

A Compact Gas Detector with Smart Sampling

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ABSTRACT

Through an internally funded research program, Defiant Technologies has developed a compact chemical detector that can be tailored for a range of target analytes. The system uses a preconcentrator (PC) to collect and screen samples from the air, and a surface acoustic wave (SAW) microbalance to detect analytes when they are released from the PC. This PC-SAW system serves as a trigger for a secondary analysis channel that uses a micro-gas chromatographic (micro-GC) column to perform a more detailed analysis of the air. This combined approach provides high-confidence results while conserving power and minimizing response time. By properly selecting coatings on the PC, micro-GC and SAW, the unit can be designed for optimum performance in detecting specific target gases while ignoring interferents. This paper presents test results from our research and discusses some of the applications for this type of system.

Keywords: Detectors, sensors, chemicals, gas analysis, monitoring, chromatography, microsystems

1. INTRODUCTION

Defiant Technologies is a small business in Albuquerque, New Mexico that produces portable chemical detection systems for military, industrial and environmental applications. Defiant's basic analysis approach is to capture a gas sample in a chemically-selective porous media, and then thermally desorb the sample in a sharp, concentrated pulse. The sample pulse moves to a microbalance where it is momentarily captured in a polymer and weighed. This process is illustrated schematically in Figure 1. The selectivity of the porous media on the preconcentrator (PC) and the coating on the surface acoustic wave (SAW) microbalance offers some ability to identify the gas sample while disregard interferants, but it has limited specificity. For greater identification specificity, Defiant offers a system with a micro-gas chromatograph (micro-GC) column (see schematic in Figure 2). A sample enters the micro-GC in a sharp pulse, then separates into individual constituents as a result of interactions with a coating (i.e., a stationary phase) on the column walls. As the constituents emerge from the column, they temporarily collect on the microbalance for weighing. The time between sample injection and when constituents emerge from the column (i.e., the elution time) is used to identify the analyte. The measured weight of the sample is related to the concentration of the analyte in the air.

Gas chromatography is accepted as one of the most versatile and reliable methods for chemical analysis, but separations can take several minutes to hours to complete. For portable systems, long analysis times can be problematic. A long analysis time means that fewer samples will be surveyed and areas of concern will be more difficult to pinpoint. Since the Canary-One™ system does not have a GC column, it can perform a relatively fast analysis (~20 seconds or less). The results may be acceptable for a quick screening, but greater detail about the sample may be needed to plan an appropriate response. The Canary-Two™ system with the GC column provides a more detailed assessment about the concentration and composition of a gas sample, but the two to three minute analysis time may be unacceptable for survey and screening situations. A system that can quickly survey the surroundings, and then switch to a more complete analysis mode when needed would have benefits over either system alone.

Defiant has developed a system that combines a fast analysis mode for quick assessments and a GC analysis mode for improved gas identification. In the normal configuration of Canary-Two™, a bypass line permits a high flow rate over the PC during the sample collection stage. The valve shown in Figure 2 switches the flow between the bypass line for sample collection and the GC path for sample separation detection. In Defiant's new system, a SAW microbalance is added to the bypass line as illustrated in Figure 3. By periodically firing the PC, the bypass SAW provides a quick check for the presence of target analytes in the air and the approximate concentration. If high concentrations are detected, the system can immediately move to an analysis mode, and if concentrations are low, collection times can be extended to collect larger volumes. An added benefit to this approach is that overwhelming (and possibly

contaminating) the system with large sample can be avoided. Also, the linear dynamic range of the sensor system is extended by collecting the optimum sample volume. Results from this new analysis approach and details about the hardware in this system are discussed in the following sections.

2. SYSTEM COMPONENTS

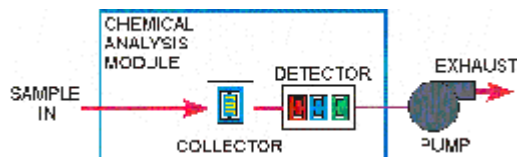


Fig. 1. Two-stage analysis system used in Canary-One™ for quick sample screening.

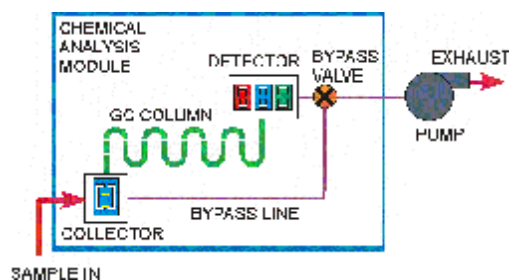


Fig. 2. Three-stage analysis with a gas chromatography (GC) column used in Canary-Two™.

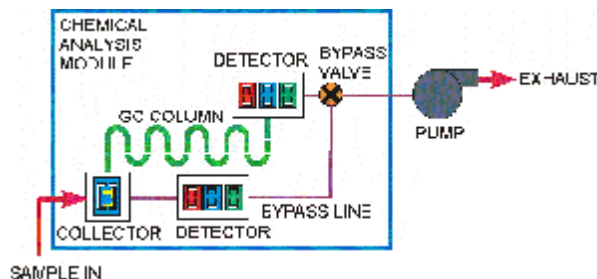


Fig. 3. Canary-Three™ system with second detector in the bypass line for quick sample screening.

2.1 Preconcentrators (PCs)

The first stage of the analysis system is a sample collector or preconcentrator (PC) where analyte samples are trapped in a coating. Upon heating, the trapped sample thermally desorbs and proceeds to the GC and detector. Defiant selects among three types of preconcentrators based on the vapor pressure of the analyte and concentrations of interest. For high vapor pressure compounds, such as volatile organic compounds, the tortuous path preconcentrator (TP-PC) shown in Figure 4a is used. The finned silicon structure provides a high surface area for sorptive coatings, yet the structure has sufficiently low mass and high thermal conductivity to permit rapid heating during the sample desorption process.



Fig. 4a. (left) high surface area tortuous path preconcentrator (TP-PC)
 4b. (center) low mass pivot plate preconcentrator (PP-PC)
 4c. (left) concentric ring preconcentrator (CR-PC)

For low-vapor pressure compounds, such as nerve or blister agents, a micro-plate suspended on two struts is used (see Figure 4b). The lower mass and enhanced thermal isolation of pivot plate preconcentrator (PP-PC) allows faster heating for a sharper injection of samples into the GC column. PC coatings are more efficient at capturing the low vapor pressure analytes, so even with the lower surface area of the PP-PC collects sufficient analyte for analysis and the sharper injection creates sharper peaks in chromatograms from the short columns (1-2 meter) used in Defiant’s systems.

A third option offered for PCs is shown in Figure 4c. The concentric ring PC (CR-PC) structure offers a higher surface area that the PP-PC and yet has a lower mass than the TP-PC. It is a cross-over design that operates over a broad cross-section of analytes. The flow-through design of the CR-PC also allows a more direct injection into the GC columns without the need for turns in the flow path. This reduces the transport distance, which can be important when prospective analytes have a tendency to adhere to walls in the connecting fluidics.

Coatings on the PC must be able to collect a vapor sample and hold onto it throughout the collection cycle. Additionally, the coating must be able to rapidly release the sample when heated. The PC coating acts more like a sponge than a bucket – target analytes will diffuse into the coating until equilibrium conditions are established with the gas stream. If analyte concentrations in the sample air change, the PC coating will move to a new equilibrium condition.

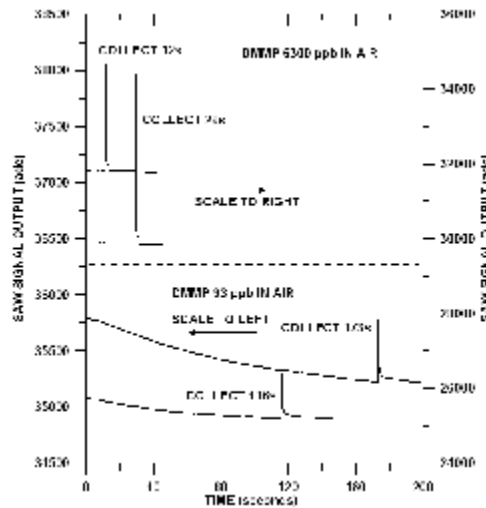


Fig. 5. Preconcentrator sample injection to a SAW detector.

Primarily, the PC functions as a sample injector since it can release a sharp pulse of an analyte relative to a steady or changing background concentration. This injector aspect characteristic is shown in Figure 5 where a SAW was located

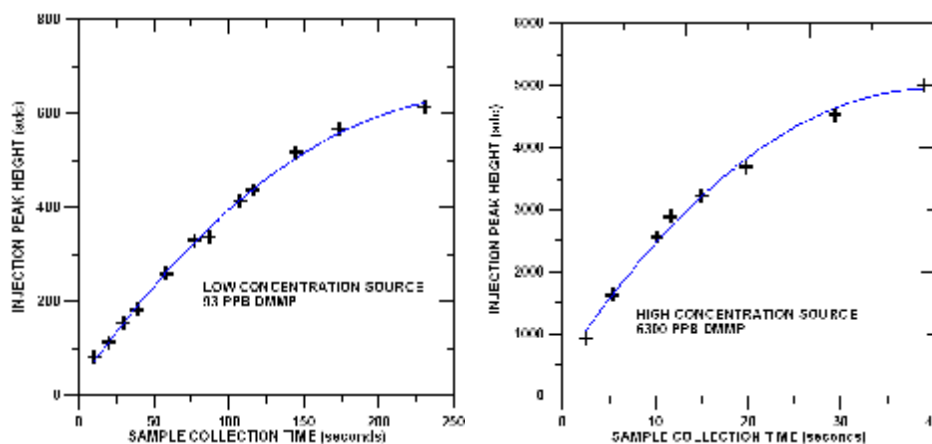


Fig. 6. Injection peak heights as a function of collection time and analyte concentration. Collection efficiency is reduced as PC coating approaches equilibrium with the sample stream.

downstream of the PC. The PC was hot until time zero, then cooled and allowed to collect for the indicated times. The PC was then heated for two seconds and the resulting peak observed on the SAW. Peak heights are proportional to the collection time, but as the coating approaches equilibrium with the sample stream, additional collecting time will not increase the peak height. Injection peak heights as a function of time and analyte concentration in the sample stream are shown in Figure 6.

Tenex and carbon coatings have been tested, but Defiant typically uses solgel coatings. The high collection capacity of solgels make them suitable for a wide range of sample concentrations – they effectively scavenge the air for analytes at low concentrations, and they can collect large amounts of analyte at high concentrations before becoming saturated. The solgels are modified to improve collection of different compounds. These modifications are achieved through additives and processing conditions during the curing process. Solgels can be selectively tailored for low-vapor pressure compounds (such as nerve or blister agents) or high-vapor pressure compounds (such as volatile organic compounds).

2.2 LIGA Gas Chromatograph Column

Commercial columns are rather bulky and the hardware necessary to maintain temperature and pressure on the column adds to the size of the overall system. To avoid these obstacles, Defiant uses the micro-GC column that is illustrated in Figure 7. The column consists of an array of holes formed in a nickel coupon, and caps on either end of the array that route the flow into a serpentine path. The center array coupon and the end caps are formed in a LIGA process, so the column is referred to as a LIGA-GC. A one-meter LIGA-GC is approximately the size of a dime, and a 10-meter column is slightly smaller than a sugar cube. Like in commercial columns, a stationary phase coating is applied to the inner wall of the column to aid in gas separation. The compact size of this GC column simplifies temperature control and allows the GC to be rapidly heated for faster chromatography.

A typical chromatographic separation for the LIGA-GC column is shown in Figure 8. This figure shows the injection of 7 analytes into a one-meter, 250-micron inner diameter, LIGA-GC. The analyte separated by the LIGA-GC were detected on a flame-ionization detector. This separation is achieved in less than 2 minutes with clear separation of 5 of the 7 analytes. The co-eluting analytes, ethyl benzene and p/m-xylene have very similar vapor pressures. Ethyl benzene and p/m-xylene could have been further separated by a smaller diameter column, but this would also lengthen the overall analysis time.

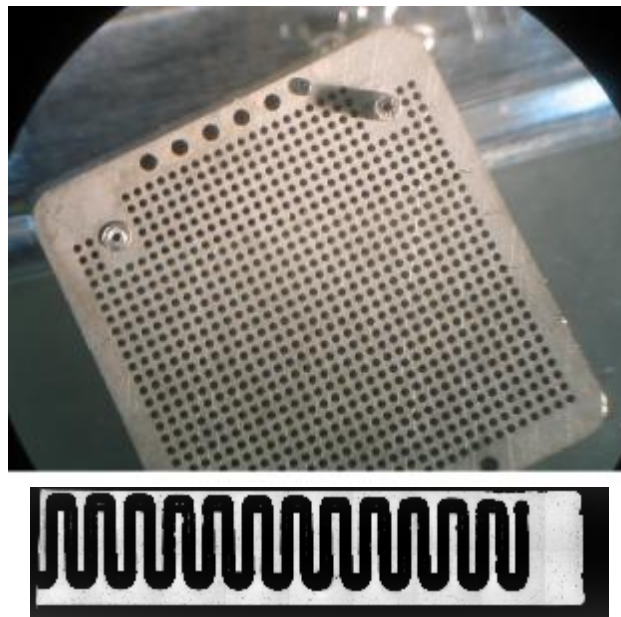


Fig. 7. LIGA GC column. An array of holes in a plate form a serpentine GC column when top and bottom caps connect adjacent holes.

The separation in Figure 8 was accomplished with a constant temperature LIGA-GC column. Figure 9 shows what can be achieved by ramping the GC temperature during the separation stage. Here, 3 analytes are collected on a micro-PC and injected into the LIGA-GC column. For this test, a SAW microbalance detects the individual analytes as they emerge from the column. With a constant temperature of 50°C, the methyl salicylate (MES) peak is so broad that it is not detectable. At 70°C, the MES peak almost co-elutes with DEMP (diethyl-methylphosphate). Like full-scale GC systems, separations can be improved by tailoring the temperature profile of the GC, but with micro-GC columns much less power is required. Figure 9 shows how separations are improved with CG ramping. Not only is there better definition on the MES peak, but all three peaks have improved separation.

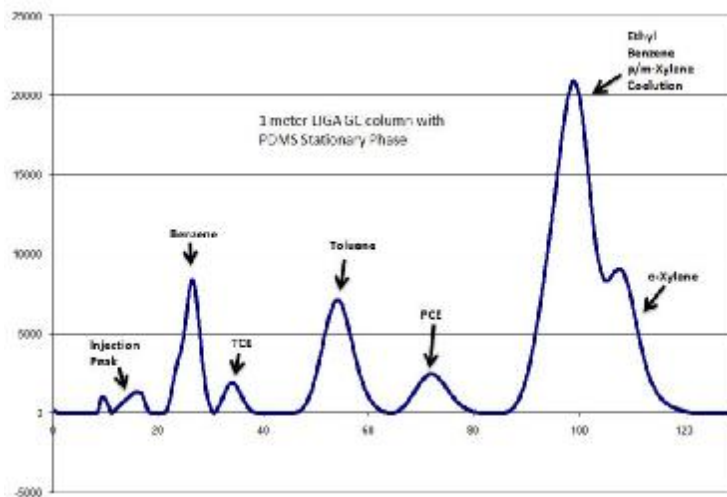


Fig 8. Separation of volatile organic compounds on a 1-meter LIGA GC columns. Time in seconds is on horizontal axis. Vertical axis shows output signal from a flame ionization detector.

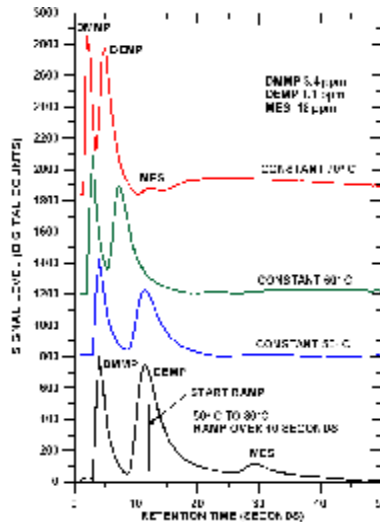


Fig. 9. The effect of ramping GC temperature on analyte separations

2.3 SAW Microbalance Detectors

A surface acoustic wave (SAW) microbalance is a resonator that operates on a principle similar to the quartz crystals in most of today's clocks. An alternating voltage in a primary pair of conductors on a quartz surface establishes a compression wave that moves across the surface. A second pair of conductors is in the path of this wave, and, as the wave passes, a current is developed in the secondary conductors. Technically this is referred to as a delay line SAW and any mass that accumulates on the quartz surface in the wave path will affect the delay in time between the launched wave from the primary conductors and the detected wave on the secondary conductors. By measuring this time delay, it is possible to measure mass down to picogram levels.

Like the LIGA-GC, the SAW is roughly the size of a dime. One of the SAWs used by Defiant is shown in Figure 10. This SAW uses a 500 MHz drive frequency so it is referred to as a 500 MHz SAW resonator. This particular design has two delay lines for measuring mass, and one reference delay line to compensate for temperature changes in the quartz. The mass sensing area is approximately 300 microns by 800 microns. The two rectangular blocks shown in Figure 10 are application specific integrated circuits (ASICs) that use a feedback amplifier to establish the wave in the quartz; a Gilbert cell mixer to measure the time delay between the launched and detected wave. A DC voltage powers the ASIC and a DC signal proportional to the mass is output. By using the ASICs, all of the high frequency signals are limited to the quartz substrate.

Introducing mass to the surface can be done by condensation directly on the quartz or sorption into a coating on the quartz. Condensing on the SAW surface is a method successfully used by some sensor manufacturers. A GC column discharges near the surface of the SAW and analytes condense onto the chilled surface. Heating the quartz at the end of the analysis cycle drives off the condensate and readies the detector for further tests.

An alternative to condensation is sorption into coatings on the quartz surface. SAW coatings must be able to sorb the target analytes when they are present in the sample stream and then the polymers must release the analytes when clean air flushes over the surface. Several SAW coatings are now available through Seacoast Sciences in Carlsbad, CA. Conceptually, an array of SAW microbalances could be used with different coatings applied to each SAW. By selecting coatings with targeted analyte preferences, a unique signature could be developed for every analyte.

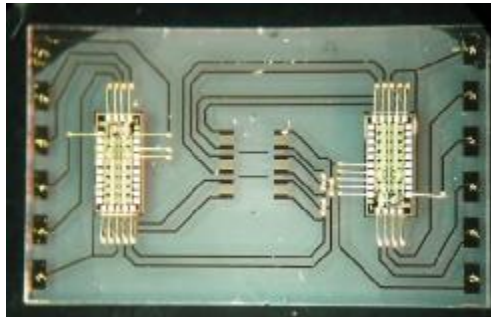


Fig. 10. Surface acoustic wave (SAW) detector.

It conceivably would be possible to eliminate the GC column and simply rely on the SAW array response for analyte identification. In practice, however, the complex interactions between SAW coatings and analytes of various concentrations make this goal hard to achieve, and calibrating the array can be extremely difficult. In the case where there are only a couple of target analytes, though an arrayed-SAW approach to analyte identification may be practical, but in general, a GC separation is preferred.

3. SYSTEM INTEGRATION

The three basic components of the gas analysis system, that is the PC, the GC, and the SAW, are microfabricated parts (or dies) and they must be integrated together to make the appropriate electrical and gas connections. Integration is achieved using the gas manifold shown in Figure 11. Individual manifolds for each component are connected together using inert tubing and epoxy, and then the assembly is screwed to a circuit board. Spring loaded probes embedded in the manifold modules make the electrical connections to the circuit card. By making relatively simple changes in the circuit card, a variety of manifold configurations can be constructed to suit different analysis needs. In addition, if a die needs to be replaced, the damaged die alone can be exchanged without destroying the manifold packaging.

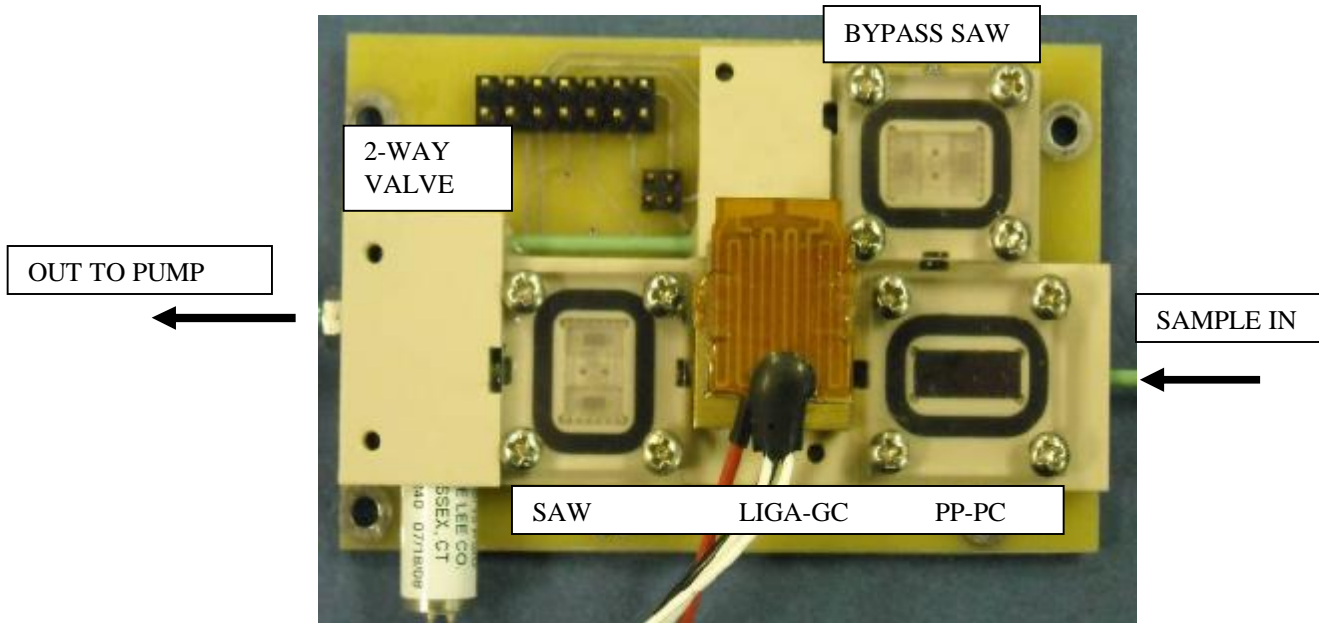


Fig. 11. Canary-Three™ gas module. Micro components drop into sockets in the manifold for easy assembly and maintenance.

Figure 11 shows the standard Canary-Three™ gas module with a PP-PC, a LIGA-GC, a SAW microbalance, and a second SAW in the bypass line. A 2-way valve alters flow through the system from the bypass path used in collection, to the analysis path through the GC. During the sample collection process, the flow across the PC is approximately 150 SCCM in Canary-Two™ systems. The capture efficiency of the PC's typically improves at higher flowrates, however, coated SAW's perform better at lower flowrates (<40 SCCM). When the system switches to the analysis mode, the additional flow restriction introduced by the GC column causes the flowrate to drop to about 5 SCCM. There is leeway in all of the flow parameters and the units are equipped with variable speed pumps to achieve optimum system performance. The most important aspect is that the flowrate remains consistent during the analysis process to provide consistent chromatography results.

4. TEST RESULTS

The object of this program is to develop a system that can automatically adjust sample collection times to optimize system performance over a wide range of sample concentrations. Results in Figures 5 and 6 showed how collection times can be tailored to achieve a desired injection peak height. The biggest injection peak will not always give the best chromatography results. Figure 12 shows that at lower concentrations, the chromatography peaks become more Gaussian in shape as collection times increase. At high concentrations though, the peaks become lopsided and tailing increases as collection times rise. Also demonstrated is that retention times become shorter when the injected sample increases. When the retention time changes with concentration, it can complicate the identification of a sample.

The gas module in Figure 11 provides a means of measuring analyte concentrations in air as it is collected. After a short collection cycle, the PC is fired and the signal change on the bypass SAW is noted. If the bypass SAW signal is small, the collection cycle is allowed to run for a full term. If the signal is large, collection is automatically abbreviated. For the tests shown in Figure 13, the full-term collection cycle was set for 80 seconds however, if the bypass SAW sees a 300 adc (analog/digital converter count) peak after collecting for 5 seconds, then the collection time is terminated after 10 seconds. The chromatogram in 13b shows SAW signals when the system continues collecting for 80 seconds because analyte concentrations are low. High analyte concentrations cause the abbreviated collection cycle shown in Figure 13a. In both cases the retention is well defined, the peaks are near Gaussian.

A side benefit to the Canary-Three™ system is that cycle times for a complete analysis is shorter when the need for a quick answer is the greatest (i.e., at high concentrations). In addition, the bypass SAW shows changes in real-time as they occur in the environment. Figure 14 shows signals from the by-pass SAW as headspace concentrations of

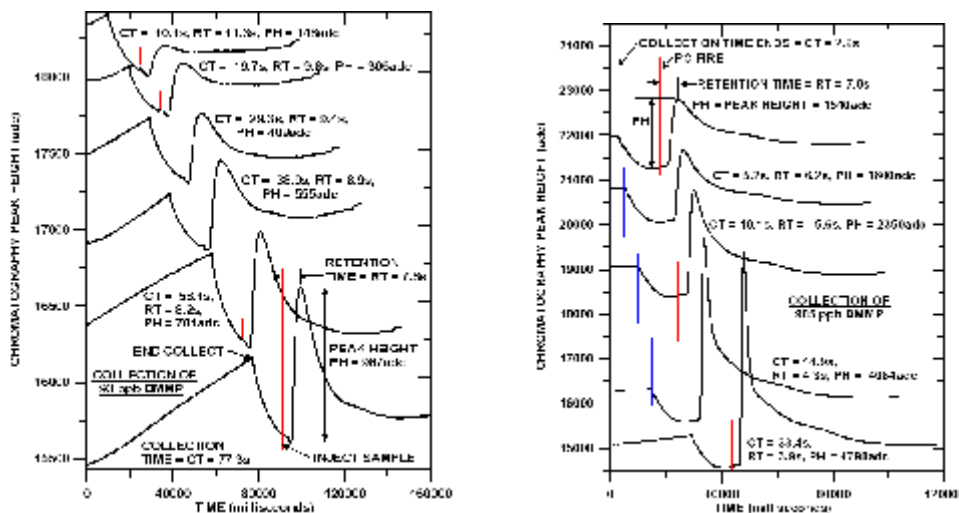


Fig. 12a. Chromatography as a function of collection time for low analyte concentrations
 12b. Chromatography as a function of collection time for high analyte concentrations.

dimethyl-methyl phosphonate (DMMP), methyl salicylate (MES), and di-isopropyl phosphonate (DIMP) are momentarily encountered. Part of the sample blows past the PC and changes the mass on the SAW. When the captured sample is subsequently released, a full analysis is performed and peaks for the three analytes show in the chromatogram.

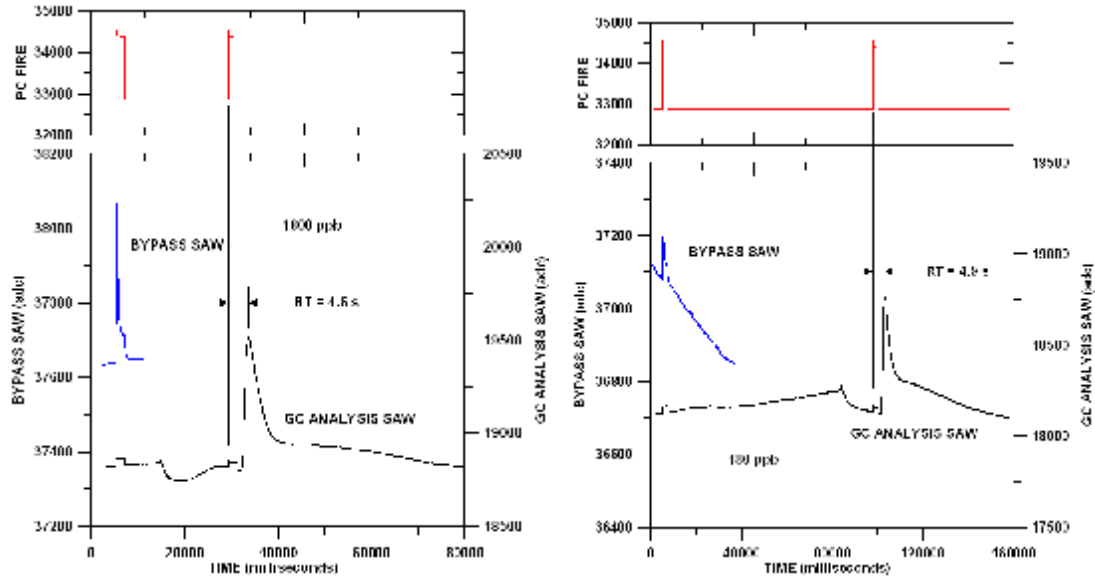


Fig. 13. Canary-Three™ operation with smart sampling function. The system automatically shortens collection times when the SAW in the bypass line senses peaks 300 counts above baseline. This approach shortens cycle times and prevents overwhelming the system with high analyte concentrations.

5. SUMMARY AND CONCLUSIONS

Traditional chemical analysis is done in a systematic manner with sample collection, separation and detection stages. By using micro-fabricated components, Defiant Technologies provides a systematic analysis of samples with a hand-held package. Measuring analytes in a sample as they are collected provides information that can improve the overall system

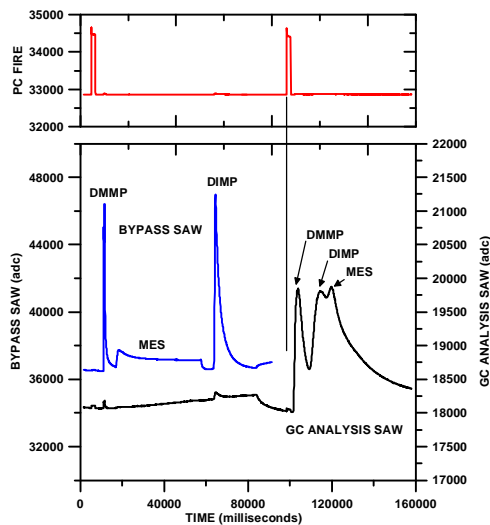


Fig. 14. Canary-Three™ results showing the real time introduction of analytes to the system and the subsequent analysis of the sample captured on the preconcentrator.

operation. Defiant has implemented this approach in its Canary-Three™ system by adding a second detector to the collection stage. Tests have shown that this approach can provide information that is useful in metering the sample mass prior to performing a full analysis. Analysis cycles are shortened and near real time detection can be achieved with this Canary-Three™ system. Future testing will explore linearity of the Canary-Three™ system and its ability to detect multiple analytes at multiple concentrations.

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