Title Page:

Title:
Rapid Screening for Polychlorinated Biphenyls and 2,3,7,8 Dioxin in Soil and Flyash Using a SAW/GC

Author:
Edward J. Staples
Electronic Sensor Technology
805-480-1994 Office
805-480-1984 Fax
staples@www.estcal.com

Key Terms: Surface Acoustic Wave (SAW), Gas Chromatograph (GC), Polychlorinated Biphenyl (PCB), 2378 Dioxin

Rapid Screening for Polychlorinated Biphenyl and 2,3,7,8 Dioxin in Soil and Flyash Using a SAW/GC

Introduction

A handheld portable chromatography system equipped with a non-specific Surface Acoustic Wave (SAW) detector is used to speciate and quantify PCB and dioxin contamination in soil and flyash with a 10 second analysis time. The SAW detector is an integrating mass detector (micro-balance) with zero dead volume and the ability to quantify chromatography peaks at the picogram level and with peak widths measured in milliseconds. Measurement speed and accuracy make the instrument well suited to rapid screening of soil samples. Early separation of those soil samples below the regulatory level from those which require laboratory validation with a GC/MS reduces the cost associated with site characterization and monitoring. The SAW/GC screening procedure, when incorporated into EPA Methods (e.g. 8080), allows for pre-dilution's optimized to the limited dynamic range of a GC/MS laboratory instrument.

A sampling pump and loop trap are used to sample and inject analyte into a GC capillary column. Speciation is based upon retention time measurements using a temperature programmed DB-5 column. Quantification is based upon the frequency shift produced by analytes or PCB isomers as they exit the GC column. By focusing the effluent onto a specific area on the surface of a temperature controlled piezoelectric crystal, high sensitivity is achieved with a 10 second analysis time. The SAW/GC is able to selectively screen and quantify PCB levels for dioxins and Aroclor compounds in soil and flyash with ppb precision.

Two procedures for extracting PCBs from soil matrices are used. These procedures have been tested on the dioxin and Aroclor mixtures shown. The **first procedure** uses an open tubular direct desorption tube (OTDDT) held at approximately 200^{o}C. The desorption tube is pre-packed with a soil sample and attached to the inlet of the SAW/GC. Heat is used to desorb vapors from a soil while the sampling pump of the SAW/GC collects the desorbed vapors. Total extraction by direct desorption is a fast and accurate method for soils with contamination levels below 250 ppb.

Analytes Tested
Aroclor 1221
Aroclor 1016
Aroclor 1248
Aroclor 1232
Aroclor 1242
Aroclor 1254
Aroclor 1260
Aroclor 1262
2,3,7,8 Dioxin

The **second procedure** is best suited to testing soil with contamination levels of 250 ppb or higher because of the sample dilution inherent in the method. A liquid extraction of the soil using a mixture of hexane, water, and methanol is first carried out and then a small amount of the liquid extract is injected into the SAW/GC inlet and the PCB content measured.

These methods should be used by, or under the supervision of, analysts experienced in the use of sampling techniques and gas chromatography. The analysts

should also be skilled in the interpretation of gas chromatograms and in the use of chromatography as a quantitative tool.

The accuracy of the SAW/GC PCB/dioxin soil screening method is based upon n-point calibrations using Standard solutions. Quality assurance measurements require GC validation using only standards certified by an independent laboratory. All spiking solutions, prior to their use in soil recovery analyses or calibration by direct injection, must first be validated by GC measurement.

Interference

Due to the universal detection capability of the SAW detector, other non-PCB compounds may co-elute with PCB standards. Any such compounds detected may be misidentified and quantified as a PCB. If the quantification level is above the alarm threshold, the method requires the soil sample to be laboratory tested and the SAW/GC screening measurement validated. It is implicit in a screening method that there are no false negatives and that all positive responses require laboratory validation.

Impurities from contaminants within the instrument or inlet train desorption tubing may interfere. Contamination by carryover can also occur whenever high-level and low-level samples are analyzed sequentially. To insure against interference, the screening method requires that acceptable (method) blanks be recorded before and after all measurements

Quality Control

The minimum required elements of quality control are as follows:

1. Initial Demonstration of Proficiency
2. Method Detection Limit Determination
3. Analysis of Blank Samples
4. Laboratory Control Sample Analysis

Expendable Materials

Laboratory Standard PCB-hexane solutions for field spikes and calibration. The concentration of the standards should provide nanogram quantities of PCB when injecting 1 to 10 µliters of standard solution. A supply of reagent grade hexane is required for method blanks.

A pre-mixed supply of hexane, methanol, and water is required for performing liquid soil extractions. Other expendable items include septa equipped vials and pipette filters for filtering soil extractions.

Weighing Balance

A weighing balance accurate to 0.1 mg is required to weigh the soil samples.

Syringes

To create soil audit samples for recovery confirmation, spiking solutions and quality assurance calibrations, a standard chromatography syringe is used. Recommended is a 10 µliter syringe available from SGE, 10R-GT, Part No. 002250.

Soil Samples

For the direct thermal desorption method a soil sample collection consists of placing homogeneous samples (approximately 0.1-0.25 grams) from a source to be analyzed into pre-weighed 6 x ¼ inch glass tubes. For the liquid extraction method soil samples are placed in 4 mL glass vials with septa caps. Sampling spatula or other utensils which come into contact with the soil should be clean so as not to contaminate the sample. If the content of the soil is not to be measured immediately the ends of the glass tube are sealed with slip-on septa covers.

Procedure No. 1 - Direct Thermal Extraction (DTE)

The SAW/GC inlet sample port is glass lined stainless steel for sampling of vapors directly into the instrument. Total extraction from soil is performed using an open heated glass tube fitted with a glass-to-luer adapter attached directly to the inlet of the instrument. Calibration is performed using a syringe needle to inject laboratory standard solutions directly into the open tubular desorption tube.

GC Analysis

1. Take Blank samples before and after each analytical run. Monitor the blank for background levels or carryover. Continue blanks until the levels are below preset minimums. Each sample tube is weighed and pre-screened before loading with soil.
2. The instrument should be used with the SAW/GC Method and instrument settings for which the calibration was performed. Use of any other method requires the generation of a new calibration curve. The operator must save all chromatograms (SAV-ALL=ON), including blanks and calibration checks performed with liquid standards.
3. After loading tube with approximately 250 mg of soil, attach luer adapter to one end of sample tube. Attach the sample tube to the luer inlet fitting of the SAW/GC.
4. Slide heater jacket, pre-heated to 200^{o}C, over the sample tube and immediately initiate soil sampling with sample time set to 30 seconds. Repeat 30 second soil sampling at 1 minute intervals until analyte concentration readings are less then 10% of initial sample values. Record the concentration mass, in nanograms, for each sample measurement, N_i, as well as the total of all sample measurements, N_T.
5. Measure the weight of the sample tube packed with soil. Subtract the weight of the empty tube and designate the result as W_{SOIL} in grams..

Procedure No. 2 - Liquid Extraction and Injection

This method is well suited to analysis of soils with high concentrations of PCBs. First the PCBs are extracted from the soil using a mixture of hexane, methanol, and water.

1. Add a weighed amount of soil (0.25-1 gram) to 1 mL of solution, shake until soil is well dispersed, and let stand until hexane solute is clearly seen to

separate and float on top of methanol-water layer with soil sediment resting on bottom of vial.

2. Extract approximately 0.25 mL of the hexane and use a disposable pipette filter to transfer into a clean vial and seal with septa cap.

Sampling of the extract solution is performed using an open tubular thermal desorption tube packed with glass wool. The tube is fitted with a glass-to-luer adapter which attaches directly to the inlet of the instrument. Calibration is performed using a syringe needle to inject laboratory standard solutions directly into the open tubular desorption tube.

GC Analysis

1. Take Blank samples before and after each analytical run. Monitor the blank for background levels or carryover. Continue blanks until the levels are below preset minimums. Each sample tube is weighed and pre-screened before loading with soil.
2. The instrument should be used with the SAW/GC Method and instrument settings for which the calibration was performed. Use of any other method requires the generation of a new calibration curve. The operator must save all chromatograms (SAV-ALL=ON), including blanks and calibration checks performed with liquid standards.
3. With the heater jacket removed and the extraction tube at room temperature inject a measured amount of extract into the tube. Initiate analysis runs with the SAW/GC to remove volatile compounds and until liquid can no longer be seen in the glass tube
4. Slide heater jacket, pre-heated to 200^{o}C, over the sample tube and immediately initiate sampling with sample time set to 30 seconds. Repeat 30 second sampling at 1 minute intervals until analyte concentration readings are less then 10% of initial sample values. Record the concentration mass, in nanograms, for each sample measurement, N_i, as well as the total of all sample measurements, N_T.

Calculations

Windows 95, SAW/GC system software (Version 4.0), and Excel and is required to operate the system, log data, and provide measurement documentation. With the system software, three calibration options are provided. The operator may select individual compound peaks and calibrate based upon the measured signal in Hz and the standard input in nanograms. Alternately the operator may select to use either the total area of all peaks over a specified range of retention times, or the sum of a set of 'tagged' peaks specified in a calibration file, to determine a response factor in terms of a standard input.

Soil contamination is expressed in either ppm (mg/kg), ppb(µg/kg), or ppt (ng/kg). To calculate soil contamination perform the following calculation:

$$Conc_{SOIL} = \frac{\sum_i N_i}{W_{SOIL}} = \frac{N_T}{W_{SOIL}}$$

For liquid extractions the above result must be multiplied by the ratio of the total amount of hexane solution divided by the amount of solution extract injected (dilution ratio).

Instrument Calibration Procedure

A calibration curve and the response factors must be entered into the Peak File software dialog screen, before analysis can begin. If the instrument has been previously calibrated in the lab, only a single mid level calibration check for each analyte is required. If the value of the check is within 30% of the lab value, then the response factor is confirmed. If the value is greater than 30%, then the instrument must be re-calibrated.

Check instrument status. Measure the instrument sample flow using the mass flow meter. Record the sample flow and enter the value in the Peak File software dialog screen under sample flow in ccm (cc/min) units.

Run an instrument blank. Assure that the background is below 10 ppb for any compounds in the peak file. The blank should be a method injection into an empty desorption tube.

Create a calibration standard solution. Fill a 4 mL vial with an appropriate amount of standard solution and an appropriate amount of solute so that a concentration (nanograms/µliter) which is mid-level to the desired measurement range, is achieved. Seal the vial with a new septa lid.

To define the instrument response factor, SF (in Hz/picogram), a liquid injection into the desorption tube with a known standard is made The instrument reading, F_m, in measurement units of frequency (Hz=Hertz) and the total amount of analyte injected, M_a, in picograms defines the response factor:

$$SF = \frac{F_m}{M_a}$$

Note: If the proper scale factor is entered into the peak file dialog screen, the software will display PCB or dioxin measurement in picograms or nanograms in the peak window. An example using a 1 µliter injection with a solution of 10 nanogram/µliter 2,3,7,8 dioxin is shown in **Figure 1**.

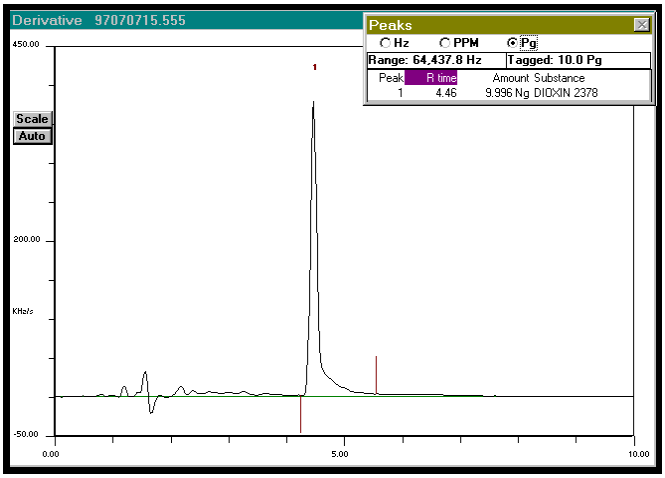

Figure 1- Calibration with 10 nanograms of 2,3,7,8 dioxin.

Peak File Setup

Confirm the retention time windows for each component to be analyzed. Make three injections of the component and calculate the standard deviation of the retention time of each component. The average retention time and response factor for each analyte is entered into the peak recognition file.

PCB Aroclor mixtures typically contain 15 or more isomers as shown in **Figure 2**. In this case the system software provides the operator with the ability to use either the sum of peaks over a retention time range or the sum of a selected peaks, as the basis for calibration. A single average response factor for the sum of the peaks within the mixture is used to calculate the concentration of the Aroclor mixture.

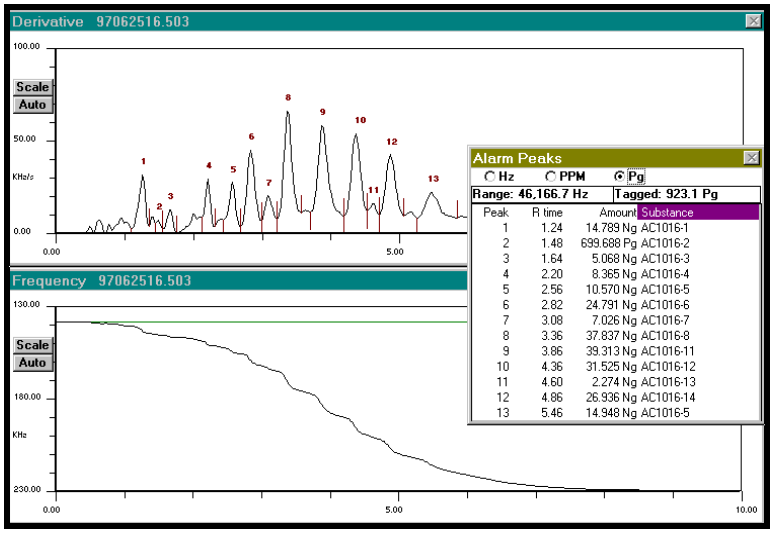

Figure 2- Calibration with Aroclor 1016.

Aroclor Pattern Recognition

Commercial Aroclor mixtures of PCB isomers are commonly found at environmental sites and their composition and vapor signature can readily be recognized by a trained operator. Five different Aroclor vapor signatures in vertically offset chromatograms are shown in **Figure 3**.

By creating peak identification files for the Aroclor mixtures, the pattern

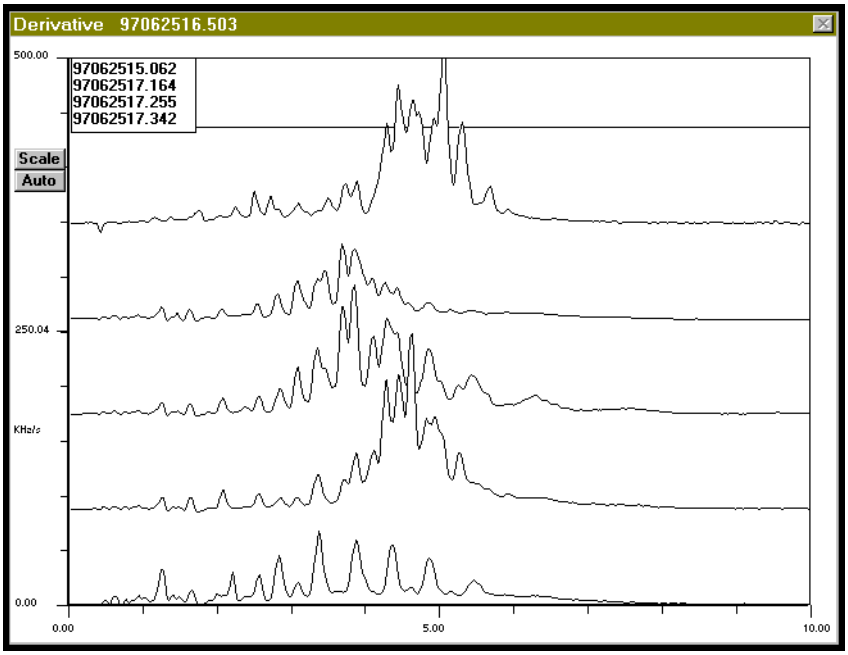

Figure 3- Vapor signatures of several Aroclor mixtures.

recognition process can be quantified and the relative degree of fit for an unknown set of PCB peak retention time determined. Data logging to Excel spread sheets using different peak recognition file patterns for the raw data, provides documentation and archival of all SAW/GC measurements.