Design, construction and validation of a simple, low-cost phi meter

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ABSTRACT

The best correlation between the yields of the major toxicants in fire smoke and the fire condition is obtained by expressing the ventilation in terms of the equivalence ratio, phi. Phi meters allow this fuel-air equivalence ratio to be determined during a large-scale fire test. The original design used a platinum catalyst, a large furnace, and required pure oxygen. This work aimed to make a simple, low-cost device which could monitor the equivalence ratio during a large-scale fire test. The current design produces the same quality of measurement with a much smaller footprint and throughput. Benefits include enhanced portability, reduction in sample gas cleaning and drying requirements and lower cost. The work showed that normal furnace components (alumina and silica) provide suitably catalytic surfaces at 900 °C eliminating the requirement for platinum catalysts and the use of pure oxygen. The ISO/TS 19700 steady state tube furnace (SSTF) was used to validate the phi meter measurements as it can both pre-set and independently quantify the equivalence ratio during a test. Long sample collection times were overcome with a larger sampling pump and effluent being split between the phi meter furnace and the exhaust. It is hoped that this simpler, optimized apparatus will encourage more widespread use and lead to better prediction of smoke toxicity.

1. Introduction

In a light-hearted paper in 1984, Harvard's Professor of Fire Science, Howard Emmons speculated that *smoke toxicity would not be understood until the 23rd century* [1]. Fortunately, in the last 40 years, prediction of smoke toxicity from unwanted fires has progressed from an insoluble problem to a relatively well-defined science.

Four factors, in roughly decreasing order of importance, influence the smoke toxicity for a particular size of fire.

1. The presence of a flame
2. The ventilation condition.
3. The presence of hetero-elements in the fuel, especially nitrogen, chlorine, bromine and phosphorus.
4. The combustion conditions controlling the temperature.

Of these factors, the ventilation condition was the most difficult to relate to toxic product formation. The breakthrough in understanding the factors controlling smoke toxicity came from detailed studies on carbon monoxide yields from burning gas and liquid fuels such as methane and hexane [5]. This led to the ventilation condition being quantified by the fuel/air equivalence ratio in the early 1990s, leading to

a better understanding of the factors affecting smoke toxicity. As part of this effort, Babrauskas [2] developed a phi-meter for direct measurement of equivalence ratio, φ, which quantifies the excess oxygen in the smoke (over-ventilation) and the oxygen requirement of the smoke (under-ventilation), thus sampling and analysis of fire effluent from the smoke plume is sufficient to quantify the ventilation condition.

In an enclosure fire, even with the windows and doors open, the ventilation rate is fixed, and provided there is sufficient fuel, the fire quickly becomes ventilation-controlled. At this stage the yields (masses of toxic products for a given mass of fuel) of carbon monoxide (CO) and hydrogen cyanide (HCN) can increase by factors between 10 and 25, creating a highly toxic fire effluent [3]. It has been established that this small under-ventilated stage of burning is responsible for the majority of fire deaths in the UK [4]. Intriguingly, in the US most fire deaths occur after flashover, away from the room of fire origin: this is believed to result from the popularity of open-plan domestic layouts.

The use of a phi meter allows the equivalence ratio to be recorded during a fire test. It has previously been used in large-scale fire tests to determine the fire condition during experimentation [6]. It facilitates direct scale comparisons with bench-scale methods. The availability of equivalence ratio measurements also allows better understanding of the fire stage(s) during large-scale fire tests. Previous phi meter designs have

used expensive catalysts and had restricted portability due to the large furnace and requirement for pure oxygen. This imposes limitations to the design, as use of an oxygen gas cylinder near a large-scale fire test presents an additional safety concern. Most reported use of phi meters have been based on the original design [2] and shown to work for monitoring the equivalence ratio during large-scale testing, but little had been added to their design and construction.

Two reports of "second generation" phi meters have appeared recently. One was reported by NIST [7]. The new design included quantification of water removed from the sample line, and was validated over a series of fire tests demonstrating its functionality, but as the fire tests did not run at set equivalence ratios, validation was based on the gas yields measured in the tests. The other report [8] came from Canterbury, NZ, which also quantified carbon dioxide in the effluent to improve the precision of the measurement. Both used a large furnace, with catalyst, and pure oxygen.

1.1. Effect of fire stages on toxic product yield

The condition of a fire has been described in terms of fire stages in ISO 19706 [9]. After ignition, a fire will typically start well-ventilated, with combustion occurring in excess oxygen favouring products of complete combustion, such as carbon dioxide (CO_2) and water. In an enclosure with fixed ventilation (such as a room with window or door opening), as the fire grows, the availability of oxygen reduces, and the fire transitions to under-ventilated flaming. During under-ventilated flaming, products of incomplete combustion, such as CO and HCN, as well as partially oxidized hydrocarbons and soot, are released causing a sharp increase in the toxicity of the smoke.

The ventilation condition of each flaming fire stage can be characterized by the fuel-to-air ratio, or equivalence ratio, φ, of a fire. φ is defined as the actual fuel-to-air ratio divided by the stoichiometric fuel-to-air ratio (Equation (1)).

$$\varphi = \frac{actual\ fuel - to - air\ ratio}{stoichiometric\ fuel - to - air\ ratio} \quad (1)$$

Typical values of equivalence ratio at defined fire conditions are shown in Table 1.

The equivalence ratio has a direct effect on the smoke toxicity of a fire. As the availability of oxygen decreases, an increase in products of incomplete combustion, such as CO and HCN, occurs. This is observed on both a bench- and large-scale. For example, the yields of CO from burning polypropylene [10] (Fig. 1) show a strong dependence on equivalence ratio. The results are consistent between bench-scale [11], tested in the steady state tube furnace, (SSTF) (ISO/TS 19700 [12]) and large-scale from fires in an ISO 9705 [13] room [14].

Fig. 2 shows a comparison [12] of the HCN yields from burning PA 6.6 in the steady state tube furnace with those from the same series of ISO 9705 room experiments [15]. This shows a dramatic increase associated with under-ventilation in relation to the other major toxic

Table 1

Fire stages and their corresponding temperatures, equivalence ratios and CO/CO_2 ratios, adapted from ISO 19706 [9].

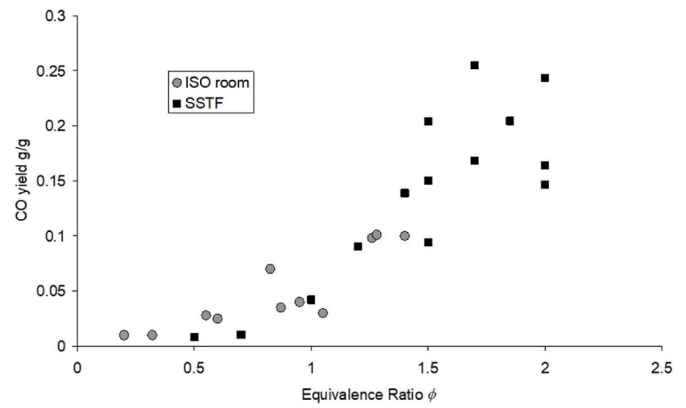| Fire Stage	Max temperature/°C		Equivalence ratio	CO/CO_2 ratio
	Fuel	Smoke		
Non-flaming				
1a. Self-sustained oxidative pyrolysis	450–800	25–85	–	0.1–1
2. Well-ventilated flaming	350–650	50–500	0.5–0.7	<0.05
3. Under-ventilated flaming				
3a. Early under-ventilated flaming	300–600	50–500	1.5–2	0.2–0.4
3b. Post-flashover	350–650	>600	1.5–2	0.1–0.4

Fig. 1. Comparison of CO yield for polypropylene from steady state tube furnace with ISO room as a function of equivalence ratio, φ [12].
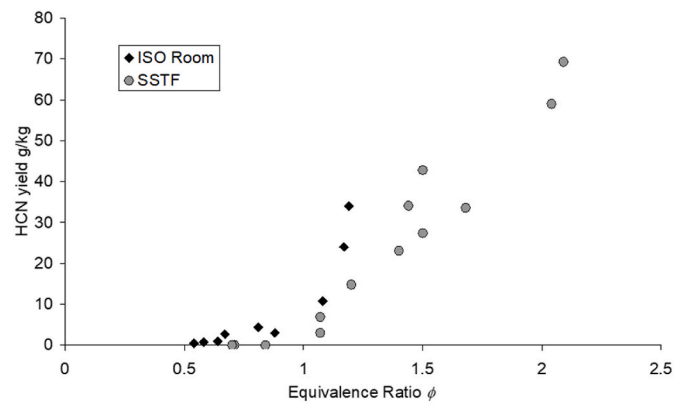

Fig. 2. Comparison of HCN yield for polyamide 6.6 from steady state tube furnace with ISO room as a function of equivalence ratio, φ [12].

product, HCN, in both the bench and large scales, and a clear dependence on equivalence ratio.

1.2. Candidate furnaces for simplified phi meter

Two working furnaces for gas phase oxidation of fire effluents were used as prototypes for the simplified phi meter design: the secondary oxidizer of the SSTF; and the main oxidizer of the microscale combustion calorimeter (MCC).

1.2.1. SSTF with secondary oxidizer

The steady state tube furnace (SSTF), Fig. 3, forces combustion at a fixed rate, independent of the material's flammability. By varying the primary air supply, the ventilation condition and hence φ can be controlled and preset. It may be set up to burn samples at a particular equivalence ratio. It does so by feeding the sample and air into a tube furnace at fixed rates, so that the flame front is held stationary relative to the furnace. This enables it to provide reliable data on the toxic product yields as a function of equivalence ratio. Unlike a flammability test where a sample's chemistry dictates the rate of burning, in the steady state tube furnace all materials are burned at a fixed rate. Samples are fed into the furnace in a silica boat typically travelling at ~35 mm min^{-1}. By varying the primary air flow, different fire conditions are created at known equivalence ratios.

The products of incomplete combustion can be quantified using an additional secondary oxidizer which reheats the fire effluent in the presence of secondary air, converting the products of incomplete combustion to CO_2 and water. The secondary oxidizer furnace is typically set to 900 °C with quartz wool inside to ensure good mixing. The additional
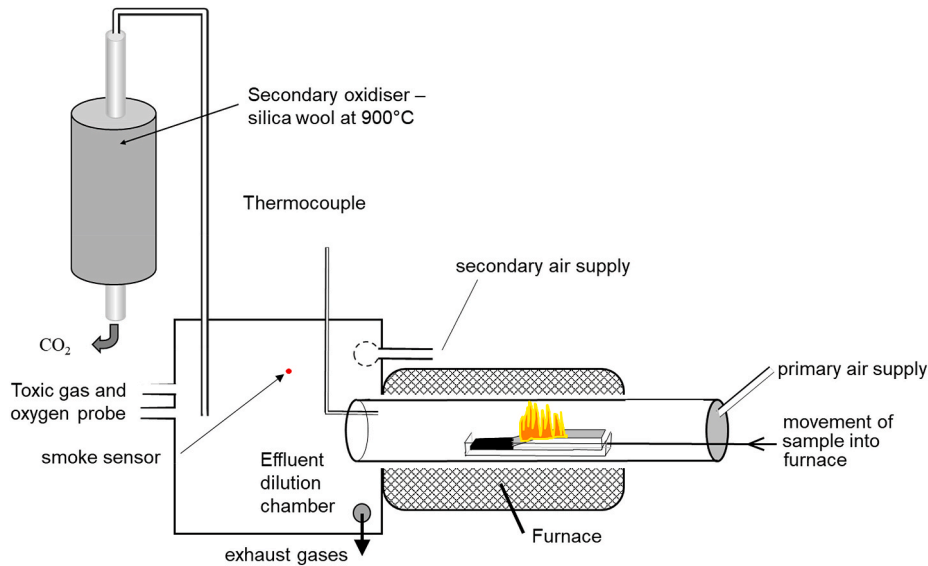
Fig. 3. Diagram of apparatus of ISO/TS 19700. The secondary oxidizer (inside dotted line) has been used to optimize furnace design.

data allow carbon balances, based on complete conversion of fuel to CO_2, to be made, and also allow the equivalence ratio to be determined for samples of unknown composition.

The equivalence ratio from the SSTF may be calculated from the oxygen concentration in the secondary oxidizer, and the primary and secondary air flows as shown in Equation (2).

$$\varphi = 1 + \frac{[O_2]_a \dot{V}_{a_s} - [O_2]_{sec} \dot{V}_T}{[O_2]_a \dot{V}_{a_p}} \qquad (2)$$

Where $[O_2]_a$ = oxygen concentration of air (=20.95%)

$[O_2]_{sec}$ = oxygen concentration of effluent from secondary oxidizer

$\dot{V}_{a_s}$ = volume flow of secondary air into mixing chamber

$\dot{V}_T$ = total volume flow into mixing chamber

$\dot{V}_{a_p}$ = volume flow of primary air to main furnace.

1.2.2. MCC oxidizer

The microscale combustion calorimeter [16,17] (MCC) was developed at the fire laboratories of the Federal Aviation Administration in the U.S. It is widely used for the assessment of fire retardant polymers. It measures heat release from small samples (2–3 mg) of polymeric materials by measuring the oxygen consumption of the products evolved from the polymer during programmed heating. The components of the apparatus are shown schematically in Fig. 4. As the sample is pyrolyzed, volatile products are released, which rise into the

Combustor – a chamber where volatiles mix with oxygen at 900 °C to ensure complete conversion to CO_2 and water. The compactness and established flows required for complete combustion made the MCC oxidizer the preferred candidate furnace for our phi meter.

The aim of this research was to design and construct a fully functioning, low-cost portable phi meter for use in large-scale fire testing. This was based around the MCC combustor furnace and operating parameters, using the SSTF secondary oxidizer as the model for equivalence ratio determination.

2. Materials and methods

2.1. Principle of operation

A schematic showing flows and measurements for our simplified phi meter is shown in Fig. 5.
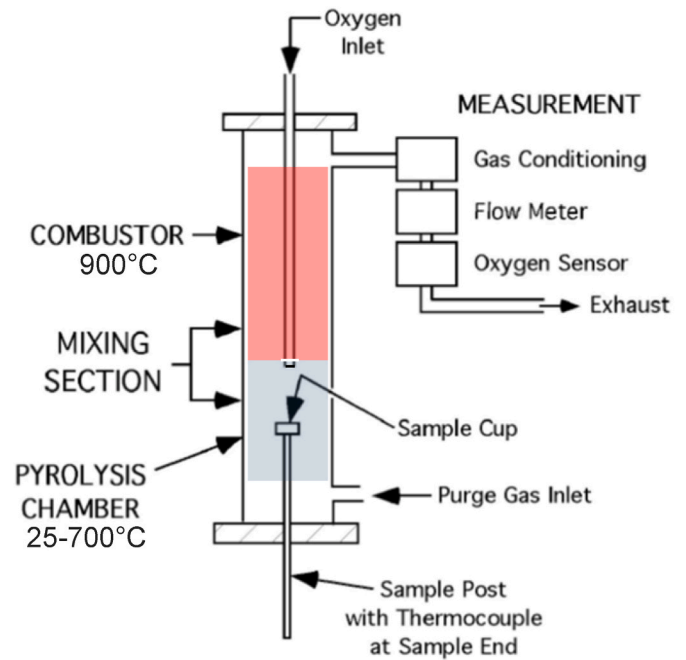

Fig. 4. Schematic of microscale combustion calorimeter.

It is based around the MCC furnace. The phi meter calculation to determine the measured equivalence ratio φ. was derived from the use of three measurements; the total air flow in the system ($\dot{V}_T$ in mL min^{-1}), the air flow to the oxidizer ($\dot{V}_a$ in mL min^{-1}), and the % concentration of oxygen in the oxidizer stream ($[O_2]_{final}$). It also used the concentration of oxygen in air ($[O_2]_a$) equal to 20.95%, and the oxygen concentration in the fire (smoke) effluent ($[O_2]_s$).

The smoke flow through the oxidizer, $\dot{V}_s$, is estimated using equation (1). It is an approximation because some of the hydrocarbon volume will be converted to carbon dioxide (which will remain), and water, which will be removed by the drying tube. However, 80% of the volume is nitrogen so any difference will be small. In the extreme case where all the oxygen is consumed, and the CO_2/CO ratio is 10, for a hydrocarbon polymer $((CH_2)_n)$ fire, the $[CO_2] = 12.6\%$, the $[H_2O(g)] = 7\%$ and the $CO = 1.4\%$. Removing water reduces the effluent volume to 93/100 of
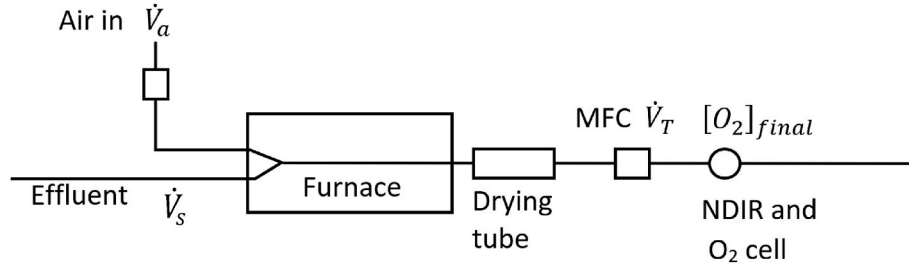
Fig. 5. Schematic flow diagram for our simplified phi meter (NDIR = Non-dispersive Infrared analyser; MFC = Mass Flow Controller).

the original, so the measured CO would be 0.93 x 1.4 = 1.3%

$$\dot{V}_s = \dot{V}_T - \dot{V}_a \qquad (3)$$

As the amount of oxygen required by the unburnt components in the smoke is equal to the oxygen consumption in the oxidizer, it can therefore be calculated using equation (4).

$$\text{Oxygen requirement of smoke} = \left(\frac{[O_2]_a}{100}\,\dot{V}_a\right) + \left(\frac{[O_2]_s}{100}\,\dot{V}_s\right) - \left(\frac{[O_2]_{final}}{100}\,\dot{V}_T\right) \qquad (4)$$

The equivalence ratio can therefore be calculated as

$$\varphi = 1 - \frac{[O_2]_s}{[O_2]_a} + \frac{\text{Oxygen requirement of smoke}}{\text{Oxygen missing from smoke}} \qquad (5)$$

The "oxygen missing from smoke" is the amount of oxygen which would be present if that volume of smoke was actually air. Equations (4) and (5) can be combined, as shown in equation (6) and simplified via equation (7), to produce two valid equations, 8 and 9, suitable for calculating the equivalence ratio using the phi meter.

$$\varphi = 1 - \frac{[O_2]_s/100}{[O_2]_a/100} + \left(\frac{\frac{[O_2]_a}{100}\dot{V}_a + \frac{[O_2]_s}{100}\dot{V}_s - \frac{[O_2]_{final}}{100}\dot{V}_T}{\frac{[O_2]_a}{100}\dot{V}_s}\right) \qquad (6)$$

$$\varphi = 1 - \frac{[O_2]_s\dot{V}_s}{[O_2]_a\dot{V}_s} + \left(\frac{[O_2]_a\dot{V}_a + [O_2]_s\dot{V}_s - [O_2]_{final}\dot{V}_T}{[O_2]_a\dot{V}_s}\right) \qquad (7)$$

$$\varphi = 1 + \left(\frac{[O_2]_a\dot{V}_a - [O_2]_{final}\dot{V}_T}{[O_2]_a(\dot{V}_T - \dot{V}_a)}\right) \qquad (8)$$

$$\varphi = 1 + \left(\frac{20.95\,\dot{V}_a - [O_2]_{final}\dot{V}_T}{20.95\,(\dot{V}_T - \dot{V}_a)}\right) \qquad (9)$$

2.2. Oxidizer design and specification

2.2.1. MCC

To find the optimal operational temperature of the phi meter, a series of experiments were conducted using a microscale combustion calorimetry (MCC), based on the FAA MCC design. Optimization experiments were undertaken at a range of furnace temperatures from 750 °C to 1000 °C (the maximum design temperature of the furnace), to study the products of combustion and measure the equivalence ratio. Polystyrene pellets (clear, food-grade, U.S. Plastic Corp.) were pyrolyzed at 1 °C min^{-1}, at a series of increasing oxidizer temperatures. A non-dispersive infrared (NDIR) sensor (Lumasense, Germany) was connected to the exhaust line of the MCC to monitor CO and CO_2 concentrations. NDIR was chosen as it has a working range of 0–4.45% for CO, and 0–4.8% for CO_2.

2.2.2. Secondary oxidizer on SSTF

The secondary furnace on the SSTF was dimensionally closer to the furnaces on the two NIST and the New Zealand phi meter designs, so was

also used in the preliminary furnace investigation. A sampling line was connected to the mixing chamber of the SSTF. The effluent was filtered on a pre-weighed dry filter before passing through a furnace set to 900 °C. The oxidized effluent then flows to a pump (Charles Austen, UK) at 1 L min^{-1} before flowing through the NDIR, continuously monitoring CO and CO_2, to a paramagnetic oxygen analyser (Servomex), and finally to an exhaust line.

The furnace temperature was varied from 750 °C to 900 °C to identify the temperatures necessary to convert all products of incomplete combustion to CO_2 and water. This enabled the operating temperature range of the phi meter to be determined. This was also used to establish whether a metal catalyst was necessary for complete oxidation.

2.3. Controlled generation of fire effluent at known equivalence ratio

The new design of phi meter was based on a hybrid of the sampling system for the SSTF and the furnace and gas supply geometry of the MCC. The SSTF's secondary oxidizer works via the same principles as the phi meter to provide measurement of equivalence ratio for an SSTF test, using the secondary air supplied to the mixing chamber, but without a metal catalyst in the furnace. It was therefore used to evaluate the phi meter constructed in this research.

A series of tests were conducted using 2 mm thick PMMA sheet, (Lucite International Ltd, UK) tested at 650 °C in well-ventilated conditions to compare the CO_2 yields measured by the secondary oxidizer of the tube furnace and the yields measured by the phi meter. A second series of tests were conducted. The primary air-flows selected for these tests were calculated to give an equivalence ratio of 1.5, to ensure plenty of products of incomplete combustion.

The SSTF was chosen because it is one of few bench-scale apparatuses available that is able to run tests at pre-defined equivalence ratios. The secondary furnace on the SSTF apparatus was used to determine the equivalence ratio during a test, and so was deemed the best means of validating the phi meter's functionality.

2.4. Construction of simplified phi meter

2.4.1. Furnace design

To enhance the design, the furnace size was reduced using a combustor with a similar design to that in the MCC, allowing much smaller flows. As the MCC furnace operates at a maximum flow of 100 mL min^{-1}, the phi meter was initially run with 50 mL min^{-1} fresh air and 50 mL min^{-1} of fire effluent. The furnace component of the phi meter was designed and constructed by Concept Equipment, UK.

2.4.2. Gas flow through phi meter setup

The gas analysis system created for the phi meter, shown in Fig. 7 was housed in a 30 x 30 × 25 cm box (Farnell Components, UK). The gas sampling system was designed so that effluent could be taken from the sampling location through a stainless steel tube (with 6.8 mm internal diameter) and drawn through a glass wool filter at 1.5 L min^{-1}. This reduces the time delay in sampling. The effluent then passed through a glass splitter, one line went to the exhaust, the other drew a known

quantity of effluent through the phi meter furnace. The effluent was drawn through the furnace system using a peristaltic pump (Verdeflex AUR 255 0120 RS1) (RS Components) connected to a mass flow controller (MFC) (Omega Engineering, UK). The flow in both mass flow controllers was set and controlled by a program written on a Raspberry Pi 3B+ (RS Components).

An oxidizer gas line was set up drawing a known volume of clean air using a peristaltic pump and controlled using an MFC. The clean air was drawn into an alumina tube to mix with the fire effluent (Fig. 8).

The gas mixture passes through the furnace at 900 °C, where the products of incomplete combustion are oxidized. The fully oxidized gas mixture then passes through a drying tube, filled with Drierite (Sigma Aldrich), held in place with glass wool plugs. After passing through a second MFC and peristaltic pump, the effluent was drawn through an NDIR to monitor CO and CO_2 concentrations, and an electrochemical oxygen cell (Lumasense) to the exhaust. All components were connected to a Raspberry Pi 3B + which was programmed as a datalogger to record the signal output from the NDIR and O_2 electrochemical cells. The Raspberry Pi had additional software to allow for remote control and data viewing on a laptop via a wireless connection to improve operator safety during large-scale fire tests. The furnace and analyser unit are shown in Fig. 6.

2.4.3. Control and data flow of phi meter

The signal and control lines are shown in red in Fig. 7. A pressure transducer was connected via two small glass T-pieces around each MFC to ensure correct pressures on either side. The signal was logged by the Raspberry Pi allowing adjustment to the MFC in the event of a partial blockage. Data from the NDIR and O_2 cell were logged by Raspberry Pi.

2.5. System testing

Before experimental validation tests, the analytical system was leak checked by connecting the sampling line to a Tedlar gas bag containing nitrogen (N_2). The mass flow controllers were set to four different air:N_2 ratios, 100:0, 75:25, 50:50, and 25:75 and the oxygen measurement was logged to test if the system was working correctly. The oxygen concentration was recorded and agreed with the pre-set ratios.

2.6. Validation

Validation tests were conducted using the ISO/TS 19700 steady state tube furnace with secondary oxidizer, and the phi meter. These comprised a series of tests at pre-set equivalence ratios, where the pre-set, secondary oxidizer (from the SSTF), and phi meter determinations of equivalence ratio were compared. Strips of PMMA were fed into the SSTF at a fixed rate with separate runs using different primary air flows to cover a range of equivalence ratios. The first series of tests looked at the well-ventilated flaming condition, while varying the flows in the phi meter. The second series of tests looked at fire stages 2, 3a and 3 b (Table 1). PMMA was chosen as it leaves no residue, so the equivalence ratio could be determined unambiguously.

Fig. 6. Photograph of Phi meter furnace and analyser unit.

3. Results

3.1. MCC preliminary tests

The CO and CO_2 concentrations from testing polystyrene in the MCC at various furnace temperatures are shown in Fig. 9.

At furnace temperatures above 800 °C, CO concentrations became negligibly small at around 50 ppm (50 mL L^{-1}). The CO_2 was observed to be the highest when the furnace temperature was set to 950 °C, but falls away rapidly above this temperature. Thermodynamically, CO is the favored product based on its greater entropy at 950 °C, but after passing through the furnace the gases will still be reactive as they cool, increasing the CO_2 concentration. As a result of the sharp change above 950 °C, a temperature of 900 °C was chosen for operating the phi meter.

3.2. SSTF secondary furnace

The steady state tube furnace used in this research had a secondary furnace, loosely filled with quartz wool. Prior to use, tests were conducted both with and without quartz wool inside the tube. No differences were found between data sets and so the use of quartz wool was deemed unnecessary. The presence of quartz wool was believed to aid mixing of the gases within the furnace, but at a flow of 1 L min^{-1} complete combustion was evident, indicating that sufficient mixing occurs, so the quartz wool is unnecessary.

In the SSTF experiments it was found that secondary furnace temperatures above 800 °C produced negligible amounts of CO. CO_2 yields are highest at temperatures of 800 °C and above, suggesting all products of incomplete combustion have fully oxidized, after passing through the furnace above this temperature.

3.3. Validation of SSTF phi measurement

The phi meter was attached to the mixing chamber of the SSTF. PMMA sheet was cut into strips of 800 mm, weighing approximately 20 g. It was burned at 650 °C in the SSTF, varying the primary air flow for each test, within a narrow range to replicate well-ventilated flaming ($0.25 < \varphi < 0.5$), to investigate the correlation between $\varphi_{sec\text{-}SSTF}$ and $\varphi_{phi\text{-}meter}$. Initially the phi meter was set up using a flow ratio of 50 mL min^{-1} fire effluent with 50 mL min^{-1} fresh air into the phi meter ($\dot{V}_s$ to $\dot{V}_a$). Secondary testing was conducted using a flow ratio of 75 mL min^{-1} effluent with 25 mL min^{-1} fresh air. The data obtained are shown in Table 2. These show the effect of the two parameters ($\dot{V}_s$ and $\dot{V}_a$) used to set up the phi meter. Consistent, repeatable results are obtained when and are equal, but not in test 6, when the effluent flow is too high. At equivalence ratios around 0.5, a 1:1 ratio ($\dot{V}_s : \dot{V}_a$) of air to effluent produced data showing very good agreement with that obtained from the SSTF.

Initial tests showed that the equivalence ratio was greatly underestimated when using a flow ratio of 3:1 air to effluent, presumably because there was not enough secondary air for complete oxidation in the phi meter furnace. Tests conducted using a 1:1 ratio showed good agreement, within 5%, with the single exception of the test 1. Well-ventilated tests conducted at equivalence ratios below 0.5 showed poorer agreement than the higher equivalence ratios tests, but were still reflective of the data obtained from the SSTF. At equivalence ratios around 0.5, the phi meter showed good agreement, with the data being representative of the values measured using the SSTF.

A second set of experiments was conducted using PMMA. This time, the air flows used on the SSTF were set to create equivalence ratios of 0.5 and 1.5 to check the response of the phi meter to conditions 2, 3a and 3 b (Table 1) including to under-ventilated flaming. Tests were run in duplicate, with data shown in Table 3.

In most cases, the phi meter measured equivalence ratios within ±0.05, although in one instance, the deviation was ±0.15. Since the
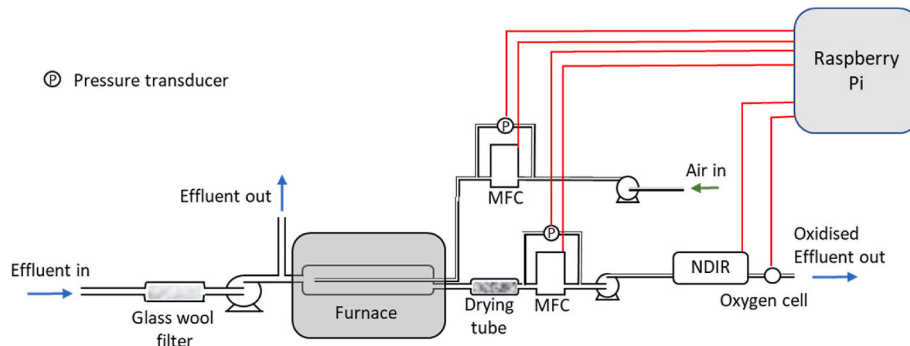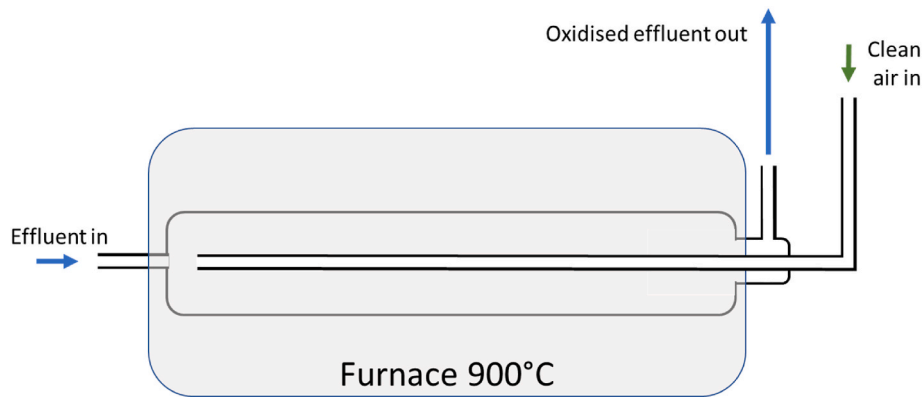
Fig. 7. Phi meter schematic.

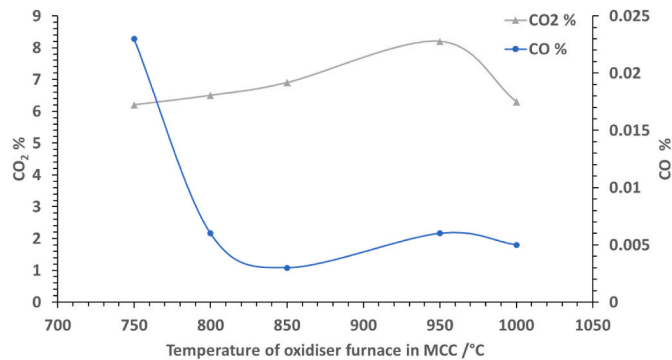**Fig. 8.** Schematic detail of air inlet and outlet.

Fig. 9. CO and CO_2 concentrations contained in the MCC effluent from polystyrene as a function of furnace temperature.

Table 2
A comparison of the data obtained from the SSTF ($\varphi_{\text{sec-SSTF}}$) and phi meter ($\varphi_{\text{phi-meter}}$) at varying flow ratios and equivalence ratios using PMMA.

Material	SSTF		Phi meter		
	Test number	$\varphi_{\text{sec-SSTF}}$	Set flow rate		$\varphi_{\text{phi-meter}}$
			Effluent flow mL min^{-1} $\dot{V}_s$	Fresh air flow mL min^{-1} $\dot{V}_a$	
PMMA	1	0.36	0.5	0.5	0.32
	2	0.24	0.5	0.5	0.25
	3	0.45	0.5	0.5	0.43
	4	0.50	0.5	0.5	0.52
	5	0.49	0.5	0.5	0.50
	6	0.35	0.75	0.25	0.20

Table 3
Validation of the phi meter using the SSTF at set equivalence ratios set for well-ventilated and under-ventilated flaming at 650 °C and 850 °C using a 1:1 ratio of fire effluent to fresh air in the phi meter.

	Fire Stage	Furnace temperature/°C	Equivalence ratio		
			φ_{preset}	$\varphi_{\text{sec-SSTF}}$	$\varphi_{\text{phi-meter}}$
PMMA	2	650	0.5	0.35	0.4
	3a	650	1.5	1.40	1.45
	3 b	850	1.5	1.45	1.47

important parameter is the extent of under-ventilation (e.g. whether $\varphi < 0.7$ or $\varphi > 1.5$), these errors will not have a significant impact on the correlation to toxic product yield. The tests showed the phi meter produced valid data that correlated with the measured equivalence ratio using the SSTF.

The final air flows for operating the phi meter were chosen to be 50 mL min^{-1} fire effluent with 50 mL min^{-1} fresh air, producing equivalence ratios closest to those obtained in the SSTF. However, more under-ventilated fire effluents could have a greater oxygen requirement, potentially necessitating a 25 mL min^{-1} effluent flow and a 75 mL min^{-1} air flow. To validate this assessment, a further series of tests were conducted using PMMA to compare the equivalence ratio measured using the phi meter and the value measured using the SSTF when testing PMMA in the SSTF. This is shown in Fig. 10. The additional experiments were run in duplicate, and the data shown is an average of the tests conducted.

During tests conducted at equivalence ratios below 0.5, φphi-meter values were more representative of the φsec-SSTF when using a flow ratio of 50 mL min-1 air to 50 mL min-1 effluent. When using the flow ratio of 25 mL min-1 effluent to 75 mL min-1 air, the phi meter typically under-predicted the equivalence ratio. This was likely due to the excess
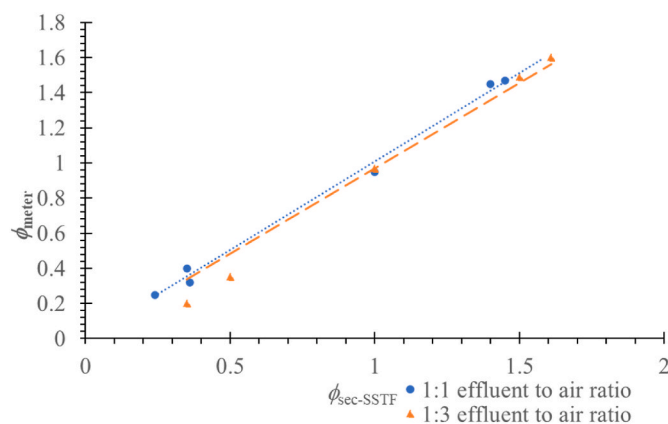
Fig. 10. Comparison of the equivalence ratio measured using the phi meter and SSTF when testing PMMA at a range of equivalence ratios in the SSTF using different air to effluent ratios in the phi meter.

air in the system. At an equivalence ratio around 1.5, the 50 mL min-1 air to 50 mL min-1 the phi meter typically under-predicted the equivalence ratio, whereas at 25 mL min-1 effluent to 75 mL min-1 was more representative of SSTF measured values. At equivalence ratios of 1.4–1.5, both the flow ratios were able to measure values reflective of those measured in the SSTF. This is probably due to the additional oxygen being almost completely consumed.

At higher equivalence ratios (>1.5), the 25 mL min^{-1} effluent to 75 mL min^{-1} air combination produced data that was representative of that measured in the SSTF, suggesting that when testing very under-ventilated fires the 1:3 effluent-to-air ratio should be used. The data show that at equivalence ratios of around 1.5 and below, both flow rates are suitable for measurement of equivalence ratio. Four higher equivalent ratios, pure oxygen, from a Tedlar bag could also be used.

3.4. Enhanced response time

Typically, the phi meter would be 3 m away from the sampling point, connected using 8 mm diameter stainless steel tube of wall thickness 0.6 mm. This gives a volume of 109 mL. Using the phi meter pump speed of 50 mL min^{-1} this would give a 2 min delay. Using the 1.5 L min^{-1} pump with a splitter decreases the delay to 4.5 s.

4. Conclusions

The phi meter designed and constructed in this work has been validated against the SSTF at pre-set equivalence ratios and has been proven to work effectively on a bench-scale. The additional research and design process conducted has allowed for the creation of a more compact and portable phi meter. The original designs for the phi meter used a significantly bigger furnace with a platinum catalyst and various gas and water traps, and pure oxygen to mix with the fire effluent.

The operating conditions for the current design were identified through a series of microscale and bench-scale experiments.

By using a smaller furnace with low flows, the system did not become blocked, and water removal was easy. Additional control over the effluent-to-air ratio was also obtained using peristaltic pumps with high precision, low flow rate mass flow controllers. However, it was necessary to minimize the time delay caused by the low system flow, with an additional 1.5 L min^{-1} pump, connected to the sampling line, which was then split between an exhaust line and the sampling line to the phi meter, reducing the response time from around 2 min to 5 s.

The low system flow could also enable the use of an atmospheric pressure Tedlar bag filled with O_2 for higher equivalence ratios. A 30 L Tedlar bag could run continuously for 20 h at an oxidizer flow of 25 mL min^{-1}. The phi meter is suitable for determining the equivalence ratio of

all flaming fires involving typical materials (hydrocarbons, polymers etc), provided the plume can be sampled in a representative manner. For highly under-ventilated fires, the modification of an oxygen-filled Tedlar bag may be required.

The phi meter made and used in this research did not require the use of a metal catalyst. The furnace design was based on the existing MCC furnace and operating conditions based on the secondary oxidizer furnace used in the SSTF. The preliminary tests were conducted to study the effects of varying furnace temperatures on combustion efficiency. It was found that at temperatures above 800 °C, negligible CO was formed, and CO_2 formation was favored. The operational temperature of the furnace was chosen to be 900 °C.

The phi meter was constructed, calibrated and then validated alongside the SSTF. The SSTF was chosen as it can both preset and independently quantify the equivalence ratio. We are not aware of other bench-scale methods with this capability. As the data were in agreement with the data obtained on the SSTF without a catalyst, no catalyst was added to the phi meter furnace. The NDIR also allowed for CO and CO_2 formation to be monitored.

It is hoped that this cheaper, optimized apparatus will encourage more widespread use and better prediction of smoke toxicity. The main problem with phi meter measurements is representative sampling. Predicting the position for the sample tube to be representative of the fire plume is not an exact science. The design challenge is to achieve greater accuracy in phi measurement, rather than higher precision through reducing errors in effluent volume by monitoring CO_2 and water.

Data availability

Data will be made available on request.

References

[1] H.W. Emmons, The further history of fire science, Combust. Sci. Technol. 40 (1–4) (1984) 167–174, https://doi.org/10.1080/00102208408923804.

[2] V. Babrauskas, W.J. Parker, G. Mulholland, W.H. Twilley, The phi meter: a simple, fuel-independent instrument for monitoring combustion equivalence ratio, Rev. Sci. Instrum. 65 (7) (1994) 2367–2375, https://doi.org/10.1063/1.1144690.

[3] T.R. Hull, A.A. Stec, K. Lebek, D. Price, Factors affecting the combustion toxicity of polymeric materials, Polym. Degrad. Stabil. 92 (12) (2007) 2239–2246, https://doi.org/10.1016/j.polymdegradstab.2007.03.032.

[4] Fire Statistics, England 2021 and preceding UK editions, Home Office, London, https://www.gov.uk/government/collections/fire-statistics.

[5] W.M. Pitts, The global equivalence ratio concept and the formation mechanisms of carbon monoxide in enclosure fires, Prog. Energy Combust. Sci. 21 (1995) 197–237, https://doi.org/10.1016/0360-1285(95)00004-2.

[6] A. Lonnermark, P. Blomqvist, M. Mansson, H. Persson, TOXFIRE-fire Characteristics and Smoke Gas Analysis in Under-ventilated Large-Scale Combustion Experiments, SP Report, 1996, pp. 1–129.

[7] R. Falkenstein-Smith, T. Cleary, NIST Technical note 2184: The design and performance of a second-generation phi meter, 2022, https://doi.org/10.6028/NIST.TN.2184.

[8] S. Rasoulipour, A. Parkes, C. Fleischmann, Enhancing the phi-meter by incorporating carbon dioxide measurement, Fire Saf. J. 129 (2022), https://doi.org/10.1016/j.firesaf.2022.103558. art. no. 103558.

[9] ISO 19706, Guidelines For Assessing the Fire Threat to People, ISO, Geneva, 2011.

[10] T.R. Hull, Bench-scale generation of fire effluents, in: A. Stec, R. Hull (Eds.), Fire Toxicity, 2010, pp. 424–460, https://doi.org/10.1533/9781845698072. Woodhead/Elsevier.

[11] T.R. Hull, K. Lebek, A.A. Stec, K.T. Paul, D. Price, Bench-scale assessment of fire toxicity, in: B. Schartel (Ed.), Advances in the Flame Retardancy of Polymeric Materials: Current Perspectives Presented at FRPM'05, p2vols. 35–248, Herstellung und Verlag, Norderstedt, 2007.

[12] ISO/TS 19700, Controlled Equivalence Ratio Method for the Determination of Hazardous Components of Fire Effluents — Steady-State Tube Furnace, ISO, Geneva, 2016.

[13] ISO 9705-1, Reaction to Fire Tests — Room Corner Test for Wall and Ceiling Lining Products — Part 1: Test Method for a Small Room Configuration, ISO, Geneva, 2016.

[14] P. Blomqvist, A. Lonnermark, Characterization of the combustion products in large-scale fire tests: comparison of three experimental configurations, Fire Mater. 25 (2) (2001) 71–81, https://doi.org/10.1002/fam.761.

[15] B. Andersson, F. Markert, G. Holmstedt, Combustion products generated by hetero-organic fuels on four different fire test scales, Fire Saf. J. 40 (5) (2005) 439–465, https://doi.org/10.1016/j.firesaf.2005.03.002.

[16] N. Walters Richard, E. Lyon Richard, Microscale combustion calorimeter for determining flammability parameters of materials, Int. SAMPE Symp. Exhib. 42 (2) (1997) 1335–1344.

[17] ASTM D 7309-07 Standard Test Method for Determining Flammability Characteristics of Plastics and Other Solid Materials Using Microscale Combustion Calorimetry, ASTM, Conshohocken, PA.