Real Time Chemical Process Measurements Using a Multi-port GC/SAW System

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ABSTRACT

The performance of a fast gas chromatograph equipped with a Surface Acoustic Wave (SAW) detector for chemical process measurement is evaluated in this paper. The performance of the GC/SAW system is measured in terms of minimum detection levels for common volatile organic compounds (VOCs) and semi--volatile organic compounds (SVOCs) at part-per-billion (ppb) levels in less than 10 seconds. The process monitor uses a new solid state detector based upon surface acoustic waves (SAW) that can detect and quantify the mass of VOC and SVOC compounds at picogram levels. These capabilities allow for real-time control decisions to be made, and in less time than previous techniques involving laboratory testing of process samples.

The ability to monitor bio-chemical processes such as metabolism of bacteria and detecting compounds such as methyl isocyanate in real time is shown.

KEY WORDS

GC/SAW, Gas Chromatography, volatile organic compounds VOC, semi-volatile organic compounds (SVOCs)

INTRODUCTION

Optimal chemical processing depends upon timely and accurate measurements of the chemical processes including emissions and impurities. Process control involving hydrocarbons and other volatile organics is important to many fields of chemistry. There is a need for fully automated instruments which can speciate and quantify process chemistry in real time.

Although a number of field screening instruments such as GCs have emerged, there is still a lack of instruments versatile enough to analyze a wide range of organic compounds. Although GCs are an effective tool, their usefulness as a process instrument is limited by retention times of several minutes or more even for relatively simple separations [1,2]. Because there is frequently no pre-concentration of the sample, the limits of detection (LOD) and quantification (LOQ) may not be adequate for many applications. On-going research has shown that GC analysis speed can be significantly improved. It has been shown that detection of organic and inorganic compounds can be enhanced with the use of a Surface Acoustic Wave (SAW) sensor. Until recently, however, no major breakthroughs in GC design had resulted in sub-minute analysis of VOCs

This paper details the development and application of a novel GC system equipped with a SAW detector for process measurement applications. Performance results are given for a SAW analyzer subjected to a number of tests in the laboratory and field conditions. These test results show that it is possible to speciate and quantify a wide range of chemicals in near real time (less than 10 seconds) with good precision and accuracy in measuring chemical processes.

DESCRIPTION OF TECHNOLOGY

High speed (10 seconds) chromatography has been achieved by combining innovations in column, injector, preconcentrator, and sensor technologies into a chemical vapor analyzer system, called the zNose® [3,4]. The major elements of a multi-port vapor analysis system are depicted in Figure 1.

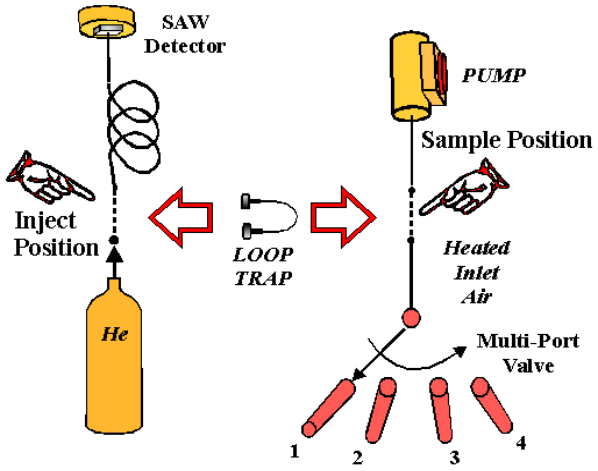

Figure 1. Multi-port process control system containing one section with helium flowing through a self-heated capillary column and the other for sampling up to 16 different vapor sources.

In this approach self-heating of the GC column is accomplished by passing electrical current directly through a metal column. The low thermal mass of the metal capillary column allows resistive heating of the column at rates as high as 20°C/second. Isothermal analysis provides maximum resolving power but temperature ramping allows the system to analyze both light and heavy compounds simultaneously.

Chemical vapors to be analyzed are pumped through a small loop trap (0.5 milliliter/second). The trap consists of a metal capillary filled with approximately 1 mg of tenax® absorbent. During sampling the trap is cooled and organic compounds are preconcentrated in the trap absorbent. After preconcentrating, the trap is switched into the helium flow by a 6-port rotary valve and becomes an injector. Preconcentrated organics are injected by rapidly heating the trap to 250°C in 10 milliseconds.

Such rapid column heating produces very short analysis times and causes effluent peak widths to be measured in milliseconds rather than in seconds or minutes as is done with a conventional gas chromatograph [5,6]. Conventional GC detectors like flame ionization or electron capture are designed to measure column flux and often contain considerable 'dead' volume which makes them unsuitable for measuring millisecond wide peaks in chemical processes.

The SAW technology was originally developed to produce miniature frequency control elements for radar and communications equipment. A quartz crystal SAW resonator has been transformed into an integrating GC detector as shown in Figure 2. Electrical signals in the piezoelectric crystal generate surface waves or elastic vibrations bound to the surface of the crystal. Material interacting with the crystal surface changes the frequency of the resonator by slowing down the surface waves. The change in frequency is a direct measure of the amount of material on the crystal surface. The stability of the acoustic resonance allows the detector to achieve picogram sensitivity. The total change in frequency, measured in hertz (Hz), provides accurate quantification of the analytes as they exit the column. Variable sensitivity is achieved by controlling the temperature of the crystal with a thermoelectric heating and cooling element.

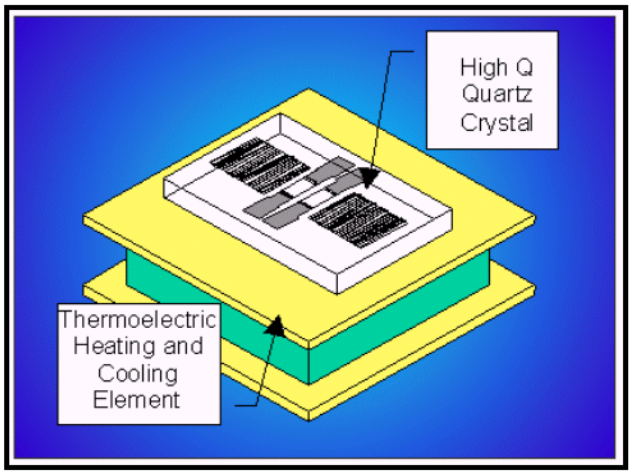

Figure 2. Design details of surface acoustic wave (SAW) detector.

Helium flowing from the GC column is directed onto the surface of the SAW crystal using a nozzle as shown in Figure 3. A thermoelectric cooling element maintains the crystal at a temperature cool enough (typically 10-20°C) to promote adsorption of VOC and SVOC vapors entrained in the column effluent. The thermoelectric element also is used to heat and remove organic films from the crystal by reversing the driving voltage. A short, 15 second, 150°C 'cleaning' step is used at the end of each chromatogram to clean the crystal before the next measurement cycle is initiated.

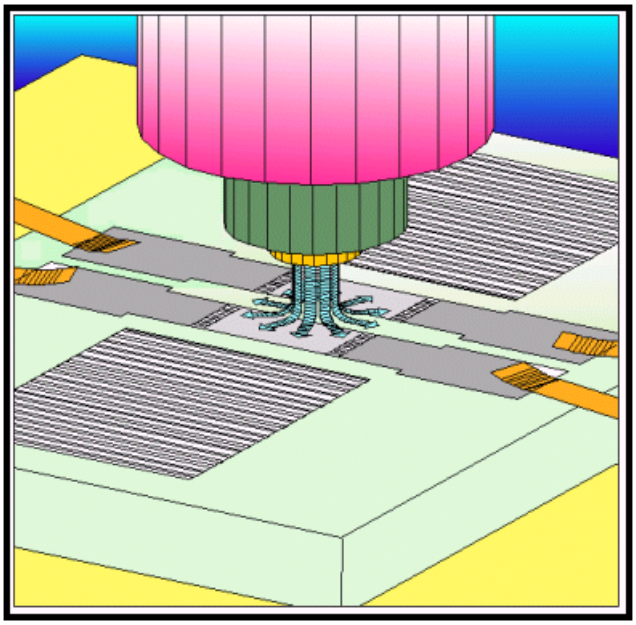

Figure 3. Surface acoustic wave GC sensor with nozzle details.

The SAW detector response is universal and non-specific. Sensitivity is controllable since it depends only upon the crystal temperature and analyte vapor pressure. No ionization source or high voltages are required to achieve picogram sensitivity. The integrating SAW detector has zero dead volume which gives it the ability to record short duration (millisecond) GC peaks accurately.

ZNOSE® FAST GC ANALYZER

The analyzer as shown in Figure 4 consists of a Fast GC enclosure and a system controller. The Fast GC enclosure contains the GC subsection which consists of the sample valve, preconcentrating trap, column and detector, and the support subsection which consists of the carrier gas bottle and power supply. The system controller is based on a laptop computer that analyzes the data and provides a user interface.

Once the materials sequentially exit the column, they interact with the SAW detector surface. The added mass of the material on the SAW surface lowers the oscillating frequency of the SAW crystal. The crystal frequency is mixed with a fixed reference frequency, which results in a difference frequency called the intermediate frequency (IF). The system electronics counts this IF and sends the information to the system controller. The system controller interprets the detector response and attempts to identify and quantify each material it has been programmed to recognize. The frequency shift caused by an analyte is proportional to the mass of material deposited on the detector.

The time required for the material to exit the column is the retention time (RT) which tags the compound by comparison with previously stored information. Unlike conventional GC columns, which are many meters in length and ramp at degree per minute rates, the columns used in the SAW/GC are 1 meter in length and can be ramped at up to 20°C/sec. This enables the GC portion of the system to produce repeatable, ten second duration chromatograms with peak widths measured in milliseconds

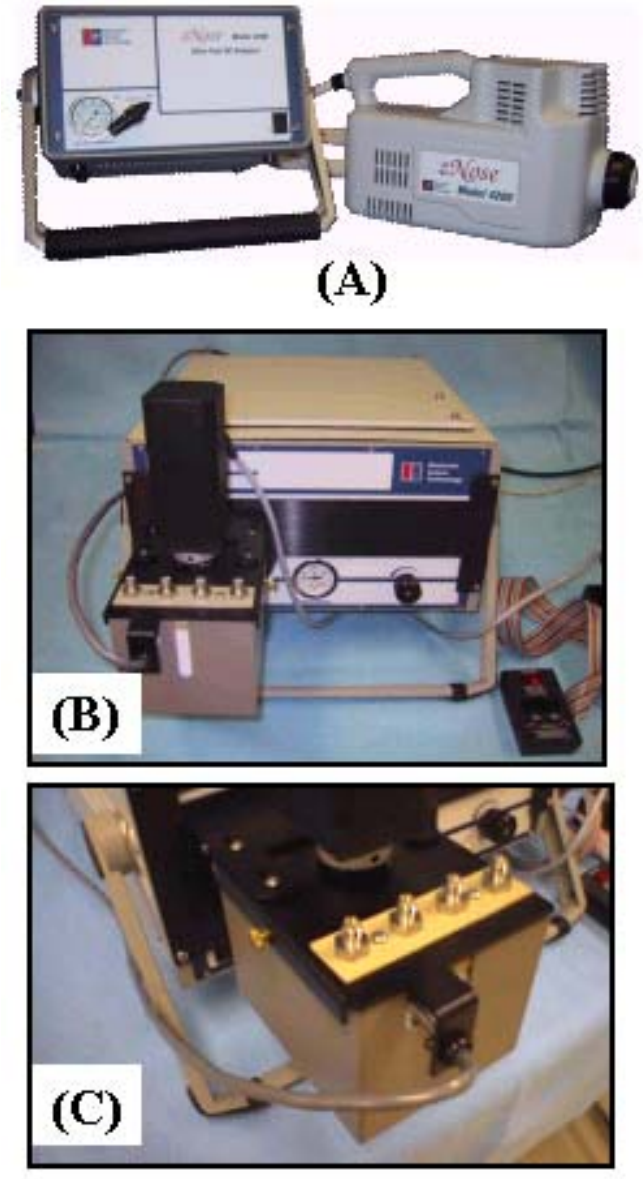

Figure 4. The zNose® ultra-fast GC design (A) re-configured as fully automatic chemical process controller (B & C) with a selectable multi-port inlet for measuring and controlling up to 16 multiple vapor sources.

Because of its picogram sensitivity the GC/SAW is a useful tool for quantifying the organic chemistry of a diverse number of chemicals. Using an uncoated solid-state mass-sensitive detector, picogram sensitivity, universal non-polar selectivity, and electronically variable sensitivity is achieved. An integrated vapor preconcentrator coupled with the electronically variable detector allows the instrument to measure vapor concentrations spanning 6+ orders of magnitude.

The zNose® system as shown in Figure 1 consists of two parts. One part or section uses helium gas, a capillary tube (GC column) and a solid-state detector. The other part consists of a heated inlet and a pump, which draws process air into the instrument at a fixed flow rate, typically 0.5 milliliter/second. Linking the two sections is a "loop" trap, which acts as a preconcentrator when it is placed in the air section (sample position) and as an injector when placed in the helium section (inject position). Operation is a two-step process. Process air is first sampled and organic compounds within the air are collected (preconcentrated) on the trap. Once the sampling is completed, the trap is switched into the helium section where the collected organic compounds are injected into the helium flow. The organic compounds are separated as they pass through a temperature programmed GC column. Each compound typically has a different velocity and exits the column at a characteristic retention time. Speciation or identification is based upon each compound's unique retention time. As each compound (analyte) exits the column, it is detected and quantified by a (SAW) crystal detector. Detector sensitivity (physical absorption onto the quartz surface) is a function of crystal temperature. Electronic temperature control is achieved by a thermoelectric element attached to the backside of the crystal.

A high-speed gate-array microprocessor controls the processing of samples and includes electronic flow control, timing, electronic injection, and temperature control for the column, inlet, detector, and other parts of the instrument. The user interface, which is responsible for sending macro instructions to the microprocessor and displaying measurement results, can be a laptop computer or a remote computer using a wireless modem (1 mile range). A software program allows users to select appropriate measurement methods and to identify specific organic compounds in process air from a library of Kovats indices.

A 20-second chromatogram showing the GC/SAW response to n-alkanes over the range C6 to C22 is shown in Figure 5. Methanol containing 125 P.M. alkanes C6 to C14 provides a convenient headspace vapor for retention time calibration. Alkanes above C14 are considered semi-volatile and will not pass through unheated sample needles. Hence they must be directly injected into the heated inlet of the zNose®. Methanol containing 500 pg/μL n-alkanes (C16-C22) is used as an injectable vapor standard for the higher alkanes.

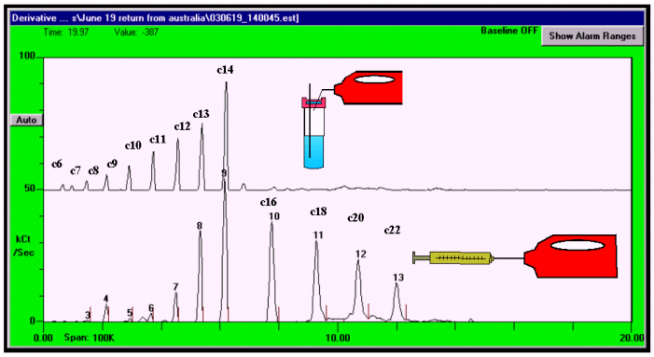

Figure 5. Typical n-alkane chromatogram response of a GC/SAW system

SENSITIVITY AND DETECTION LEVELS

Every GC instrument for process measurement has to be evaluated by the sensitivity and delectability of various analytes. The GC/SAW system was subjected to a series of tests. One of the first series of tests was to measure minimum detection level (MDL) of common organics. The MDL was based on the standard deviation of 7 replicate analyses at a concentration that gave a signal-to-noise ratio in the range of 5 to 10. The standard deviation, σ, of the 7 replicates was determined and then MDL was calculated based on the relationship, MDL = $3.14 \bullet \sigma$ where 3.14 is the students' t value for 7 replicates at 99% confidence level. The results of measurements are shown in Tables 1 and 2 and Figure 6.

Table 1. Minimum Detection levels of common volatile organic compounds (VOC).

Analyte	MDL (ppb in Air)
Chloroform	45
Cis 1,2 Dichloroethene	47
Benzene	42
Carbon Tetrachloride	130
Trichloroethylene	6
Toluene	10
Tetrachloroethylene	6
Ethylbenzene	2.5
o-xylene	2.5
1,1,2,2 Tetrachloroethane	3.6
o-xylene	2.5

These measurements were taken by sampling gas standards from a Tedlar bag for 30 seconds and using a detector temperature of 0°C. MDL levels lower than those indicated can be achieved by using a longer sampling time. These MDLs are typically one to one hundredth of MDLs that can be achieved using conventional systems under similar conditions[7].

The absolute precision and accuracy of these measurements were also made using certified Scott gas. The accuracy varied from 90-97% over the measurement range[7]. The data clearly showed that the GC/SAW system can make accurate and precise measurements.

PROCESS MONITORING APPLICATIONS

The GC/SAW system was tested on a number of process measurements. Two such measurements are listed below.

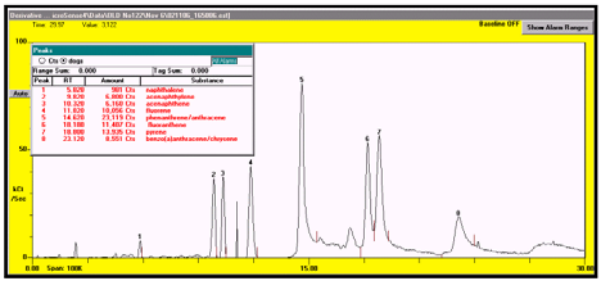

Figure 6. Typical GC/SAW chromatogram of common SVOCs as shown in Table 1.

Table 2. Minimum detection levels for some common polyaromatic hydrocarbon (PAH) compounds.

Analyte	MDL (pg)
Naphthalene	1
Acenaphthylene	0.1
Acenaphthene	0.1
Fluorene	0.5
Anthracene	0.2
fluoranthene	0.5
Pyrene	0.3
Chrysene	0.5

METHYL ISOCYANATE MEASUREMENT

Methyl isocyanate (also isocyanatomethane, methyl carbonyl amine, MIC. C2H3NO; H3C-N=C=O) is an important intermediate chemical in the production of carbamate pesticides and herbicides (such as sevin, carbofuran, methomyl, and aldicarb). It is also used in the production of rubbers and adhesives.

The standard deviation from a series of replicate measurements of MIC at relatively high concentration levels (1000 ppm) is shown in Table 3 and demonstrates the accuracy and precision of the GC/SAW for process control.

Table 3. Standard deviation of replicate measurements at high MIC concentrations *(0-1000 ppm ,13.8 Cts/ppm)*

Vapor Pressure (ppm)	Std Deviation (ppm)
971	**35**
70	**0.6**
55	**2.2**
5	0,25

Because MIC is also extremely toxic and can damage by inhalation, there is a need to monitor ambient air concentrations for safety. OSHA limits are 20 ppbv in air or 0.05 mg/m3, thus replicate measurements at 0-50 ppbv levels were also carried out. A typical series of replicate chromatograms, offset and overlaid for viewing, are shown in Figure 7. Standard deviations at several concentrations within this range are tabulated in Table 4.

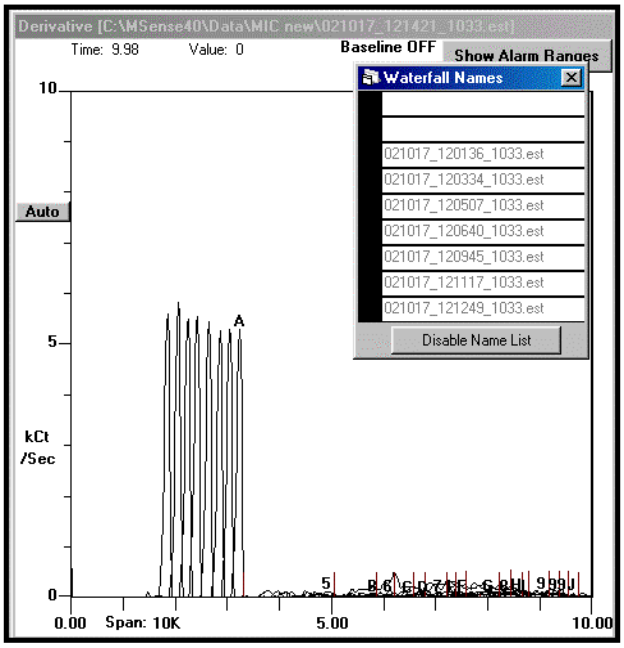

Figure 7. Replicate MIC chromatogram measurements, horizontally offset, using 55 ppbv vapor standard. Sample time was 30 seconds (15 milliliter) and detector temperature 20°C.

Table 4. Standard deviation of replicate measurements at low MIC concentrations (0-50 ppb , 1.76 Cts/ppb)

Vapor Pressure (ppm)	Std Deviation (ppb)
55	**1.05**
30	**1.15**
7.8	**0.26**

MONITORING BIOCHEMICAL PROCESSES

Biochemical processes are important for a wide range of industrial and pharmaceutical products. These processes frequently involve growing and maintaining a healthy colony of bacteria. There is a need to monitor the viability, health, and production of chemicals by bacteria in real time.

The GC/SAW was used to monitor the chemistry of headspace vapors from a liquid culture containing e. Coli bacteria. The real time chemical analysis provided information on nutrient levels as well as the number of colony forming units present. The concentration of compounds solely produced by the bacteria provides a convenient method of quantification and is illustrated in Figure 8. Measuring the concentration of indole (produced by e. Coli) with the GC/SAW provided a method of quantifying the bacterial population in real time. After a period of exponential growth the nutrient in the culture is exhausted and the bacteria population

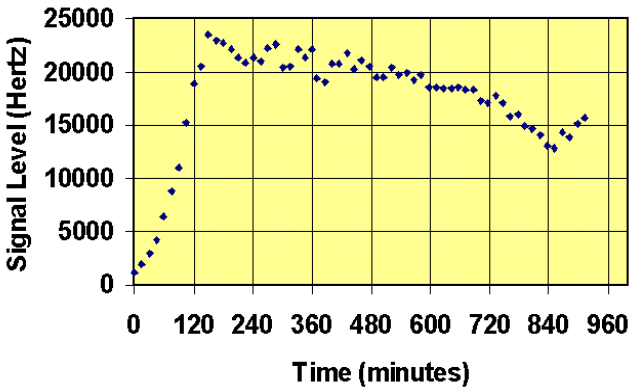

Figure 8. Indole signal level (headspace concentration) vs time for e.Coli liquid culture in a biochemical process.

reaches a plateau. Without further nutrient the population begins to decline and eventually die.

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SUMMARY

The Surface Acoustic Wave gas chromatography sensor developed in this program represents advancement in the art of chromatography for process measurements. The SAW detector is the first and only known integrating detector for GC systems. The device operating in the frequency domain directly requires no high voltages or radioactive ionization sources. It can process millisecond duration peaks, and is a true solid state chip technology with high accuracy at low cost.

This new technology represents a significant advancement in fast chromatographic methods as evidenced by the instruments ability to accurately measure in real time (10 seconds) a wide range of compounds and thus be used to improve productivity without sacrificing precision or accuracy

ACKNOWLEDGMENTS

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DEFINITIONS

SAW Detector – Surface Acoustic Wave Detector