NCC2-5185: "Evaluation of Relative Sensitivity of SAW and Flexural Plate Wave Devices for Atmospheric Sensing"

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1. Acknowledgements

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2. Abstract

The objective of this project is to evaluate the suitability of the ultrasonic flexural plate wave (FPW) device as the detector in a gas chromatograph (GC). Of particular interest is the detection of nitrous oxide (N_20). From experimental results we conclude analyte detection is achieved through two mechanisms: changes in gas density, and mass loading of the device membrane due to the sorption of gas molecules. Reducing the dead volume of the FPW chamber increased the FPW response. A comparison of the FPW response to that of the surface acoustic wave (SAW) detector provided with the GC (made by MSI, Microsensor Technologies, Inc.), shows that for unseparated N_20 in N_2, the FPW exhibits a sensitivity that is at least 550 times greater than that of the SAW device. A Porapak Q column was found to separate N_20 from its carrier gas, N_2 or He. With the Porapak Q column, a coated FPW detected 1 ppm N_20 in N_2 or He, with a response magnitude of 7 Hz. A coated SAW exhibited a response of 25 Hz to pure N_20. The minimal detectable N_20 concentrations of the sensors were not evaluated.

3. Background

The flexural plate wave (FPW) device has been shown to function well as a gravimetric sensor for measuring the concentration of a vapor (see "Acoustic Wave Sensors", Ballantine et al., Academic Press, 1997). As illustrated in Figure 1, the micromachined FPW device has a thin silicon nitride membrane peripherally supported by a silicon frame.

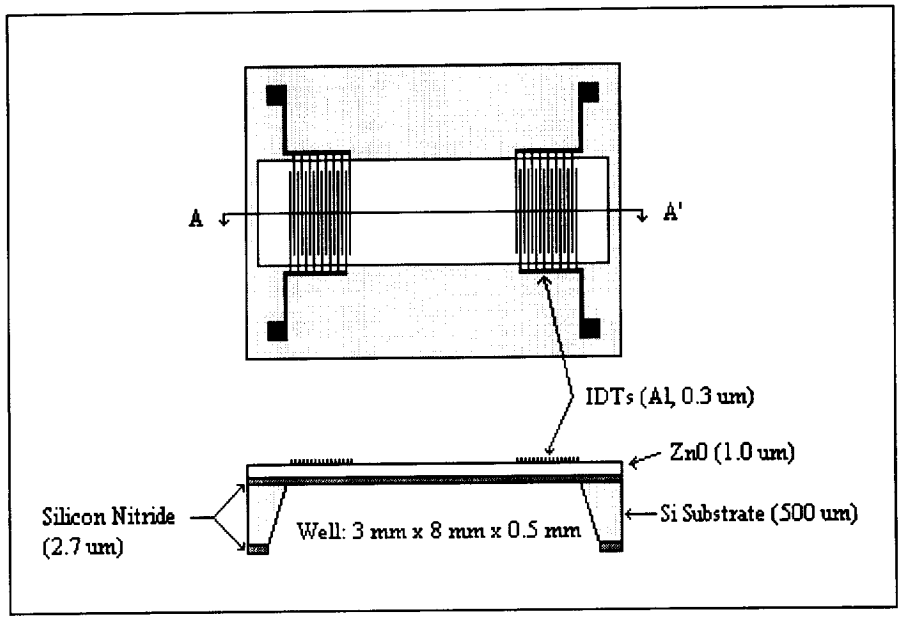

Figure 1. FPW Delay Line: Top View and A-A' Cross Section

Input and output transducers, which are formed by a piezoelectric film and patterned aluminum electrodes, can generate and detect anti-symmetric ultrasonic plate waves in the megahertz frequency range. Sorption of gas into a polymer film deposited on the membrane shifts the phase velocity of the plate wave. Using a delay-line oscillator, which is formed by an electronic amplifier connected between the delay-line output and input, a change in this wave velocity is readily measured as a frequency shift. Alternatively, a bare FPW delay-line configuration measures the density of the surrounding medium.

The reaction of the FPW delay-line to a change in mass per unit area, Δm, can be characterized by a gravimetric sensitivity factor S_m. This reaction is governed by the equation $(\Delta f / f) = S_m \cdot \Delta m$, where f is the resonant frequency of the oscillator and Δf is the shift in resonant frequency induced by the change in mass Δm. The value of S_m may be approximated from the expression $S_m = - \frac{1}{2} \cdot M$, where M is the mass per unit area of the membrane. With a high value of gravimetric sensitivity and a well-developed fabrication process, the FPW delay-line offers several attractive features for gas detection.

When sensing gas density, the FPW device is characterized by a density sensitivity S_ρ. This mode of operation is described analogously as $(\Delta f / f) = S_\rho \cdot \Delta \rho$, where $\Delta \rho$ is the change in gas density. The density sensitivity, S_ρ, is related to the gravimetric sensitivity, S_m, by the equation $S_\rho = \delta \cdot S_m$. The evanescent decay distance of the device, δ, is roughly $\lambda / 2\pi$, where λ is the ultrasonic wavelength of the structure.

In practice, the use of two sensors, a reference device and an active device, can minimize spurious responses to environmental variables such as temperature and air pressure. As configured in this experiment, both devices experience ambient conditions, but only the active device is exposed to the vapor of interest (in some experiments a voltage source with constant frequency was used as the reference FPW device).

4. Equipment

An MSI-301 gas chromatograph with SAW detectors was modified to incorporate FPW devices. As illustrated in Figure 2, the MSI-301 is comprised of a sampling pump, a sample concentrator, a Porapak column, an air pump and scrubber to generate carrier gas, and a pair of surface acoustic wave (SAW) devices. As the bulk gas sample propagates through the column, column-molecule interaction gradually separates the sample into its constituents. With the proper column, each constituent emerges at a different retention time. Each component induces a shift in the resonant frequency of the active SAW or FPW device.

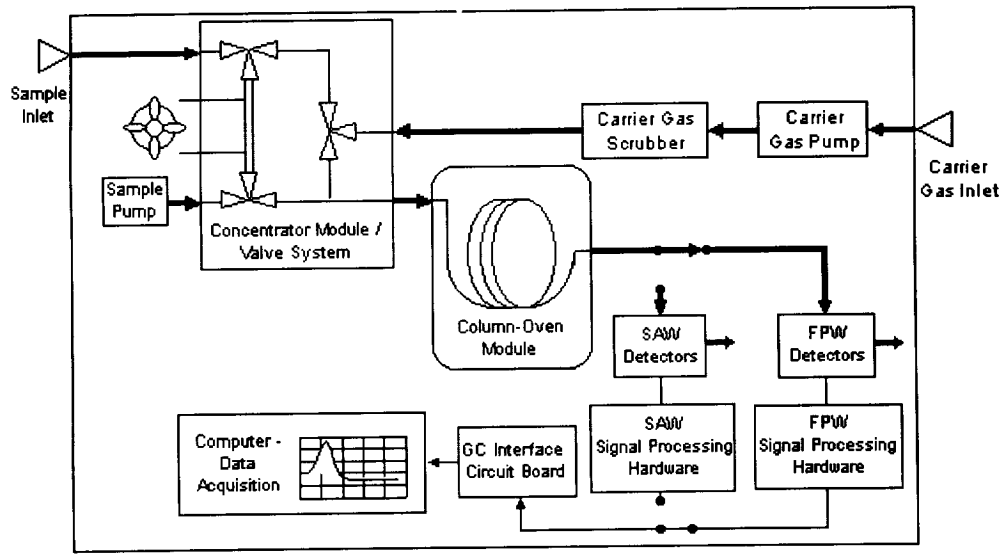

Figure 2. Schematic of Modified MSI-301 Gas Chromatograph

To incorporate the FPW sensors into the MSI-301, the gas flow from the GC column was redirected over the active FPW sensor. A circuit board (developed by Bryan Chen) modifies the FPW voltage output signal into a form indistinguishable from that of the SAW devices. Switching the GC

interface board leads between the FPW and SAW devices allows data collection with the MSI-301 software, GC_RAP.

The FPW housing, illustrated in Figure 3, was a modified version of the SAW housing. Unlike the SAW device, in which the wave travels only on one side, the entire membrane of the FPW oscillates with a sinusoidal displacement. To take advantage of this unique feature, flow from the GC column can be directed over both sides of the FPW through two chamber inlets.

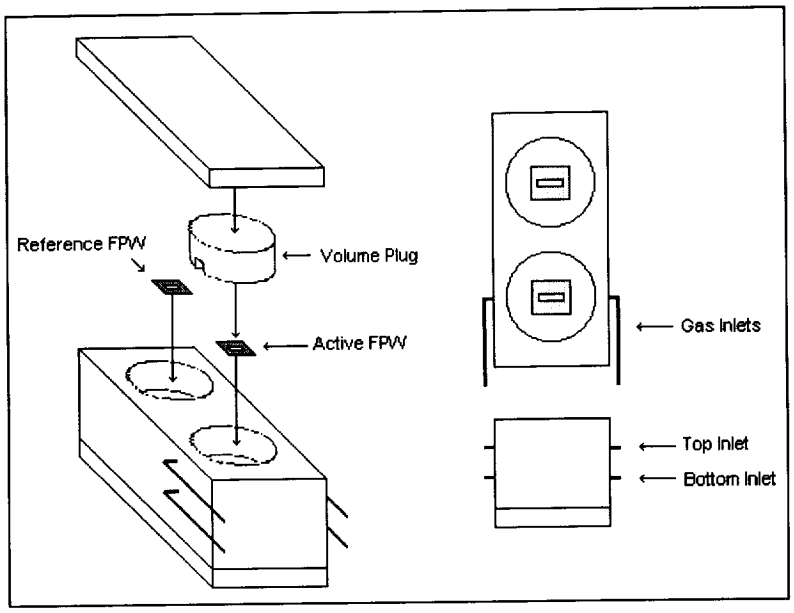

Figure 3. FPW Housing: Perspective, top, and side views

Gas Samples

The 100 ppm N_20 in N_2 or He experiments were conducted with gas canisters acquired from Aldrich Chemical Company. The 1 ppm N_20 in N_2 results were obtained with gas samples from Scott Specialty Gases. Richard Quinn provided the 300 ppb N_20 in He samples.

5. Experiments

Coatings

In order to investigate the effects of coating on device sensitivity, the devices were coated with a polymeric adsorbent, polyisobutylene (PIB). While the coated SAW devices were furnished by MSI, the FPW devices were coated with an airbrush at U.C. Berkeley. The PIB thickness on the SAW devices was nominally 200 kHz (resonant frequency 250 MHz), and the FPW coating was 50 kHz (resonant frequency ~3.5 MHz). For initial experiments, only the well of the FPW device was coated. Although the PIB coating improved both SAW and FPW device sensitivity, it was not N_20 selective.

Sensor Chamber Volume

Early experiments showed that a bare FPW was sensitive to N_20 in He. It was hypothesized that the FPW device was responding to a change in the density of gas near its membrane, and that this response could be improved by reducing the volume of the chamber. As shown above in Figure 3, a brass plug was fabricated which eliminated most of the dead space around the active FPW sensor. The initial volume around the active FPW was approximately 0.42 in^3. With the plug, this volume was reduced by a factor of seven to 0.06 in^3. The volume of the SAW chamber was less than 0.01 in^3.

Detector Noise

A problem encountered with both sensors is initial baseline frequency drift. This drift occurs when the active device must equilibrate to the temperature of the column air flow, usually a few tenths of a degree Celsius different than ambient air. Temperature equilibration takes twenty to thirty minutes, but lasts longer for coated devices.

Measurements indicate that the noise levels of the SAW and FPW devices are comparable, and that the PIB coating has variable effects. The minimum meaningful frequency shifts are shown below in Table 1.

Table 1. Device Noise Levels (+ / - Hz per second)

	Bare	Coated
FPW	0.40	0.43
SAW	0.42	1.06

Reproducibility

Results achieved with both the SAW and FPW devices are readily reproducible at high N_20 concentrations, such as 100 ppm, and with other vapor samples such as ethanol. The reproducibility at lower concentrations has not been sufficiently evaluated. Samples run successively (during the same day for instance) exhibit highly reproducible results. Figure 4 shows two such N_20 trials performed within hours of each other. This chromatogram was produced with the Porapak P column, which does not separate N_20 from the carrier gas N_2. External variables such as temperature and air pressure can also cause shifts in peak size over time.

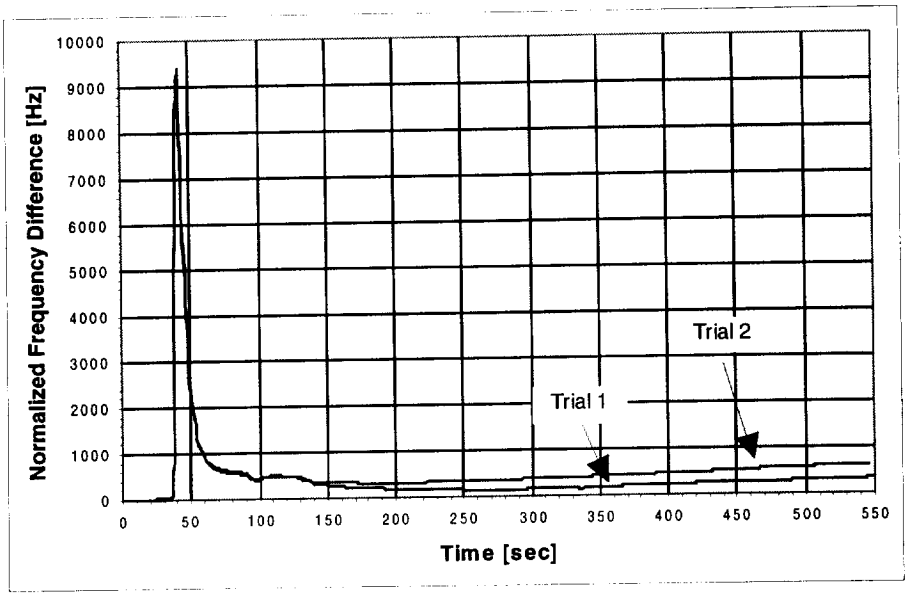

Figure 4. Coated Plugged FPW Response to Unseparated 100 ppm N_20 in N_2, Successive Trials

5.1 Porapak Q Column

Two GC columns were investigated -- the Porapak P and Q. Only the Porapak Q column separated N_20 from the carrier gases, N_2 and He. The magnitude of the coated SAW response to **pure N_20** was 25 Hz (not shown). The SAW could not sense 1 ppm N_20 in N_2 or He (the detection limit of the SAW was not investigated). As shown in Figure 5, the coated FPW detected 1 ppm N_20 in He or N_2. The magnitude of the response was 7 Hz.

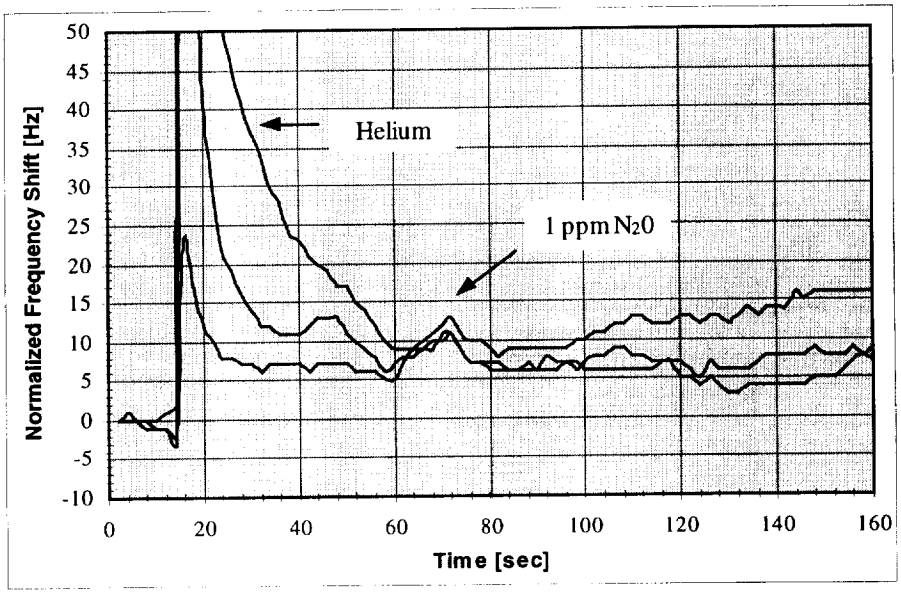

Figure 5. Coated, Plugged FPW Response to 1 ppm N_20 in Helium – Three Trials

5.2 Porapak P Column

With the Porapak P column the N_20 and carrier gases, N_2 and He, elute simultaneously. Thus the results shown below are the aggregate response of the sensors to both the N_20 **and** the carrier gases, N_2 or He. In this report, the term 'unseparated' is used to denote the simultaneous elution of N_20 and the carrier gases He or N_2. Conclusions about N_20 sensitivity can not be made with this unseparated data because the FPW also shows a large response to both He and N_2 gas.

5.2.1 FPW and SAW Response to Unseparated 100 ppm N_20 in N_2

Table 2 summarizes SAW and FPW detection results for N_20 in N_2. Results are expressed in terms of peak height, in Hz, and peak area, which is the dimensionless product of Hz and seconds. The PIB coating improved the SAW device sensitivity by a factor of 3, and the FPW sensitivity by a factor of around 40. The reason for this difference in improvement remains unclear.

Table 2. SAW and FPW Response to Unseparated 100 ppm N_20 in N_2

	SAW Device		Unplugged FPW Device		Plugged FPW Device	
	Peak Area	Peak Height	Peak Area	Peak Height	Peak Area	Peak Height
Bare	25	5	--	--	3,300	200
Coated	75	-17	17,800	730	123,000	9300
Improvement (absolute value): $\frac{\Delta Area_{coated}}{\Delta Area_{uncoated}}$, $\frac{\Delta f_{coated}}{\Delta f_{uncoated}}$	3.0	3.4	--	--	37.3	46.5

Figure 6 shows the coated SAW and coated, plugged FPW aggregate responses to 100 ppm N_20 in N_2. The graph has a different axis for the SAW, with a scale of Hz, than for the FPW, with a scale of kHz. Additional tubing between the MSI-301 column to the FPW housing causes the longer elution time for the FPW.

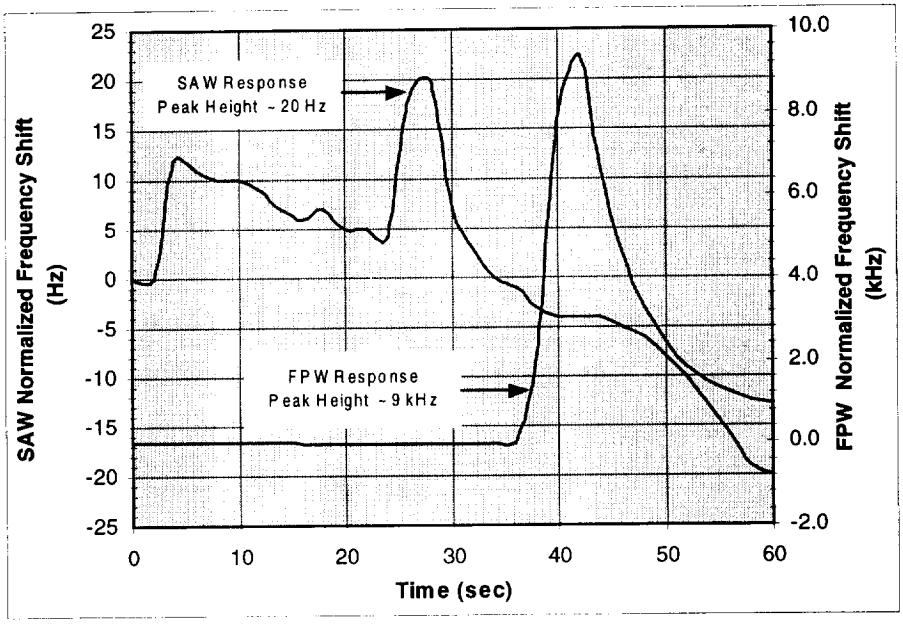

Figure 6. Coated SAW and FPW Response to Unseparated 100 ppm N_20 in N_2

Table 3 shows the relative sensitivities of the SAW and FPW sensors (FPW response divided by SAW response). Using peak area, the response to unseparated N_20 in N_2 samples of a coated and plugged FPW is up to three orders of magnitude greater than the response of the SAW. Using peak height, the FPW device is 550 times more sensitive to unseparated N_20 in N_2 samples than the SAW device. It is presently unclear why the PIB coating affects the relative sensitivities.

Table 3. Relative Sensitivities of SAW and FPW Detectors to Unseparated N_20 in N_2

	Unplugged FPW		Plugged FPW	
	$\frac{\Delta Area_{FPW}}{\Delta Area_{SAW}}$	$\frac{\Delta f_{FPW}}{\Delta f_{SAW}}$	$\frac{\Delta Area_{FPW}}{\Delta Area_{SAW}}$	$\frac{\Delta f_{FPW}}{\Delta f_{SAW}}$
Bare Devices:	--	--	130	--
Coated Devices:	240	40	1640	550

Figure 7 illustrates FPW sensitivity before and after the plug volume reduction. Table 4 provides these results in numerical format. With a coated FPW, the unseparated N_20 in N_2 peak area jumped from 17,800 to 123,000 as a result of the volume reduction. Thus a seven-fold reduction in volume produced a seven-fold increase in FPW sensitivity. Since the volume of the SAW chamber is less than 0.01 in^3, further reductions in the FPW volume promise to yield even greater sensitivities.

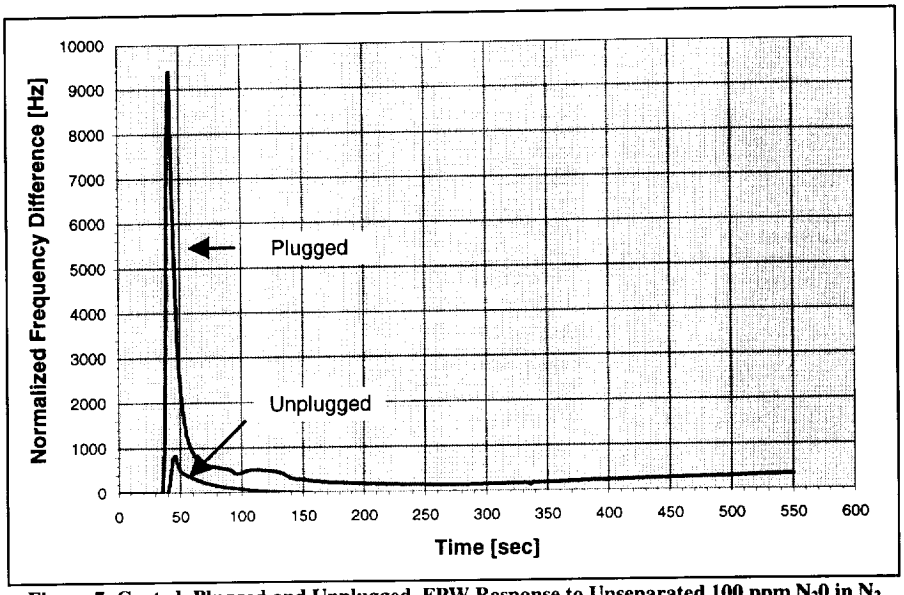

Figure 7. Coated, Plugged and Unplugged, FPW Response to Unseparated 100 ppm N_20 in N_2

Table 4. Improvement in FPW Sensitivity to Unseparated N_20 in N_2 with a Reduction in Chamber Volume

	Unplugged FPW		Plugged FPW		Improvement	
	Peak Area	Peak Height	Peak Area	Peak Height	$\frac{\Delta Area_{plugged}}{\Delta Area_{unplugged}}$	$\frac{\Delta f_{plugged}}{\Delta f_{unplugged}}$
Coated FPW	17,800	730	123,000	9300	6.9	12.7

5.2.2 FPW and SAW Response to Unseparated 100 ppm N_20 in He

Experiments analogous to those presented above were also conducted with 100 ppm N_20 in He. Although the detection of N_20 in He has little practical use, this gas mixture was initially used because it was readily accessible. The reader is reminded that results shown below represent the aggregate response of sensors to N_20 and the carrier gas He. Tables 5 and 6 gives SAW and FPW response to unseparated 100 ppm N_20 in He. The PIB coating improved the sensitivity of the SAW device by a factor of 2 or 3.

Table 5. SAW Response to Unseparated 100 ppm N_20 in He

	100 ppm N_20 in He		300 ppb N_20 in He	
	Peak Area	Peak Height	Peak Area	Peak Height
Bare SAW	400	110	100	30
Coated SAW	1310	250	not performed	not performed
Improvement (absolute value): $\frac{\Delta Area_{coated}}{\Delta Area_{uncoated}}$, $\frac{\Delta f_{coated}}{\Delta f_{uncoated}}$	3.3	2.3	--	--

Table 6. FPW Response to Unseparated 100 ppm N_20 in He

	Unplugged FPW		Plugged FPW		Plug Improvement	
	Peak Area	Peak Height	Peak Area	Peak Height	$\frac{\Delta Area_{plugged}}{\Delta Area_{unplugged}}$	$\frac{\Delta f_{plugged}}{\Delta f_{unplugged}}$
Bare FPW	--	2100	--	21000	--	10
Coated FPW	330,000	7250	$1.68*10^6$	34000	5.1	4.7
Improvement: $\frac{\Delta f_{coated}}{\Delta f_{uncoated}}$	--	3.5	--	1.6		

Figure 8 shows the coated SAW and plugged, coated FPW responses to unseparated 100 ppm N_20 in He. The SAW, with a scale of Hz, is given on a different axis than the FPW, with a scale of kHz.

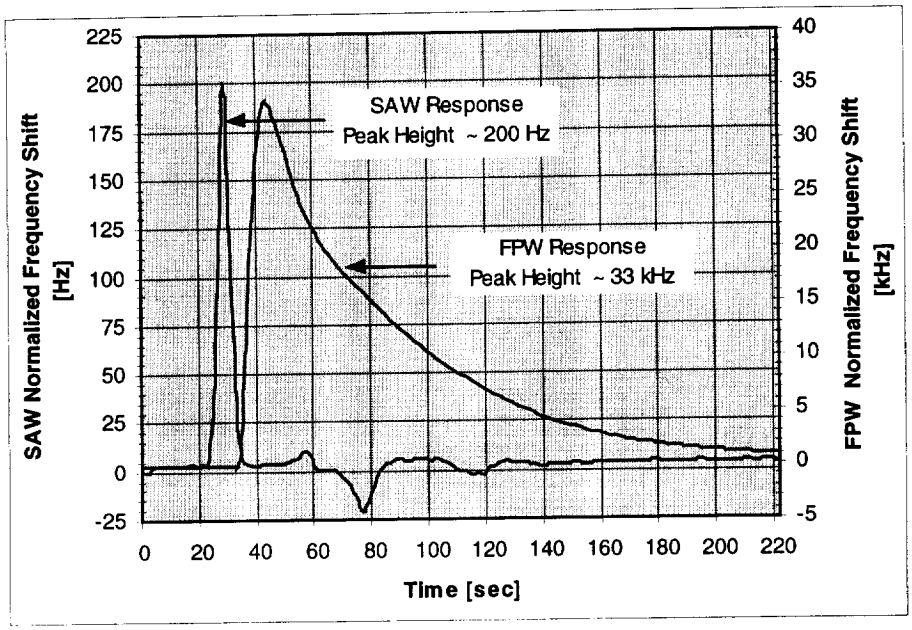

Figure 8. SAW and FPW Response to Unseparated 100 ppm N_20 in He

The relative sensitivities of the SAW and FPW devices to unseparated 100 ppm N_20 in He are given in Table 7. The plugged and coated FPW device is considerably more sensitive than the SAW.

Table 7. Relative Sensitivities of SAW and FPW Detectors to Unseparated 100 ppm N_20 in He

	Unplugged FPW		Plugged FPW	
	$\frac{\Delta Area_{FPW}}{\Delta Area_{SAW}}$	$\frac{\Delta f_{FPW}}{\Delta f_{SAW}}$	$\frac{\Delta Area_{FPW}}{\Delta Area_{SAW}}$	$\frac{\Delta f_{FPW}}{\Delta f_{SAW}}$
Bare Devices:	--	20	--	190
Coated Devices:	250	30	1280	130

The response of the FPW sensor to unseparated 100 ppm N_20 in He is given in Figure 9. The bare FPW exhibits what is believed to be an N_20 peak embedded in a helium peak. Using peak height instead of area, the PIB coating improved the FPW device sensitivity by a factor of 1.6 or 3.5.

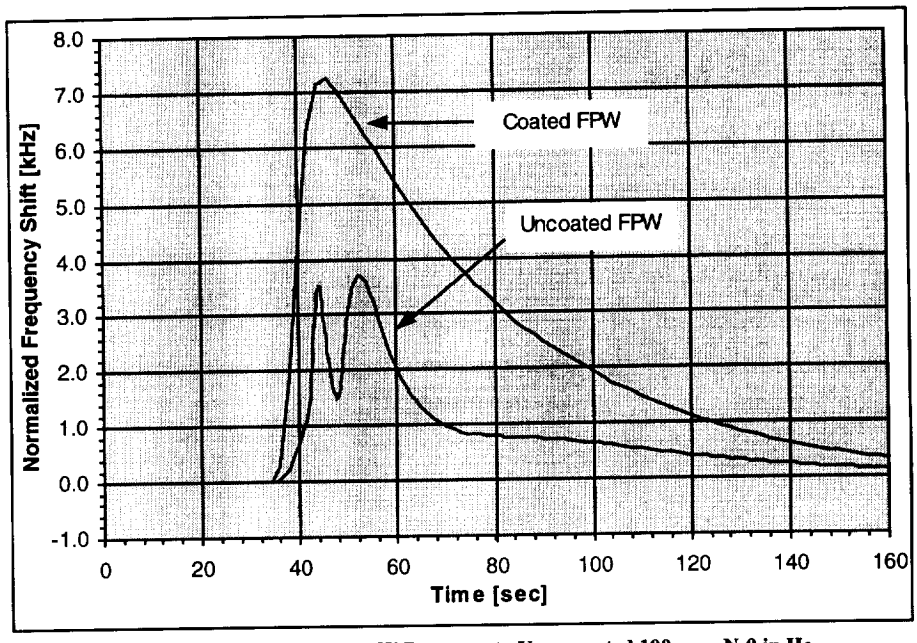

Figure 9. Bare and Coated FPW Response to Unseparated 100 ppm N_20 in He

As shown in Figure 10 and Table 6, a reduction in the dead volume around the FPW sensor significantly improved sensitivity. With the addition of the plug, the 100 ppm N_20 in He peak jumped from an area of 330, 000 to 1.68 x 10^6. Thus the seven-fold reduction in volume produced a five-fold improvement in sensitivity.

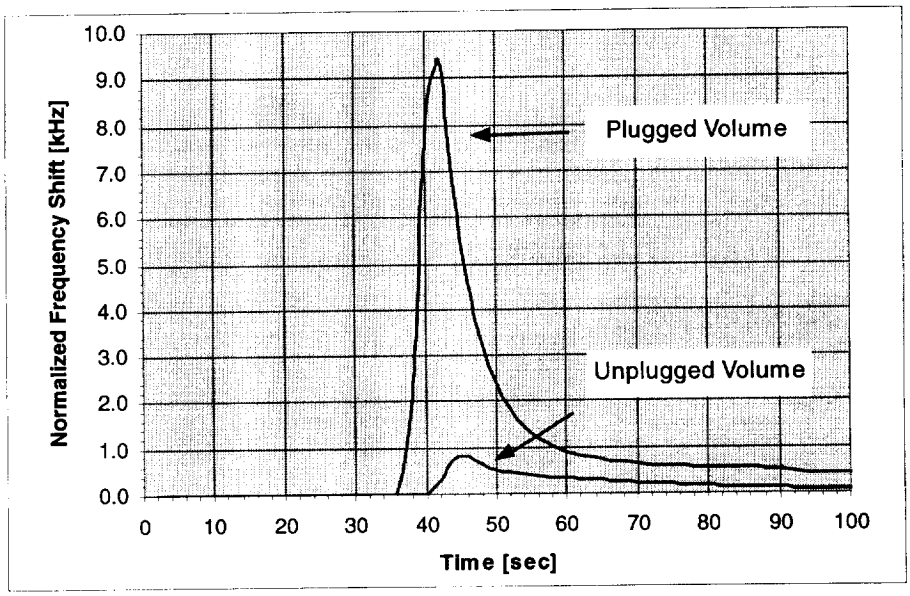

Figure 10. Coated, Plugged and Unplugged, FPW Response to Unseparated 100 ppm N_20 in He

Conclusions

With a Porapak P column, the FPW is several orders of magnitude more sensitive than the SAW to unseparated samples of N_20 in He or N_2. With the Porapak Q column, which separated N_20 from the carrier gases, a PIB-coated, plugged FPW exhibited a response of 7 Hz to 1 ppm N_20 in He or N_2. The magnitude of the SAW response to **pure** N_20 was 25 Hz . It should be noted that the sensor coating, polyisobutylene, was chosen as a "starting point", and is more suited for the detection of organic volatiles.