



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.

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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

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

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