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Rapid, Automated Gas Chromatographic Detection of Organic Compounds in Ultra-Pure Water

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Abstract

An automated gas chromatograph was used to analyze water samples contaminated with trace (parts-per-billion) concentrations of organic analytes. A custom interface introduced the liquid sample to the chromatograph. This was followed by rapid chromatographic analysis. Characteristics of the analysis include response times less than one minute and automated data processing. Analytes were chosen based on their known presence in the recycle water streams of semiconductor manufacturers and their potential to reduce process yield. These include acetone, isopropanol, butyl acetate, ethyl benzene, p-xylene, methyl ethyl ketone and 2-ethoxy ethyl acetate. Detection limits below 20 ppb were demonstrated for all analytes and quantitative analysis with limited speciation was shown for multianalyte mixtures. Results are discussed with respect to the potential for on-line liquid process monitoring by this method.

Introduction

In the manufacturing of semiconductor devices ultra-pure water (UPW) is used primarily as a cleaning/rinsing solvent. Organic contamination of this water which occurs during routine operations such as wafer rinsing affects the ability of the manufacturer to reuse the water. Currently, due to limited on-line monitoring

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methods, this process water is commonly diverted to waste or large holding tanks until adequate chemical analysis can be performed. However, to conserve the resource and subsequently reduce operating costs, it is desirable to reuse the water in the same process or recycle it for other applications such as industrial cooling. For such practices, however, rapid and reliable on-line monitoring methods must be available to identify contaminants that can upset processes or damage equipment. Process monitors are commercially available that measure total organic carbon (TOC) and have low parts-per-billion (ppb) detection limits. These monitors are based on the oxidation of organics to CO_2 (1) or combustion-ion chromatography (2) and several were recently evaluated (3,4). Unfortunately this type of monitor is limited due to its relatively large sampling/analysis times, typically greater than three minutes, and its inability to speciate. This paper discusses a method developed at Sandia National Laboratories for the rapid on-line detection of several organic compounds commonly found as contaminants in the UPW systems of semiconductor manufacturing facilities. The method combines an interface (5) that introduces and vaporizes an untreated UPW sample with rapid gas chromatographic techniques.

This work was undertaken to address the need cited by members of the semiconductor manufacturing community for an on-line chemical analyzer that can perform rapid analysis for organic compounds in water at low ppb concentrations. The primary analytes of concern, and those that prove difficult for traditional analytical approaches, were polar organic molecules, specifically acetone and isopropanol. The difficulty in detecting these analytes in water is due primarily to their infinite miscibility in water. Their low Henry's law constants makes partitioning- and preconcentration- based sampling approaches of limited efficacy. The feasibility of using gas chromatography (and also chemical sensors based upon surface acoustic wave detectors) to rapidly detect the target analytes was previously demonstrated (6).

Previous work using gas chromatography for on-line detection of organic analytes in water has been reviewed and desirable characteristics outlined (7,8). Two general sampling methods, preconcentration and direct injection, have been utilized. Specific preconcentration methods include membrane separation, trapping using sorbents or cyrogenics, extraction using gas (purge and trap) or liquid-liquid methods. While these methods may have characteristics suitable for on-line monitoring, preconcentration can significantly increase the overall time of analysis (9,10,11). Direct injection methods into a gas chromatograph have the potential to be much faster (12,13). Through automated valving, such an approach can be used as a process monitor, where the sampling rate is uniquely dependent upon the time required for analyte separation in the chromatographic column. Due to the high volumetric flow rates commonly encountered in process-streams, rapid sampling and analysis rates improve the accuracy of the chemical contaminant identification and the ability to define the precise volume of the process water being analyzed.

In this work, gas chromatographic analysis of water samples with trace (parts-per-billion) contaminant levels was achieved in analysis times less than one minute using flame ionization detection, while still providing chromatographic separation (speciation) for most analytes studied. The system configuration includes a short column, high carrier flow rates, isothermal operation, automated valves and computer control, allows for rapid and automated detection at low parts-per-billion detection limits. These features, combined with automatic data logging and alarm functions, demonstrate the ability of the system to perform as a stand alone process monitor.

Experimental Details

Instrument and System Optimization

A Varian Model 3600 single column gas chromatograph was operated isothermally at temperatures between 40 and 120 degrees Celsius (°C) and was

equipped with a flame ionization detector (FID). The injector and detector were held at 250 °C and 325 °C respectively to prevent sample condensation. Helium carrier gas (Ultra-high purity, Trigas, Albuquerque, New Mexico) was used with flow rates between 5 and 17 milliliters per minute (mL/min). The capillary column used during the evaluation was a 15 meter carbowax column (Supelco Wax, 0.5 µm film thickness, 0.32 mm I.D., P/N 10-24084, Supelco, Bellafonte, PA).

Optimization of the instrument operating parameters was accomplished by varying the injected sample size, column length, oven temperature, and carrier gas flow rate. Optimized conditions were chosen such that baseline deviations were minimized and the detector response was stabilized while maintaining high analyte sensitivity. Initially, the system parameters were optimized for parts-per-billion (ppb) concentrations of isopropyl alcohol and acetone. These general conditions were then used for examining the instrument response to similar concentrations of other analytes.

A schematic of the automated sample injector system is shown in Figure 1. A four-port pneumatically operated valve (Valco Instruments Model A2C14WF.5) with a 0.5 microliter (µL) internal injection loop was installed above the GC injection port. To minimize sample condensation in the sampling loop, a heating block was placed over the loop and injector and maintained isothermally at 150 °C. The standard GC injector was bypassed by extending the capillary column through the injection port and coupling it directly to the valve. A three-way valve was used upstream of the four-port injector to select one of two sampling lines. One line was used for clean water and one was dedicated to sample solutions. In practice, one line would be used for calibration solution(s) and the other would be the sample stream. A Teflon-lined peristaltic pump provided flow. During operation a given line was selected via computer control which activated the appropriate line pump and set the three-way valve to the proper configuration.

Figure 1

The GC was interfaced to a PC based system using a Perkin Elmer Series 900 interface and Turbochrom™ 4.1 software (Perkin Elmer Corporation, Norwalk, Connecticut). This system controlled the sampling time and rate, run time, valve sequencing, and the rate and number of samples taken. Furthermore, the software package defined the location of data storage and ran a post processing data analysis algorithm. A Turbochrom™ method was written that established peak picking parameters and identified peaks of interest based on their retention times. The method was also used to integrate the chromatographic peaks. This information was then used as input for an alarm program based on peak area and written in Quickbasic™. Both Turbochrom™ and the alarm analysis were performed immediately after data acquisition and concurrently with collection of the next chromatogram. The alarm program was designed to function real-time, alerting an operator that a particular analyte was above a predetermined concentration while also creating a log of integrated area of detected analyte.

Experimental Procedure

Aqueous solutions of isopropanol and acetone were prepared by serial dilution in concentrations varying from 30 to 1000 ppb (by volume). Deionized water and HPLC-grade chemicals (Fisher Scientific, Fairlawn, New Jersey) were used. Transport lines were flushed for at least five minutes after sample solutions were switched to prevent sample carryover. The system was then operated in a fully automated mode, which injected a 0.5 µL sample while recording and storing the subsequent chromatogram (detector response versus time). The number of analyses was defined by the operator. In each series of experiments a minimum of five replicate samples of each concentration were analyzed. Water blanks were analyzed periodically to ensure that cross-contamination or carryover was not occurring.

Five other analytes (butyl acetate, ethyl benzene, p-xylene, methyl ethyl ketone and 2-ethoxy ethyl acetate) were examined at three concentrations: 50, 100 and 500 ppb. All chemicals were purchased at 99% or greater purity from Fisher Scientific (Fairlawn, New Jersey).

Results and Discussion

Acetone and Isopropanol

Two polar organic compounds that are widely used in semiconductor manufacturing include acetone and isopropanol. Therefore, system parameters for acetone and isopropanol were determined that would achieve a rapid analysis time yet still provide speciation. Figure 2 presents an example of the automated analysis of an UPW sample containing 50 ppb of both acetone and isopropanol. Acetone elutes in 7.9 seconds while isopropanol elutes in 18.6 seconds after injection (indicated by time equals zero). Data collection in these tests was underway prior to the sample injection and the negative peaks are indicative of injection valve actuation. Because the carrier gas is flowing through the injection valve, actuation causes a pressure pulse that is detected by the FID. To achieve the short (less than one minute) analysis time yet retain speciation, a column length of 15 m, a gas flow rate of 15 mL/min, and a constant oven temperature of 50 °C were used. The cause of the doublet feature observed in the acetone peak in Figure 2, which was also observed intermittently on various analyte peaks, is unknown. A number of conditions, such as dead volume at the column/valve interface or even an unknown contaminant, could be responsible.

The acetone peak, even with the doublet feature, has a full-width at half maximum (FWHM) of 2 seconds while the isopropanol has a larger FWHM of 3 seconds. The faster elution time and narrower bandwidth is consistent with the relatively high polarity of acetone compared to isopropanol, which results in fewer interactions between acetone and the stationary phase of the column. The

baseline separation of these peaks suggests that response time can be further reduced while still retaining speciation of these two analytes.

Figure 2

Quantitation is necessary for informed decision making in process monitoring. To achieve quantitation the instrument response function to the analyte must be known. The response function of the flame ionization detector towards organic analytes is typically linear but varies among compounds (14), however it was not known if the injection system described here would introduce any non-linearities or bias at low levels. The response function of this instrument was therefore examined versus analyte concentration for both acetone and isopropanol. Utilizing the same conditions described above, the integrated chromatographic peak area (μV•sec) is plotted as discrete points versus analyte concentration (ppb) for acetone (Figure 3) and isopropanol (Figure 4). The linear response for both analytes across this concentration range can be observed and a least squares fit to each set of data is shown as a solid line in each figure. From the least squares concentration model overall concentration residuals were randomly distributed around zero with standard deviations of 51 and 30 ppb for acetone and isopropanol, respectively, over the concentration range examined. Higher concentrations were not examined because this was the range of concern for the application of UPW monitoring.

Figure 3

Figure 4

A large spread in the acetone response at 175 ppb is observed in Figure 3. This spread is due to changes in the chromatographic baseline as determined during the automated software signal integration. The software baseline defines the lower "y" limit of the integration and minor changes in the slope and

intersection of this line with the peak can result in significant changes in the integrated area. For this reason integration parameters must be carefully defined in the software, otherwise the variance in detected peak area will be increased artificially and increase the calculated error in system response.

The linearity of the plots in Figures 3 and 4 demonstrate that automation does not adversely affect detection in this concentration range. From these plots average response factors, defined as integrated chromatogram peak area (μV•sec) per analyte concentration (ppb), of 12.9 (acetone) and 13.3 μV•sec ppb^{-1} (isopropanol) were calculated. The similarity in response factors is consistent with the similarity in chemical formula of these analytes.

Detection limits were estimated assuming a linear extrapolation of both noise and detector response at low concentrations. The detection limits for both acetone and isopropanol were determined at 15 ppb based on the analyte peak height at 3 times the baseline standard deviation. Frequently in industrial applications a more conservative value, the determination limit, which is 25 times the baseline noise, is cited as a useful lower concentration value. For both analytes the determination limit was 125 ppb. This approach for estimating the detection limits assumes error is due exclusively to instrumental noise and not associated with any errors in analyte concentration. It remains nonetheless a useful parameter for understanding and quantifying system performance.

Other Polar Analytes

Other polar organic compounds used in semiconductor manufacturing, and therefore likely to be found in a UPW recycling stream, include butyl acetate, ethyl benzene, p-xylene, methyl ethyl ketone (MEK), and 2-ethoxy ethyl acetate. In this specific process control application is important to rapidly detect and quantitate these compounds as are acetone and isopropanol. These compounds represent a wide range of polarities, molecular weights, and boiling points. Despite their range of properties, it is possible using the instrumentation

described here to detect them in less than 60 seconds. Figure 5 shows the chromatogram of an automated GC analysis of a UPW sample containing 500 ppb of each of the five compounds. The same 15 m column was used as before but slightly modified conditions from those that separated acetone and isopropanol were necessary. Please note, due to their higher boiling points and molecular weights a faster carrier gas flow rate of 17 mL/min and a higher constant oven temperature of 80 °C were used to obtain the signal in the specified time.

Figure 5

This chromatogram illustrates the compromises necessary for rapid analysis. In order to achieve a total analysis time less than 60 seconds, chromatographic separation had to be compromised because ethyl benzene and p-xylene coelute under these conditions. A longer run time (slower carrier gas flow or cooler oven), more specialized column, dual column or multidimensional GC analysis would be required to speciate all of these analytes. Of course, a different list of analytes would potentially require a different set of instrumental parameters. The advantage in an industrial setting is that the list of potential contaminants is generally known, and there are a variety of columns and instrumental parameters available to tailor the analysis.

The instrument response function for the analytes shown in Figure 5 was investigated individually using the same instrumental conditions at three different concentrations. Isopropanol (500 ppb) was added as an internal standard. Under these conditions, however, MEK coeluted with isopropanol. To aid separation the flow rate and temperature were reduced to 15 mL/min and 45 °C for the response study of MEK. The automated analysis of a UPW sample containing 50 ppb MEK and the 500 ppb isopropanol internal standard under these conditions is shown in Figure 6. The small peak prior to MEK, centered at 11.7 seconds, is an unknown contaminant. No long-term column degradation or

change of detector response, as determined by changing retention times or integrated intensity of the isopropanol peak, was observed.

Figure 6

Integrated detector response versus concentration for all 5 analytes is plotted in Figure 7, and indicates a linear detector response with respect to concentration for all analytes except butyl acetate. As with acetone and isopropanol, a linear detector response was expected, and therefore the automated injector performed without bias in this concentration range. For butyl acetate, a linear response function was also expected due to its similarities to the other analytes for properties such as molecular weight and boiling point. For these reasons it is unlikely that the injector or detector produced the non-linearity observed for this analyte, and it is assumed that the high concentration sample was prepared in error. The data for this sample was therefore not included during calculation of the average response factor.

Figure 7

The calculated average response factors for each analyte (acetone and isopropanol included for completeness) are listed in Table A. Note that the response factor for ethyl benzene is three times larger than that for acetone or isopropanol. This means that for a sample with the same concentration of both analytes, the ethyl benzene peak area would be three times larger. This is no different than what occurs in TOC analyses, where different analytes produce different signal levels. For example, a contamination of decane would be oxidized to produce twice as much CO2 and therefore signal as the same concentration (moles/liter) of pentane. In the typical implementation of TOC technology this is accounted for by the end user in determining the alarm levels

of the instrument. The same would be expected in the application of automated GC analysis.

Table A

Detection limits for these analytes were calculated as described for acetone and isopropanol, assuming a linear extrapolation of both noise and detector response at low concentrations. Both detection and determination limits were calculated using the data in Figure 7 and are shown in Table B (with acetone and isopropanol for completeness).

Table B

Post processing software allowed an alarm function to be added to the system. The integrated peak area information generated by the control software was processed such that an alarm condition was generated if a specific analyte was detected above a defined threshold. Depending upon the utilization of the instrument, the alarm could be used to trigger a process-line valve or other control device. More sophisticated analysis and control procedures could be employed; the work here was intended only to demonstrate that unattended, continuous operation is feasible.

Conclusions

The rapid detection of trace, parts-per-billion, concentrations of organic analytes in liquid phase water samples has been demonstrated using an automated gas chromatograph with flame ionization detection. Multianalyte mixtures were quantitatively analyzed with the instrument, providing limited speciation of the analytes. A linear response, and therefore a constant response factor, was demonstrated for each analyte of concern. Capabilities include detection limits below 20 ppb and a sufficient dynamic range to make it useful for

expected contaminant levels in semiconductor manufacturing facilities. Analysis times of less than one minute and automated data processing demonstrate the ability of the instrument to be utilized as a rapid process monitor, employing only commercial parts and flexible chromatographic techniques. The instrument does not generate any waste water and requires only a small (0.5 μL) sample for each analysis.

The data from both a TOC and the on-line monitor described here provide data that can be used to make process flow (recycle or divert) decisions. The automated instrument however has an improved response time relative to commercially available TOC monitors and also provides speciation. Speciation, or separation in time of analytes, along with linear response factors, allows each analyte to be identified and quantitated. In a process control environment this would provide information valuable in tracing the source of the contamination – information not provided by TOC monitors. While TOC monitors may detect a very broad range of analytes, the flexibility of instrumental conditions available to the system described here allows tailoring to many contaminants; the system is not limited to those investigated.

There are several issues that remain to be investigated prior to commercial application. Ease of implementation, long-term stability and reproducibility, application specific methodologies, and failure modes were not addressed here but will affect marketplace acceptance. Because the instrument was assembled using commercial parts these investigations should not be difficult. Implementation in an actual UPW recycling system for longer-term testing would also be desirable, especially with regard to column lifetime.

While a trade off between speciation for analysis time may sometimes be necessary in the case of multiple contaminants, a secondary analysis using other (speciating) conditions (or perhaps sample collection) is possible. This would require more sophisticated software or hardware, but these are currently available and would only increase the price of a final system rather than require additional research for proof of principle.

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Figure Captions:

Figure 1: Schematic diagram of automated gas chromatographic system.

Figure 2: Signal intensity versus time for the automated chromatographic analysis of a UPW sample containing 50 ppb acetone and isopropanol. For conditions see text.

Figure 3: Integrated peak area (μV•sec) versus acetone concentration (ppb).

Figure 4: Integrated peak area (μV•sec) versus isopropanol concentration (ppb).

Figure 5: Signal intensity versus time for the automated chromatographic analysis of a UPW sample containing 500 ppb each of methyl ethyl ketone (MEK), butyl acetate, ethyl benzene, xylene, and ethoxy ethyl acetate. For conditions see text.

Figure 6: Signal intensity versus time for the automated chromatographic analysis of a UPW sample containing 50 ppb MEK and 500 ppb isopropanol.

Figure 7: Integrated peak area (μV•sec) versus concentration (ppb) for methyl ethyl ketone (MEK), butyl acetate, ethyl benzene, xylene, and ethoxy ethyl acetate. For conditions see text.

Table A

Average response factors (integrated area in µV•sec / analyte concentration in ppb) for analytes of concern using automated GC-FID detection.

Table B

Detection and determination limits (ppb) for the analytes of concern using automated GC-FID detection.

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This document contains figures, tables, and captions for 99_FID paper to be submitted to the publication Ultrapure Water.

Figure 1: Schematic diagram of automated gas chromatographic system.

Figure 2: Signal intensity versus time for the automated chromatographic analysis of a UPW sample containing 50 ppb acetone and isoporpanol. For conditions see text.

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Table A

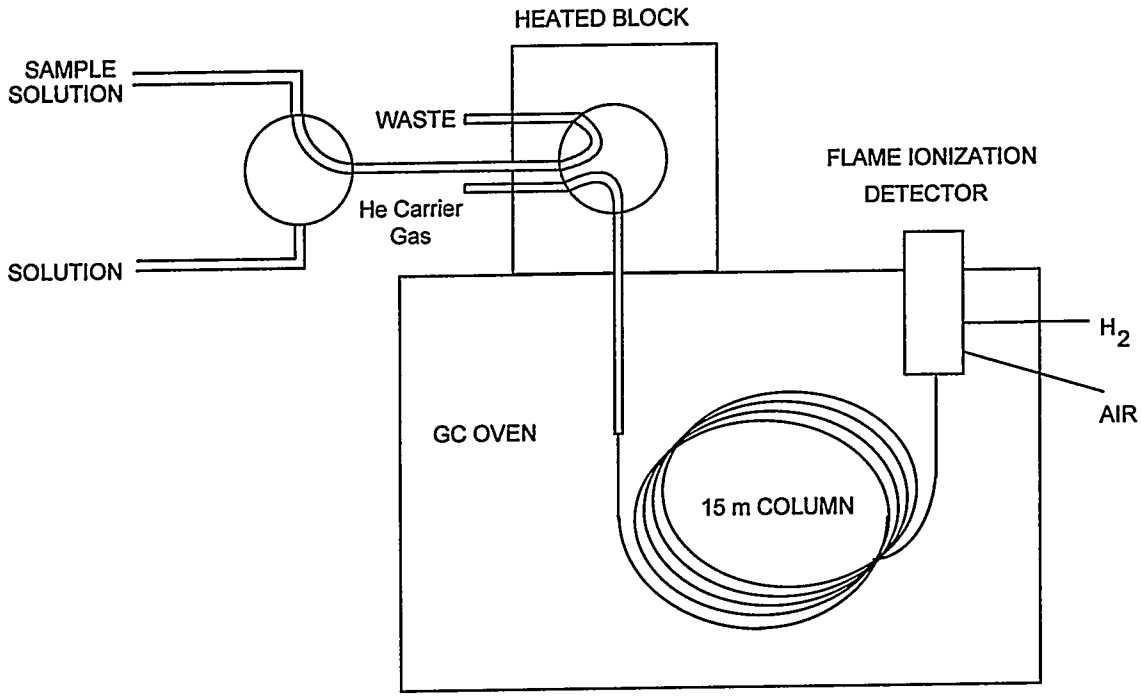
Average response factors (integrated area in μV•sec / analyte concentration in ppb) for analytes of concern using automated GC-FID detection.

Analyte	Response Factor
butyl acetate	30
ethyl benzene	39
p-xylene	36
methyl ethyl ketone	27
2-ethoxy ethyl acetate	16
acetone	13
isopropanol	13

Table B

Detection and determination limits (ppb) for the analytes of concern using automated GC-FID detection.

Analyte	Detection Limit (ppb)	Determination Limit (ppb)
butyl acetate	7	58
ethyl benzene	5	42
p-xylene	5	42
methyl ethyl ketone	7	58
2-ethoxy ethyl acetate	12	97
acetone	15	125
isopropanol	15	125



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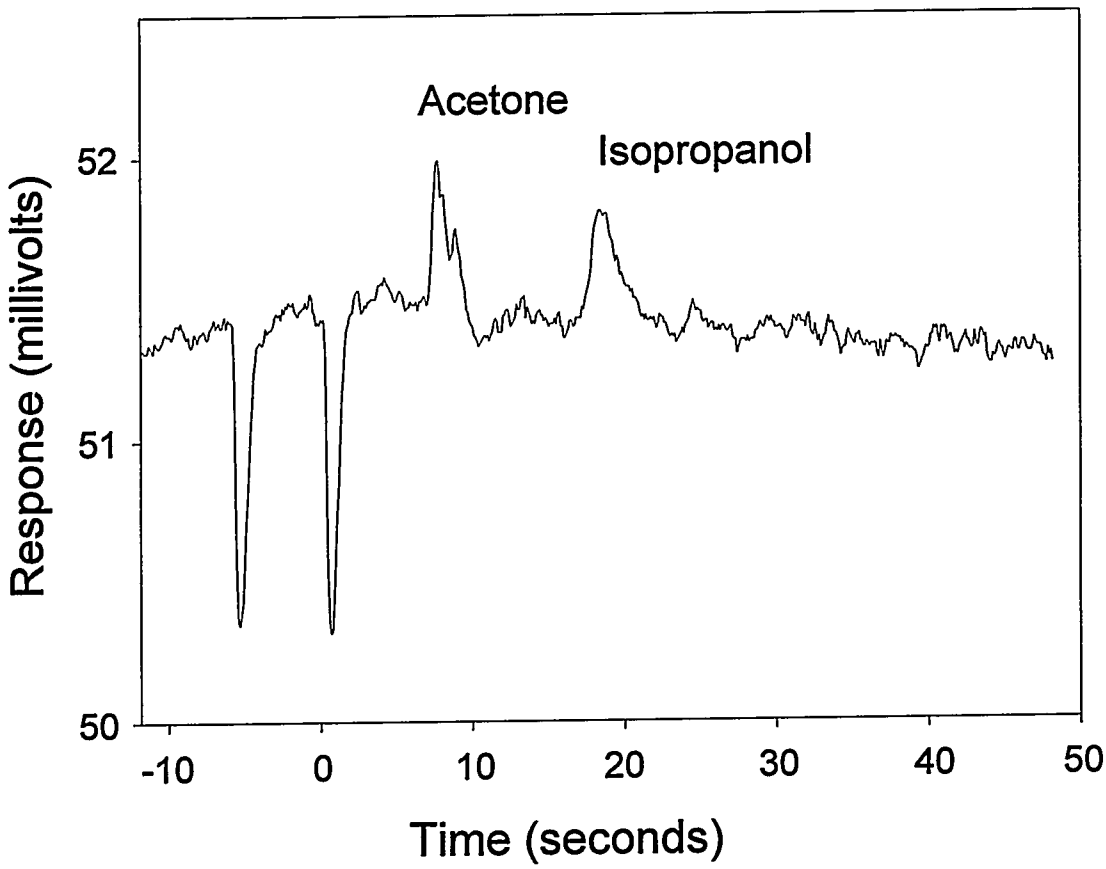

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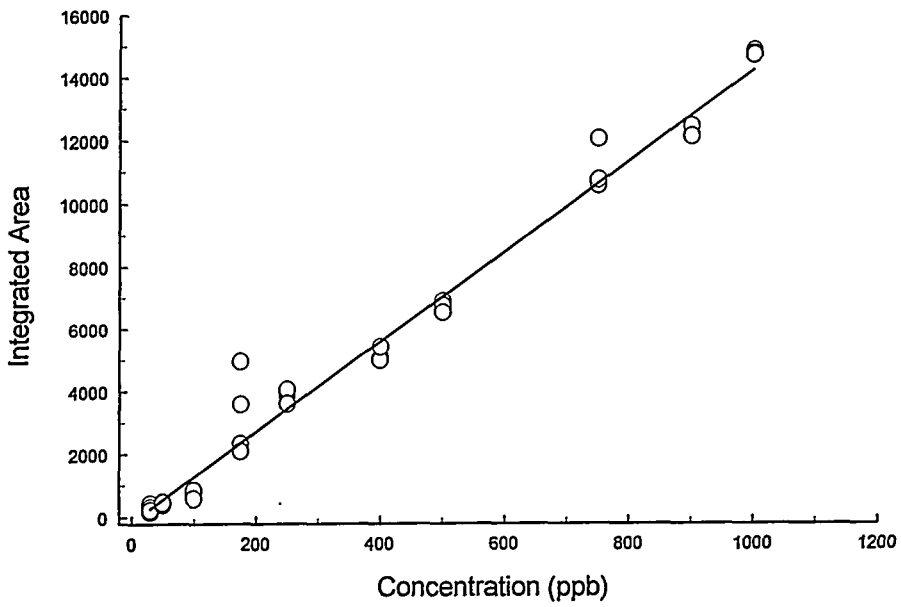

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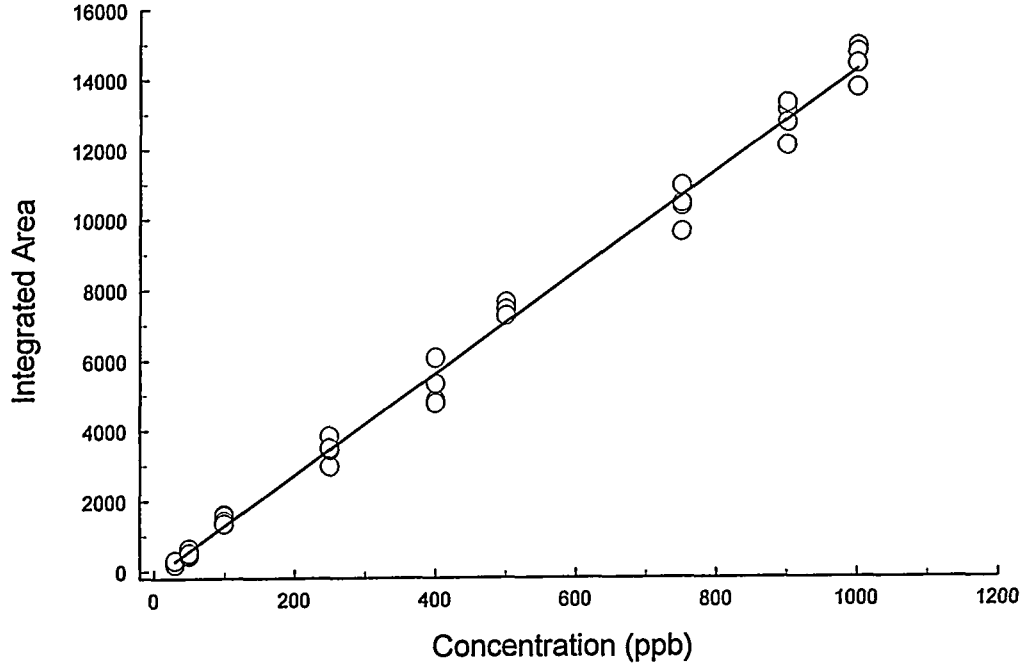
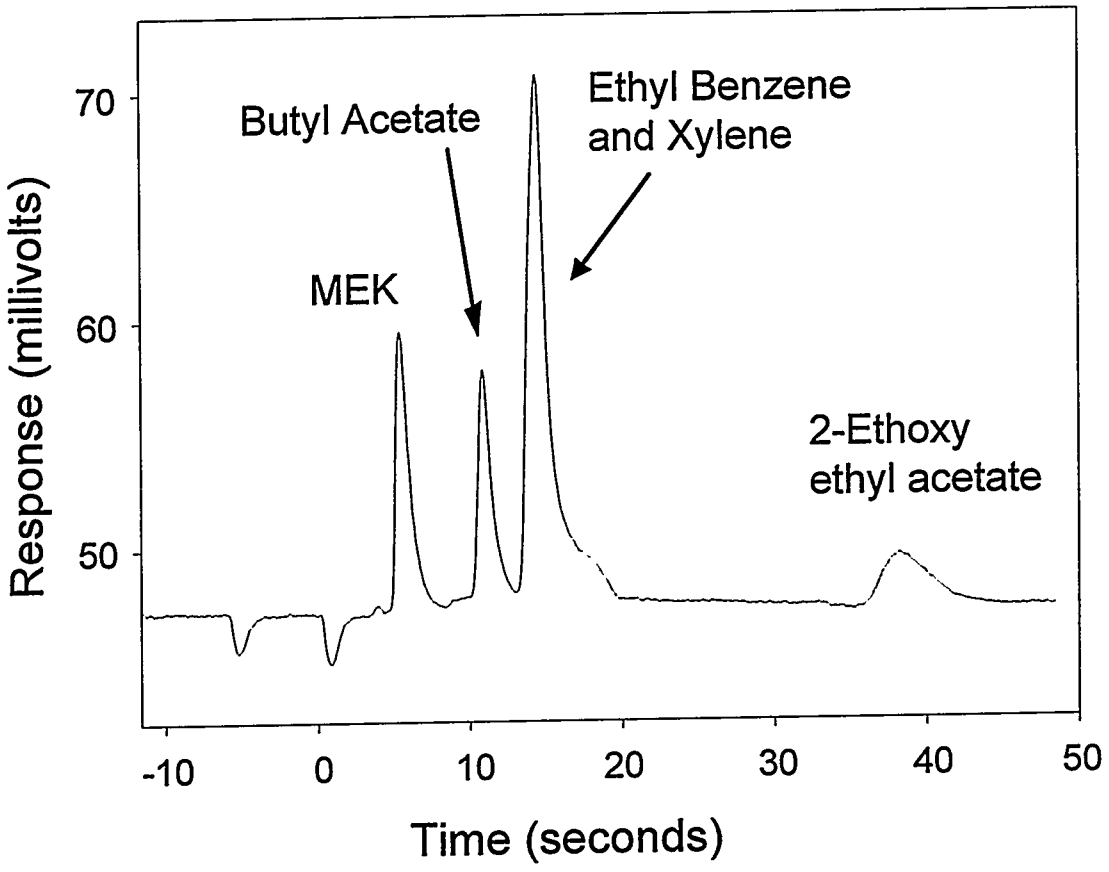


Figure 4: Integrated area (μV•sec) versus isopropanol concentration (ppb).



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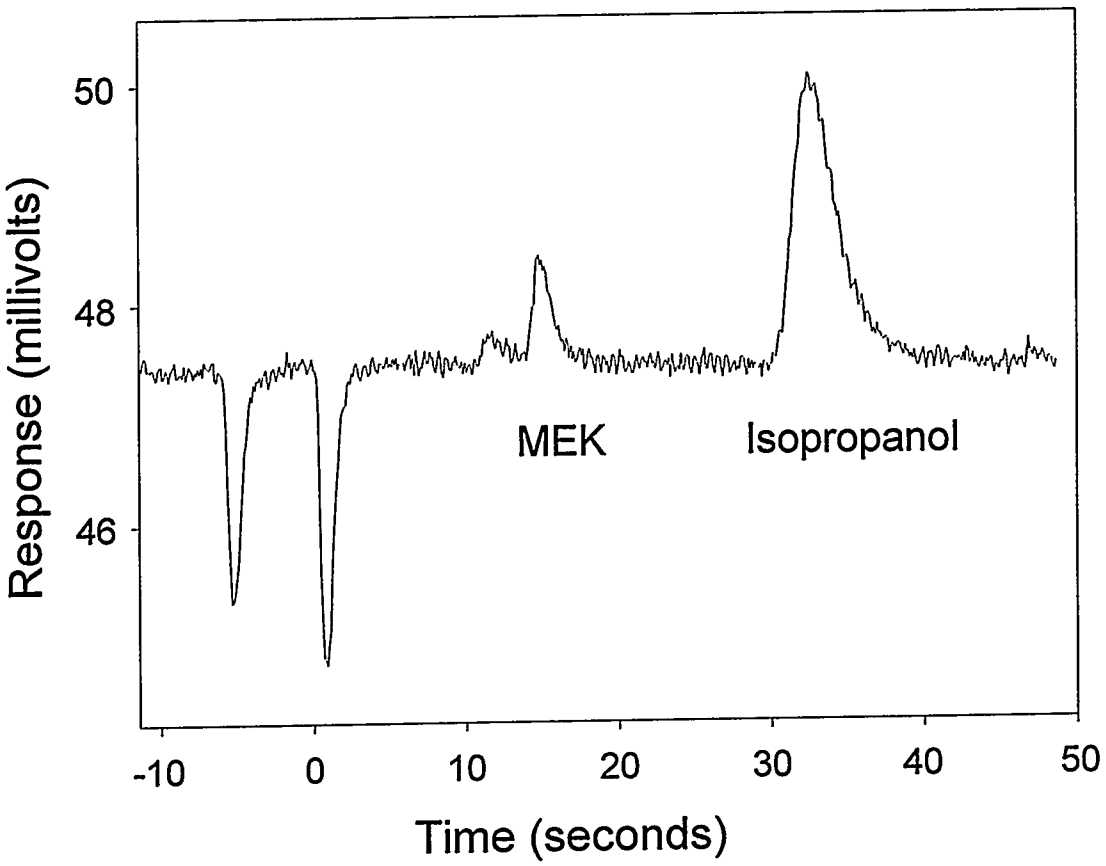

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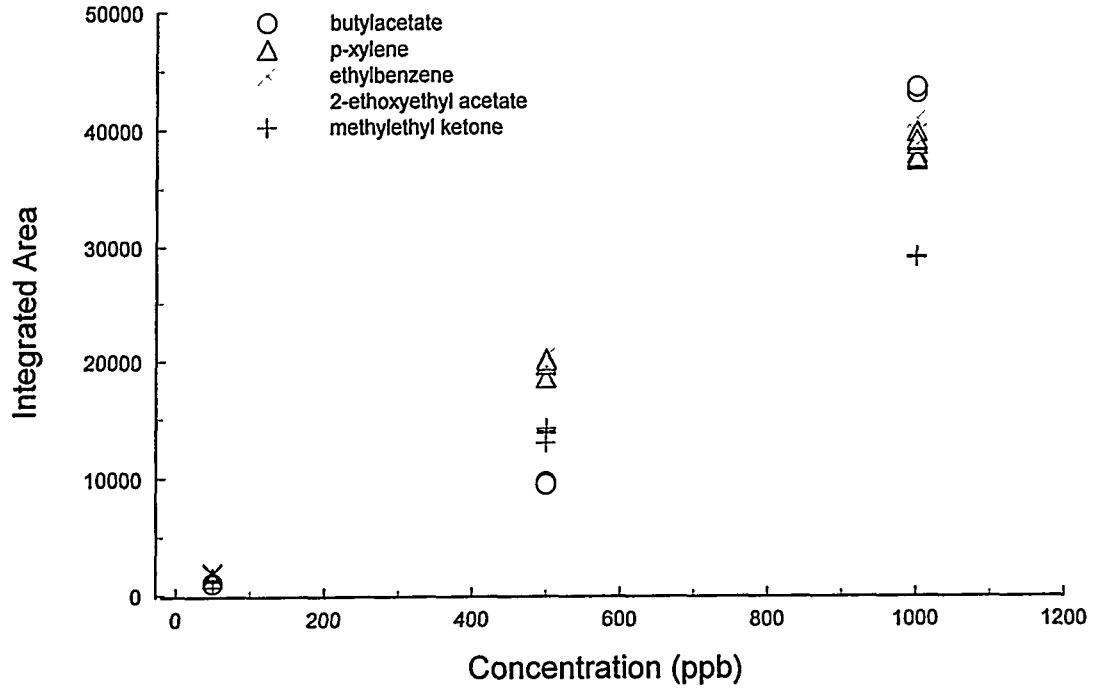

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