

NIST Technical Note XXXX

Mapping the Chemical Structure of Centerline Profiles in Medium-Scale Pool Fires

Ryan Falkesntein-Smith
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Abstract

This report documents a series of time-averaged local gas species measurements made throughout the centerline profile of moderate-sized methanol, ethanol, and acetone pool fires steadily burning in a quiescent environment. All gas species measurements are obtained using a Gas Chromatograph/ Mass Spectrometer system (GC/MSD). The volume fraction of each species was calculated via the number of moles identified by the GC/MSD at each location throughout the centerline profile of the fire. Soot mass fractions are measured during the gas sampling process. The gas species volume and soot mass fractions were compared at different heights within the fire and across a variety of different fuels.

Key words

Acetone fuel, Ethanol fuel, Gas species measurements. Methanol fuel, Moderate-sized pool fire

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1. Introduction

Use of fire modeling, such as the Fire Dynamic Simulator (FDS) [1], in fire protection engineering, has increased dramatically during the last decade due to the development of practical computational fluid dynamics fire models and the decreased cost of computational power. Today, fire protection engineers use models to design safer buildings, nuclear power plants, aircraft cabins, trains, and marine vessels, to name a few types of applications. To be reliable, the models require validation, which involves an extensive collection of experimental measurements. An objective of this report is to provide data for use in fire model evaluation by the research community.

A pool fire is a fundamental combustion configuration of interest in model development. In pool fires, the fuel surface is isothermal, flat and horizontal, which provides a well-defined and straightforward setup for testing models and furthering the understanding of fire phenomena. In moderate and large-scale pool fires, radiative heat transfer is the dominant mechanism of heat feedback to the fuel surface. Species concentrations and temperatures have a significant influence on the radiative heat transfer. A zone of particular interest is the fuel rich-core between the flame and the pool surface, where gas species can absorb energy that would otherwise have been transferred to the fuel surface. Few studies in the literature studies have reported local chemical species measurements, which provide a deep understanding of the chemical structure of a pool fire and provide insight on critical kinetic, heat, and mass transfer processes.

The purpose of this study is to characterize the spatial distribution of stable gas-phase chemical species in a moderate-scale liquid pool fire steadily burning in a well-ventilated quiescent environment. Here, methanol, ethanol, and acetone are the fuels of interest. Contrary to ethanol and acetone, fires established using methanol are unusual as no carbonaceous soot is present or emitted.

In this study, measurements are made in a 30.0 cm diameter pool fire using various fuels. These particular fires are selected for research since the measurements complement results from previous studies, including analyses of the mass burning rate, the temperature and velocity fields, radiative emission, flame height, and pulsation frequency [2, 3]. Additional characterization of this fire enables a more comprehensive understanding of its detailed structure, enhancing the understanding of fire physics.

2. Description of Experiments

The methods used in this work to investigate pool fires have been documented previously [3–7]. Experiments are conducted under a canopy hood surrounded by a 2.5 m x 2.5 m x 2.5 m enclosure made of a double-mesh screen wall. The walls of the enclosure were formed by a double layer of the wire-mesh screen (5 mesh/cm) that reduced the influence of compromising room flows that could disrupt the pool fire's flow field. All measurements were made once the burning conditions, specifically the mass burning rate, reached steady-state, achieved approximately 10 min after ignition.

2.1 Pool Burner Setup

A circular, stainless-steel pan with an outer diameter of 30.0 cm, a depth of 15.0 cm, and a wall thickness of 0.16 cm was used as the pool burner. As shown in Fig. 1, the burner was placed within an overflow basin, which extended 3.00 cm beyond the burner wall. The burner is fitted with legs such that the burner rim was positioned 30 cm above the ground. The bottom of the burner was maintained at a constant temperature by flowing water ($20^{\circ}\text{C} \pm 3^{\circ}\text{C}$) through a 3 cm section on the bottom of the fuel pan. Additionally, a fuel level indicator was positioned near the center of the burner to aid in maintaining the fuel level while burning.

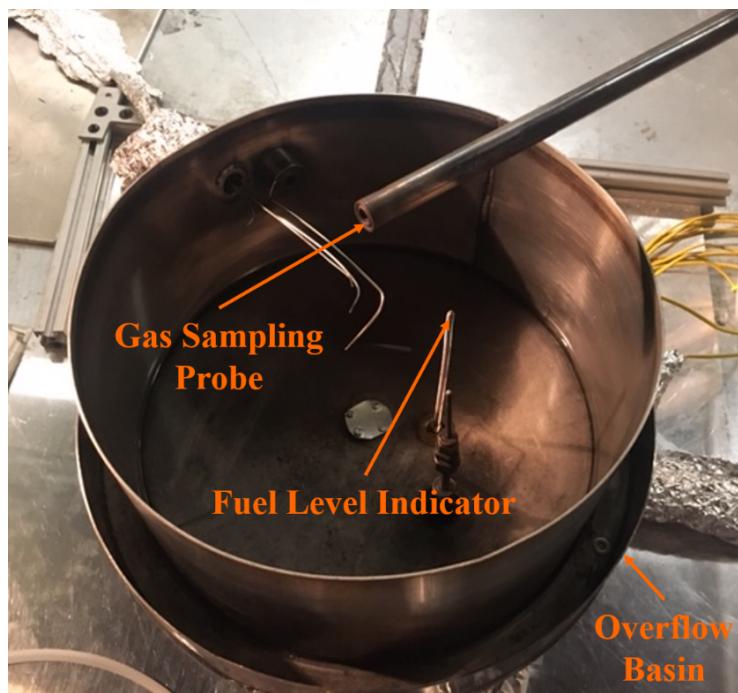


Fig. 1. A 30 cm Pool Burner with fuel level indicator, overflow section, and quenching probe

Figure 2 shows how the fuel level was monitored by a fuel flow operator via live video feed. The live video feed provided a close up of a barely discernable dimple made from the fuel level indicator on the fuel surface. The fuel flow was manually adjusted using a needle valve to maintain a fuel level 10 mm below the burner rim. Fuel to the burner was gravity fed from a reservoir positioned on a mass load cell located outside the enclosure and monitored by a data acquisition system. The expanded uncertainty with a coverage factor of 2 of the fuel level was estimated to be 0.5 mm for these experiments.

2.2 Measuring the Volume Fraction of Gas Species via GC/MSD

Gas-species measurements were made using an Agilent 5977E Series GC/MSD fitted with a thermal conductivity detector (TCD). The GC/MSD was able to quantify a variety of



Fig. 2. Photo of fuel flow operators monitoring the fuel level via live video feed (top) and a close up image of the live video feed used to maintain a consistent fuel level relative to the fuel level indicator (bottom)

stable reactants, intermediates, and combustion product species collected from the pool fire. The GC/MSD was equipped with a 2 ml sample loop maintained at a 200 °C. Chro-

matographic separation of species was achieved using a Select for Permanent Gases-Dual Column (CP7430) comprised of mole-sieve and Porapak Q columns working in parallel and using a helium carrier gas. The sample analysis time was 62 min wherein the carrier gas flow leading into the TCD and MSD was 3.00 ml/min and 1.00 ml/min, respectively. During the analysis, the GC oven temperature was maintained at 30 °C for 12 min, then ramped at 8 °C/min for 2 min until a temperature of 300 °C was obtained.

Figure 3 displays the flow diagram for gas sampling into the GC/MSD. After achieving steady-state burning conditions, approx. 10 min after ignition, flow prompted by a vacuum pump located downstream from the GC/MSD was initiated. Gas samples were collected using a quenching probe. The quenching probe was composed of two concentric, stainless-steel tubes with outer annular coolant flow and inner, extracted, gas-sample flow. The inner and outer tube diameters were 7.9 mm and 16 mm, respectively. Water at 90 °C flowed through the sampling probe for the duration of the experiment. The remainder of the sampling line leading into the GC/MSD was heated with electrical, heating tape to 140 °C to prevent condensation of water and liquid fuels through the line.

Gas sampling was conducted for a minimum of 12 min, ensuring that the gas sample had completely swept through the GC/MSD sample loop. The gas sampling period varied from 12 min to 25 min depending on the sampling location within the fire. The sampling flow was controlled using a mass flow controller (Alicat Scientific MC-Series) located in front of the vacuum pump within the sampling line. During the gas sampling procedure, the volumetric flow was approximately 200 ml/min and recorded using DAQ at 2 Hz for the entire duration of the gas sampling procedure. The mass flow controlled also provided temperature readings of its internal gas flow.

After the gas sampling period, two quarter-turn valves located on opposite ends of the GC/MSD sample loop within the sampling line are closed. Once the sampled gas reached equilibrium, 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, were collected at 2 Hz for 50 s. After collecting pressure and temperature measurements, the sampled gas was injected into the GC/MSD.

The volume fraction, \bar{X}_i , was calculated from the ratio between the number of moles of a given gas species, n_i , and the total number of moles identified, n_{tot} . The moles of a given species were measured from the Thermal Conductivity Detector (TCD) within the GC/MSD. The total number of moles was determined from the summation of moles for each species identified by the TCD.

$$\bar{X}_i = \frac{n_i}{n_{tot}} \quad (1)$$

All measurements were repeated at least twice at each location along the centerline of the pool fire. Gas species concentration measurements made at the same location were averaged. The variance in the gas species volume fraction was a function of location and species. A detailed description of the uncertainty analysis for the gas species measurement

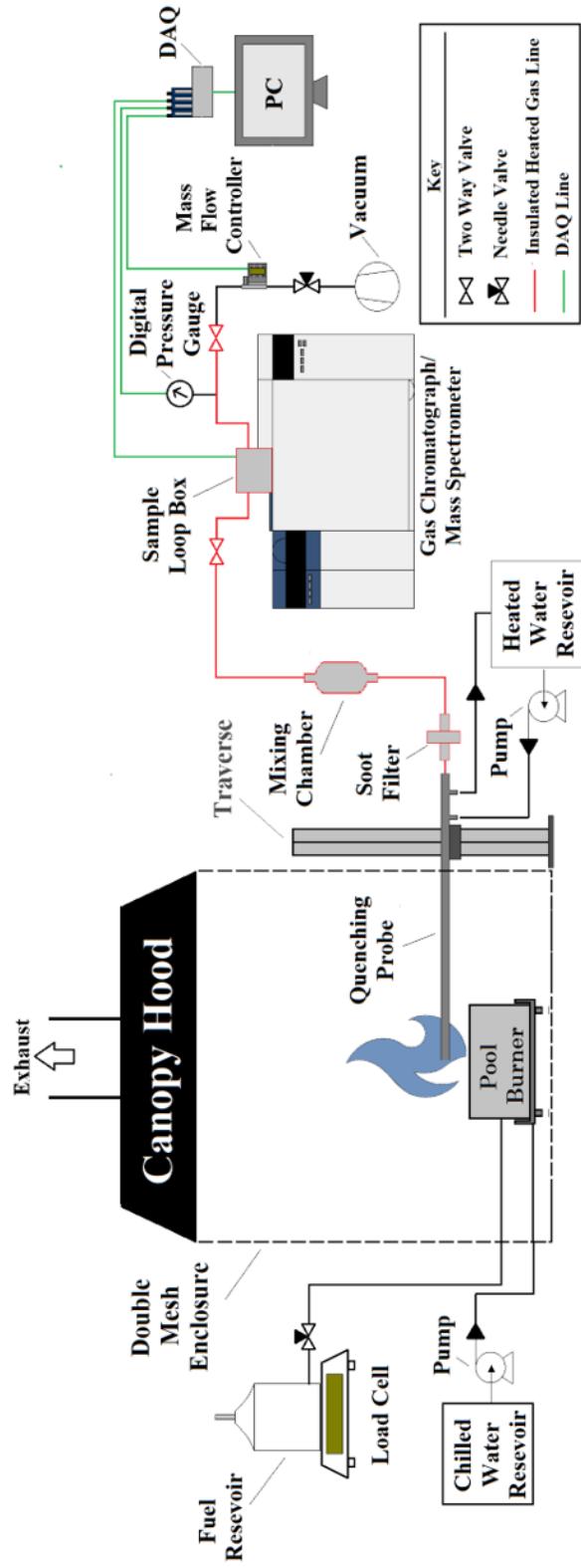


Fig. 3. A schematic of the extractive sampling setup used to transport gas samples from the pool fire to the GC/MSD

and its calibration is discussed in Appendices A and B, respectively.

2.3 Determining Soot Mass Fraction

Soot was collected simultaneously with gas samples using the sampling procedure described in Section 2.2. Before a test, a dessicated 47 mm Polytetrafluoroethylene (PTFE) filter was weighed and subsequently placed into an in-line stainless steel particulate filter holder [8]. During a test, the filter holder was positioned within the gas sampling line behind the quenching probe and heated to 140 °C using heating tape to prevent condensation of water and liquid fuels on the filter. After testing, the PTFE filter was removed from the filter holder and dried in a desicator. After desiccating for 48 hrs, the PTFE filter's final weight was measured. Approximately 2 mg of soot was collected during the gas sampling period which varied from 12 min to 25 min depending on the sampling location within the fire.

After some tests, soot deposits were observed on the inner walls of the quenching probe. As shown in Fig. 4 desicated gun cleaning patches were used to clean the inside of the quenching probe. At least two patches were used to collect soot on the inside of the probe. Soot collection using patches concluded once a patch was observed to have no soot after being swept through the inner walls of the quenching probe. Patches were weighed immediately before and 48 hrs after cleaning the inside of the probe. The soot collected from the dry patches was accounted for when calculating the soot mass fraction. The portion of the soot collected on the inner walls of the quenching probe relative to the PTFE filter varied based on the sampling location. The mass of the PTFE filter and cleaning patches were measured three times before and after each test.

The soot mass fraction, M_s , was computed from the mass of the soot collected from the PTFE filter and gun cleaning patches, m_s , the ratio of the mass flow controller's temperature reading, T_∞ , to the temperature at the probe entrance, T_p , the total mass of gas sampled, M_t , based on the mass flow controller readings:

$$M_s = \frac{m_s}{M_t} \frac{T_\infty}{T_p} \quad (2)$$

The total mass of gas sampled was estimated from product of the average volumetric flow rate measured by the mass flow controller, \dot{V} , the density of the sample gas injected into the GC/MSD, ρ_g , and the gas sampling time, t .

$$M_t = \dot{V} \cdot \rho_g \cdot t \quad (3)$$

In Eq.3, the density of the sample gas was determined from the total mass detected in the TCD chromatogram, m_{tot} , for the injected sample volume, V_s .

$$\rho_g = \frac{m_{tot}}{V_s} \quad (4)$$

The uncertainty of the soot mass fraction was estimated from a combined uncertainty of the Type A evaluation of standard uncertainty in the variation of temperature and mass



Fig. 4. Process of collecting soot from the internal walls of the quenching probe using gun cleaning patches

measurements and the Type B standard uncertainty in the bias errors of the instrumentation. A detailed description of the soot mass fraction uncertainty is provided in Appendix C.

3. Mixture Fraction

4. Results

Brief observations of each pool fire burning different fuels are described in the first portion of this section. The key results of this work are the local gas species and soot measurements made at incremental heights along the centerline of medium-scale pool fires using various fuels such as methanol, ethanol, and acetone. A more in-depth analysis of the relationships between different measured gas is also provided in this section.

Table 1. List of measurements obtained in a well-ventilated round, steady, 30.0 cm diameter pool fire burning in a quiescent environment. The uncertainty of measurements of fire parameters are discussed in detail in Appendix D

Parameter (units)	Methanol	Ethanol	Acetone
Mean Flame Height (cm)	40.5 ± 1.4	61.1 ± 14.1	87.3 ± 16.4
Mass Burning Flux ($\text{g}/\text{m}^2\text{s}$)	12.4 ± 1.1	13.9 ± 0.8	17.6 ± 2.7
Heat Release Rate (kW)	17.4 ± 1.4	26.3 ± 1.5	35.5 ± 5.4

4.1 Flame Observations

Figure 5 displays a series of snapshots depicting the flame pulsation of the methanol, ethanol, and acetone pool fires in the 30.0 cm stainless-steel water-cooled burner. A repeated cycle was observed in each of the pool fires; uniformly curved flame sheets present at the burner rim would roll towards the fire centerline to form a long and narrow plume.

The shape and visible color of the fires differed between the different fuel types. The methanol fire appeared to be completely blue, whereas the ethanol and acetone fires primarily consisted of vibrant yellow and orange colors. The methanol pool fire was observed to exhibit a weak turbulent structure compared to the fully developed fires of the other two fuels. The sequential order from smallest to largest of the time-averaged flame height of each pool fire was as follows: methanol, ethanol, acetone. Table 1 provides a list of measurements of each pool fire. The observed dynamic shapes were consistent with previous experiments [3–7].

4.2 Gas Species Concentrations

4.3 Soot Mass Fraction

4.4 Mixture Fraction Results

4.5 Carbon Balance

5. Conclusion

Acknowledgments

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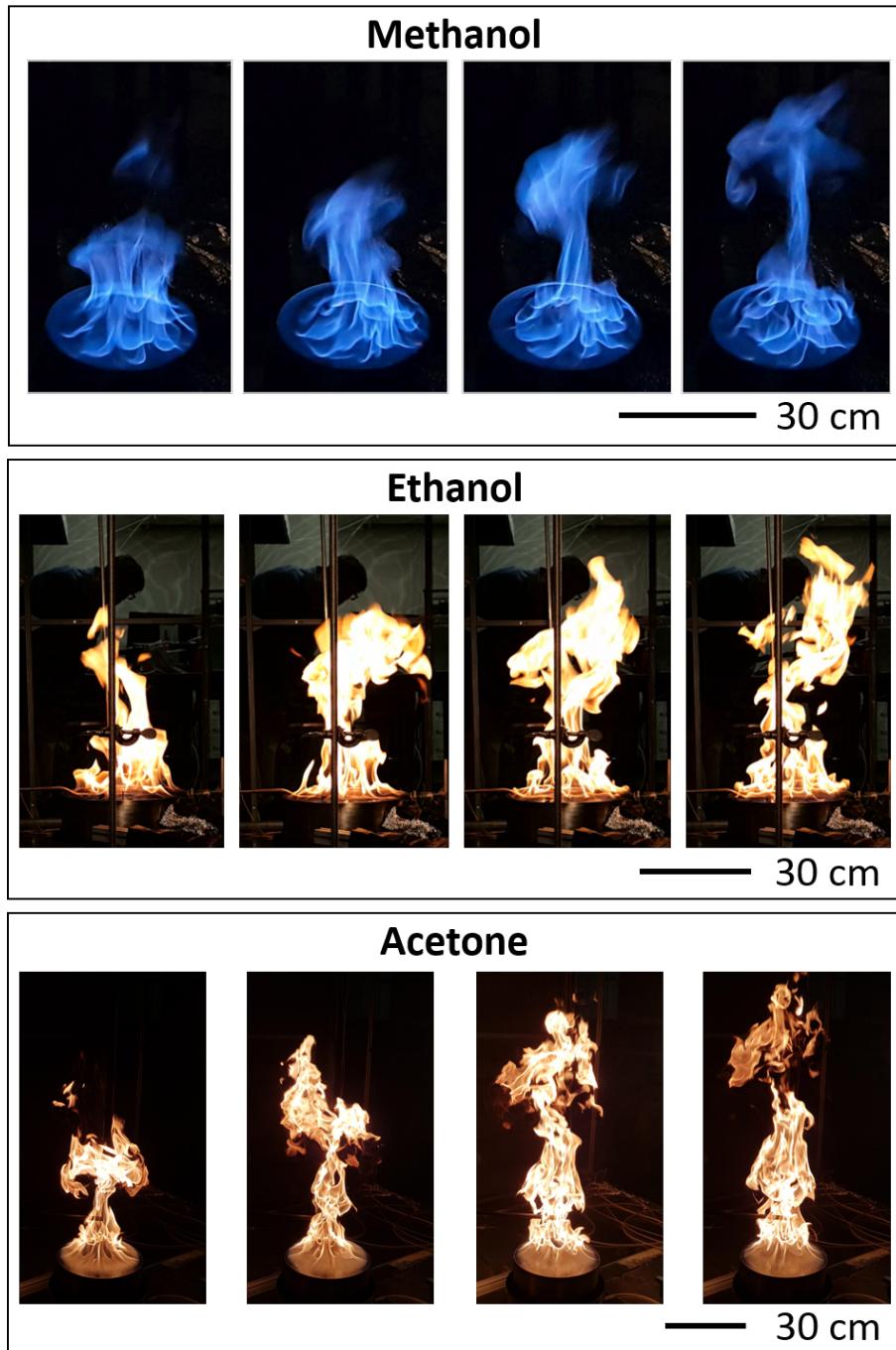


Fig. 5. Flame structures of methanol (top), ethanol (middle), and acetone (bottom) pool fires during their pulsing cycles

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A. Uncertainty Analysis of Gas Species Concentration

As shown in Eq. 1, volume fraction, \bar{X}_i was calculated from the ratio between the number of moles of a given species, n_i , and the total number of moles identified, n_{tot} . The uncertainty of the measured volume fraction was estimated using the law of propagation of uncertainty after determining the volume fraction of each species:

$$u_{\bar{X}_i} = \sqrt{\left(\frac{\partial \bar{X}_i}{\partial n_i} u_{n_i}\right)^2 + \left(\frac{\partial \bar{X}_i}{\partial n_{tot}} u_{n_{tot}}\right)^2} \quad (\text{A.1})$$

A coverage factor of 2 was applied to the combined uncertainty to produce a 95 % confidence interval.

A.1 Number of Moles of a Given Species

The number of moles of a given species was determined from a calibration function of the integrated peak area of the respective species obtained from the TCD chromatogram. The Type A evaluation of standard uncertainty of the number of moles of a given species was taken as the standard deviation of the measurements obtained from the repeated tests. The Type B evaluation of standard uncertainty was determined from the error in the calibration functions for each species measured by the TCD further detailed in Appedix B. The combined uncertainty was found via quadrature:

$$u_{n_i} = \sqrt{u_{n_i, \text{cal}}^2 + s_{n_i}^2} \quad (\text{A.2})$$

A.2 Total Number of Moles Identified

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

$$u_{n_{tot}} = \sqrt{\sum_{n=1}^N s_{n_i}^2} \quad (\text{A.3})$$

where N is the number of a species identified species in the TCD chromatogram.

B. Uncertainty Analysis of Gas Species Calibrations

A calibration function is a relationship between an integrated peak area on the TCD chromatogram, $Area_i$, and the number of moles of a given species injected into the GC/MSD, n_i . A calibration function was determined by injecting a known amount of moles of a given species into the GC/MSD, $n_{i,cal}$, and identifying the peak area corresponding to the individual species. For this work, the calibration functions are approximately linear consisting of a slope, a , and intercept, b .

$$n_{i,cal} = a(Area_i) + b \quad (\text{B.1})$$

Calibration functions were weighted to account for the error of each gas standard used in the calibration procedure. The uncertainty of a calibration function was determined using the law of propagation of uncertainty:

$$u_{n_i} = \sqrt{\left(\frac{\partial n_i}{\partial a} u_a\right)^2 + \left(\frac{\partial n_i}{\partial b} u_b\right)^2} \quad (\text{B.2})$$

The uncertainties of the slope and intercept in a weighting linear regression are as follows:

$$u_a = \sqrt{\frac{\sum \frac{1}{u_{n_{i,cal}}^2}}{\left(\sum \frac{Area_i^2}{u_{n_{i,cal}}^2}\right)\left(\sum \frac{1}{u_{n_{i,cal}}^2}\right) - \left(\sum \frac{Area_i}{u_{n_{i,cal}}^2}\right)^2}} \quad (\text{B.3})$$

$$u_b = \sqrt{\frac{\sum \frac{Area_i^2}{u_{n_{i,cal}}^2}}{\left(\sum \frac{Area_i^2}{u_{n_{i,cal}}^2}\right)\left(\sum \frac{1}{u_{n_{i,cal}}^2}\right) - \left(\sum \frac{Area_i}{u_{n_{i,cal}}^2}\right)^2}} \quad (\text{B.4})$$

where $u_{n_{i,cal}}$ is the uncertainty of the known number of moles of the respective species.

During calibration, the number of moles of a given species $n_{i,cal}$ was calculated from the product of the total moles injected into the GC/MSD, $n_{tot,inj}$ and the known concentration of the particular species in the calibration standard, C_i .

$$n_{i,cal} = C_i(n_{tot,inj}) \quad (\text{B.5})$$

A collection of gas calibration standards for a variety of species were pre-selected to provide a broad range of concentrations. All calibration standards were mixtures of the target gas species with a Nitrogen balance, with the exception of 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 in Appendix B.2.

The uncertainty of the number of moles of a given species injected into the GC/MSD for calibration was estimated using the law of propagation of uncertainty:

$$u_{n_{i,cal}} = \sqrt{\left(\frac{\partial n_{i,cal}}{\partial C_i} u_{C_i}\right)^2 + \left(\frac{\partial n_{i,cal}}{\partial n_{tot,inj}} u_{n_{tot,inj}}\right)^2} \quad (\text{B.6})$$

B.1 Total Moles Injected into the GC/MSD for Calibration

The total moles injected into the GC/MSD for calibration was determined from the pressure, P , temperature, T , and volume, V , of the gas sample injected into the GC/MSD using the experimental setup described in Section 2.2. The injected sample was assumed to be an ideal gas:

$$n_{tot,inj} = \frac{PV}{RT} \quad (\text{B.7})$$

where R is the universal gas constant (287 J/(mol · K)).

Pressure and temperature measurements were made using an Omega Digital Pressure Gauge (DPG409-030DWU) and K Type Thermocouple located at the GC/MSD Sample Loop injection valve, respectively, sampling at 2 Hz for 50 s. The volume of the GC/MSD sample loop, V_{sl} , was assumed to be 2 ml. The Type A evaluation of uncertainty of the total moles injected into the GC/MSD for calibration was determined from the standard error of the pressure, s_P , and temperature, s_T readings from the sampling period. The Type B evaluation of uncertainty for the total moles injected into the GC/MSD for calibration is determined from the bias error sources in the instrumentation, u_{inst} , used to measure pressure (0.008% accuracy of the reading), temperature (1.5 °C), and volume (0.02 ml) of gas sample injected. The combined uncertainty of the pressure, temperature, and volume was found via quadrature:

$$u_P = \sqrt{u_{inst}^2 + s_P^2} \quad (\text{B.8})$$

$$u_T = \sqrt{u_{inst}^2 + s_T^2} \quad (\text{B.9})$$

$$u_{V_{sl}} = \sqrt{u_{inst}^2} \quad (\text{B.10})$$

The standard uncertainty of the total moles injected into the GC/MSD for calibration was estimated using the law of propagation of uncertainty:

$$u_{n_{tot,inj}} = \sqrt{\left(\frac{\partial n_{tot,inj}}{\partial P} u_P\right)^2 + \left(\frac{\partial n_{tot,inj}}{\partial T} u_T\right)^2 + \left(\frac{\partial n_{tot,inj}}{\partial V_{sl}} u_{V_{sl}}\right)^2} \quad (\text{B.11})$$

B.2 Table of Gas Standards with Error

A table of the gas standards with their respective concentrations and Type B evaluation of standard uncertainty, used for calibrating the GC/MSD is provided below. Lot numbers for all standards are provided for traceability.

Table 2. Gas Standards used to Calibrate GC/MSD

Components	Uncertainty(%)	Distributor	Lot No.
200 ppm Acetone	2.00	Gasco Affiliates, LLC.	DNJ-ACE-200N-1
0.26% Acetylene	2.00	Gasco Affiliates, LLC.	FBJ-M24-0.25%-1
1.04% Acetylene	2.00	Gasco Affiliates, LLC.	FBJ-M24-1
1.02% Argon	2.00	Gasco Affiliates, LLC.	DBJ-2-1N-1
88.5% Argon	2.00	Gasco Affiliates, LLC.	DBJ-2-90N-1
100 ppm Benzene	2.00	Gasco Affiliates, LLC.	FBJ-21-100-3
15.6% Carbon Dioxide	0.04	NIST Gas Sensing Metrology Group	9-C-44
24.5% Carbon Dioxide	2.00	Gasco Affiliates, LLC.	KBI-35-25-1
1.00% Carbon Dioxide	2.00	Matheson Tri-Gas	9306620888
2.51% Carbon Dioxide	2.00	Roberts Oxygen	1002080917
7.00% Carbon Dioxide	2.00	Roberts Oxygen	1009010318
0.30% Carbon Monoxide	2.00	Roberts Oxygen	1009010318
9.00% Carbon Dioxide	2.00	Praxair Distribution Inc.	304113044702
0.02% Carbon Monoxide	2.00	Matheson Tri-Gas	9306620888
0.11% Carbon Monoxide	2.00	Roberts Oxygen	1002080917
4.00% Carbon Monoxide	2.00	Praxair Distribution Inc.	304113044702
7.81% Carbon Monoxide	0.02	NIST Gas Sensing Metrology Group	??????
0.51% Ethane	2.00	Gasco Affiliates, LLC.	FBJ-62N-0.5-1
1.00% Ethane	2.00	Gasco Affiliates, LLC.	FBJ-152N-1-1%-1
2.55% Ethane	2.00	Gasco Affiliates, LLC.	FBJ-152N-2.5-1
0.51% Ethylene	2.00	Gasco Affiliates, LLC.	FBJ-62N-0.5%-1
1.02% Ethylene	2.00	Gasco Affiliates, LLC.	FBJ-62N-1%-1
2.55% Ethylene	2.00	Gasco Affiliates, LLC.	FBJ-62N-2.5%-1
0.26% Hydrogen	2.00	Gasco Affiliates, LLC.	FBJ-84-0.25-1
0.50% Hydrogen	2.00	Gasco Affiliates, LLC.	KBI-84-0.5-1
1.00% Hydrogen	2.00	Gasco Affiliates, LLC.	KBI-84-1-3
2.00% Hydrogen	2.00	Gasco Affiliates, LLC.	FBJ-84-2-5
4.03% Hydrogen	2.00	Gasco Affiliates, LLC.	FBJ-84-4-2
0.40% Methane	2.00	Gasco Affiliates, LLC.	DBJ-135N-0.4-1
3.95% Methane	2.00	Gasco Affiliates, LLC.	DBJ-135N-4-2
40.8% Methane	2.00	Gasco Affiliates, LLC.	DBJ-135N-40-1
0.50% Oxygen	2.00	Gasco Affiliates, LLC.	DBJ-2-90N-1
1.97% Oxygen	0.01	NIST Gas Sensing Metrology Group	73-D-03
5.02% Oxygen	2.00	Gasco Affiliates, LLC.	DBJ-161-5-5
9.92% Oxygen	0.02	NIST Gas Sensing Metrology Group	72-D-60
10.2% Oxygen	2.00	Gasco Affiliates, LLC.	KBI-161-10-6
20.7% Oxygen	0.04	NIST Gas Sensing Metrology Group	71-D-51
0.42% Propane	2.00	Gasco Affiliates, LLC.	DBJ-176N-0.4-1
39.6% Propane	2.00	Gasco Affiliates, LLC.	DBJ-176N-40-1

B.3 Concentration of Vapors from Bubblers

Liquid material concentrations were calibrated from the ratio of the liquid-vapor pressure to the total pressure injected into the GC/MSD.

$$C_{vap} = \frac{P_{vap}}{P} \quad (\text{B.12})$$

The vapor pressure of any given liquid can be calculated and modified using the bubbler setup shown in Fig. 6:

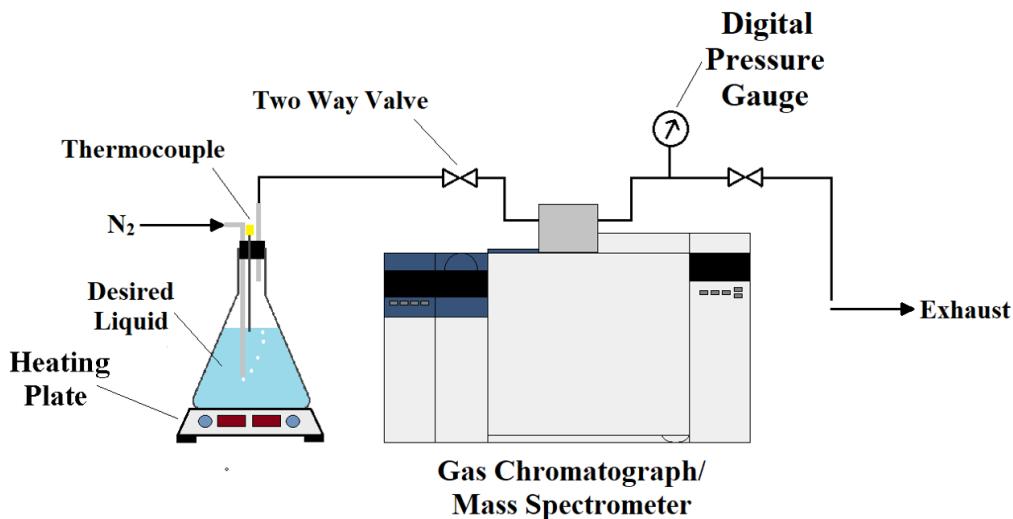


Fig. 6. Flow diagram for bubble calibration system used for liquid materials (acetone, ethanol, methanol, and water)

Nitrogen, acting as a carrier gas, was bubbled at the bottom of a liquid bath which after reaching the liquid surface transport vapor molecules through a heated gas line and into the GC/MSD sample loop. The concentration of the vapor injected into the GC/MSD was calculated from a liquid-vapor pressure correlation provided by DIPPR®.

$$P_{vap} = e^{A + \frac{B}{T} + C \ln T + D T^E} \quad (\text{B.13})$$

In this correlation, P_{vap} is the vapor pressure calculated from the temperature of the liquid bath, T , with the coefficients (A, B, C, D, E) specific to the liquid material. Table 3 lists all coefficients for each calibrated liquid, including the uncertainty of their respective correlations, u_{corr} .

The concentration range of each calibrated liquid typically spanned between 2 % and 50 %. Liquid bath temperatures were controlled using a heating plate positioned underneath

Table 3. Liquid Vapor Pressure Correlation Coefficients for Various Calibrated Liquids

Liquid Material	A	B	C	D	E	Uncertainty(%)
Acetone	69.006	-5599.6	-7.0985	6.2237E-6	2.00	3.00
Ethanol	73.304	-7122.3	-7.1424	2.8853E-6	2.00	1.00
Methanol	82.718	-6904.5	-8.8622	7.4664E-6	2.00	3.00
Water	73.649	-7258.2	-7.3037	4.1653E-6	2.00	0.20

the insulated bubbler. The temperature of the bath, T_b , was measured using a K Type thermocouple placed at the liquid bath's surface. The liquid bath temperature measurements were sampled at 2 Hz for 50 s simultaneously with pressure and temperature measurements of the GC/MSD sample loop. Liquid-vapor calibrations were conducted once the bath a steady-state temperature (approximately 1 hour) and the Nitrogen/vapor gas mixture has swept through the GC/MSD sample loop. Upon injection into the GC/MSD, pressure and temperature measurements of the sample loop are made as previously describe in Appendix B.1.

The uncertainty of the concentration determined using Eq. B.12 was estimated using the law of propagation of uncertainty:

$$u_{C_{vap}} = \sqrt{\left(\frac{\partial C_{vap}}{\partial P} u_P\right)^2 + \left(\frac{\partial C_{vap}}{\partial P_{vap}} u_{P_{vap}}\right)^2} \quad (\text{B.14})$$

The uncertainty of the pressure measured upon injected was calculated from Eq. B.8. The uncertainty of the vapor pressure was found by combining the propagated error of liquid bath temperautre and the uncertainty in the correlation via quadrature:

$$u_{P_{vap}} = \sqrt{\left(\frac{\partial P_{vap}}{\partial T_B} u_{T_B}\right)^2 + u_{corr}^2} \quad (\text{B.15})$$

The Type A evaluation of uncertainty of the liquid bath temperautre readings is determined from the standard error of the temperature, s_{T_B} readings from the sampling period. The Type B evaluation of uncertainty for the liquid bath temperature was the bias error source (1.5°C) in the thermocouple, u_{inst} . The combined uncertainty liquid bath temperature was determined via quadrature:

$$u_{T_B} = \sqrt{u_{inst}^2 + s_{T_B}^2} \quad (\text{B.16})$$

C. Uncertainty Analysis of the Soot Mass Fraction

The local soot mass fraction measurements, M_s made at various heights above the fuel surface in pool fires of different fuels were calculated through a combination of Eq. 2, 3, and 4:

$$M_s = \frac{m_s V_{sl}}{\dot{V} t m_{tot}} \frac{T_\infty}{T_p} \quad (\text{C.1})$$

where m_s is the mass of soot collected on the PTFE filter and gun cleaning patches, \dot{V} is the volumetric flow rate measured by the mass flow controller, V_{sl} is the volume of the sample loop, $\sum n_i \cdot \bar{M}_i$ is the total mass of the gas sample detected in the TCD chromatogram calculated from the summation of the product of the number of moles of a given species and their respective molar mass, T_∞/T_p is the ratio of the internal gas flow temperature readings of the mass flow controller to the temperature of the probe, and t is the total sampling time. The uncertainty of the measured soot mass fraction was estimated using the law of propagation of uncertainty after determining the soot mass fraction:

$$u_{M_s} = \sqrt{\left(\frac{\partial M_s}{\partial m_s} u_{m_s}\right)^2 + \left(\frac{\partial M_s}{\partial \dot{V}} u_{\dot{V}}\right)^2 + \left(\frac{\partial M_s}{\partial V_{sl}} u_{V_{sl}}\right)^2 + \left(\frac{\partial M_s}{\partial m_{tot}} u_{m_{tot}}\right)^2 + \left(\frac{\partial M_s}{\partial T_\infty} u_{T_\infty}\right)^2 + \left(\frac{\partial M_s}{\partial T_p} u_{T_p}\right)^2} \quad (\text{C.2})$$

A coverage factor of 2 was applied to the combined uncertainty to produce a 95 % confidence interval.

C.1 Mass of Soot

The mass of soot was measured from the difference in mass of a dried PTFE filter and dried gun cleaning patches immediately before and 48 hrs after each test. The Type A evaluation of standard uncertainty of the mass of soot, m_s was taken as the standard deviation, s_{m_s} , of the measurements sampled three times before and after each test. The Type B evaluation of Uncertainty was determined from the instrumentation error sources of the scale and was found to be $u_{inst} = 1\%$ of the reading. The combined uncertainty was found via quadrature:

$$u_{m_s} = \sqrt{u_{inst}^2 + s_{m_s}^2} \quad (\text{C.3})$$

C.2 Mass Flow Controller Volumetric Flow Rate

A mass flow controller was used to measure the volumetric flow rate, \dot{V} , within the gas sampling line. The Type A evaluation of standard uncertainty was taken as the standard deviation of the flow measurements sampled at 2 Hz during the gas sampling period which varied from 12 min to 25 min depending on the sampling location within the fire. The Type B evaluation of standard uncertainty was determined from the calibration error, u_{cal} , and the precision error sources at calibration conditions, u_p , defined as 2 ml and 0.8 % of

the reading + 0.2 % of the full scale (2 Lpm), respectively. The combined uncertainty is calculated via quadrature:

$$u_V = \sqrt{u_p^2 + u_{\text{cal}}^2 + s_V^2} \quad (\text{C.4})$$

C.3 GC/MSD Sample Loop Volume

All gas sampling experiments and calibrations were conducted using a 2 ml sampling loop. The Type B evaluation of standard uncertainty of the GC/MSD sample loop volume was assumed to be 1 %.¹

C.4 Total Mass Injected into the GC/MSD

The total mass detected in the TCD chromatogram, m_{tot} , was calculated from the summation of products of the moles of given species and their respective molar mass.

$$m_{tot} = \sum_{n=1}^N n_i \cdot \bar{M}_i \quad (\text{C.5})$$

The uncertainty in the total mass detected was defined as the combined uncertainty of all identified species multiplied by their corresponding molar mass via quadrature:

$$u_{m_{tot}} = \sqrt{\sum_{n=1}^N (s_{n_i} \cdot \bar{M}_i)^2} \quad (\text{C.6})$$

where N is the number of a species identified species in the TCD chromatogram.

C.5 Mass Flow Controller Internal Gas Flow Temperature Reading

The mass flow controller provides an internal gas flow temperature reading that was recorded manually during the gas sampling process. The uncertainty of the temperature reading was determined from the Type B evaluation of standard uncertainty of the mass flow controller temperature measurement defined as 0.75 % of the reading.

C.6 Temperature Reading at the Entrance of the Probe

¹The uncertainty of the sample loop was assumed to be 1 % after contacting the manufacturer.

D. Uncertainty Analysis of Pool Fire Parameters

D.1 Mean Flame Height

D.2 Mass Loss Rate

D.3 Heat Release Rate