A calibration and sampling technique for quantifying the chemical structure in fires using GC/MSD analysis

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Abstract

This work presents an approach to measure, calibrate, and verify local concentrations of combustion products in pool fires steadily burning in a quiescent environment. This study describes a method that can be used to measure and verify the chemical species present in a fire. Such information is needed to assist in the development and validation of the chemistry subroutines in computational fluid dynamic fire models. Samples are extracted along the centerline of pool fires using a thermal quenching probe. Gas species volume fractions are analyzed using a custom Agilent 5977E Series Gas Chromatograph fitted with a permanent gas dual-column comprised of a Molsieve 5 Å and PoraBOND Q capillary columns in parallel flowing into mass selective and thermal conductivity detector. The system can identify and quantify a variety of stable reactant, intermediate, and product species collected from the fire, including several condensable species (e.g., water, methanol, ethanol, and acetone). The time-weighted average soot mass fraction is determined using a gravimetric sampling method. In order to solidify the legitimacy of the measured gas composition, the results are verified by implementing different techniques, including the determination of the carbon to hydrogen ratio, calculating the argon to nitrogen ratio, and comparing the total moles estimated from the chromatogram peaks to the total moles of the injected sample.

1 Introduction

Computational Fluid Dynamics (CFD) fire models are an important tool for performancebased design as practiced by fire protection engineers¹. A critical objective of fire protection design of buildings and structures is human tenability. In this regard, the yield of CO, CO₂, soot, and other fire combustion products are of interest. Although, the current generation of CFD fire models provide reasonable transport models of hot smoke and gases about a structure, the predictions of fire yields are not as accurate. In order to guide the development and validation of CFD fire models, local chemical species datasets are needed for fires burning a range of fuel types. Little such data is available in the literature^{2–4}.

A requirement of acceptance in the fire protection design process is an evaluation of the models, which involves comparing the computational results to experimental measurements for scenarios analogous to those of interest. A better understanding of the evolution of chemical species in a fire is required to model the yield of fire products quantitatively for an arbitrary fire scenario. The purpose of this study is to describe in detail the methodology used to create an experimental database comprised of the major and minor species in a fire for use to guide the development and validation of the CFD fire models such as FDS¹. A search of the last 20

years of the fire research literature suggests that are few studies of the chemical structure of fires. The major fire science conferences, including Interflam and the IAFSS symposia, have a negligible number of contributions on this topic – with the word chemistry typically used to refer to studies of pyrolysis and decomposition chemistry.

Furthermore, there are few practical diagnostic options to quantify chemical species in pool fires. While many combustion studies and some fire studies have successfully employed various optical methods alone or in tandem to quantify the local concentration of individual or even several chemical species in a fire⁵⁻⁷; they are not readily able to provide a comprehensive survey of the full profile of chemical species. Shaddix et al.⁸ reports "very little temporally and spatially resolved chemical species information has been reported in fires" in an overview of the state of gas species and soot measurement methods in pool fires. Optical methods such as FTIR, emission spectroscopy, Raman, laser transmission, and tunable diode laser studies enable temporally resolved quantification of individual chemical species. Yet, they are expensive, limited in terms of capability particularly in the presence of soot, and not practical for characterization of the entire suite of major and minor species in a fire. An effective approach to comprehensive chemical examination is the use of extractive sampling in concert with soot gravimetric filtering and GC analysis, which has been used in compartment fires and pool fires⁹⁻¹¹, in addition to laminar flames¹².

Fire chemistry is very complex, such that it occurs over a wide range of temperatures and involves many chemical processes. In its earliest stage, a typical compartment fire scenario can be seen as an over-ventilated laminar non-premixed flame. As a fire grows and spreads, an under-ventilated turbulent fire scenario may arise. Quantitative predictions of chemical species yields for all possible fire conditions must consider chemical processes such as fuel pyrolysis, oxidation, and molecular and soot growth.

Here, a technique is described to characterize the lateral distribution of the major and minor chemical species, including water and other condensable species, in moderate-scale (approximately 30 cm diameter) pool fires steadily burning in a well-ventilated, quiescent environment. This paper supplements the information presented in other works^{3;4;11;13;14}, providing a comprehensive description of the experimental method and presenting new measurement results. The method is demonstrated for a series of pool fires burning a range of fuels: methane, propane, methanol, ethanol, and acetone. Pool fires are a convenient testbed for model validation due to their well-defined boundary conditions, including the isothermal, flat, and horizontal fuel surface. Gaseous species and soot concentration measurements are made at various lateral heights on the centerline of the pool fire. The study emphasizes the determination of measurement uncertainty, as models cannot be deemed more accurate than the data by which they are validated.

2 Experimental Method

2.1 Measuring the volume fraction of gas species

Figure 1 displays the flow diagram for gas and particulate sampling. The GC/MSD is equipped with a 2 mL sample loop maintained at approximately 200 °C. The characteristic length of the regime of influence was estimated to range between 0.5 cm \pm 0.1 cm to 3.9 cm \pm 0.7 cm. The characteristic length of the regime of influence was calculated using through the approximation provided in Supplemental Material, S1. The gases are extracted by a vacuum pump located downstream of the GC/MSD. Gas samples are collected using a thermal quenching probe composed of concentric, stainless-steel tubes with outer annular coolant flow and inner extracted sample flow. The outer and inner tube diameters are 16 mm and 8 mm, respectively. Water at approximately 90 °C flows through the sampling probe for the duration of the experiment. The remainder of the sampling line leading into the GC/MSD is heated to approximately 140 °C with electrical heating tape to prevent condensation of water and other condensable species (e.g., methanol, ethanol, benzene, etc.).

Directly behind the sampling probe is a heated soot filter which was used to make a gravimetic soot measurement and eliminate soot from the gas sample injected into the GC. An in-line, heated, 50 ml chamber helps to ensure that the sample is well-mixed and representative of the local sampling volume. Depending on the probe's lateral location within the fire, the sampling period varies from 12 min to 25 min, ensuring a significant soot measurement is made and that the gases are representative of the sampling location and have completely swept through the sample loop. The sample flow is controlled using a mass flow controller (Alicat Scientific MC-Series^{*}) located in upstream of the vacuum pump in the sampling line. All measurements are replicated at least two times to provide an average concentration measurement.

During the gas sampling procedure, the volumetric flow is approximately 200 mL/min and recorded at 2 Hz. After the gas sampling period, two quarter-turn valves located on opposite ends of the sample loop are closed, at which point pressure measurements, obtained from a digital pressure gauge (OMEGA DPG409-030DWU), and temperature measurements, acquired by a K-type thermocouple located at the GC/MSD sample loop injection port, are collected at 2 Hz for 50 s directly followed by sample injection.

Gas species measurements are made using an Agilent 5977E Series GC/MSD. The GC/MSD quantifies a variety of stable reactant, intermediate, and product species collected from the fire plume using helium as the carrier gas. The GC/MSD utilizes an Agilent J&W Select Permanent Gases/CO₂ High-Resolution column, which separates permanent gases (i.e., gases that are incapable of liquefaction). As shown in Fig. 2, the column is a parallel configuration consisting of a 25 m x 0.32 mm PoraBOND Q capillary column coupled with a 50 m x 0.53 mm Molsieve 5 Å capillary column. The PoraBOND has high retention for several species, including carbon dioxide, but struggles to separate oxygen, nitrogen, and other species resulting in a single composite peak. The Molsieve 5 Å column includes zeolite-based materials with a pore size of 5 Å, allowing for separation and very high retention of permanent gases. Due to the multi-component setup of the column, some species (e.g., methane or propane) are observed to elute twice from the composite column causing two distinct peaks on the chromatogram.

The sample components elute from the column through a capillary tee splitter (Agilent G3184-60065), which divides the flow into two deactivated fused silica tubes (Agilent 160-2615-10) of different lengths leading to the thermal conductivity (TCD) and mass selective detectors. The deactivated fused silica tubing flowing into the TCD and MSD are cut to 1 m and 5 m to maintain carrier gas flows of approximately 3 mL/min \pm 5% and 1 mL/min \pm 5%, respectively, such that the TCD and MSD chromatograms are synchronized. Gas species are identified using the total ion chromatogram generated by the MSD and quantified from the TCD's chromatogram.

For the methane, propane, ethanol, and acetone pool fires, the GC/MSD run time is approximately 60 min. During that time the GC oven temperature is maintained at 30 °C for 10 min, then ramped at 8 °C/min to 300 °C which is then held constant for the remainder of the run. For methanol pool fires, the GC oven has the same set-point temperature hold time and ramp rate, but only ramps to 192 °C to reduce overall analysis time. During a GC/MSD run,

^{*}Certain commercial products are identified in this report to specify adequately the equipment used. Such identification does not imply a recommendation by the National Institute of Standards and Technology, nor does it imply that this equipment is the best available for the purpose.

the TCD is maintained at 300 °C with a helium makeup and reference flow of 12 mL/min and 27 mL/min, respectively. The TCD polarity is negated from 8.5 to 10 min to obtain an inverted hydrogen peak. The MSD source and quad temperatures are 250 °C and 200 °C, respectively, for the entire sample analysis. The MSD scan parameters are set to a mass range of 10 to 120 m/z at a sampling rate of 16 units per scan.

A typical TCD chromatogram is shown in Fig. 3. The elution times for individual gas species are provided in supplementary material; see S2. Many species elute twice, once through the PoraBOND Q column, and then again through the Molsieve column. In some cases, the PoraBOND Q is unable to separate species, which results in two composite peaks eluting at approximately 6.4 and 9.2 minutes; the initial composite peak is composed of gas species found in air while the second composite peak is comprised of ethane, ethylene, and acetylene.

The area associated with each peak is proportional to the number of moles of a particular species. Peaks are manually integrated within the Agilent analysis software. Integration bounds of each peak are determined based on the total ion chromatogram. As shown in Fig. 3, there are instances where peaks overlap, and a tangential "skim" integration is implemented to resolve the overlapping region. The area associated with a peak, A, must be adjusted to account for the variation in the measured injection pressure, P, and temperature, T, at the sample loop, using the ideal gas law:

$$A_{\rm corr} = A \left(\frac{P T_{\infty}}{P_{\infty} T}\right) \tag{1}$$

where P_{∞} and T_{∞} are a reference pressure (14.7 psia) and temperature (298.2 K). The range of temperature and pressure at injection are relatively narrow (180 °C ± 2 °C and 14.7 psia ± 0.2 psia).

The corrected area of each peak, representing a specific species, is correlated to the number of moles of that species using a linear regression model. Once the mole count for all detected species is determined, the total number of moles is determined from the summation of the moles for each species quantified from the TCD chromatogram. The volume fraction of a given species, X_i , is calculated from the ratio of the number of moles of a given gas species, n_i , and the total number of moles identified by the GC/MSD, n_{tot} , as shown in Eq.2.

$$\bar{X}_{i} = \frac{n_{i}}{n_{\text{tot}}} = \frac{n_{i}}{\begin{pmatrix} \# \text{ of species} \\ \sum \\ i=1 \end{pmatrix}}$$
(2)

2.2 Calibration of Chemical Species

As previously stated, all calibrations factors are based on the linear correlation between the number of moles of a given species and the corrected area estimated from integration, $n_i \sim f(A_{\text{corr}})$. During calibration, the number of moles of a given species $n_{i,\text{cal}}$ are calculated from the product of the total moles injected into the GC/MSD inlet, n_{inj} , and the known concentration of the particular species in the calibration standard, C_i .

$$n_{i,\text{cal}} = C_i \, n_{\text{inj}} \tag{3}$$

A collection of gas calibration standards for a variety of species is selected to provide a broad range of concentrations. All calibration standards are mixtures of the target gas species with a nitrogen balance, except for one standard balanced in Air. A list of gas standards used in this work, with their respective concentrations and Type B evaluation of standard uncertainty, is provided as supplementary material; see S3. The total moles injected into the GC/MSD inlet, n_{inj} , for calibration is determined from Eq. (4) using the pressure, P, temperature, T, and volume, V_s , of the gas sample injected into the GC/MSD.

$$n_{\rm inj} = \frac{PV_{\rm s}}{RT} \tag{4}$$

Here, $R = 8.314 \text{ (Pa} \cdot \text{m}^3)/(\text{mol} \cdot \text{K})$ is the universal gas constant, $V_{\text{s}} = 2 \times 10^{-6} \text{ m}^3 \pm 1\%$ is the injected sample volume, and P (Pa) and T (K) are the mean sample injection pressure and temperature measurements made on the GC/MSD sample loop, respectively.

Chemical species that are liquid at room temperature and atmospheric pressure (e.g., water, methanol, ethanol, acetone) are calibrated using a different calibration procedure shown in Fig. 4. The calibration is performed by partially filling a leak-tight 500 ml Pyrex flask with the liquid of interest, then bubbling helium through the liquid, forcing the saturated vapor to pass through a heated line and into the GC/MSD sample loop. The concentration in the sample loop varies depending on the vapor pressure of the liquid, which is calculated from the measured temperature using a liquid-vapor pressure correlation provided by DIPPR¹⁵. A list of the correlations for each calibrated liquid, including their respective uncertainties, is provided as supplementary material; see S4.

The concentration of vapor from liquid materials is determined from the ratio of the liquidvapor pressure in the heated flask to the total pressure in the sample line measured by the digital pressure gauge, shown in Fig. 1. The concentration range of each calibrated liquid is approximately 1 % to 50 %. Liquid bath temperatures are controlled using a heating plate positioned underneath the insulated bubbler. The temperature of the bath is measured using a stainless steel sheathed, 3.2 mm diameter, K-type thermocouple positioned at the liquid surface. The bath temperature is measured simultaneously at 2 Hz for 50 s with the pressure and temperature measurements of the GC/MSD sample loop. Helium is quasi-statically bubbled through the solvent reservoir. Calibration sample injection is conducted once the bath reaches a steady-state temperature (approximately 1 h), and the nitrogen/vapor gas mixture has swept through the sample loop. Upon injection into the GC/MSD, pressure and temperature measurements on the sample loop are made as described above.

Figure 5, shows the calibration of water using the TCD. The linear regression presented here is typical of all calibrated species. For all TCD calibrations, the regression is forced through the origin and the relative error of the slope is estimated to be between 1% and 3%. Linear regressions being forced through the origin is done under the notion that detection limits of all calibrated species are approximately ppm or less (i.e., close, if not equivalent, to zero). In previous studies, the concentration of water and other condensable substances have been challenging to estimate due to the inability to maintain a controlled amount of substance used for calibration consistently. Figure 5, however, demonstrates the capability of the bubbler setup to repeatedly produce a consistent peak area over a wide range of concentrations. In doing so, the amount of water and other condensable substances can be directly measured from the chromatogram, eliminating the indirect approximations via stoichiometric balance.

2.3 Determining the time-weighted average soot mass fraction

Soot mass fraction, Y_s , is quantified using a well-established gravimetric technique¹⁶. Soot is filtered out of the gas stream using a 47 mm polytetrafluoroethylene (PTFE) filter positioned in a stainless steel particulate filter holder (PALL 2220). A desiccated PTFE filter is weighed three times before and after each test, then placed into the holder. The filter holder is positioned in the gas sampling line behind the quenching probe and maintained at approximately 140 °C using heating tape to prevent condensation of water and condensable substances on the filter.

After sampling, the filter is removed and dried in a desiccator for 48 h, then weighed three times again to obtain the final mass. To collect a significant mass of soot ($\geq 1 \text{ mg of soot}$), the sampling time is varied from 12 min to 25 min depending on the sampling location; sample locations high in the plume of the fire have smaller soot volume fraction, requiring longer sampling times to gather a sufficient sample. In some cases, as much as 38% of the total collected soot mass is observed on the inner walls of the quenching probe. Dedicated gun cleaning patches (Hoppe's 9 1203S) are used for solvent-free cleaning on the inside of the quenching probe. At least two patches are used to collect soot on the inside of the probe. A petri dish is placed below one end of the probe to catch dislodged soot and patches. Soot collection on the inside of the probe to reach dislodged soot and patches. Patches are also weighed three times before and 48 h after cleaning the inside of the probe.

The soot mass fraction, $Y_{\rm s}$, is computed from the ratio of the mass of the soot collected from the PTFE filter and gun cleaning patches, $m_{\rm s}$, to the total mass of gas sampled, $m_{\rm tot}$, based on the mass flow controller:

$$Y_s = \frac{m_s}{m_{\rm tot}} \tag{5}$$

The total mass of gas sampled is the product of the average volumetric flow rate measured by the mass flow controller, \dot{V} , the density of the sample gas, $\rho_{\rm g}$, the gas sampling time, Δt and the ratio of the average temperature of the gas calculated from Eq. (8), $T_{\rm g}$ to the the mass flow controller's temperature reading, T_{∞} .

$$m_{tot} = \dot{V} \rho_{\rm gas} \,\Delta t \, \left(\frac{T_{\rm g}}{T_{\infty}}\right) \tag{6}$$

In Eq. (6), the density of the sample gas is determined from the total mass detected from the TCD and MSD, m_{gas} , per the injected sample volume, V_{s} . The total mass of the gas samples determined from Eq. (6) neglects the mass of the soot since it is substantially less (< 1 %) than the total mass of the gas.

$$\rho_{\rm gas} = \frac{m_{\rm gas}}{V_{\rm s}} \tag{7}$$

The effective temperature of the extracted gas is determined from time-averaged temperature measurements made along the vertical centerline of the fire. An identical approach has been conducted in larger diameter pool fires, as reported in Sung et al.¹⁷. Temperature measurements are obtained using S-type (Pt 10% Rh/Pt), bare-wire thermocouples (OMEGA P10R-001) with wire diameters of approximately 13 μ m and 25 μ m, respectively, and bead diameters approximately three times greater. Temperature measurements are sampled at 250 Hz for 2 min, approximately 300 pulsing cycles of the fire¹⁸.

The measured thermocouple temperatures are corrected for heat losses and thermal inertia using the formula described by Shaddix¹⁹:

$$T_{\rm g}(t) = T_{\rm b}(t) + \tau \, \frac{\mathrm{d}T_{\rm b}}{\mathrm{d}t} + \frac{\epsilon\sigma}{h} \left(T_{\rm b}(t)^4 - T_{\infty}^4 \right) \tag{8}$$

where $T_{\rm g}$ is the "true" gas temperature, $T_{\rm b}$ is the measured bead temperature, T_{∞} is the ambient temperature, $\sigma = 5.67 \times 10^{-11} \text{ kW}/(\text{m}^2 \cdot \text{K}^4)$ is the Stefan-Boltzmann constant, ϵ is the thermocouple emissivity, and h is the convective heat transfer coefficient. The temperature-dependent emissivity of the platinum is taken from Shaddix¹⁹ and shown below:

$$\epsilon = -0.1 + 3.24 \times 10^{-4} T - 1.25 \times 10^{-7} T^2 + 2.18 \times 10^{-11} T^3$$
(9)

h and τ are defined as:

$$h = \frac{\operatorname{Nu} k_{\mathrm{g}}}{D_{\mathrm{b}}} \quad ; \quad \tau = \frac{\rho_{\mathrm{b}} c_{\mathrm{b}} D_{\mathrm{b}}^{2}}{6 \operatorname{Nu} k_{\mathrm{g}}} \tag{10}$$

where $k_{\rm g}$ is the thermal conductivity of the gas, Nu is the Nusselt number, and $\rho_{\rm b}$, $c_{\rm b}$, and $D_{\rm b}$ are the density, specific heat, and diameter of the bead, respectively. The thermal conductivity of the gas is determined by interpolating the instantaneous temperature-dependent data²⁰. The density of the thermocouple bead is assumed constant at 21.45 g/cm²¹. The specific heat of the bead is calculated from the formulae provided from Jaeger et al.²². The Nusselt number is calculated using the Ranz-Marshall correlation¹⁹:

$$Nu = 2 + 0.6 \,\text{Re}^{1/2} \,\text{Pr}^{1/3} \quad ; \quad \text{Re} = \frac{\rho_{\text{air}} \,U_{\text{g}} \,D_{\text{b}}}{\mu_{\text{air}}} \quad ; \quad \text{Pr} = 0.7 \tag{11}$$

The temperature-dependent gas properties for Reynolds number, Re, and Prandtl number, Pr, are taken as those of air from report tables²³. The gas velocity is assumed to be equal to 2 m/s. The corrected temperature is relatively insensitive to gas velocities between 1 m/s and 3 m/s, consistent with the results of Shaddix¹⁹. Consistent with Weckman and Strong²⁴, the thermal inertia term in Eq. 8 is found not to influence the mean temperature, but only its variance. Details of the temperature calculation are provided elsewhere¹⁷.

2.4 Uncertainty analysis

A detailed uncertainty analysis of measurements discussed in this work is provided from Falkenstein et al.⁴. The uncertainty of the volume fraction measurements is determined via the law of propagation of uncertainty using Eq. 2.

$$u_{\bar{X}_{i}} = \sqrt{\left(\frac{\partial \bar{X}_{i}}{\partial n_{i}} u_{n_{i}}\right)^{2} + \left(\frac{\partial \bar{X}_{i}}{\partial n_{\text{tot}}} u_{n_{\text{tot}}}\right)^{2}}$$
(12)

The uncertainty of the number of moles of a given species, u_{n_i} , is calculated through a combined Type A and B evaluation of uncertainty²⁵. The Type A evaluation of uncertainty is the standard deviation in the measurements made during replicate GC/MSD runs, s_{n_i} . The Type B evaluation of uncertainty is the reported bias in the instrumentation and calibration, $u_{n_{i,\text{bias}}}$.

$$u_{n_i} = \sqrt{\underbrace{s_{n_i}^2}_{\text{Type A}} + \underbrace{u_{n_{i,\text{bias}}}^2}_{\text{Type B}}}$$
(13)

The total number of moles detected is determined from the summation of the number of moles for each species identified by the TCD and TIC chromatograms. Therefore, the uncertainty in the total number of moles identified is the combined uncertainty of all the identified species via quadrature:

$$u_{n_{\text{tot}}} = \sqrt{\sum_{n=1}^{N} u_{n_i}^2} \tag{14}$$

where N is the number of a species identified species in the TCD and TIC chromatogram. All uncertainties are expressed using a 95% confidence level. For calculated values, the uncertainty is calculated using the law of propagation of uncertainty. It is observed that the majority of measurements' uncertainties are dominated by the Type A measurement (i.e., the standard deviation between GC/MSD runs).

3 Results and Discussion

Gas extractions and analyses of gas composition are conducted at various heights along the centerline of the pool fires with measurements made between 1 cm to 75 cm, relative to the fuel surface, at varying increments in order to capture gas species concentrations in the flame, intermittent, and plume regimes of the fire. Once enough measurements are made within the fire, a profile of individual species' concentration throughout the fire is produced. Overall, measured species concentrations of all repeated measurements are observed to be within their respective error bounds, suggesting a well-mixed sample. The volume fraction of gas species extracted from methanol, ethanol, acetone, methane, and propane fires, using the methods described here, is reported in various works^{4;11;13;14} and provide validation datasets for CFD fire models.

Although these datasets provide some comparison between the practical and predicted, they are useless unless their accuracy is authenticated within some error. Therefore a series of verification techniques that confirm the accuracy of the results are implemented to evaluate the volume fraction measurements. These techniques include the comparison between the total number of moles determined from the chromatogram and injection conditions, the estimation of the carbon to hydrogen ratio, and the estimation of the inert gas ratio (i.e., Ar to N_2).

3.1 Total Number of Moles

The first verification technique identifies any prediction error in the measured mole fraction of all detected species. This technique compares the total number of moles estimated from the TCD chromatogram and injected into the GC/MSD inlet. The total moles estimated from the TCD chromatogram, n_{tot} , is defined as the sum of the moles of all detected species in the chromatogram obtained in a GC/MSD run. The total moles injected into the GC/MSD inlet, n_{inj} , is defined by the ideal gas law (Eq. 4) using the pressure and temperature measurements recorded just before injection.

Figure 6 shows the comparison between n_{tot} and n_{inj} at various positions within the centerline of the examined fires. In most cases, this ratio is close to unity, indicating that the total moles injected into the GC/MSD inlet are accounted for in the chromatogram via the calibration of each species. At locations close to the fuel surface, the ratio is greater than unity, possibly indicating an over-prediction of the quantity of the fuel species found at high concentrations near the liquid surface, which suggests some bias in the calibration. In comparison, the expected values and estimated results are consistent within the experimental uncertainty, validating the calibration process of all detected species.

3.2 Carbon to Hydrogen Ratio

The second verification technique utilizes the carbon to hydrogen ratio to verify the conservation of carbon and hydrogen atoms throughout the fire. The carbon to hydrogen ratio, C/H, is calculated using the equation below

$$\frac{C}{H} = \frac{W_C}{W_H} \frac{\sum x_i \bar{X}_i}{\sum y_i \bar{X}_i}$$
(15)

where the summation is over all measured gas species, and x_i and y_i are the numbers of carbon and hydrogen atoms in the parent fuel molecule, respectively, and W_C and W_H and the molecular weights of carbon and hydrogen. Soot is included, assuming all measured soot is carbon. Each of the parent fuels examined in this work has a unique carbon to hydrogen ratio that can be compared to the estimated values, determined using Eq. 15.

Figure 7 shows the comparison between the hydrogen to carbon ratio of the parent fuel, indicated by the dotted lines, and the calculated ratio at various positions within the centerline

of the fires. In all cases, the calculated C\H is within the experimental uncertainty of the parent fuels' ratios. In several cases, the expected and calculated values are nearly matching, indicating that the concentration measurements of species that consist of carbon and hydrogen are accurately estimated using the experimental method. The consistency of the C/H at different positions along the centerline of the fires also suggests that each of the extracted gas samples are well-mixed, as expected, showing no uneven distribution of carbon or hydrogen atoms when measured throughout the fire.

3.3 Inert Gases Ratio

The last verification technique considers the ratio between the inert gases present in the room air at STP and those measured within the fire. Since Ar and N_2 do not react, the ratio between them should be constant at every position within the fire. Figure 8 shows the ratio of Ar to N_2 at different positions along the centerline of the fires. The error band is estimated from the measured Ar/N₂ ratio is obtained from extracted ambient air samples taken at different locations throughout the room.

Accounting for all cases, the average measured Ar/N_2 ratio is observed to be 0.0117 ± 0.0005 . All calculated ratios are observed to fall within the uncertainty bounds of the ambient air measurement, indicating that measurements of the concentrations of argon and nitrogen are reasonable throughout the fire. Similarly to the C/H, the consistency of the inert gas ratio suggests the extracted sample is well-mixed, further supporting the validity of the experimental methods.

4 Conclusion

This work details a technique used to characterize the chemical structure of medium-scale pool fires steadily burning in a quiescent environment. Principal combustion species, including liquid-vapor species, are calibrated and measured using the extractive sampling and GC/MSD method described. Verification techniques are adapted to authenticate the accuracy, within some error, of the measurement. These techniques include comparing the total number of moles, estimating the carbon to hydrogen, and calculating the ratio between inert gases. All techniques are shown to be in agreement with the theoretical values, which verifies the accuracy of the measurements and the experimental approach. A major limitation of the approach is its ability to provide time-average species measurements as opposed to measurements made in real-time. Despite this limitation, this method does provide a thorough insight into the chemical structure of fires by quantifying major and minor species in the fire, including difficult to measure condensable species. In addition to pool fires, this technique can be implemented for other fire configurations, which would not only aid in the development and accuracy of computational fire models but provide a more in-depth insight into the chemistry of fire.

References

¹ McGrattan K, Hostikka S, McDermott R, Floyd J, Weinschenk C, Overholt K. *Fire Dynamics Simulator, Technical Reference Guide.* National Institute of Standards and Technology, Gaithersburg, Maryland, USA, and VTT Technical Research Centre of Finland, Espoo, Finlandsixth ed. 2013. Vol. 1: Mathematical Model; Vol. 2: Verification Guide; Vol. 3: Validation Guide; Vol. 4: Software Quality Assurance.

- ² Fischer SJ, Hardouin-Duparc B, Grosshandler WL. The structure and radiation of an ethanol pool fire *Combustion and Flame*. 1987;70:291-306.
- ³ Hamins A, Lock A. The Structure of a Moderate-Scale Methanol Pool Fire NIST Technical Note 1928, National Institute of Standards and Technology, Gaithersburg, MD, USA 2016.
- ⁴ Falkenstein-Smith R, Sung K, Chen J, Harris K, Hamins A. The Structure of Medium-Scale Pool Fires NIST Technical Note 2082, National Institute of Standards and Technology, Gaithersburg, MD, USA 2020.
- ⁵ Choi MY, Hamins A, Rushmeier H, Kashiwagi T. Simultaneous optical measurement of soot volume fraction, temperature, and CO2 in heptane pool fire in *Symposium (International) on Combustion*;25:1471–1480Elsevier 1994.
- ⁶ Andrews GE, Daham B, Mmolawa MD, et al. FTIR investigations of toxic gases in air starved enclosed fires *Fire Safety Science*. 2005;8:1035–1046.
- ⁷ Meier W, Barlow RS, Chen YL, Chen JY. Raman/Rayleigh/LIF measurements in a turbulent CH4/H2/N2 jet diffusion flame: experimental techniques and turbulence–chemistry interaction *Combustion and Flame*. 2000;123:326–343.
- ⁸ Shaddix CR, Allendorf SW, Hubbard GL, Ottesen DK, Gritzo LA. Diode Laser Diagnostics for Gas Species and Soot in Large Pool Fires in *Diode Laser Diagnostics for Gas Species and Soot in Large Pool Fires. Sandia Report, SAND2001-8383* 2001.
- ⁹ Bundy M, Hamins AP, Johnsson EL, Kim SC, Ko G, Lenhert DB. Measurements of heat and combustion products in reduced-scale ventilation-limited compartment fires NIST Technical Note 1483, National Institute of Standards and Technology 2007.
- ¹⁰ Lock A, Bundy M, Johnsson EL, et al. Experimental Study of the Effects of Fuel Type, Fuel Distribution, and Vent Size on Full-Scale Underventilated Compartment Fires in an ISO 9705 Room NIST Technical Note 1603, National Institute of Standards and Technology, Gaithersburg, MD, USA 2008.
- ¹¹ Falkenstein-Smith R, Sung K, Chen J, Hamins A. The Chemical Structure of a 30 cm methanol pool fire *Fire and Materials.* 2020.
- ¹² McEnally CS, Pfefferle LD, Robinson AG, Zwier TS. Aromatic hydrocarbon formation in nonpremixed flames doped with diacetylene, vinylacetylene, and other hydrocarbons: evidence for pathways involving C4 species *Combustion and flame*. 2000;123:344–357.
- ¹³ Falkenstein-Smith R, Sung K, Chen J, Hamins A. Chemical Structure of Medium-Scale Liquid Pool Fire *Fire Safety Journal.* 2020.
- ¹⁴ Falkenstein-Smith R, Sung K, Hamins A. Mixture Fraction Analysis of Combustion Products in Medium-Scale Pool Fires in *Proceedings of the Combustion Institute* Accepted.
- ¹⁵ DIPPR[®] . Design Institute for Physical Properties (DIPPR 801) 2019.
- ¹⁶ Choi MY, Mulholland GW, Hamins A, Kashiwagi T. Comparisons of the soot volume fraction using gravimetric and light extinction techniques *Combustion and Flame*. 1995;102:161-169.
- ¹⁷ Sung K, Chen J, Bundy M, Fernandez M, Hamins A. The thermal character of a 1 m methanol pool fire NIST Technical Note 2083, National Institute of Standards and Technology, Gaithersburg, MD, USA 2020.
- ¹⁸ Wang Z, Tam WC, Lee KY, Chen J, Hamins A. Thin Filament Pyrometry Field Measurements in a Medium-Scale Pool Fire *Fire Technology*. 2020;56:837–861.
- ¹⁹ Shaddix CR. Correcting thermocouple measurements for radiation loss: a critical review Tech. Rep. CONF-990805, Sandia National Laboratories, Livermore, CA, USA 1999.
- ²⁰ Touloukian YS, Liley PE, Saxena SC. Thermophysical Properties of Matter—The TPRC Data Series. Volume 3. Thermal Conductivity—Nonmetallic Liquids and Gases TEPIAC Technical Note ADA951937Thermophysical and Electronic Properties Information Analysis Center 1970.
- ²¹Wise EM. , ed. The Platinum Metals and Their Alloys. Literary Licensing, LLC1st ed. 2012.
- 22 Jaeger FM, Rosenbohm E. The exact formulae for the true and mean specific heats of platinum between 0 and 1600 C *Physica*. 1939;6:1123-1125.

- ²³ Incropera FP, Lavine AS, Bergman TL, DeWitt DP. Fundamentals of Heat and Mass Transfer. Hoboken, NJ, USA: Wiley 2007.
- ²⁴ Weckman EJ, Strong AB. Experimental investigation of the turbulence structure of mediumscale methanol pool fires *Combustion and Flame*. 1996;105:245-266. ²⁵ Taylor Barry N, Kuyatt Chris E. Guidelines for evaluating and expressing the uncertainty of
- NIST measurement results 1994.

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Fig. 1. A schematic of the experimental setup, including the extraction sampling setup used to transport gas samples from the pool fire to the GC/MSD.



Fig. 2. An internal schematic of the GC detailing the column configuration and extension tubing feeding into the detectors.



Fig. 3. TCD chromatogram of a pool fire gas sample and a magnified image of overlapping peaks with an example of the tangential skim integration technique used to determine peak area. Peaks eluting from the PoraBOND Q and Molsieve 5 Å are denoted as Q and MS, respectively. Identified peaks include CH₄, CO₂, H₂, H₂O, Ar, O₂, C₃H₈, CH₃OH, N₂, C₂H₅OH, C₃H₅OH, CO, C₆H₆, C₂H₆, C₂H₄, and C₂H₂. Some peaks are not shown above.



Fig. 4. Schematic of the calibration system used for condensed chemical species.



Fig. 5. TCD calibration curve for water. The solid black line is the linear regression determined from the calibration values, with the calibration coefficient listed in the legend of the plot.



Fig. 6. Ratio of moles identified to moles injected, with uncertainty, as a function of position. The uncertainty of the ratio is defined by Falkenstein et al.⁴.



Fig. 7. Carbon to hydrogen ratio calculated from all measured gas species compared to the theoretical values as a function of position. The uncertainty of the ratio is defined in Falkenstein et al.⁴.



Fig. 8. Ar/N_2 mole ratio at different elevations compared to the uncertainty bounds of the measurement in ambient air. The uncertainty of the ratio is defined by Falkenstein et al.⁴.