



Analysis of trace contaminants in hot gas streams using time-weighted average solid-phase microextraction: Pilot-scale validation



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HIGHLIGHTS

- TWA-SPME method (retracted fiber) was developed for high temperature process gases.
- All major tars (benzene, toluene, styrene and indene) were quantified.
- Pilot-scale gasifier was used for method comparison and validation.

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ABSTRACT

A new method was developed for collecting, identifying and quantifying contaminants in hot process gas streams using time-weighted average (TWA) passive sampling with retracted solid-phase microextraction (SPME) and gas chromatography. The previous lab scale proof-of-concept with benzene was expanded to include the remaining major tar compounds of interest in syngas: toluene, styrene, indene, and naphthalene. The new method was tested on high T (≥ 100 °C) process gas from a pilot-scale fluidized bed gasifier feeding switchgrass and compared side-by-side with conventional impingers-based method. Fourteen additional compounds were identified, representing 40–60% improvement over the conventional method's detection capacity. Differences between the two methods were 1–20% and as much as 40–100% depending on the sampling location. Compared to the inconsistent conventional method, the SPME-TWA offered a simplified, solvent-free approach capable of drastically reducing sampling and sample preparation time and improving analytical reliability. The improved sensitivity of the new method enabled identification and quantification of VOCs beyond the capability of the conventional approaches, reaching concentrations in the ppb range (low mg/m^3). RSDs associated with the TWA-SPME were <10%, with most lab-based trials yielding <2%. Calibrations were performed down to the lowest expected values of tar concentrations in ppb ranges (low $\text{mg}/\text{N m}^3$, with successful measurement of tar concentrations at times >4000 ppm (up to $10 \text{ g}/\text{N m}^3$). The new method can be a valid alternative to the conventional method for light tar quantification under certain conditions. The opportunity also exists to exploit TWA-SPME for process gas streams analysis e.g., pyrolysis vapors and combustion exhaust.

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1. Introduction

Thermochemical processing is the application of heat and catalysts to break apart solid carbonaceous materials to produce heat, power, fuels, and chemicals [1]. Many thermochemical processes create a vapor stream as either a direct or intermittent product.

These vapor phases must be analyzed to determine product purity and process efficiency. However, many conventional methods of analysis require substantial time and material investment. Developing an alternative means of analysis using fewer steps and less material (i.e. solvents), while maintaining or improving levels of detection and quantification are highly desirable.

1.1. Solid phase microextraction

Solid-phase microextraction (SPME) has been developed to address these issues by combining sampling and sample

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preparation into a single step [2]. Volatile analytes are collected on a thin sorbent coating the tip of a fused-silica or metal alloy fiber. This fiber can be retracted into protective syringe-like needle housing. The SPME-based samples can then be transferred and introduced into a GC or LC coupled with a FID, MS or other detector [3–5].

Unlike conventional SPME in which the fiber is exposed to the sampling environment, time-weighted average (TWA) sampling keeps the fiber coating retracted a known distance (δ) within the needle opening [6]. Analytes diffuse from the needle opening into the retracted fiber and are not subject to variable extraction rates and boundary layer conditions that can be associated with sampling onto exposed SPME fiber. Fick's first law of diffusion is used to describe this extraction and estimate the TWA concentration of analytes using their molecular diffusion coefficient (D_g), the retraction depth (δ), sampling time (t), and the cross-sectional area (A) of the SPME needle. This protects the fiber coating (e.g., from particulates in fast moving gas) while enabling sampling in a variety of conditions by simply varying the (δ) and (t) at first order sampling rates. Properly designed TWA-SPME sampling maintains zero-sink sorption, and minimizes the effects of competitive adsorption onto the SPME coating. Similar to work by Koziel et al., a special SPME holder was modified to enable δ of 5 mm, 10 mm, 15 mm, and 20 mm (Fig. S-1) [7,8].

The objective of this work is to test at the pilot scale the proof-of-concept work described in a previous article [9]. Specifically, this paper expands the quantification of a single analyte (benzene) in a high-temperature (115 °C) standard gas stream (N_2) to include a matrix of benzene, toluene, styrene, indene, and naphthalene (BTSIN). These analytes represent the primary components of syngas tar existing downstream of a syngas cleaning device [9]. The secondary objective is to demonstrate the newly developed quantification method for BTSIN on a pilot-scale gasification and syngas cleaning process development unit (PDU) feeding 20 kg/h (i.e. ~0.5 metric ton per day) of switchgrass. The new method was compared with conventionally approved quantification methods for syngas tar [10].

1.2. Syngas tar analysis

Syngas exiting a gasification process is contaminated by feedstock impurities as well as an array of larger MW aromatic hydrocarbons developed from the process known as 'tars'. These tars are typically found in concentrations ranging from 10 to 100 g/m³ (3–30 ppm_w at standard conditions) or higher depending on the method of gasification [11]. They are a particularly menacing problem given their tendency to condense as temperatures fall below ~400 °C, potentially clogging pipes and fouling downstream equipment. Tar reduction also usually becomes more intense and expensive as the removal efficiency is increased, making it beneficial to only reduce tar to levels necessary for downstream applications [11,12].

Conventional analysis of syngas tar is performed offline using wet chemical methods [13–15]. They typically involve passage of a slipstream (i.e. a small sample stream diverted isokinetically from the main process stream) into a series of impingers containing solid or liquid-phase sorbents, where the condensable components in the syngas are collected and the non-condensable gases (NCGs) are passed to a gas measurement device such as a micro-gas chromatograph (microGC). The gas stream is ultimately passed through a flow meter to determine the volume of gas analyzed (see Fig. 1). The final stage is a multi-step sample preparation process to analyze the collected components via GC–MS or GC–FID for the volatile analytes, and gravimetric analysis for the non-GC detectable components. The concentration is derived by the overall mass of analytes collected divided by the standardized volume of

gas analyzed. These methods suffer from long and complicated solvent extraction steps, often requiring days for analysis and suffering from a plethora of potential errors, such as inherently difficult isokinetic sampling trains (see 'Section 2.2'), glassware contamination, insufficient measurement accuracy and precision, and complicated sample matrices and solvent separations. Long sampling times inherent to conventional methods may also confound tar analyses due to difficulty of attaining consistent steady state conditions in the reactor and exhaust gas. It may also be impossible to analyze reactions and gases in a shorter time scale inherent to non-steady state kinetics and research-grade nature of pilot-scale operations. In addition, experimental errors typically result in relative standard deviations ranging from 20% to 50%, but can extend beyond 100% for many kinds of analytes [10,13].

Previous attempts to mitigate the analytical challenges with tars in gas streams have included adoption of a pressure cooker (PC) vessel for collection of non-GC detectable components [16] (primarily heavier tars). This dry-condenser process was compared to the conventional analysis and showed accuracy within 10% of the heavy tar fraction from the conventional approach. However, the light tar fraction, i.e. compounds with vaporization temperatures less than or near 105 °C set point of the PC (such as benzene and toluene), could make up a substantial fraction of the syngas tar. Benzene, T, and other light tars may typically represent 10–30%, and as much as 50% or more of the overall tar fraction [12,15,17–20]. These compounds are still a significant threat to end-use applications that require high purity syngas, like catalysis for synthetic fuels [21]. They are also difficult to completely eliminate via typical cleaning methods (e.g. oil washing) without creating waste water issues from the low condensation point [22,23]. Thus, identifying the optimal concentration of these light tar fractions in the syngas is essential to operating a gasification-based synthetic fuels plant at peak operational and financial efficiency.

1.3. Suitability of retracted SPME for fast moving process gas

An accurate, rapid, and dependable light tar quantification method is also needed for research-grade pilot scale reactors and processes where operational steady-state conditions are relatively rare and where the reaction kinetics might be of particular interest. The syngas temperatures found downstream of cleaning equipment and the dry condenser typically fall between 100 and 150 °C and provide an ideal side-by-side testing environment for the TWA-SPME method. Woolcock et al. showed that the benefits of the TWA-SPME found in typical ambient air temperature would still apply to contaminant measurement in hot process gas streams in lab conditions [9]. The results indicated potential for the method to effectively determine contaminant concentrations at elevated temperatures. The benefits might potentially include lower detection limits than conventional methods, shorter sample preparation and analysis time, and more accurate measurements.

The retracted TWA-SPME approach also offers several advantages compared to conventional extractions using an exposed SPME fiber, which have only been attempted for laboratory scale proof-of-concept tar measurement [24]. These advantages include: controlling sample extraction conditions to enable a much broader range of analyte concentrations, broader range of sampling times that could be adjusted to expected ranges of concentrations, and eliminating the need to consider changing boundary layer conditions, fouling and mechanical stress on the exposed fiber in a rapidly moving process gas stream [25]. Sorptive capacity of retracted SPME is still limited. First order extraction conditions need to be maintained so that a SPME fiber coating is not saturated [9]. This means, in extreme conditions, using shorter sampling time in conditions characterized by high concentrations or using

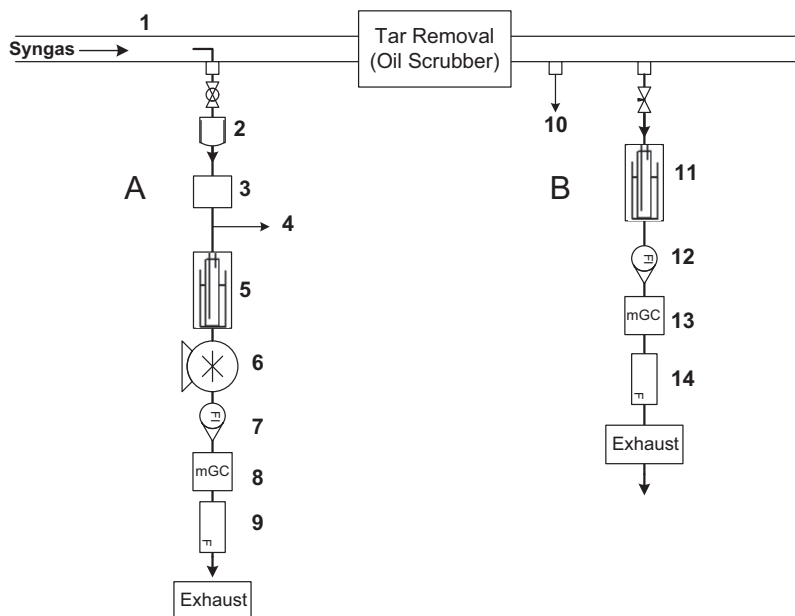


Fig. 1. Schematic of the conventional tar sampling and collection system (all process piping and sampling lines are heat traced to reduce probability of tar condensation): (1) syngas process piping; (2) isokinetic sampling probe and particulate thimble filter; (3) pressure cooker (PC) heavy tar sampling system (refer to [16]); (4) TWA-SPME sampling port; (5) 4 impingers each with 200 mL 2-propanol immersed in a dry ice 2-propanol bath; (6) vacuum pump; (7) rotameter; (8) micro gas-chromatograph (mGC); (9) wet-test meter; (10) SPME sampling port sample; (11) 3 impingers each with 200 mL 2-propanol immersed in a dry ice 2-propanol bath; (12) rotameter; (13) mGC; (14) wet-test meter.

longer sampling times in conditions characterized by low concentrations.

This work aimed to test the TWA-SPME method in a pilot-scale gasifier for quantification of BTSI and to compare results with the impinger based dry-condenser gas sampling technique. The TWA-SPME approach can close the gap on analytical methods capable of avoiding problematic condenser trains associated with conventional method and providing rapid feedback on process conditions. Numerous additional analytically challenging process gas environments can benefit from successful application of this technique, e.g. combustion exhaust and pyrolysis vapor streams, and may also enable monitoring of reaction kinetics in much shorter timescales.

1.4. Theory of TWA-SPME sampling

TWA-SPME with retracted fiber operates on the premise derived from Fick's first law that the amount of analyte extracted is proportional to the integral of the concentration over a sampling time (t):

$$n = D_g \frac{A}{\delta} \int C_g(t) dt \quad (1)$$

where A = opening area of SPME needle (L^2 , cm^2), t = sampling time (t , s), D_g = molecular diffusion coefficient for the sample in the gas stream (L^2/t , cm^2/s), C_g = instantaneous concentration in the gas stream (M/L^3 , $g/cm^3 \rightarrow g/m^3$), n = mass extracted on SPME (determined by analytical equipment) (M , g), δ = boundary layer (length of diff. path, retraction of SPME fiber inside the needle) (L , cm).

In practice, this can be reduced to the following relationship as long as a few essential sampling requirements are met, which are detailed thoroughly in [2,9].

$$\bar{C}_g(t) = \frac{n(t)\delta}{D_g A t} \quad (2)$$

The work aimed to expand the original lab scale proof of concept (developed for one model compound only) to the mixture of all

main tars expected in the actual syngas process stream located downstream of the dry-condenser and the start of the gas cleaning system (Fig. 1) [9].

2. Materials and methods

2.1. Chemicals

Benzene, T (Sigma-Aldrich CHROMASOLV®Plus, for HPLC $\geq 99.9\%$), S (Sigma-Aldrich ReagentPlus® $\geq 99\%$), I and N (Sigma-Aldrich $\geq 99\%$) were used to generate a model tar stream within an ultra-high-purity N_2 gas stream (99.995%). Impingers were filled with either DI water (18.2 $M\Omega\text{-cm}$) or 2-propanol (Sigma-Aldrich CHROMASOLV®Plus, for HPLC $\geq 99.9\%$). 2-Propanol and dry ice were used in the impinger ice bath during later experiments to ensure analyte capture by reducing temperature. Permanent gases calibrated and analyzed in the Agilent microGC included CO_2 (6–45%), CO (1–45%), H_2 (2–22.5%), CH_4 (2–6%), N_2 (0–66.5%), ethane (0.25–1%), ethylene (0.75–5%), acetylene (0.15–1%), and O_2 (0.2–1%). All work with chemicals was performed following lab safety protocols, using vented fume hoods and approved personal protection gear.

2.2. Materials

A manual SPME device was equipped with a Carboxen/Polydimethylsilosane (85 μm Car/PDMS – Supelco) fiber. This fiber was chosen based on performance criteria for testing syngas streams (see [9]). The high sorptive capacity of Carboxen was an additional benefit for TWA sampling of high analyte concentrations potentially found in process gas [26].

This work was performed in two phases requiring different experimental setups. Fig. 1 in [9] shows the laboratory setup used for experimental validation of D_g values for target light tars. This original setup was modified with extensive heat tracing upstream of the oven to preheat the gas flowing through the glass bulb to 80 °C. Initial testing showed this was necessary to maintain a

homogenous concentration of the synthetic BTSI tar mixture in the gas stream. The conventional tar sampling system was significantly more complex. Glassware used on the pilot-scale testing included two sets of impinger trains (seven total impingers) for sampling multiple locations in the syngas process lines simultaneously.

Syngas exits the gasifier and enters the cleaning system shown in Fig. 2 (detailed in [27]). The hot syngas is maintained at 400 °C or higher using high performance cable heaters (Tempco) on the process piping. Cyclones remove most of the particulate matter, and the remaining char is quantified using the thimble filter located in the isokinetic sampling line (A). This heat traced sampling line enters a PC downstream of the thimble filter, where syngas passes through a 3 m polymer tube (Santoprene or Trelleborg) submerged in water heated to 105 °C.

This environment rapidly transfers heat from the syngas to condense the heavier molecular weight tars from the vapor stream. Syngas exiting the PC enters another heat traced ~9.5 mm (3/8") sampling line equipped with a stainless steel tee, which serves as an SPME sampling port by placing an 11 mm septum into the top nozzle of the tee. Four impingers filled ~1/3 full with 200 mL of 2-propanol follow this ~0.5 m sampling line.

3. Results and discussion

Validating the TWA-SPME concept for analysis of syngas tar at elevated T required two separate experimental segments: (1) verifying D_g for the primary analytes of interest at lab-scale, and (2) comparing the retracted SPME gas sampling technique to conventional tar measurement techniques on a pilot-scale gasifier and gas cleaning system.

3.1. Phase I: lab-scale experiments to estimate D_g for target analytes at elevated T

D_g is the only parameter on the right side of Eq. (2) that is not provided by analytical equipment or known a priori. Proof-of-concept work performed in [9] on a standard benzene/ N_2 hot gas stream indicated the possibility of a secondary boundary layer existing at the face of the SPME fiber's Car/PDMS extraction phase [6,7]. This boundary layer has the potential to significantly affect D_g under certain conditions. A series of tests was performed as described in [9] using a mixture of BTSIN compounds (the main tars remaining in cleaned syngas) to determine this phenomenon's impact on a sample matrix that contains multiple analytes. An equal weight mixture of these five compounds was created and used in the injection syringe of the sampling system depicted in Fig. 1 of [9]. Hot gas mixture stream was maintained at temperatures simulating ranges of process equipment parameters and gas sampling ports of the pilot-scale reactor (i.e., between 105 and 130 °C). Despite several attempts to address repeated difficulties with N (described in Supplementary Information and [27]), this tar vapor mixture was reduced to BTSI to substantially improve precision of the small laboratory system.

BTSI adsorption onto the fiber was highly linear with small sample variations as a result of retraction depth (Figs. 3, S-2, and S-3), despite the secondary boundary layer effect that was shown in the first paper [9] and described in depth in the Supplementary Information and [27]. RSDs for B were all <5% with an average of 3.0%, and remaining RSD averages were 2%, 3.5%, and 5% for T, S, and I, respectively). These results warranted continuing trials of the retracted SPME method in real-world pilot-scale testing and comparison of measured tar concentrations with conventional tar analysis technique.

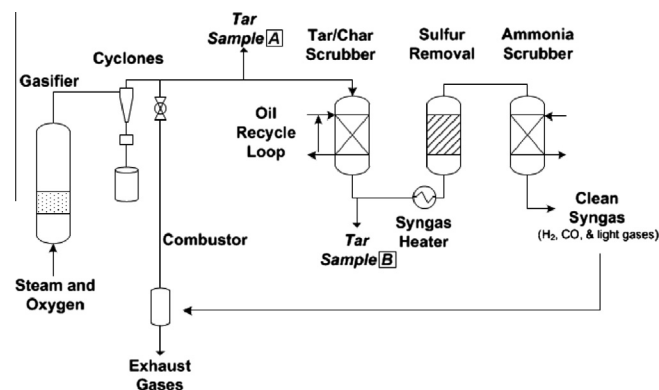


Fig. 2. Schematic of the pilot-scale gasifier and gas cleaning system at ISU's BioCentury Research Farm (gas samples taken immediately prior to and downstream of the tar/char scrubber, with A taken at ~135 °C and B at ~110 °C).

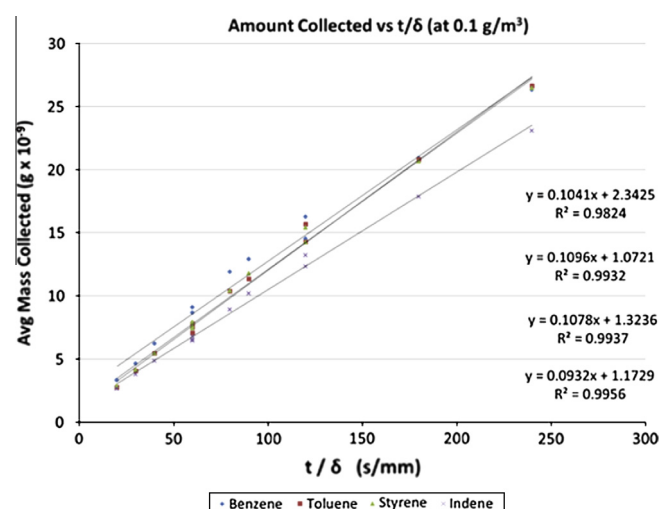


Fig. 3. Mass of the target analytes adsorbed on SPME fiber vs. changes in sampling time and SPME fiber retraction depth (see Figs. S-2 and S-3 for benzene and toluene extractions individually).

3.2. Phase II: method comparison between retracted TWA-SPME and conventional impingers

Field testing of the TWA-SPME approach was performed on a fluidized bed gasification and gas cleaning pilot-plant located at Iowa State University's BioCentury Research Farm (BCRF) [28]. Due to the scale of the system and the expense of pilot operation, the comparison between the conventional analytical approach and the TWA-SPME approach was performed jointly with other experimental research, which made it difficult to reach acceptable sampling conditions during more than a few tests over a 6 month period (see SI for more information) [29].

Syngas samples were taken at two different locations during each test (Figs. 1 and 2). The TWA-SPME sampling location for B was located immediately downstream of the tar scrubber and ~1.5 m upstream from the impinger sampling point at a process temperature of between 110 and 125 °C depending on the test. Typical sampling time was 5 min with retraction depth of 5 mm. See SI for further details on sampling design. An inherent challenge to side-by-side comparisons of sampling methods is the difference in sampling time scales: the conventional methods require much longer sampling time and long sampling preparation.

Raw results from the TWA-SPME analysis required multiple adjustments to account for temperature, pressure, and sampling

variables according to Eqs. (1) and (2). Initial D_g values were based on lab experiments (discussed in Section 3.1 results) conducted at 115 °C and 101 kPa using a gas stream composed only of N₂ and the analytes of interest. However, the samples taken from the PDU were at different conditions which varied slightly with each testing environment. Accounting for these conditions was done using a combination of approaches. The T and p were easily accounted for by utilizing the three theoretical equations previously discussed (Wilke-Lee, FSG, and Huang et al) [9,30–32]. The baseline analyte adsorption was also accounted for by alternating samples in the PDU with SPME assemblies that were missing a Car/PDMS coating. The corresponding mass of analytes that adsorbed onto the outer and inner surface of SPME needle was then subtracted from the amount collected on the SPME fiber coating.

The effects of gas mixture composition on D_g required a more thorough investigation (Table 1). Most D_g are calculated only in a bimolecular mixture, and very few theoretical equations are available to accurately adjust for multiple gas phase species [33]. Adjustments were made using the technique described in [33], in which the FSG equation is calculated for each bimolecular species and adjusted for the total depending on C_g of each major species. The microGC used at the end of the impinger trains during all PDU research was used to estimate the average gas composition during each test. This composition was normalized to the six major gas species (N₂, CO₂, CO, H₂, CH₄, and H₂O) which accounted for 95% or more of the hot stream gas phase. Unfortunately H₂O has at times been shown to affect the Car/PDMS adsorption process as well, by taking up active sites in the Carboxen [34–36]. However, its effect is varied and may sometimes be insignificant due to molecular analyte size and hydrophobicity [37,38]. Due to this uncertainty, mathematical adjustments were not made for the effect of H₂O on the SPME adsorption process, and this is cited as a potential source of error to be considered for further analysis in future experiments.

Initial results from the impinger analyses also required substantial revision. The 2-propanol impingers were chilled to –70 °C, which caused significant amounts of NCG to dissolve and collect into the impingers (e.g., Fig. S-6). This dissolved gas was subsequently not accounted for in the wet-test meter results. Immediately after sampling, the impinger samples were weighed and then allowed to reach ambient conditions to vent the dissolved gases. This was done to prevent violent release of the samples once bottled and readied for transport. Once the dissolved NCGs were released, the samples were weighed again and the difference was accounted for in the wet-test meter as CO₂. The complicated matrix of 2-propanol, H₂O from the steam/O₂ gasification process, and similarly low boiling point analytes of interest also created significant problems in GC-FID analysis. A separate analysis was performed by an independent lab (Minnesota Valley Testing Laboratory – MVTL) to verify the in-house GC-FID results, and showed potential matrix effects were possible with the varied concentration of H₂O in the impinger samples. Despite matching readings between in-house and third party analyses, all subsequent tests were also sent to MVTL to consistently verify analyte concentrations prior to final comparison of the conventional and TWA-SPME analytical methods.

Final results from the three successful comparison trials (summarized in Table 2) indicate a general level of success in terms of a comparable light syngas tars C_g . Differences between runs are expected given the non-steady state and varying operating conditions. The tar values in Table 3 correspond as expected with the equivalence ratios [39]: lower equivalence ratio yields more heavy tars [12,40]. The overall trend in light tar is difficult to discern from the two different methods of measurement, but may indicate according to data from location A (prior to the cleanup stage in

Table 1

D_g values derived experimentally from lab-scale testing and adjustments made for pilot-scale experiments at sampling locations A and B. Note: D_g was only significant to 2 digits and adjustments for H₂O were only for molecular diffusion effects and not the effect of humidity on the Car/PDMS adsorption process.

	Original	Revised	
		A	B
Benzene	0.133	0.164	0.120
Toluene	0.109	0.134	0.097
Styrene	0.101	0.124	0.090
Indene	0.083	0.103	0.075
<i>Conditions</i>			
Temperature (°C)	115	131	115
Pressure (kPa)	101	101	129
Gas composition	N ₂	(N ₂ , CO ₂ , CO, H ₂ , CH ₄ , H ₂ O*)	

H₂O was accounted for via molecular weight only, not any effect due to CAR/PDMS coating interference.

* Note: D_g only significant to 2 digits.

Table 2

Summary and comparison of measured BTS concentrations using the newly developed TWA-SPME and conventional impingers (L.D. = values below limit of detection).

Location	A		B	
	TWA-SPME g/m ³	Impinger g/m ³	TWA-SPME g/m ³	Impinger g/m ³
<i>Run 1</i>				
Benzene	9.0	16.2	6.4	7.7
Toluene	0.25	0.33	0.41	0.26
Styrene	0.26	0.45	0.07	L.D.
<i>Run 2</i>				
Benzene	4.9	13.6	6.9	7.2
Toluene	2.2	5.1	0.69	0.29
Styrene	1.0	2.0	0.14	L.D.
<i>Run 3</i>				
Benzene	7.4	17.8	10.3	10.5
Toluene	1.1	2.2	0.83	0.54
Styrene	0.59	0.96	0.13	L.D.

Table 3

Comparison of the total light tar C_g estimates from conventional impinger and TWA-SPME analyses. All totals were calculated using BTSI calibrated compounds and adjusting for the percentage of the total tar compounds present in the chromatogram (see Fig. S-9 for the three side-by-side test runs). BTSI in all cases was 50–90% of the total peak area.

Location	A		B	
	TWA-SPME	Impinger	TWA-SPME	Impinger
<i>Run 1</i>				
Total tars (g/m ³)	15.4	25.4	10.4	9.6
W/out light Ends	12.4	24.2	7.7	7.7
STDEV TT (g/m ³)	4.0		4.4	
STDEV WoLE	3.4		3.0	
RSD TT (%)	26%		42%	
RSD WoLE	27%		39%	
<i>Run 2</i>				
Total tars (g/m ³)	16.0	43.8	18.1	13.4
W/out light ends	12.0	38.0	8.3	7.2
STDEV TT (g/m ³)	3.1		3.4	
STDEV WoLE	1.4		3.0	
RSD TT (%)	19%		19%	
RSD WoLE	12%		36%	
<i>Run 3</i>				
Total tars (g/m ³)	9.3	28.6	17.6	14.0
W/out light ends	8.2	26.7	11.2	10.5
STDEV TT (g/m ³)	1.7		2.0	
STDEV WoLE	2.2		1.4	
RSD TT (%)	18%		11%	
RSD WoLE	27%		12%	

the tar scrubber) a tendency of heavier tars to crack at higher T and yield larger quantities of lighter tars (Runs 1 and 3 compared to 2). This phenomenon directly corresponds to conventional knowledge of tar formation and methods of destruction: multi-ring tars may crack above 850 °C and single ring tars remain intact until temperatures exceed 1000 °C [21,41]. More fundamental kinetic studies in the laboratory may further confirm this phenomenon.

The tar samples taken with the TWA-SPME method at sampling point A were always less than that of the impinger approach, but still aligned closely with literature values. Typical literature values for benzene for instance may range from a few g/m³ to up to 45% by weight of the total tar volume quantified [12,15,18–20].

Measured C_g from the conventional and TWA-SPME analyses were substantially more similar at sampling location B, with relative differences typically < 10%. This is beneficial when considering deployment in commercial gasification systems since trace tars are of greatest concern downstream of the cleaning processes. The inability of the impingers to detect the S while it was detected in the TWA-SPME-based analysis also shows the significance of the new method's ability to quantify otherwise undetected compounds.

A variety of potential issues could be responsible for differences occurring between samples taken at different locations. The different methods of removal for heavy tar may play a primary role. The PC method utilizes indirect contact heat exchange limited by convection to reduce the syngas temperature. Tar is collected via condensation and deposition on the surface of the tubing and small canister of glass wool inside the PC. The tar scrubber utilizes a much more efficient direct-contact heat exchange process with cooler heat transfer oil. In addition to rapid condensation, it also applies a counter-flowing oil spray to achieve a very efficient removal of aerosol vapors. Compounds such as N should condense in the PC and be included in the heavy tar fraction of Table 2 as its dew point is > the 105 °C set point. However, as seen by the coloration in Fig. S-6 and noted in Table S-3, compounds such as N are less efficiently removed with the PC and may also deposit in the impinger train, yielding much higher tar concentrations when compared against the post cleanup location. Lower tar C_g at location B compared to location A may also be due to the much lower T attained at times in the syngas cleaning unit. Due to the short sampling times allowed by the gasifier, there was insufficient time to reach a steady operating state in the oil scrubber. Typical operating conditions were ~115 °C, but periods of operation occurred < 80 °C. This causes greater tar condensation and potentially absorption into H₂O condensed from the high concentration of steam in the syngas. Some discrepancy between the two sampling methods at location A could also be explained by the inconsistent vacuum pump and thimble filter p disturbances located on the sampling line. These devices made it difficult to accurately predict the p at the SPME sampling point for proper adjustment of the D_g values during analysis.

The high inherent variability in the conventional method may also be a source of discrepancy between the two techniques. According to Neeft et al. and Bahng et al., the overall variability in the conventional impinger approach is typically 20–40% for many analytes [12,14]. In addition, the high quantity of H₂O vapor in the syngas from the steam/O₂ gasification process may cause analytes to preferentially separate in the impinger containers and vials while awaiting analysis. GC-FID trials were conducted to test this hypothesis using a calibration standard of the analytes of interest that was spiked with 20% water. Results reflected the hydrophobicity of the analytes with a minimal but noteworthy 2%, 5%, 10%, 14% and 17% increase in response for B, T, S, I, and N respectively. The sampling at location A also requires isokinetic sampling to maintain proper collection of heavy tars. Data analysis later indicated that isokinetic rates were missed by up to 30% on occasion during the 6 months of trials, and was attributed to

random error with no discernible association to the wet-test and rotameter discrepancies. This would also affect the collection of heavy tars giving a false indication of the light/heavy tar ratio.

TWA-SPME sampling configurations during gasification were also altered from the lab-scale analysis due to higher than expected tar C_g . Despite the higher concentrations, the adjustments in sampling depth and time of extraction were able to keep analyte quantity on the fiber for all tests within an order of magnitude of the calibrations performed in the lab. This should be noted however as a potential source of error, resulting in a possible under-estimate of tar via the TWA-SPME technique at location A. However, because there was zero carry over in the fiber after analysis and the samples stayed below the 5–10% saturation levels required by the zero-sink hypothesis (the high capacity of Carboxen is orders of magnitude higher yet), it is unlikely that the under-estimate was off by more than a few percent [42]. Evidence for this is seen by the linear response in the higher C_g lab experiments of previous work [9].

Total light tar concentrations in Table 3 were estimated from the relative abundance of quantified compounds in the chromatograms. The light tars were calculated as BTSI and then a correction was applied to account for the missing mass percentage in the chromatograms that was not due to those 4 calibrated compounds. A second calculation was performed by discounting all compounds smaller than B (termed: without light ends, or WoLE). This adjustment was made to reflect the inability to detect some analytes in the impingers due to the co-elution in the GC-FID with the solvent. It also more accurately reflects the true definition of 'tar', which is typically considered as benzene compounds and larger [11].

The discrepancies between samples become exacerbated when comparing total tars using only 4 calibrated analytes, but the table is useful for comparing typical light tar values to those reported in aforementioned literature. As many as 14 additional compounds were identified and quantified with the retracted SPME method (Fig. S-8, Table S-4). A majority of the compounds identified are single ring aromatics, as shown in Table S-4. For each test, three extractions and three baselines were taken successively for TWA-SPME in the PDU trials, which allowed for an average, a standard deviation and RSD calculation. Unfortunately the impinger-based analysis was not amenable to taking several different samples from each location given the longer time required per sample. RSD information for the impingers is limited to the 2% or less RSD values attained during direct injection of liquid samples into the GC-FID for analysis.

Large RSD values for the SPME samples in the pilot scale trials may reflect the drastic changes that can occur in the sampling train at a shorter time-scale. Samples for the conventional method were collected over a 50 min period on average, whereas TWA-SPME samples were collected over several different 5 min sampling periods. Inconsistent pump performance, changes in sampling line pressure drop, or changes in gas composition are captured by the TWA-SPME method but are averaged out in the conventional analysis. Unlike commercial-scale operations, the gasification pilot plant is only operated when research tests are conducted. The large thermal mass of the gasifier and cleaning equipment make it difficult to attain true steady state conditions in all aspects prior to sampling. Commercial operations will still suffer from inconsistencies in sampling lines, but the TWA-SPME method can extract samples directly from the process stream eliminating this unwanted variation while providing the possibility of capturing the dynamic nature of the system if desired. Finally, the TWA-SPME-based measured C_g was available within hours, whereas the conventional analysis required 1–3 days for estimating C_g , further increasing the potential for data corruption. Summary of possible sources of errors in both methods is presented in Table S-5.

4. Conclusions

The TWA-SPME concept for analysis of syngas tar at elevated T is a valuable technique compared to the conventional solvent-based impinger approach. The presence of a secondary boundary layer at the SPME surface (unrelated to δ) as shown in original proof-of-concept testing was confirmed in multicomponent testing, but was found again to have minimal effect on the usefulness of the method [9]. Comparison of the new and conventional method was performed using a pilot-scale gasification and gas cleaning system. The complicated nature of the conventional method made it difficult to collect reliable samples during every test. However, the few sample collections that were successful showed the new method was capable of staying within 20% of the conventional method for light tars downstream of a syngas cleaning unit. Some of the difficulties that were experienced during conventional sampling included: deviation of isokinetic sampling rates from their intended set points; T and p fluctuations in the PC and sample lines making steady-state sampling and C_g measurements difficult; and complicated sample matrices requiring repeated wet chemical analyses for verification of analyte concentrations. The TWA-SPME samples also required multiple corrections for temperature, pressure, and gas-phase composition, but still provided useful data for comparison. In addition, the new method was capable of showing the dynamic nature of the syngas, and was able to identify and quantify more analytes than that of the conventional solvent-based approach.

Future TWA-SPME comparisons to other conventional approaches that do not suffer from the same difficulties as the impingers would be highly useful to confirm and more accurately test this method. Solid phase extraction (SPE) and multibed solid phase adsorbent (SPA) are potential candidates given their resemblance to SPME, despite the need for solvent-based lab work [43–45]. Expanding the laboratory testing environment to include multiple other temperatures may help develop an improved model for compounding effects of different T , p , and analytes (C/H numbers or MW correlation).

A major disadvantage of the method is the 300 °C or lower T limit on the SPME fibers, which currently restricts sampling to only GC-detectable tars. An internally-cooled SPME device that would enable sample extraction from higher T environments may overcome this limitation. Future work may also consider testing the effects of thermophoresis on this device and its potential for sampling all high T contaminants directly from process gas streams such as pyrolysis or combustion processes. This technique would potentially avoid the time consuming and complicated conventional sampling trains.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.fuel.2015.02.101>.

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