

Dioxin/Furan Detection and Analysis Using A SAW Based Electronic Nose

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Abstract - The rise in birth defects in Japan and other countries throughout the world has been traced to high concentrations of dioxins and furans in the environment resulting from widespread incineration of waste. There is a need for real time instruments to test for the presence of these toxic compounds in air, water, and soil. To meet this need a new Surface Acoustic Wave (SAW) based electronic nose was evaluated and the technical results of this investigation are presented in this paper.

Introduction

Dioxins and Furan emissions from incinerators in Japan have become a serious public health problem since these are known to cause birth defects and cancer. The US EPA normalizes toxicity [1] to 2,3,7,8 dioxin, which has a Toxicity Equivalent Quotient (TEQ) of 1.0. TEQ factors are used to convert detected amounts of each analyte within a sample into total TEQ for the sample, usually measured in picograms (pg) or nanograms (ng) per meter³. Only recently (December 1997) has the Japanese Environmental Agency (EA) mandated that all incinerator emissions be below 80 pg-TEQ/m³.

Recent investigations involving volatile organic and semi-volatile compounds [2-3] have suggested that this technology could provide a means of monitoring dioxin and furan levels in real time. This paper describes research to determine linearity, minimum detection limits, and potential application of this of this new electronic nose technology to detecting dioxins and furans

SAW Sensor

Unlike previous electronic nose technology utilizing arrays of polymer coated sensors, the GC/SAW electronic nose utilizes a single tem-

perature controlled 500 MHz SAW resonator crystal (Figure 1) to measure the adsorption and desorption characteristics of analytes as they exit a temperature programmed GC capillary column [Ref. 4-6]. The sensing crystal and oscillator cir-

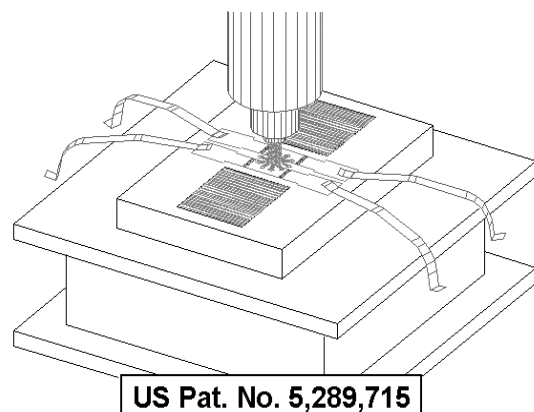


Figure 1- Temperature controlled SAW Sensor

cuitry are enclosed within a 2 inch diameter enclosure as shown in Figure 2. The SAW crystal is used to provide closed loop frequency control of an oscillator circuit and the oscillator frequency is a direct measure of the amount of material deposited.

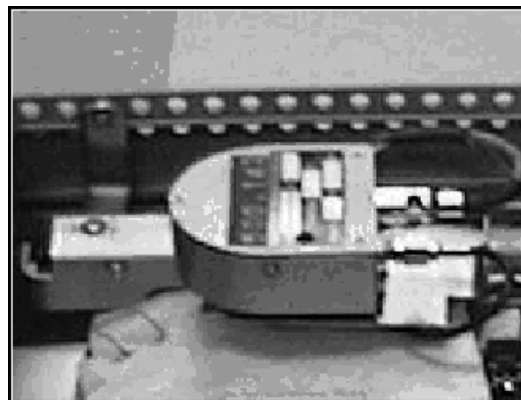


Figure 2- Packaged SAW Sensor module

A heated nozzle is used to focus the He carrier gas of the GC such that it impinges the acoustic standing wave pattern in an optimal manner. Focusing column effluent and the inherent high Q of an uncoated crystal results in a 10,000 fold increase in sensitivity over polymer coated delay line SAW sensors.

The detection limit of the SAW sensor was determined by the oscillator phase noise and crystal temperature (60°C). Precise control of the crystal temperature over the range 0°-150°C was by means of a thermoelectric element. Using a counter sample time of 20 milliseconds resulted in an Allan variance of 1-2 Hz. Sensitivity to dioxin and furan isomers was approximately 10 Hz/picogram, hence detection levels for the SAW sensor were at the part per trillion (picogram) level.

System Description

The GC/SAW electronic nose system consisted of a heated inlet and sample pump, a vapor preconcentrator and injector, a temperature programmed GC capillary column, and a SAW resonator sensor as shown in Figure 3.

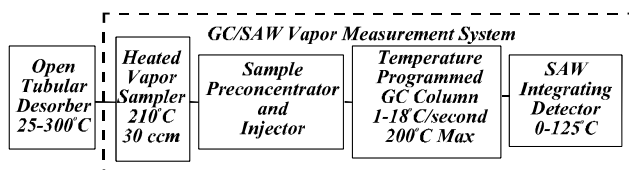


Figure 4- GC/SAW Vapor Analyzer System

The GC/SAW Electronic Nose system was contained within a handheld sensor module as shown in Figure 4. To test the system with liquid injections of standard solutions an open tubular desorber (OTD) was attached to the inlet of the system and a desorption temperature of 280°C was used. The OTD is used to desorb soil samples as well as liquid injections of stock or extract solutions.



Figure 3- Desorbtion tool attached to fast GC/SAW

Electronic Nose VaporPrints™

The SAW sensor output frequency and derivative of output frequency form natural VaporPrint™ images [Ref. 7] of any fragrance without the need for artificial intelligence software and examples for some common substances are shown in Figure 5.

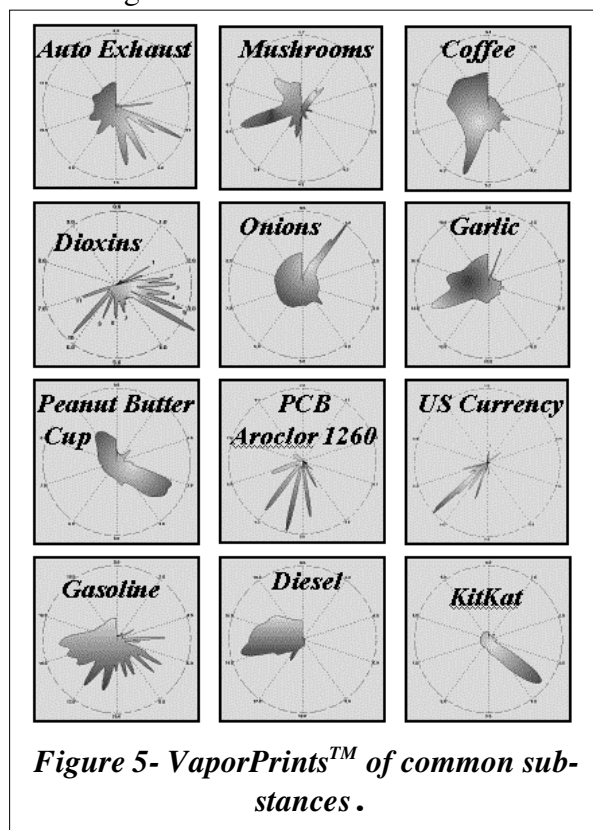


Figure 5- VaporPrints™ of common substances .

Test Method

Hexane stock solutions with known concentrations of dioxin and were used to calibrate the instrument with response factors for all analytes. A typical response to desorbtion of a solution containing five dioxin congeners is shown in Figure 6. The derivative of SAW sensor frequency and frequency are shown in top and bottom traces respectively.

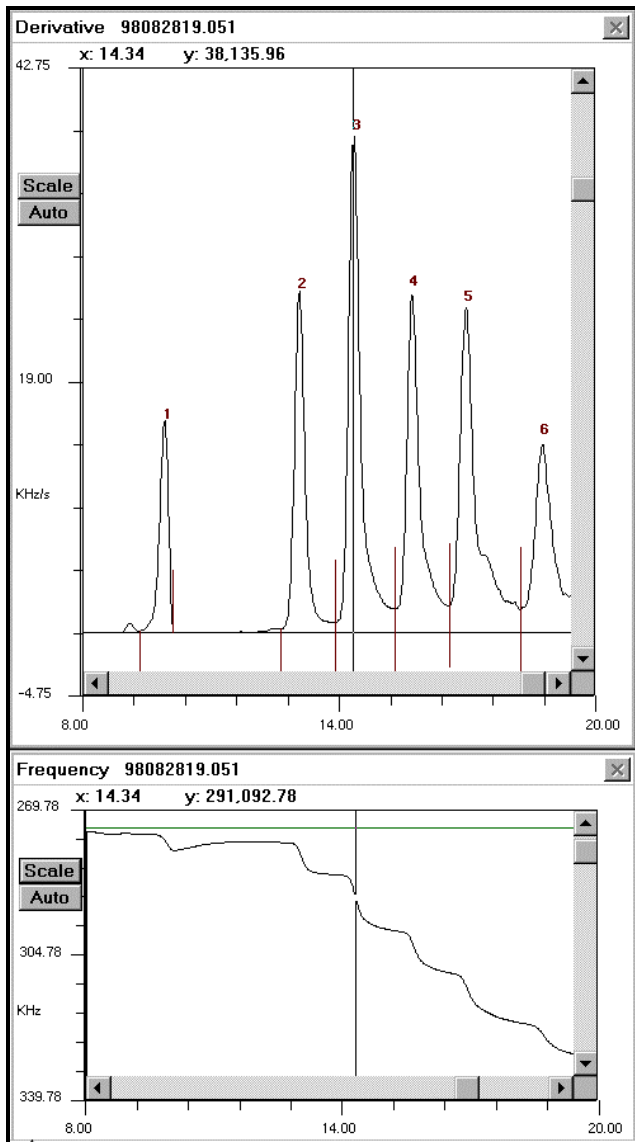


Figure 6- Frequency vs time and derivative of frequency vs time for SAW sensor.

Stock hexane solutions containing five dioxin and five furan analytes of known non-zero TEQ were used to calibrate the sensor response in this study:

Solution No. 1- 5 ng/μliter each of 2,3,7,8 TCDD; 1,2,3,7,8 PCDD; 1,2,3,4,7,8 HexCDD; 1,2,3,4,6,7,8 5 HepCDD; and OctaCDD.

Solution No. 2- 5 ng/μliter each of 2,3,7,8 TCDF; 1,2,3,7,8 PCDF; 1,2,3,4,7,8 HexCDF; 1,2,3,4,6,7,8 5 HepCDF; and OctaCDF.

Each solution contained a tetra, penta, hexa, hepta, and octa member from the respective dioxin or furan congener groups.

Experimental Results

An 5-point calibration using serial dilutions was performed over the range 50 to 5000 picogram using stock solution dilutions and the results are plotted in Figure 7. Accuracy and precision were quite good even at 1 pg levels.

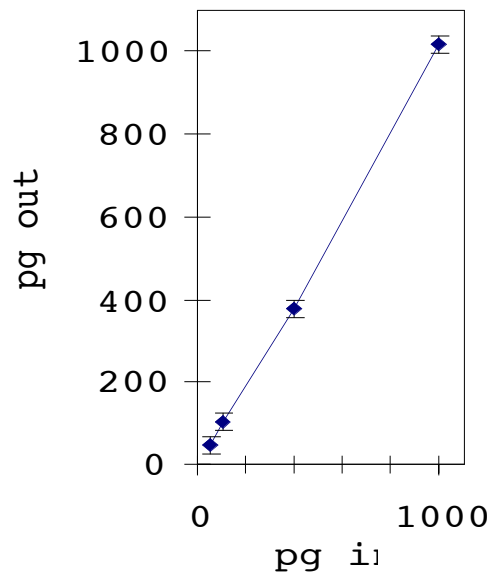


Figure 7 -Plot showing linearity for 2,3,7,8 TCDD.

Individual furan and dioxin isomers can be identified by retention time matching with known standards. An QA-sample chromatogram with overlays of chromatograms for 5 dioxin and 5 furan calibration standards are shown below. This figure shows expanded portions of a 50 second duration chromatogram. Good retention time identifications can be seen for 12378 Penta Furan, 123478 Hexa Furan, 1234678 Hepta Furan. Similarly good identifications for 123478 Hexa Dioxin and 1234678 Hepta Dioxin are also apparent.

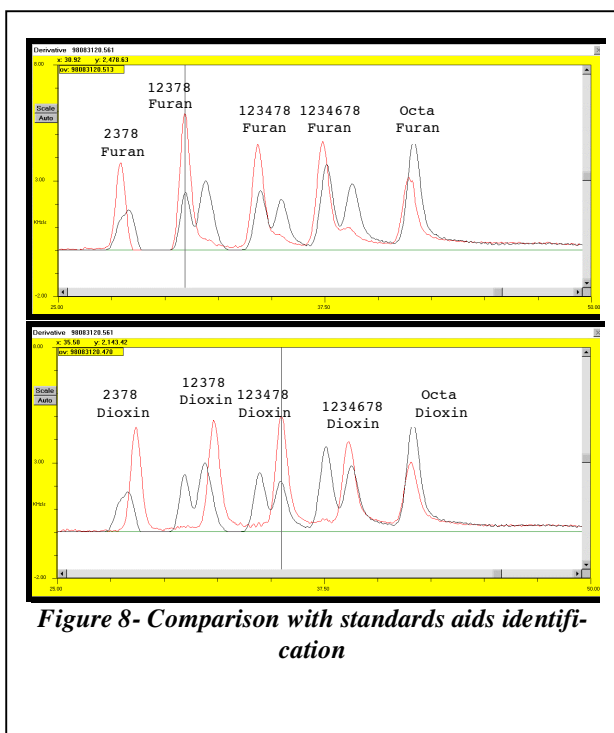


Figure 8- Comparison with standards aids identification

The peak containing tetra- isomers contains two major peaks, which are not well resolved. The leading edge shoulder is a good match with the retention time of 2378 furan while the peak detected by the software peak detector is not a good match for 2378 dioxin. Based upon this longer chromatogram it is estimated there is approximately 250 pg/ μ liter of 2368 Furan present in the previously identified 478.7 pg/ μ liter 2378 dioxin peak (undiluted sample). The remainder of this peak is not 2378 dioxin but more likely contains other isomers such as 1234 or 1368 tetra dioxin.

Summary and Conclusions

The results discussed in this paper show that it is possible to test for the presence of dioxins and furans at the picogram level using SAW sensors. Testing for dioxin/furan in soil and liquid matrices surrounding the source of dioxin/furan emissions (e.g. incinerators) is also possible. In these cases the concentrations are higher (nanograms) and more dangerous to humans because they have accumulated over time.

In addition, the SAW sensor output frequency forms a natural VaporPrint™ image of any fragrance without the need for artificial intelligence software. The detection limit of the SAW detector is determined by the spectrum of SAW oscillator phase noise. Sensitivity to dioxin and furan isomers is nominally 10-20 Hz/picogram, hence detection levels are at the part per trillion (picogram) level.

References

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- 7 VaporPrint™ images can be seen at the following website: WWW.ESTCAL.COM