PASSIVE CALIBRATION-VAPOR SOURCE FOR A MICRO GAS CHROMATOGRAPH

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Abstract

Micro-electro-mechanical systems (MEMS) fabrication techniques have been used to create a calibration-vapor source for a micro gas chromatograph (μGC) that employs a porous silicon (PS) reservoir and continuously generates a known quantity of n-decane by passive diffusion through a DRIE-Si channel. Sources containing PS layers with vertical pores 3±0.6 μm (diam.) x 280 μm (depth) provided an average generation rate at 25 °C within 5% of theoretical predictions. The temperature dependence of the n-decane generation rate (10-60 °C) was slightly higher than predicted. Results indicate that this source design is suitable for extended μGC field deployment.

Keywords: Calibration; vapor source; diffusion; gas chromatography; MEMS

1. Introduction

The accurate analysis of air contaminants by gas chromatography (GC) requires the generation of standard atmospheres to calibrate and verify instrument response. Direct injection of a standard atmosphere into the GC can be used to detect and compensate for errors in sampling and analysis as well as retention time shifts arising, for example, from changes in the operating environment or deterioration of system components.

Diffusion sources rely on the gradient-driven diffusion of a vapor through a tube of specified dimensions into a flowing gas stream and are commonly used to generate standard atmospheres. The behavior of these sources is described by Equation 1 [1]

\[ q_d = \frac{DMPA \ln \left( \frac{P}{P-P} \right)}{LRT} \]

where \( q_d \) is the diffusion rate (g/sec), \( D \) is the vapor diffusion coefficient (cm²/sec), \( M \) is...
the vapor molecular weight (g/mol), P is atmospheric pressure (mm Hg), \( A \) is the diffusion channel cross-section (cm\(^2\)), \( P_c \) is the calibrant vapor pressure (mm Hg), \( L \) is the diffusion length (cm), \( R \) is the gas constant (mL-mmHg/mol-K), and \( T \) is the source temperature (K).

Thus, the source generation rate is governed by the nature of the calibrant, the diffusion channel dimensions, and the source temperature. Both \( D \) and \( P_c \) increase with increasing temperature. Varying the temperature of the source allows the diffusion rate to be changed in a predictable manner.

2. Experimental

The source is a three-tiered structure consisting of a base Si layer containing a porous-Si (PS) reservoir, a Pyrex spacer with a machined aperture, and a cap with a deep reactive ion etched (DRIE) Si diffusion channel and outlet port that permits surface-mounting of the inverted structure onto a fluidic substrate upstream from the \( \mu \)GC preconcentration and separation stages (Fig. 1). The calibrant liquid is immobilized in the PS reservoir. Vapors saturate the headspace and pass down the narrow-bore diffusion channel into the sample inlet channel of the \( \mu \)GC. The source was designed for use in a \( \mu \)GC that samples at 25 mL/min and has an adsorbent preconcentrator with a finite capacity. Three diffusion channel lengths were chosen to provide inlet concentrations ranging from 45-122 ppb of n-decane at 25 °C.

The component parts and an assembled \( \mu \)GC source are shown in Fig. 2. A diffusion channel cross-section of \( \sim 0.04 \) mm\(^2\) and lengths of 7.5, 13.0 and 20.3 mm have been utilized. The cap and spacer chips were anodically bonded and then joined with the base layer using a laser-patterned polymer adhesive (VHB, 3M Corp.) after loading the reservoir with \( \sim 2.5 \) \( \mu \)L of n-decane.

Initial PS reservoirs (3.5 x 3.5 mm, square) were made from phosphorus-doped Si via a standard anodization procedure that yielded mesoporous PS layers \( \sim 180 \) \( \mu \)m deep with a broad pore size distribution ranging from 5-200 nm in diameter (PS-1). Efforts were then mounted to create deeper PS layers with larger pores and a narrower pore size distribution. To this end, boron-doped <100> Si substrates (17-23 \( \Omega \)-cm) were anodized using a Pt-grid counter electrode. An etching solution containing \( 10^{-3} \) M...
cetyltrimethylammonium chloride in a solution of HF (49%): ethanol: water (1:1:1) and a current density of 85 mA/cm² provided the best tradeoff among etch rate, morphology, and mechanical strength [2,3]. Macroporous PS reservoirs with a circular cross section 3.5 mm in diameter were produced using this process.

4. Results and Discussion

Fig. 3 illustrates that straight macropores with diameters of 3 ± 0.6 μm can be produced to a depth of 280 μm with the latter process. On-going studies are comparing randomly initiated vs. pre-patterned PS layers and layer depths up to 400 μm.

Assembled sources were surface-mounted over ports in a machined block of PEEK® having inlet/outlet capillaries connected to a downstream bench-scale GC-FID. Tests have been performed on one sample made with the initial PS process (PS-1) and two samples made with the latter process (PS-2). In all cases at least 2 hrs was required to achieve steady-state, presumably due to off-gassing of vapors adsorbed to the block walls during storage. Fig. 4 shows the steady-state generation rates at 25°C. The PS-2 samples differ by about 20% and their average value, 0.199 ng/sec (82 ppb in the 25 mL/min sample stream), is within 5% of the theoretical value of 0.189 ng/sec (78 ppb). The rate for the PS-1 sample is about 30% lower than predicted, which is within the range predicted by the Kelvin Equation to arise from surface-tension
induced vapor-pressure depression of n-decane for the PS-1 pore size range [4]. Day-to-

day reproducibility for the PS-2 samples was measured at ±2% over several days. 

Accelerated aging tests (PS-1 sample) show the generation rate to decline over time but 
to stay within 10% of the initial rate for 31 days at 25 °C. The generation rate exhibits a 
positive Arrhenius-type temperature dependence that is somewhat greater than predicted 
(Fig. 5). Testing with other MEMS components in a μGC prototype subsystem has been 
performed and is described elsewhere [5].

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