



Development of a standard gas generating vial comprised of a silicon oil–polystyrene/divinylbenzene composite sorbent



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ABSTRACT

In this work, a highly reproducible standard gas generating vial is proposed. The vial is comprised of a silicon diffusion pump oil spiked with an appropriate calibration compound, such as modified McReynolds probes (benzene, 2-pentanone, pyridine, 1-nitropropane, 1-pentanol, and n-octane), and then mixed with polystyrene/divinylbenzene (PS/DVB) particles. The concentrations of these compounds in gaseous headspace were found to substantially decrease in comparison to previously developed hydrocarbon pump oil based vials; hence, the amount of standard loaded onto SPME fibers was at most, half that of the previous vial design. Depletion for all compounds after 208 successive extractions was shown to be less than 3.5%. Smaller quantities of standards being used resulted in a vial that depleted slower while remaining statistically repeatable over a wider number of runs. Indeed, it was found that depletion could be largely predicted by using a mass balance theoretical model. This behavior allowed a further increase in the number of loadings that could be performed repeatedly. At a 95% level of confidence, the ANOVA test demonstrated that the prepared vials were statistically identical, with no significant intra- or inter-batch differences. In addition, it was found that vials stored under different conditions (e.g. under light exposure, room temperature, and within a refrigerator) were stable over 10 weeks. Silicon based vials proved to be ideal for performing instrument quality control and loading of internal standards onto fibers, both of which are of great importance when performing on-site analysis using portable GC–MS instrumentation and high throughput determinations in laboratory.

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1. Introduction

Since its introduction in 1989, solid phase microextraction (SPME) has been well accepted by the analytical chemistry community due to its miniaturized format, ability for high throughput analysis, minimal need for organic solvent [1,2], and combination of sampling and sample preparation into one easy to perform step, which have revealed SPME to be an ideal technique for on-site chemical analysis [3–6]. One issue presented however, is that environmental factors such as temperature, and air/water velocity can be very difficult to control. Since SPME is an equilibrium based extraction technique driven by diffusion, uncontrollable temperatures and fluid velocities can have a major impact on the amount of analyte extracted, as the distribution constant, K_{fs} , and the diffusion rate across the fiber boundary layer are, respectively, dependent on these factors [5–8]. These effects render many classical SPME calibration techniques, such as equilibrium extraction and in-lab external calibration, impractical for on-site analysis [1]. To address

these issues, diffusion based calibration methods such as the interface model have been proposed, allowing SPME calibration to be performed while accounting for measured fluid velocity and temperature. Nonetheless, these techniques are susceptible to fluctuations in these factors and do not account for matrix effects in complex samples [1]. In such scenarios, it may be preferential to perform a kinetic type calibration, where an internal standard is loaded onto the fiber prior to performing an extraction from the sample matrix [2,7–13]. Desorption of this standard will then occur as sampling takes place. The use of internal standards also brings the advantage of correcting for potential signal drifts incurred by field portable GC–MS instruments.

In order to effectively perform such calibrations on-site, one must be able to deliver standard to the fiber in a highly reproducible manner with a portable standard source. It is also essential that the amount of standard loaded is representative of the analyte concentration found in the sampling environment [14]. Previous efforts by Koziel et al. were able to demonstrate that a standard gas of VOC's could be generated in-lab by placing neat standards into a series of PTFE permeation tubes that were then placed into an enclosed gaseous flow through system [15]. Although this system was found to be appropriate for SPME and needle trap sampling

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it is inappropriate for onsite use due to size [15]. Wang et al. demonstrated that even when extremely short extraction times were used, a very large amount of standard are extracted onto the fiber if headspace extraction of pure standard spiked into a vial was performed [14]. Such quick extraction times are also difficult to perform repeatedly when manual injection is used on-site. Spiking standards into a polydimethylsiloxane (PDMS) membrane or Tenax particles was also shown to generate too great of a headspace concentration to be useful [14]. It was subsequently found that an appropriate standard gas generating vial could be produced by spiking a few milligrams of standard into a hydrocarbon based, ultra-low volatility mechanical pump-oil [11,14]. Furthermore Xie et al. were also able to demonstrate that an easy-to-use multiple standard gas generating system could be prepared by spiking nanoliters of pure standard onto a solid PDMS powder [16]. These PDMS based vials were shown to exhibit acceptable intra-vial repeatability, as demonstrated by percent relative standard deviations (%RSD's) of about 4.5% after 114 headspace extractions were performed for 30 s using a 100 μm PDMS fiber [16]. However, PDMS vials were still found to generate too high of a headspace concentration for trace applications, as several hundreds of nanograms of standards were still extracted. Additionally, where such small quantities, in the nanoliters, of the more volatile standards were spiked, it would be very difficult to produce multiple vials in a reproducible manner. Concurrently, another design was proposed by Gómez-Ríos et al., who addressed these major shortcomings by spiking a couple of microliters of pure standard into a hydrocarbon pump-oil solution, which was then mixed with PS/DVB particles to produce a highly reusable and durable standard gas generating vial [10]. In this study, it was demonstrated that these vials were highly repeatable, showing that intra-vial RSD's were less than 4% for all McReynolds probes [17] after 160 extractions were performed for 1 min, using the strongly sorbing, 50/30 μm divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) SPME fiber [10]. Furthermore, it was demonstrated that different vials prepared from the same batch of pump oil were statistically identical at a 95% level of confidence [10].

In this study, a significant enhancement of the previous standard gas generation system was achieved by using a silicon based, ultra-low volatility diffusion pump fluid. Similar to the previous design, the oil was first spiked with pure standards and then mixed with PS/DVB resin particles [10]. The use of silicon oil in combination with the PS/DVB particles proved to better retain the standards. Consequently, a lower headspace concentration of the standard was obtained, and a smaller fraction of the analytes was removed per extraction. Hence, a lesser extraction of standard resulted in a vial that depleted slower, giving a standard gas generating vial that remained repeatable over a greater number of extractions. Additionally, better precision of the amount loaded was obtained when longer loading times were used.

2. Experimental

2.1. Materials and reagents

Benzene, 2-pentanone, pyridine, 1-nitropropane, 1-pentanol, and n-octane standards, as well as the styrene/divinylbenzene (PS/DVB) particles (Amberlite® XAD-4) [18] were purchased from Sigma–Aldrich (Mississauga, ON, Canada). Varian general purpose mechanical pump oil was supplied by Varian Vacuum Technologies (Lexington, MA). KJLC 704 silicon pump fluid (tetramethyl tetraphenyl trisiloxane) was ordered from Kurt J. Lesker Company (Toronto, ON, Canada). 20 mL screw top vials and caps with 20 mm PTFE/silicone septa were purchased from Canada Life Sciences (Peterborough, ON, Canada). 40 mL screw

top vials and caps with 22 mm PTFE/silicone septa and 15 mL screw top vials with PTFE Mininert® valves were purchased from Sigma–Aldrich. HPLC grade methanol was obtained from Caledon Laboratories Ltd. (Georgetown, ON, Canada). Nano-pure water was obtained using a Barnstead/ThermoFisher NANO-pure ultrapure water system (Dubuque, IA, USA). Ultra high purity helium was supplied by Praxair (Kitchener, ON, Canada). Drierite desiccant was purchased from W. A. Hammond DRIERITE Co. (Xenia, OH, USA). Hamilton brand, 10 μL microsyringes were purchased from Sigma–Aldrich. Flex-Foil® gas sampling bags were supplied by SKC (Eighty Four, PA, United States). The vial heater block was constructed by the University of Waterloo electronics shop (Waterloo, ON, Canada). 65 μm divinylbenzene/polydimethylsiloxane (DVB/PDMS) and 50/30 μm divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS,) SPME fiber assemblies were provided by Sigma–Aldrich.

2.2. Instrumentation

An Agilent 6890 GC-5973 quadrupole mass spectrometer (Agilent Technologies, Mississauga, ON, Canada) was used in this study. Chromatographic separations were performed using a SLBTM-5MB (30 m \times 0.25 mm \times 0.25 μm) fused silica column from Sigma–Aldrich with a helium flow rate of 1 mL min⁻¹. The column temperature was initially held at 40 °C for 1 min, gradually increased to 50 °C at a rate of 5 °C min⁻¹, then to 70 °C at a rate of 6 °C min⁻¹, and then held for 0.47 min. An injector temperature of 260 °C was used to desorb the DVB/PDMS fibers. Calibration was performed using liquid injection at the same split ratio to generate a nanograms injected versus instrument response relationship curve. During analysis, the transfer line, quadrupole and ion source were set at 280 °C, 150 °C and 230 °C, respectively. Ionization was achieved using electron impact ionization mode. Full scan mode (40–250 *m/z*) was used for all compounds, and quantitation was achieved using extracted ion chromatograms.

Chromatographic separations on the Acme 6100 GC-FID (Young-Lin, South Korea) were performed using a RTX-WAX (30 m \times 0.25 mm \times 0.5 μm) fused silica column from Restek with a helium flow rate of 1.3 mL min⁻¹. The column temperature was initially held at 45 °C for 1.5 min and then raised to 145 °C at a rate of 12 °C min⁻¹, then raised to 180 °C at a rate of 35 °C min⁻¹ and held there for 30 s. Desorption of the DVB/PDMS and DVB/CAR/PDMS fibers were carried out for 1 min at a temperature of 260 °C with a split setting of 3:1. Calibration was performed using liquid injection at the same split ratio. The flame ionization detector (FID) was held at a constant temperature of 300 °C with a fuel mixture consisting of 30 mL min⁻¹ of hydrogen, 300 mL min⁻¹ of air and 30 mL min⁻¹ of helium.

2.3. Comparison of the different pump oil matrices

To determine the superior pump oil matrix, 4 standard gas generating vials were prepared using the Varian® general purpose mechanical pump oil (hydrocarbon oil), the silicon diffusion pump oil, a hydrocarbon oil–PS/DVB mixture, and a silicon oil–PS/DVB composite mixture. In order to maintain a consistent headspace volume with the oil–PS/DVB composite vials, standard pump oil vials were prepared by placing 6 mL of the spiked oil solutions into an empty 20 mL headspace vial. Vials were then heated to 50 °C in a Gerstel agitator unit. Extractions were performed for 30 s using a 65 μm DVB/PDMS stableflex fiber. Automated SPME injections were performed using a CTC Combi-PAL system (Zwingen, Switzerland) installed on the Agilent 6890 GC and 5973 qMS. Replicate extractions were randomized to minimize the effects of any potential signal drift of the mass analyzer.

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