Nanoporous-Carbon Coated SAWs for ppb Detection of Trihalomethanes in Water

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Motivation—The treatment of water results in many disinfection products; trihalomethanes (THMs) are among the most common and of greatest concern to regulatory bodies and the public due to their known adverse health effects, which include cancer and miscarriage. The Environmental Protection Agency (EPA) regulatory limit for THMs (chloroform, bromodichloromethane, dibromochloromethane, and bromoform) is 80 parts-per-billion (ppb). Current detection methods involve retrieving water samples from reservoirs, wells, etc. and sending them to a chemical laboratory for analysis, often taking many months for results to be reported. A need exists for a reliable, light-weight, low-cost, highly-sensitive, and easily deployable water sensor that performs THM analysis in just a few minutes.

Accomplishment—We developed a portable system for THM detection in water using purge and trap, followed by isothermal gas chromatography and finally detection using a nanoporous-carbon (NPC) coated surface acoustic wave (SAW) sensor device. The SAW sensor device is at the heart of this detection scheme. SAWs respond to increased surface mass as a function of analyte concentration, which changes the acoustic propagation speed and can be measured as a phase shift in the wave over a fixed length. Sorbent coatings on a SAW surface can increase device response. We find that NPC coatings are reproducible, sensitive, and stable for long term use. Fig. 1 shows a 100 MHz SAW device coated with 1-µm-thick NPC (mass density ~ 1 g/cm^3), previously shown to be sufficient to achieve limits-of-detection (LOD) < 1 ppb for most volatile analytes studied. Fig. 2 shows the detection of each THM from fixed mixtures that are separated via a gas chromatograph and directed over the NPC-coated SAW. Chloroform elutes first, followed in succession by each chemical in order of molecular weight, with bromoform appearing last. Each response peak is integrated and plotted versus the known concentration for each THM in Fig. 3. We find similar functional behavior at these near-ppb concentration levels as we did previously for other volatile analytes at higher concentration levels, i.e. power-law behavior that fits to a straight-line on a log-log graph. These results demonstrate that 1 µm-thick NPC-coated SAW devices have LODs < 1 ppb for chloroform and ~ 1 part-per-trillion for bromoform!

Finally, we studied the relationship between the NPC coating thickness and the SAW response to controlled chloroform exposures, shown in Fig. 4, for thicknesses ranging from 0.25 to 2.5 µm, this time using only the response peak height, or phase shift. These results provide a defining property for NPC used for SAW device chemical detection. The chloroform LODs decrease exponentially with increasing NPC thickness, not linearly, as expected. Increasing NPC thickness from 1.1 to 2.5 µm, a factor of 2.2, improves the LOD by 20-fold, nearly an order-of-magnitude greater than expected!

Significance—Nanoporous-carbon coatings sorb volatile chemicals better than any other materials ever reported, improving SAW device microsensor LODs by multiple orders-of-magnitude. In particular, optimally NPC-coated SAW devices can detect THMs at part-per-trillion levels. This enables the development of portable chemical analysis systems for numerous field applications, including Homeland Defense, ES&H, Industry, and EPA regulations for our Nation's clean (and safe) water supply.

Sponsors for various phases of this work include: Laboratory Directed Research & Development and Work for Others

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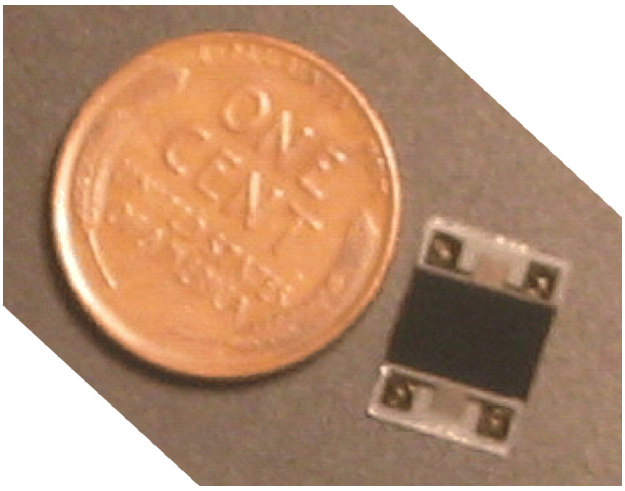

Figure 1. Photo of an NPC-coated 100 MHz SAW device next to a penny. Electrical contacts are made to the four large Au contact pads, and the Au transducer lines between them generate and detect the acoustic wave.

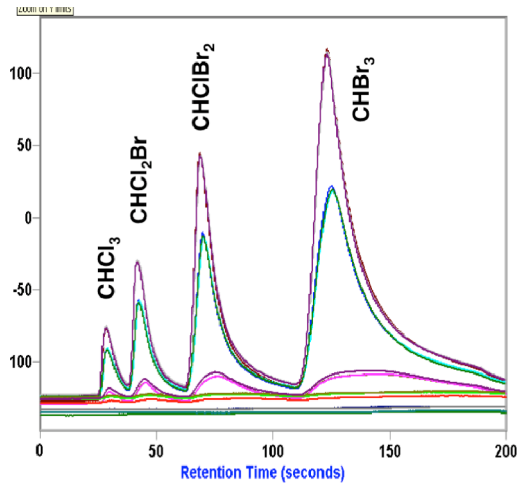

Figure 2. Phase-shift response from a 1 µm thick NPC-coated SAW device for controlled exposures to various concentration THM mixtures.

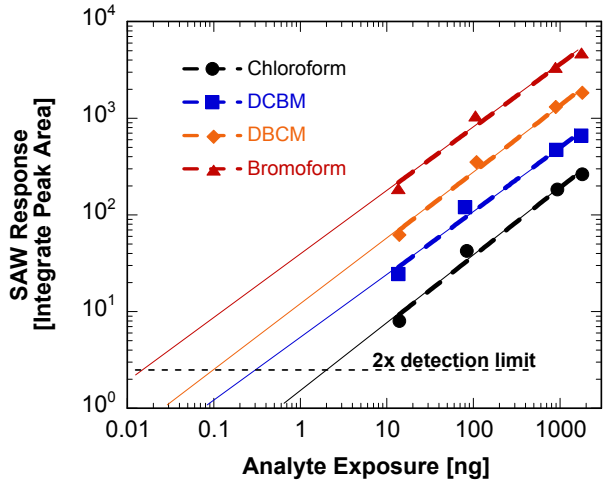

Figure 3. SAW response vs. analyte exposure for all four THMs, using the data shown in Fig. 2. (Note: 12 ng ~ 1 ppb.) The dashed line is placed a factor of two times above the SAW device detection limits, due to signal-to-noise. Therefore, the LODs for chloroform, DCBM, DBCM and bromoform are 0.16, 0.026, 0.0088, and 0.0013 ppb, respectively.

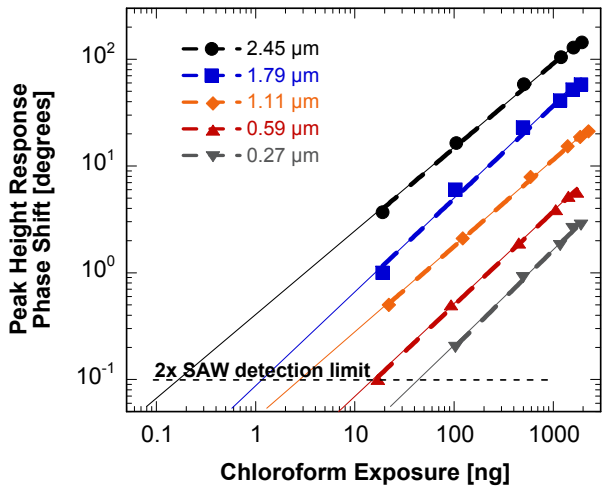

Figure 4. SAW response for chloroform detection as a function of NPC coating thickness. The LODs improve from 3.8 to 0.008 ppb for thicknesses ranging from 0.27 to 2.45 µm.