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Analysis of trace contaminants in hot gas streams using time-weighted average solid-phase microextraction: Proof of concept

Patrick J. Woolcock[a,b], Jacek A. Koziel[b,*], Lingshuang Cai[b,1], Patrick A. Johnston[a], Robert C. Brown[a,b]

[a] Iowa State University, Center for Sustainable Environmental Technologies (CSET), 3122 Biorenewables Research Laboratory (BRL), Ames, IA 50011, USA
[b] Iowa State University, Department of Agricultural and Biosystems Engineering, 3202 NSRIC, Ames, IA 50011, USA

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ABSTRACT

Time-weighted average (TWA) passive sampling using solid-phase microextraction (SPME) and gas chromatography was investigated as a new method of collecting, identifying and quantifying contaminants in process gas streams. Unlike previous TWA-SPME techniques using the retracted fiber configuration (fiber within needle) to monitor ambient conditions or relatively stagnant gases, this method was developed for fast-moving process gas streams at temperatures approaching 300 °C. The goal was to develop a consistent and reliable method of analyzing low concentrations of contaminants in hot gas streams without performing time-consuming exhaustive extraction with a slipstream. This work in particular aims to quantify trace tar compounds found in a syngas stream generated from biomass gasification. This paper evaluates the concept of retracted SPME at high temperatures by testing the three essential requirements for TWA passive sampling: (1) *zero-sink assumption*, (2) *consistent and reliable response by the sampling device to changing concentrations*, and (3) *equal concentrations in the bulk gas stream relative to the face of the fiber syringe opening.* Results indicated the method can accurately predict gas stream concentrations at elevated temperatures. Evidence was also discovered to validate the existence of a second boundary layer within the fiber during the adsorption/absorption process. This limits the technique to operating within reasonable mass loadings and loading rates, established by appropriate sampling depths and times for concentrations of interest. A limit of quantification for the benzene model tar system was estimated at 0.02 g m^{-3} (8 ppm) with a limit of detection of 0.5 mg m^{-3} (200 ppb). Using the appropriate conditions, the technique was applied to a pilot-scale fluidized-bed gasifier to verify its feasibility. Results from this test were in good agreement with literature and prior pilot plant operation, indicating the new method can measure low concentrations of tar in gasification streams.

1. Introduction

1.1. Sampling and analysis in thermochemical processing

Thermochemical processing of carbonaceous materials, such as biomass or municipal solid waste, is a potential pathway for producing renewable fuels and chemicals. Gasification in particular is a robust technology that is capable of converting contaminated feedstock into a useable product, in this case, a hot (800–1200 °C) synthetic gas stream composed primarily of carbon monoxide (CO) and hydrogen (H_2). This ‘syngas’ is valuable for many commercial applications, from fuel and chemical synthesis to raw heat and power operations.

Raw syngas produced by gasification contains numerous contaminants either derived from impurities in the feedstock or created as a byproduct of the process. These contaminants include particulate matter, ammonia (NH_3), hydrogen chloride (HCl), hydrogen sulfide (H_2S), and heavier oxygenated compounds known as “tars.” Tars are a particularly serious issue as they tend to condense from the vapor-phase as the temperatures fall below 400 °C, which leads to deposits that clog pipes and equipment. Cleaning methods often leave residual contamination that can still be problematic in several highly sensitive technologies, such as catalysis [1].

Numerous analytical techniques are available for quantifying these contaminants, but they are largely based on preparation steps that use wet chemical methods [2]. These methods are performed offline, which is a significant disadvantage to monitoring and quickly controlling a process in real-time to maintain optimum efficiency. Some devices may monitor specific contaminants online during the process, including GC–TCD (thermal conductivity detector), NCD (nitrogen chemiluminescence detector), and SCD

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[*] Corresponding author. Tel.: +1 515 294 4206; fax: +1 515 294 4250.
E-mail address: koziel@iastate.edu (J.A. Koziel).
[1] Formerly with Iowa State University, now with Ricerca Biosciences, Concord, OH 44077, USA.

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(sulfur chemiluminescence detector) among others. However these devices are typically expensive and limited to detecting single types of contaminants (i.e. NH_3 or H_2S).

Heavy molecular weight, slightly oxygenated compounds known as tars are a particularly difficult contaminant to quantify [1]. Due to their varied composition (usually hundreds of different compounds), they are typically collected by exhaustive extraction and gravimetrically measured. A slipstream (i.e. a small sample stream diverted from the main process stream) of the syngas is passed through a series of condensers or impingers, sometimes with isopropanol as a solvent. Differences in mass are calculated for the equipment before and after the tars are collected. Clear guidelines for this conventional tar measurement and a closely related solvent-free technique have been documented in the literature [3,4].

The method of exhaustive extraction is difficult to apply at low concentrations due to low mass accumulation. For example, removing tar by 99% from a typical fluidized bed gasifier would still yield ~100 mg m^{-3} of tar (~30 ppm_w at standard conditions) [5]. Only ~0.5 g of sample would be collected after nearly 17 h of sampling at a higher than typical flow rate of 5 SLPM. In addition to this inefficient data gathering technique, maintaining steady-state process conditions and the sampling equipment for that extended timeframe is often difficult. The conventional tar measurement techniques are therefore impractical for monitoring low concentrations, which can still cause damage to catalysts and reduce process efficiency.

Sampling and sample preparation are notorious for taking the most time during an analytical process, typically accounting for over 80% of analysis time [6]. In the case of trace tar analysis, this could be even greater due to the long sample times required for collecting significant gravimetric tar data. More likely is the inability of maintaining steady state conditions long enough to collect meaningful samples. In the event that a statistically meaningful amount of tar can be collected, the light tars condensed in the impinger train are likely to be highly diluted with water that has condensed from the many hours of sampling. This makes it increasingly difficult to obtain accurate and precise data on the quantity of light tar that has also condensed. Any ability to obtain information on process kinetics also becomes extremely complicated if not impossible with such a slow and time-consuming technique. The result in many cases is that potentially useful data is discarded as unquantifiable. Developing an alternative analytical technique based on representative sampling to quantify trace tars will eliminate these issues of tar quantification. This in turn will improve the performance of gas cleaning equipment and downstream applications.

1.2. Time-weighted average (TWA) sampling with SPME

Solid-phase microextraction (SPME) is a sample collection and preparation method that does not require long sample times to obtain a representative sample using exhaustive extraction. It is a relatively new approach that has been extensively applied to environmental, agricultural, and pharmaceutical applications [7–9]. It operates by collecting volatile analytes on a small fiber that is coated with an extraction phase, which is then directly injected into a gas chromatograph (GC) or liquid chromatograph (LC) coupled to a detector, such as flame ionization (FID) or mass spectrometry (MS) [8,10,11].

SPME can detect pico-grams or less of some compounds, equating to part per trillion (ppt) levels or lower [6,12]. Tar concentrations can be several hundred parts per million (ppm), and can easily saturate a fiber's extraction phase when exposed to the gas stream. This leads to samples that may not be representative of the average concentration in the gas stream. Retracted time-weighted average (TWA) SPME sampling addresses this issue by keeping the extraction phase retracted within the protective needle housing. Diffusion of the analytes from the environment to the extraction phase occurs through the stagnant boundary layer between the tip of the fiber and the tip of the needle housing. Under conditions where diffusion can be approximated as a constant value, the rate of sample collection can be controlled by the depth of fiber retraction. Retracting the fiber farther within the needle housing can facilitate sampling at higher concentrations, or the sampling time can be extended to several minutes or hours to establish a more representative average analyte concentration.

Other advantages of SPME-TWA using a retracted fiber include (a) reducing analysis time from several hours per sample to several minutes, (b) simplified quantification because a retracted fiber is independent of gas stream velocity [13–15], (c) small particles in the gas stream are not a concern since the fiber is protected by the outer needle housing, (d) the SPME sampler is sealed at the top to eliminate the possibility of gas flowing through the fiber syringe, which could alter results or damage the fiber. Unlike the equilibrium SPME techniques, applying the TWA-SPME method avoids the need for extra sampling equipment (heated chambers, sampling lines, and vacuum pumps) since it is used directly on process piping, and may potentially eliminate the need to calibrate the fiber for compounds of interest [16]. Finally, SPME sampling experience continues to grow, offering information on many different organic and inorganic compounds at a wide range of molecular weights and sampling environments, which aids in more rapid development for future applications [7,17–20].

The principle of the TWA sampling technique follows Fick's first law of diffusion: the amount collected on the fiber is proportional to the molecular diffusion rate (D_g) of the analytes in the vapor and the area (A) of the needle housing opening, and is inversely proportional to the diffusion path length (δ), which is the boundary layer of stagnant gas inside the needle housing between the tip of the needle and the tip of the coated fiber. As long as the concentration at the tip of the coated fiber is small compared to the free-stream value, the amount extracted is proportional to the integral of the concentration over a sampling time (t):

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

where A is the open area of needle housing [L^2], t is the sampling time [t], D_g is the molecular diffusion coefficient for the sample in the gas stream [L^2 t^{-1}], C_g is the instantaneous concentration in the gas stream [M L^{-3}], n = mass extracted (determined by analytical equipment) [M], and δ is the boundary layer (or length of diffusion path inside the needle) [L].

The overall objective of this work is to develop a TWA-SPME technique to improve the speed and accuracy of analyzing process gas streams for difficult-to-measure species. Unlike previous TWA applications, this research involves rapidly moving gas streams at elevated temperatures (~115 °C), with application to a complicated gas matrix in actual process environments. This paper in particular examines the TWA-SPME passive sampling concept for application to trace tar measurements in syngas process streams. As the authors are unaware of any application of SPME directly to gasification streams, this work also forms a basis for future analysis of syngas. Specifically, the three necessary requirements for TWA passive sampling were addressed: (1) *zero-sink assumption*, (2) *consistent and reliable response by the sampling device to changing concentrations*, and (3) *equal concentrations in the bulk gas stream relative to the face of the fiber syringe opening*. Benzene in nitrogen was used as a model compound in this proof-of-concept evaluation. Multiple concentrations, sampling times, and boundary layer lengths (i.e. depths of SPME fiber retraction) were tested to determine the limits of method application.