecular ion, whereas butanal is known to fragment at 2.4 mbar with only 43% of its ion intensity being detected at m/z 73. It is uncertain to what extent butanal will fragment under the conditions of the present experiment. A reaction rate constant of 2×10^{-9} ml/s has been assumed for the quantification of the sum of these two compounds, because the reaction rate constant for methylglyoxal is not known. The normalized emission ratio determined for these compounds is observed to be low (−51%) relative to that reported by Spicer et al. [2]. This result might be expected, because methylglyoxal, like glyoxal, is a sticky compound and some fraction of this compound could be lost to the walls of the sample line. Fragmentation of butanal has not been accounted for and so both of these circumstances are thought to lead to the low reported measurement for these two compounds. At best, the measurement reported here represents a lower estimate of the sum of methylglyoxal and butanal.

I. Benzene

Proton transfer to benzene forms only the pseudomolecular ion that is detected at m/z 79. Benzene is expected to be the most dominant aromatic component in aircraft exhaust and so virtually all of the ion intensity detected at m/z 79 can be attributed to benzene. Spectral interference from the fragmentation of ethyl and propylbenzene is not expected to affect this measurement based on their relatively low concentrations in the exhaust matrix. The normalized emission ratio measurement reported here for benzene is in good agreement with that of Spicer et al. [2].

J. 1-hexene

Proton transfer to 1-hexene produces a variety of ionic products, with only 24% of ion intensity being detected at the pseudomolecular ion m/z 85. This mass is not unique and there are higher molecular weight alkanes and alkenes that will contribute intensity to this mass [19]. Assuming that all of the ion intensity detected at m/z 85 is derived solely from 1-hexene produces a normalized emission ratio approximately six times larger than that reported by Spicer et al. [2] and suggests previously unidentified hydrocarbon species are present in the exhaust samples. Unresolved large alkane and alkene compounds are the most likely candidates, but unsaturated 5-carbon carbonyl compounds are also plausible exhaust components that would contribute intensity to this ion mass. The PTR-MS measurement of 1-hexene in this study is not considered reliable and an emission index for this compound is not reported.

K. Toluene

Proton transfer to toluene produces only the pseudomolecular ion that is detected at m/z 93. There are no other previously identified compounds in the exhaust matrix that interfere with the measurement of toluene. The normalized emission ratio determined for toluene in this study is high by 34%, but is still in reasonable agreement with that derived from Spicer et al. [2].

L. Phenol

Proton transfer to phenol is expected to produce only the pseudomolecular ion m/z 95. Phenol has been previously identified as an aircraft emission product [2]. This ion mass is reasonably unique and there are only a few compounds that would potentially interfere. Vinyl furan and dimethyldisulfide represent potential interferences, but there is not evidence for their presence in aircraft exhaust. The normalized emission ratio determined in this study for phenol is approximately five times larger than that reported by Spicer et al. [2]. Christian et al. [16] have measured phenol using both PTR-MS and Fourier transform infrared (FTIR) methods and observed good agreement between the two methods. Because of the polarity and low volatility of phenol, sampling losses of phenol in the canister samples appear to be the most likely reason for the discrepancy in the data sets.

M. 1-heptene

Proton transfer to 1-heptene produces only a very small amount (2%) of the pseudomolecular ion at m/z 99. As a result, this ion mass is not a good indicator of the presence of this exhaust component. The proton transfer reaction products of the higher alkane and alkene components are the most likely contributors to the ion intensity at this mass. The PTR-MS measurement of 1-heptene is not considered to be reliable and the emission index for this compound is not reported.

N. Styrene

Proton transfer to styrene produces only the pseudomolecular ion m/z 105. Styrene has been previously identified as an aircraft exhaust emission product and there are no other emission components that are expected to interfere with this measurement. The proton transfer reaction products of peroxy isobutyryl nitrate [29] are detected at m/z 105. However, because previous studies show that peroxyacyl nitrate species are present in engine exhaust plumes at exceedingly small concentrations [5], we do not expect any significant interference from this compound. The normalized emission ratio determined for styrene appears to be in excellent agreement with that of Spicer et al. [2].

O. C2-benzenes and Benzaldehyde

The isomeric xylenes and ethyl benzene are referred to as the C2-benzenes. Benzaldehyde is detected along with the C2-benzenes, as it has the same nominal molecular weight. All of these compounds form pseudomolecular ions and are detected at m/z 107. There are several minor perturbations toward quantifying this collection of compounds. Ethylbenzene fragments upon ionization and only 70% of the intensity of this ion is detected at m/z 107. A single calibration factor based on the response of p-xylene is assumed to apply to all of these compounds. Although the reaction rate constants for all of the C2-benzenes are quite similar, the proton transfer reaction rate constant for benzaldehyde is substantially larger [14]. The use of a single sensitivity factor may not be totally appropriate, because the predicted benzaldehyde concentration is only slightly less than that of the C2-benzenes. However, Warneke et al. [15] have measured the sensitivity factors for the C2-benzenes and benzaldehyde and report that the sensitivity factor for benzaldehyde is lower than that of C2-benzenes. No correction has been made to the data, however. If the sensitivity factor was adjusted to compensate for benzaldehyde, the new sensitivity factor would be equal to 0.99. Without any correction to the data, the normalized emission ratio for this collection of compounds is 7% higher than that reported by Spicer et al. [2]. Application of the new sensitivity factor would reduce the normalized emission ratio to 0.20, which would then be 20% lower than the reported value. Regardless of which result is used, both are considered to agree within the stated uncertainty of the method.

P. C3, C4, and C5-benzenes

These designations are not exact, as they represent the sum of all the compounds that have the same molecular weight as the parent hydrocarbon, that is, C_9H_{12} for the C3-benzenes plus the isobaric (same molecular weight different molecular formula) aldehydes and ketones. For the C3-benzenes, 13 compounds contribute ion intensity to m/z 121, which includes the eight isomeric forms of C_9H_{12} plus the five isomeric carbonyl compounds C_8H_8O. The C4-benzenes actually represents the sum of all isomeric forms of $C_{10}H_{14}$ and $C_9H_{10}O$, whereas the C5-benzenes will reflect the contributions of the $C_{11}H_{16}$ and $C_{10}H_{12}O$ isomers. We quantified these species by assuming that a single sensitivity factor or reaction rate constant adequately reflects the reactivity of all of the components. Most of these compounds are expected to only form the pseudomolecular ion. The singly substituted forms like propyl and isopropylbenzene do fragment substantially in the PTR-MS and their contributions, although minor, will not be properly represented in the current measurements. Comparison with previous studies has only limited utility, because only a small number of these components are typically resolved during gas chromatographic analysis [2,5]. No data was reported by Spicer et al. [2] for any of the C3-benzenes and there is only data for one C4-benzene isomer and one C5-benzene isomer. It is not surprising that the PTR-MS results are larger by about a factor of three for the C4-benzenes. Given that the PTR-MS results are only slightly higher (17%) for the C5-benzenes probably indicates that some line loss exists for these high molecular weight compounds. The PTR-MS results indicate that some of the unidentified mass component of the Spicer et al. study contains aromatic components within this group.

Q. Naphthalene and Substituted Naphthalenes

The naphthalenes were the only polycyclic aromatic compounds monitored using the PTR-MS, and proton transfer to these compounds exclusively forms pseudomolecular ions. These compounds have been previously reported as exhaust emission components and there are no other emission components that are expected to interfere with these measurements. The naphthalenes are an important class of compounds, because they are present in both the particle and gas phase and understanding their emission characteristics may provide insight into the gas-to-particle conversion mechanism. The normalized emission ratios determined here for naphthalene and the methylnaphthalene are considerably lower, by factors of two and three, respectively, than those reported by Spicer et al. [2]. The emission ratios for these components are quite small, and so it is uncertain as to whether these differences are related to experimental errors or reflect real differences in the emissions. Given the low volatility of these compounds, sample line loss is at least partially responsible for some of the discrepancy between the two data sets.

IV. Conclusions

The PTR-MS technique was applied as an online monitor of the volatile organic compounds emitted from a commercial aircraft turbine engine. This approach was demonstrated to be a rapid, sensitive, and reliable quantitative approach for determining selected hydrocarbon emissions within the engine exhaust matrix. We observed that plots of the HC emission indices vs that of the emission index determined for formaldehyde (normalized plots) were linear and essentially independent of power setting and fuel composition. This result suggests that all of the HC emissions scale together and that the HC speciation is not significantly altered as a function of fuel composition or power setting, even as the magnitude of the HC emissions vary dramatically. Normalizing the emission data relative to that of formaldehyde provided a convenient means for removing the effect of ambient temperature from the data and allowed us to compare our observations with those from previous studies that were conducted under potentially quite different environmental conditions. The emission characteristics of the CFM-56 engine examined in this study were found to be generally in good agreement with the results of Spicer et al. [2]. Eighteen ion masses were quantified, representing individual compounds or grouping of compounds, and the emission indices derived from these measurements agreed with Spicer et al. to within ±35% for the majority of these components. Nine different compounds including methanol, acetaldehyde, acetic acid, benzene, toluene, phenol, styrene, naphthalene, and the methylnaphthalenes were identified as components in the engine exhaust matrix that are free of spectral interferences and quantifiable using the PTR-MS. Two new compounds, methanol and acetic acid, have been tentatively identified for the first time as turbofan aircraft exhaust emission products. The PTR-MS represents a new and valuable quantitative online analysis tool for studying the hydrocarbon emissions from commercial aircraft turbofan engines.

Future effort will be needed to address the question regarding the level of the acrolein present in the exhaust. Acrolein is an important air toxic compound and its reported presence in commercial aircraft exhaust has raised considerable concern. Although the conventional PTR-MS approach results does not provide quantitative information about acrolein, because it is incapable of resolving the $C_4H_9^+$ and $C_3H_5O^+$ species, ion trap proton transfer reaction based methods [30] might be capable of resolving these ions and thus provide needed quantitative information for this species. Resolution of the acrolein content also has important consequences to measurement of the total alkene content within the exhaust. Considerable effort was expended in interpreting the PTR-MS ion masses at m/z 43, 57, 71, and 85, which reflect the presence of the alkene, large (>C7) alkane and unsaturated carbonyl compounds (i.e., acrolein) in the exhaust matrix. The anticipated concentration distribution of these components, alkenes (76%), large alkanes (6%), and acrolein (18%) allows us to dismiss the alkane contribution (on the basis of concentration bias and low ionization efficiency) to these ion masses. Should the contribution from acrolein be found to be less important, then the sum of signals at m/z 43, 57, 71, and 85 could be used to provide quantitative information about the total alkene concentration within the exhaust. Alkene emissions are important because they are photochemically reactive species that lead to the formation of ozone and secondary aerosol particles.

Acknowledgments

Funding for the purchase of the PTR-MS instrument was through the National Science Foundation Major Research Instrumentation Program, Murdock Charitable Trust, and Montana State University. The authors would like to thank Chowen Wey (NASA Glenn) and Phil Whitefield (University of Missouri–Rolla) for the opportunity to participate in the APEX measurement campaign. A portion of this material is based on work supported by the National Science Foundation under grant no. 0242922. We would like to thank NASA Dryden for the use of their facilities and their assistance, as well as all the members of the APEX team who made this experiment possible.

References

[1] Pison, I., and Menut, L., "Quantification of the Impact of Aircraft Traffic Emissions on Tropospheric Ozone Over Paris Area," *Atmospheric Environment*, Vol. 38, No. 7, 2004, pp. 971–983.

[2] Spicer, C. W., Holdren, M. W., Riggin, R. M., and Lyon, T. F., "Chemical-Composition and Photochemical Reactivity of Exhaust from Aircraft Turbine-Engines," *Annales Geophysicae: Atmospheres, Hydrospheres and Space Sciences*, Vol. 12, Nos. 10–11, 1994, pp. 944–955.

[3] Slemr, F., Giehl, H., Slemr, J., Busen, R., Schulte, P., and Haschberger, P., "In-Flight Measurement of Aircraft Non-Methane Hydrocarbon Emission Indices," *Geophysical Research Letters*, Vol. 25, No. 3, 1998, pp. 321–324.

[4] Slemr, F., Giehl, H., Habram, M., Slemr, J., Schlager, H., Schulte, P., Haschberger, P., Lindermeir, E., Dopelheuer, A., and Plohr, M., "In-Flight Measurement of Aircraft CO And Nonmethane Hydrocarbon Emission Indices," *Journal of Geophysical Research: Atmospheres*, Vol. 106, No. D7, 2001, pp. 7485–7494.

[5] Anderson, B. E., Chen, C., and Blake, D. R., "Hydrocarbon Emissions from a Modern Commercial Airliner," *Atmospheric Environment*, Vol. 40, No. 19, 2006, pp. 3601–3612.

[6] Wey, C. C., "A Study of Aircaft Engine Emissions: Aircraft Particle Emissions eXperiment (APEX) Project Overview," *Journal of Propulsion and Power* (submitted for publication).

[7] Anderson, B. E., "Formation and Growth of Secondary Aerosols in Turbine Engine Exhaust Plumes," *Journal of Propulsion and Power* (in this issue).

[8] Herndon, S. C., Nelson, D. D., Li, Y. Q., and Zahniser, M. S., "Determination of Line Strengths for Selected Transitions in the nu(2) Band Relative to the nu(1) and nu(5) Bands of H_2CO," *Journal of Quantitative Spectroscopy and Radiative Transfer*, Vol. 90, No. 2, 2005, pp. 207–216.

[9] Smith, M. A. H., Rinsland, C. P., Fridovich, B., and Rao, K. N., "Intensities and Collision Broadening Parameters From Infrared Spectra," *Molecular Spectroscopy: Modern Research*, Academic Press, New York, 1985.

[10] De Gouw, J., Warneke, C., Karl, T., Eerdekens, G., van der Veen, C., and Fall, R., "Sensitivity and Specificity of Atmospheric Trace Gas Detection by Proton-Transfer-Reaction Mass Spectrometry," *International Journal of Mass Spectrometry*, Vol. 223, Nos. 1–3, 2003, pp. 365–382.

[11] Herndon, S. C., Rogers, T., Dunlea, E. J., Jayne, J. T., Miake-Lye, R., and Knighton, B., "Hydrocarbon Emissions from In-Use Commercial Aircraft During Airport Operations," *Environmental Science and Technology*, Vol. 40, No. 14, 2006, pp. 4406–4413.

[12] Rogers, T. M., Grimsrud, E. P., Herndon, S. C., Jayne, J. T., Kolb, C. E., Allwine, E., Westberg, H., Lamb, B. K., Zavala, M., Molina, L. T., Molina, M. J., and Knighton, W. B., "On-Road Measurement of Volatile Organic Compounds in the Mexico City Metropolitan Area Using Proton Transfer Reaction Mass Spectrometry," *International Journal of Mass Spectrometry*, Vol. 252, No. 1, 2006, pp. 26–37.

[13] Lindinger, W., Hansel, A., and Jordan, A., "On-Line Monitoring of Volatile Organic Compounds at pptv Levels by Means of Proton-Transfer-Reaction Mass Spectrometry (PTR-MS): Medical Applications, Food Control And Environmental Research," *International Journal of Mass Spectrometry*, Vol. 173, No. 3, 1998, pp. 191–241.

[14] Zhao, J., and Zhang, R. Y., "Proton Transfer Reaction Rate Constants Between Hydronium Ion ($H_3O(+)$) and Volatile Organic Compounds," *Atmospheric Environment*, Vol. 38, No. 14, 2004, pp. 2177–2185.

[15] Warneke, C., de Gouw, J. A., Kuster, W. C., Goldan, P. D., and Fall, R., "Validation of Atmospheric VOC Measurements by Proton-Transfer-Reaction Mass Spectrometry Using a Gas-Chromatographic Preparation Method," *Environmental Science & Technology*, Vol. 37, No. 11, 2003, pp. 2494–2501.

[16] Christian, T. J., Kleiss, B., Yokelson, R. J., Holzinger, R., Crutzen, P. J., Hao, W. M., Shirai, T., and Blake, D. R., "Comprehensive Laboratory Measurements of Biomass-Burning Emissions, 2: First Intercomparison Of Open-Path FTIR, PTR-MS, And GC- MS/FID/ECD," *Journal of Geophysical Research: Atmospheres*, Vol. 109, No. D2, 2004

[17] Midey, A. J., Arnold, S. T., and Viggiano, A. A., "Reactions of $H_3O^+(H_2O)_{(n)}$ with Formaldehyde and Acetaldehyde," *Journal of Physical Chemistry A*, Vol. 104, No. 12, 2000, pp. 2706–2709.

[18] Hansel, A., Jordan, A., Warneke, C., Holzinger, R., Wisthaler, A., and Lindinger, W., "Proton-Transfer-Reaction Mass Spectrometry (PTR-MS): On-Line Monitoring of Volatile Organic Compounds at Volume Mixing Ratios of a Few pptv," *Plasma Sources Science & Technology*, Vol. 8, No. 2, 1999, pp. 332–336.

[19] Jobson, B. T., Alexander, M. L., Maupin, G. D., and Muntean, G. G., "On-Line Analysis of Organic Compounds in Diesel Exhaust Using a Proton Transfer Reaction Mass Spectrometer (PTR-MS)," *International Journal of Mass Spectrometry*, Vol. 245, Nos. 1–3, 2005, pp. 78–89.

[20] Steinbacher, A., Dommen, J., Ammann, C., Spirig, C., Neftel, A., and Prevot, A. S. H., "Performance Characteristics of a Proton-Transfer-Reaction Mass Spectrometer (PTR-MS) Derived from Laboratory and Field Measurements," *International Journal of Mass Spectrometry*, Vol. 239, Nos. 2–3, 2004, pp. 117–128.

[21] Midey, A. J., Williams, S., Arnold, S. T., and Viggiano, A. A., "Reactions of H3O + (H2O)(0, 1) with Alkylbenzenes from 298 to 1200 K," *Journal of Physical Chemistry A*, Vol. 106, No. 48, 2002, pp. 11726–11738.

[22] Spanel, P., and Smith, D., "Reactions of Hydrated Hydronium Ions and Hydrated Hydroxide Ions, with Some Hydrocarbons and Oxygen-Bearing Organic-Molecules," *Journal of Physical Chemistry*, Vol. 99, No. 42, 1995, pp. 15551–15556.

[23] Warneke, C., van der Veen, C., Luxembourg, S., de Gouw, J. A., and Kok, A., "Measurements of Benzene and Toluene in Ambient Air Using Proton-Transfer-Reaction Mass Spectrometry: Calibration, Humidity Dependence, and Field Intercomparison," *International Journal of Mass Spectrometry*, Vol. 207, No. 3, 2001, pp. 167–182.

[24] Hunter, E. P., Lias, S. G., "Proton Affinity Evaluation," *NIST Chemistry Webbook* [online database], http://webbook.nist.gov [cited June 2005].

[25] Yelvington, P. E., Herndon, S. C., Knighton, B., Jayne, J. T., Wormhoudt, J. C., and Miake-Lye, R. C., "Chemical Speciation of Hydrocarbon Emissions from a Commercial Aircraft Engine During the NASA APEX Measurement Campaign," *Journal of Propulsion and Power* (in this issue).

[26] Herndon, S. C., Shorter, J. H., Zahniser, M. S., Nelson, D. D., Jayne, J., Brown, R. C., Miake-Lye, R. C., Waitz, I., Silva, P., Lanni, T., Demerjian, K., and Kolb, C. E., "NO AND NO_2 Emission Ratios Measured from In-Use Commercial Aircraft During Taxi and Takeoff," *Environmental Science & Technology*, Vol. 38, No. 22, 2004, pp. 6078–6084.

[27] Diskin, A. M., Wang, T. S., Smith, D., and Spanel, P., "A Selected Ion Flow Tube (SIFT), Study of the Reactions of H_3O^+, NO^+ and O_2^+ Ions with a Series of Alkenes; in Support of SIFT-MS," *International Journal of Mass Spectrometry*, Vol. 218, No. 1, 2002, pp. 87–101.

[28] Spanel, P., and Smith, D., "Selected Ion Flow Tube Studies of the Reactions of H_3O^+ NO^+, and O_2^+ with Several Aromatic and Aliphatic Hydrocarbons," *International Journal of Mass Spectrometry*, Vol. 181, Nos. 1–3, 1998, pp. 1–10.

[29] De Gouw, J. A., Goldan, P. D., Warneke, C., Kuster, W. C., Roberts, J. M., Marchewka, M., Bertman, S. B., Pszenny, A. A. P., and Keene, W. C., "Validation of Proton Transfer Reaction-Mass Spectrometry (PTR-MS) Measurements of Gas-Phase Organic Compounds in the Atmosphere During the New England Air Quality Study (NEAQS) in 2002," *Journal of Geophysical Research: Atmospheres*, Vol.108, No. D21, 2003.

[30] Warneke, C., Kato, S., de Gouw, J. A., Goldan, P. D., Kuster, W. C., Shao, M., Lovejoy, E. R., Fall, R., and Fehsenfeld, F. C., "Online Volatile Organic Compound Measurements Using a Newly Developed Proton-Transfer Ion-Trap Mass Spectrometry Instrument During New England Air Quality Study: Intercontinental Transport and Chemical Transformation 2004: Performance, Intercomparison, and Compound Identification," *Environmental Science & Technology*, Vol. 39, No. 14, 2005, pp. 5390–5397.

L. Maurice
Associate Editor