

Electronic Sensor Technology GC/SAW Performance
Evaluation Report

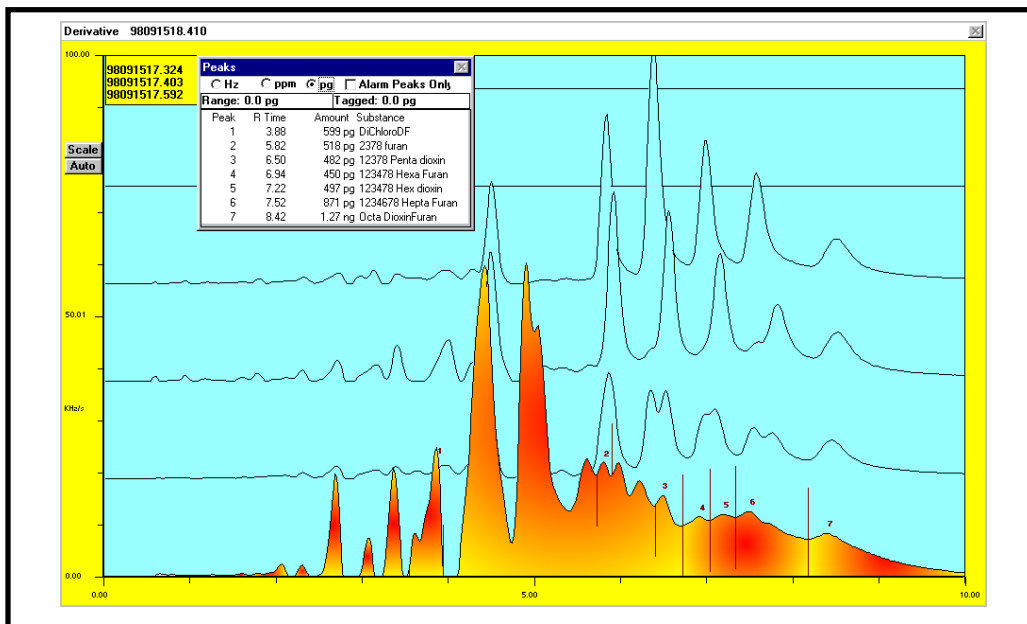
For

Detection of Dioxin/Furan Isomers in Flyash

Prepared for:
A Japanese Company

December 12, 1998

Speed of an Electronic Nose



and the Precision and Accuracy of a GC!!

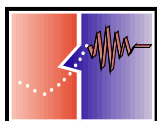
Detection of Dioxin/Furan Isomers in Flyash

Report Summary

There is a worldwide need to measure dioxin/furans in real or near real time in flyash matrices from incinerators to meet the Environmental Standards. This report describes the performance of a fast GC/SAW measurement system, which was successfully used to analyze flyash samples supplied by A Japanese Company. Although a GC by itself cannot positively identify dioxins/furans, it can provide a near real time field measurement and is a cost effective screening tool which can minimize expensive laboratory GC/MS testing.

A simple field extraction method, calibration procedure, and the instrument's associated minimum detection level (10 picograms) were determined before extracts from flyash samples were tested. The total flyash dioxin/furan concentration was typically 100-1000 nanograms/gram of flyash. The Japanese Company laboratory test results were compared with preliminary GC/SAW findings and recovery and accuracy evaluated. In general, the recovery achieved with the simple field extraction was within 50% of that of laboratory results. Quantification of individual isomer concentrations was done at several screening speeds. Although screening times as short as 10 seconds gave acceptable levels of detection, longer analysis times of 20 seconds or even 150 seconds gave improved peak separation.

Because the field extraction did not utilize acid washing or filtering there was a substantial background level of compounds which might interfere and cause false alarms at low levels. Recommendations for future work include detailed analysis of recovery, method detection limits, and filtering using solid phase micro-extraction.



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Performance Evaluation Report:

Detection of Dioxin/Furan Isomers in Flyash

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December 12, 1998

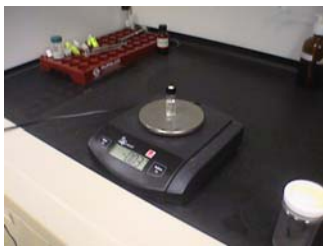
Purpose and Scope:

A Japanese Company has identified the need to measure dioxin/furans in real or near real time in flyash matrices from incinerators to meet the Environmental Agency's (EA) Standards. As part of a preliminary evaluation of promising technologies such as fast chromatography flyash samples were sent to Electronic Sensor Technology for evaluation using a GC/SAW. This report includes a description of the GC/SAW measurement system, sample analysis procedures, calibration procedures, values obtained and minimum detection levels.

Evaluation Protocol:

The flyash samples contained unknown concentrations of dioxins and furans. Flyash samples were first extracted using a solvent mixture of hexane and methanol. After centrifuging to separate solids samples of the hexane were extracted into vials. Evaluation was performed by injecting microliter quantities of the sample extract into an open-tubular desorber attached to the inlet of a GC/SAW vapor analyzer. For each sample the concentration of individual dioxins and furans were recorded and referenced to calibration standards of similar concentration.

The basic steps of the extraction procedure are shown in the following pictures. It should be noted that no special attempt was made to perform any type of clean up procedures such as acid washing or silica column filtering in this preliminary evaluation.



Step 1- Weigh vial containing 1 mL methanol and 0.5 mL hexane.



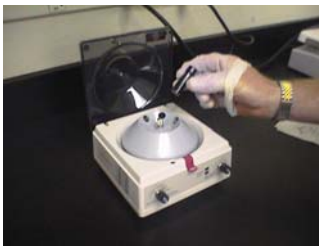
Step 2- add approximately 1 gram of flyash to vial.



Step 3- Shake for 1 minute.



Step 4- re-weigh vial. Subtract previous solvent weight to obtain weight of flyash added.



Step 5- Centrifuge for 2 minutes at 5000 rpm.



Step 6- Pipette extraction sample from top layer of hexane in vial.

Figure 1- Steps used in solvent extraction of flyash samples.

Description of GC/SAW Technology

Electronic Sensor Technology currently manufactures fast chromatographs in two different models. Both models use surface acoustic wave (SAW) integrating detectors. One system, the model 4100, features a handheld GC and sampling preconcentrator attached to a support case by means of a 6 foot umbilical cable. The second, a model 7100, is designed for laboratory or portable use and the chromatograph and vapor preconcentrator are integrated into a benchtop case. Both systems interface with a Pentium laptop running proprietary control software using an RS232 connection. A full range of post processing analysis and communications software is provided by links to features inherent in Windows 95 and Microsoft Office.



**Figure 3- Benchtop Model 7100
GC/SAW Vapor Analyzer.**



**Figure 2- Handheld Model 4100
GC/SAW vapor Analyzer.**

These instruments can be configured to quickly analyze a wide range of volatile and semi-volatile compounds using the patented integrating SAW detector. Using a temperature ramped DB-5 column the GC/SAW typically can speciate and quantify dioxins and furans at the picogram level within a 10 second chromatogram. For the evaluation of the Japanese Company samples a 4100 system was used together with a model 3100 open-tubular desorber attached to the inlet of the system. This accessory thermally vaporizes liquid injections and these vapors are then sampled by the GC/SAW measurement system.

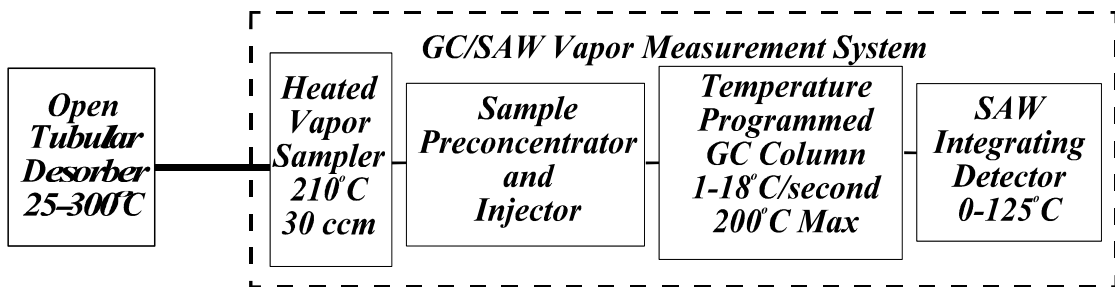


Figure 4- block diagram of GC/SAW vapor measurement system.

Sample Preparation and Injection

Standard calibration solutions were used and two additional dilutions were carried out in hexane. A 50 to 1 dilution was prepared by injecting 20 μ liters of stock solution into 1 milliliter of hexane. A 1000 to 1 dilution was prepared by injecting 1 μ liter of stock into 1 milliliter of hexane.



Figure 5- Attachment of Open-Tubular sample desorber attached in inlet of GC/SAW Vapor Analyzer.

All samples extracts and calibration standards were injected using a 10 μ liter glass syringe. The sample injection and measurement was carried out in two steps:

Step 1 - 1-10 μ liters of sample is injected into middle of glass wool wick within a six inch long desorbtor tube attached to the inlet of the GC/SAW vapor analyzer.

Step 2- A desorbtor tube heater (280°C) is placed over the glass desorbtor tube and vapor sampling (measurement cycle) by the GC/SAW is initiated by the operator.

The remainder of the measurement process was automatic and required no further operator actions other than to annotate notes which identified the actions being taken or other relevant sample identification information.

Calibration Standards

Two calibration standards were purchased from AccuStandard Inc. (25 Science Park, New Haven CT 06511). Each kit contained five dioxins (M8280A) and five furans (M8280B) as required by EPA 8280 Method. The concentration of each analyte within the mixture was 5.0 nanograms per μ liter of toluene. A 10-to-1 dilution was used as a calibration level of 0.5 ng/ μ liter. The following table provides the full analyte specifications as well as their TEQ rating.

Analyte	CAS No.	TEQ*
2,3,7,8-tetrachlorodibenzo-p-dioxin	51207-31-9	1.00
1,2,3,7,8-Pentachlorodibenzo-p-dioxin	40321-76-4	0.50
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin	39227-28-6	0.10
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin	35822-46-9	0.01
Octachlorodibenzodioxin	3268-87-9	0.001
2,3,7,8-Tetrachlorodibenzofuran	1746-01-6	0.1
1,2,3,7,8-Pentachlorodibenzofuran	40321-76-4	0.05
1,2,3,4,7,8-Hexachlorodibenzofuran	55684-94-1	0.10
1,2,3,4,6,7,8-Heptachlorodibenzofuran	35822-46-9	0.01
Octachlorodibenzofuran	39001-01-0	0.001

Figure 6- Analyte Standards Used in Sample Evaluation.

No other standards were available for comparison with the Japanese Company samples. Hence in this study any quantification of isomers lower than tetra is based upon an estimated response factor and not upon a calibration standard.

Selection of GC Method

The GC/SAW vapor analyzer is capable of performing dioxin analysis and quantification within a 10 second chromatogram as well as at slower speeds such as 20, 50, or more seconds. There is a trade-off in resolving power with better resolution being achieved at slower and longer chromatograms as shown in Figure 5.

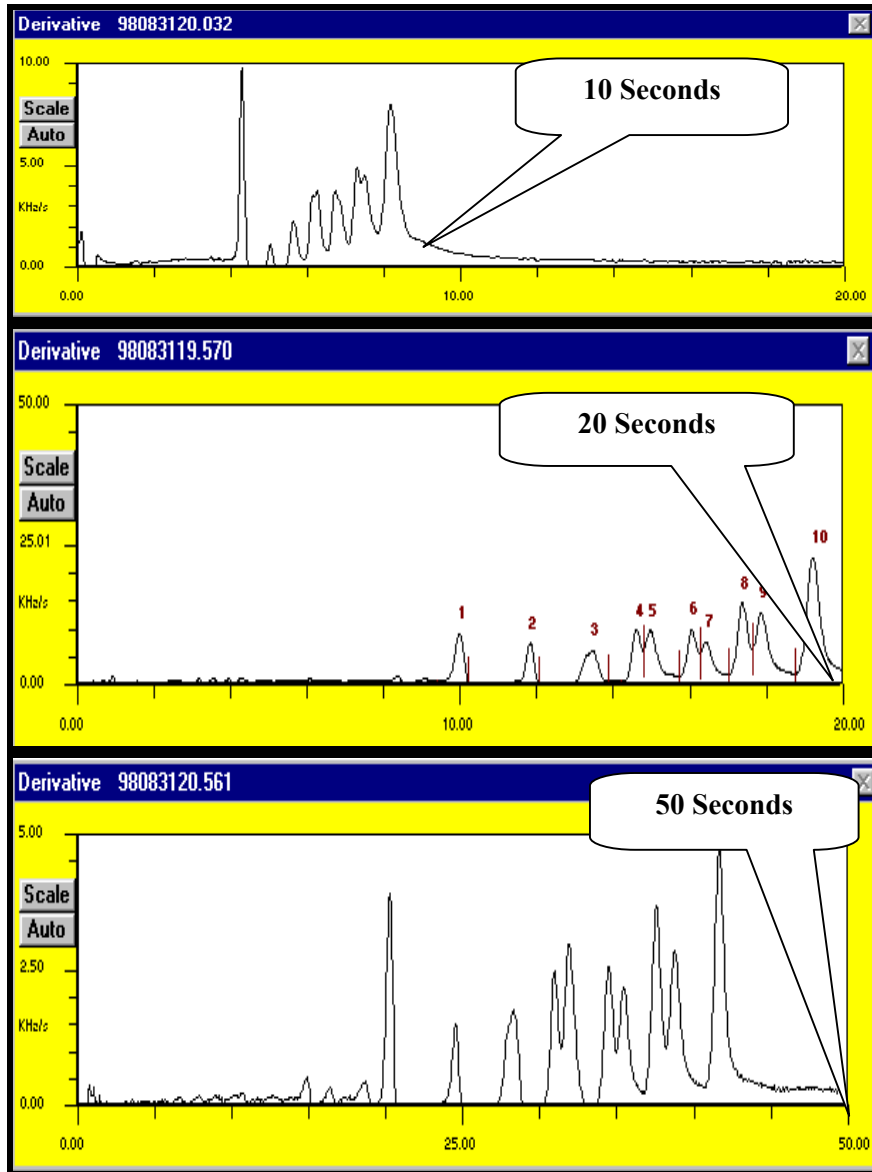


Figure 6- Resolution vs speed displayed for 18° C/sec, 7° C/sec, and 3° C/sec column ramping rates.

For quantification of the Japanese Company sample, a 20 second chromatogram was achieved with a linear increase of column temperature from 60°C to 200°C within 20 seconds. The complete GC method was constructed using a graphical method as shown in Figure 6. The GC method steps are created by dragging placeholders from the vertical

toolbar into a horizontal line at the bottom of the dialog screen of Figure 6. Each placeholder corresponds to a step or action with parameters set by the operator. This method begins with a 30 second sample (preconcentrate) time, move valve to inject position, inject sample, ramping of the column temperature, and taking of data for 20 seconds following the injection. At the end of the method is a 15 second bake cycle to ‘clean’ the crystal detector is activated and the column temperature is returned to 60°C..

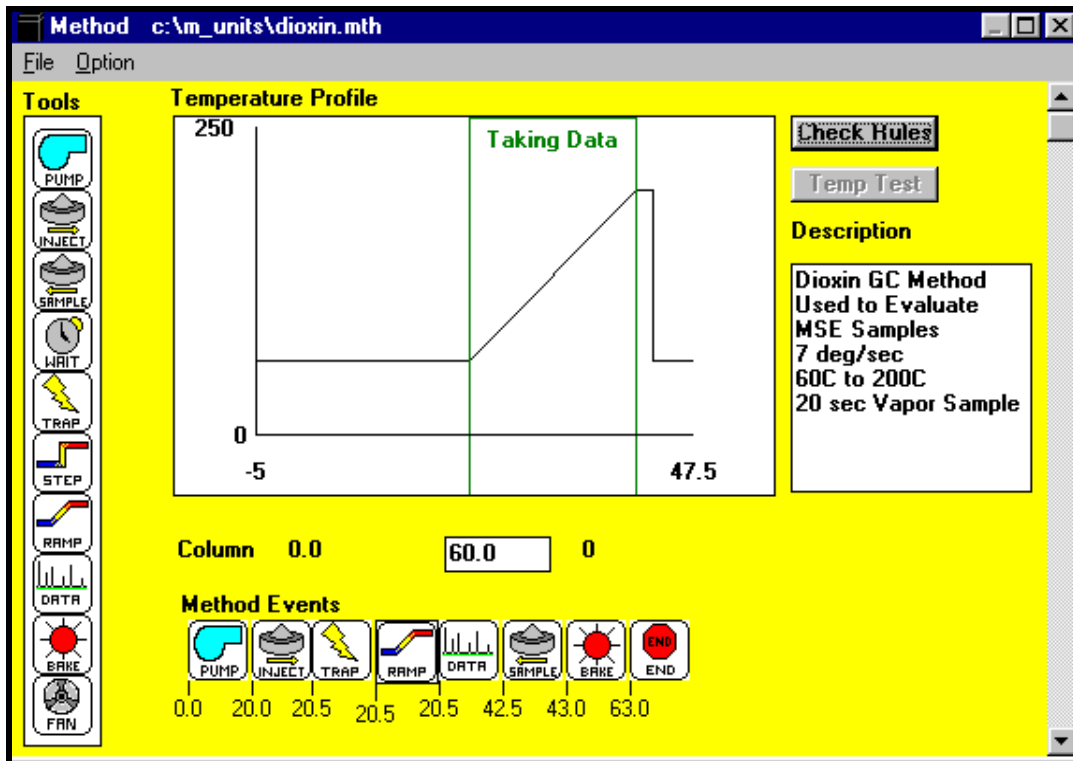


Figure 7- GC Method dialog screen showing method used to evaluate MSE samples.

Analysis Time Requirements

In automatic mode each analysis must contain the following basic steps with their minimum values. The values used for the Japanese Company samples is shown for

	Minimum (Sec)	BHK Sample (Sec)
Inject Sample into Desorber	2	5
Preconcentrate Vapor Sample	15	30
GC Analyze	10	20
Recovery of Column & Detector	15	30
Total Cycle Time	42	85

comparison.

Calibration Procedures

Calibration of the instrument involved injection of standards of known concentration. Division of SAW detector 'counts' by the concentration produced a response factor specific to each analyte. The response factor (Hz/pg), peak name, retention time, and

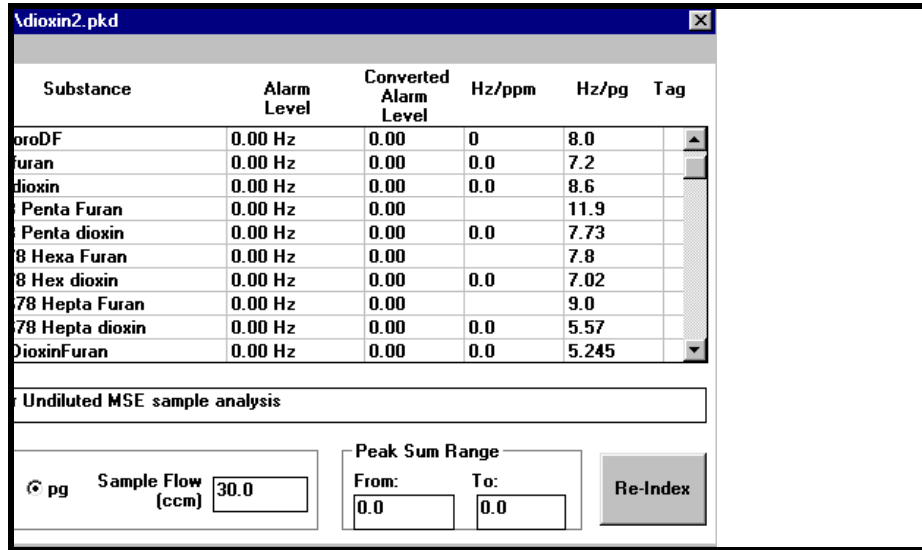


Figure 9- Operator entry of retention time windows, peak labels, and response factors completes system software calibration.

percentage variation allowed in retention time (Percent spread) were entered into a calibration table and this completed calibration (Single point). Multiple point calibration and interpolation were also available features within the software. Proper calibration was routinely checked by injecting furan or dioxin mixtures of known concentration.

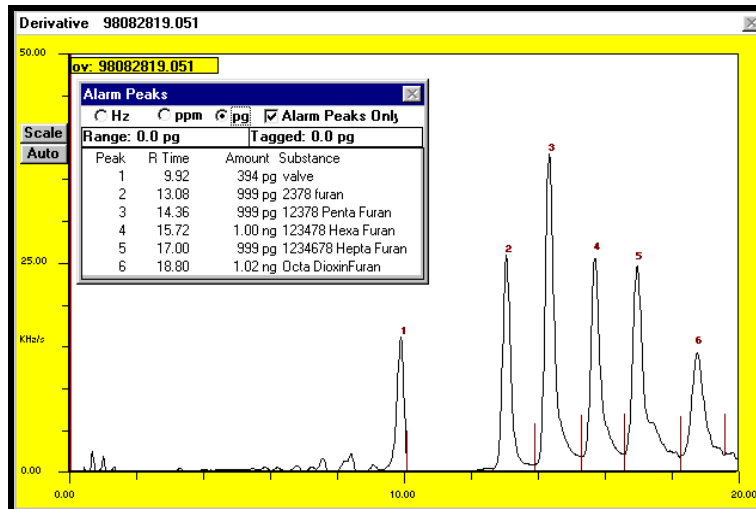


Figure 8- Chromatogram of furan standards after entry of proper response factors and retention times into peak identification file.

Minimum Detection Limit

Detection limits for instruments the GC/SAW is determined by signal to noise and the noise or detected peak amplitudes obtained with a blank injection of pure hexane into the GC/SAW are specified to be less than 1 picogram. Operating the system at a signal to noise ratio of 3 would then give a 3 picogram minimum detection level while operating at a higher signal-to-noise ratio of 10 would give a minimum detection level of 10 picograms.

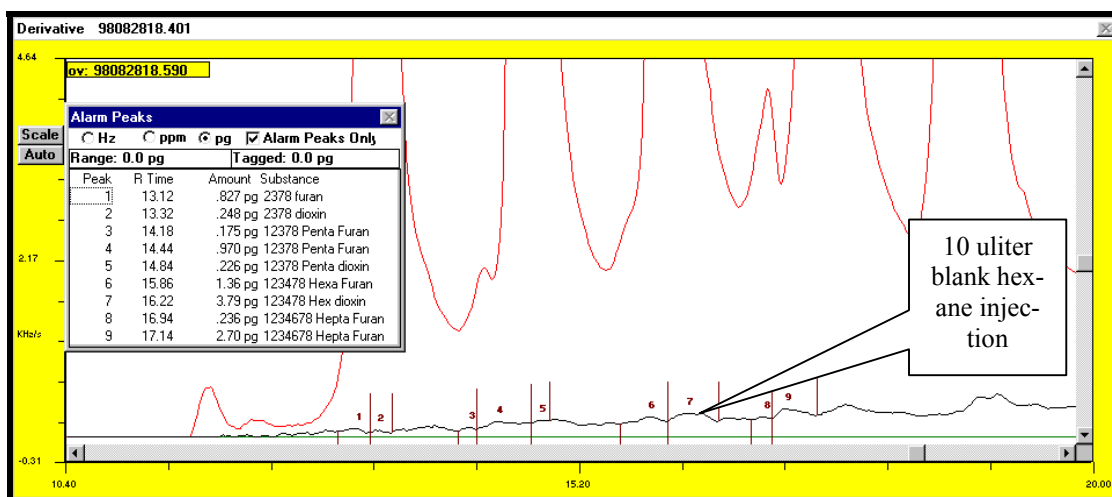


Figure 9- Blank injection chromatogram of 10 uliters of hexane compared with 2 uliter dioxin standard (0.5 ng/uliter).

EPA Method detection limits were evaluated by multiplication of the standard deviation of seven replicate measurements by 3.14. Method detection limits varied between 10 and 30 picograms using this method with 10 picogram injections. RSD values for manual injections were typically 20% or less.

Quality Control/Assurance Procedures

Electronic Sensor Technology utilizes ISO9000 procedures throughout the manufacture and testing of all GC/SAW instruments. In addition the company maintains an on-site calibration laboratory where EPA quality control and quality assurance methods for all performance tests are practiced.

Samples obtained from JAPANESE COMPANY were logged and maintained by the laboratory director. In addition the quality of calibration standards were controlled by the laboratory operators throughout the testing of the JAPANESE COMPANY samples. All GC data taken on the JAPANESE COMPANY samples was logged and archived on the company server. Each data record was labeled and time-stamped according to the Quality Assurance procedures of the laboratory.



Figure 10- The EST Quality team tests and certifies the performance of each and every system before it is delivered the customer

Evaluation Results

At this time a comprehensive evaluation of the extraction method has not been performed and only preliminary results on isolated samples has been done. Extract chromatograms were compared with chromatograms obtained from standard solutions. An example of a 4 microliter flyash extract chromatogram is shown in Figure 11. The three background traces correspond to (top to bottom) a standard mix of furans (1 nanogram per isomer), a mix of dioxins (1 nanogram per isomer), and a standard mix of furans and dioxins (0.5 ng per isomer).

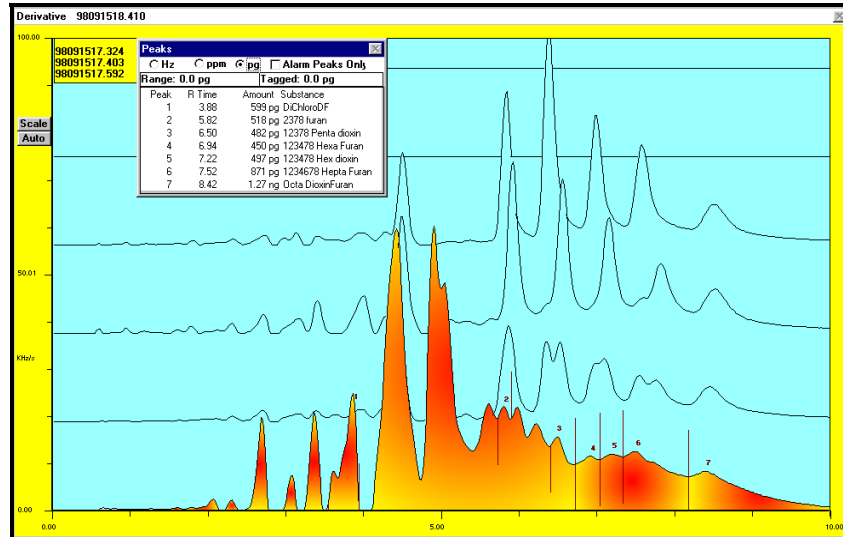


Figure 11- Comparison with individual and mixed dioxin furan standards

The inset table displays the amount of each isomer detected as well as its recorded retention time. The following table summarizes the measurement results as total di, tri, tetra, penta, hexa, hepta, and octa dioxins and furans detected. Quantification is based upon response factors as determined from calibration standards and identification was based upon a retention time which matched the standard's retention time within 5%.

Quantities of each isomer detected in this sample ranged from 500 pg to 1.3 ng. Since the 4 microliter sample represented only 1/80 of the total amount extracted, these results indicate the sample contained 40 to 104 ng/g of furan or dioxin isomers.

	Measured pg	Flyash ng/g
Di/Tri DF	599	48
Tetra DF	518	41
Penta DF	482	39
Hexa DF	947	76
Hepta DF	871	70
Octa DF	1227	98
total DF	4644	372

Ten second chromatograms represent the fastest analysis time available. Although peak separation is not complete a useful detection of compounds can be still achieved. Improved resolution was achieved by slowing the column temperature program of the GC method. An example performed on the same extract but with a slower temperature ramp is shown in Figure 12. For comparison a mixed furan/dioxin standard (1 nanogram per isomer) is shown in the background of this figure. The peak separation is greatly improved expected in a 20 second chromatogram.

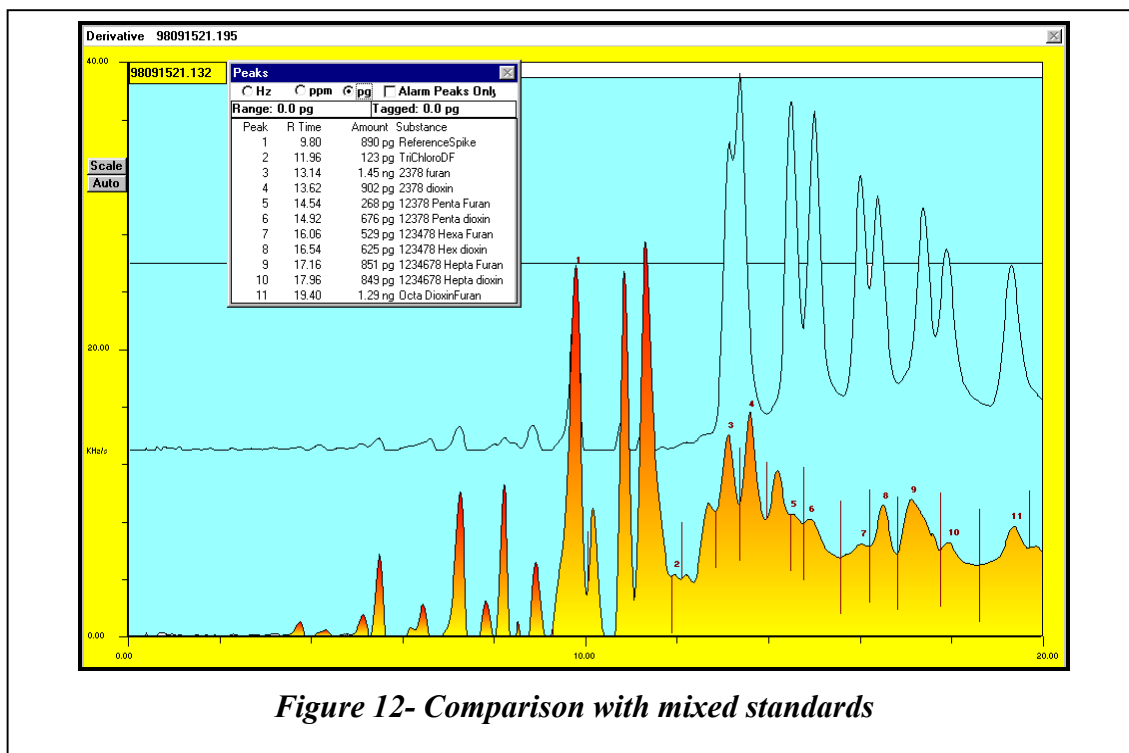


Figure 12- Comparison with mixed standards

Quantitatively the amount of furan/dioxin isomers detected was quite similar. In this case the concentrations again ranged from 500 pg to 2 ng for the isomers detected. This then predicted a concentration of furans and dioxins in the flyash sample of from 40 to 160 ng/g. The total amount of dioxins furans was approximately 500 ng/g.

	Measured pg	Flyash ng/g
Di/Tri DF	123	10
Tetra DF	1352	108
Penta DF	944	76
Hexa DF	625	50
Hepta DF	1700	136
Octa DF	1290	103
total DF	6034	483

Not all flyash samples gave the same result as indicated by the result shown in Figure 13. A very slow temperature ramp was used to produce a 150 second analysis time and the resolution achieved illustrates perhaps the best separation which can be achieved

with the length of column used. In this flyash sample the amount of furan/dioxin isomers detected was relatively low spanning a range of 100 to 300 picograms. Thus this extract had a normalized concentration of from 8 to 24 ng/g. For comparison a mixed standard (1 nanogram per isomer) is shown in the background.

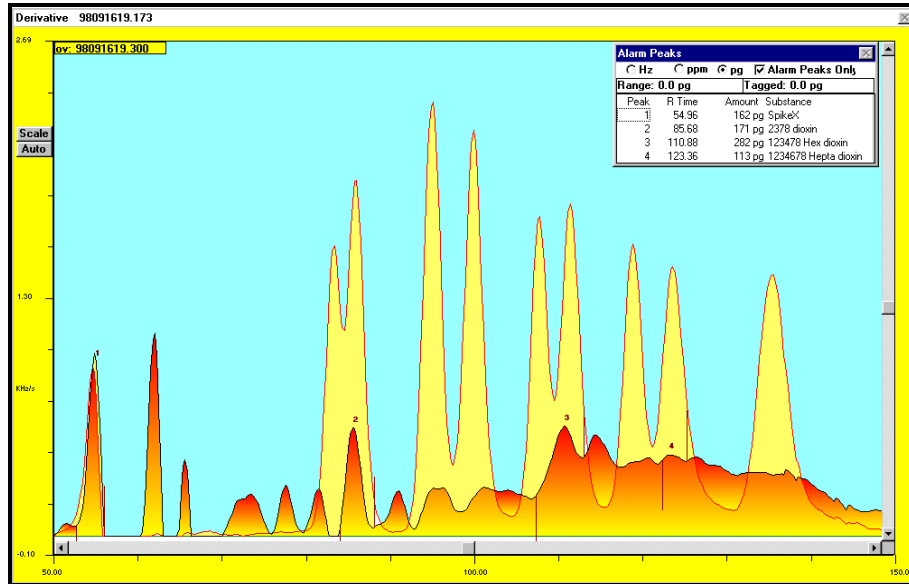
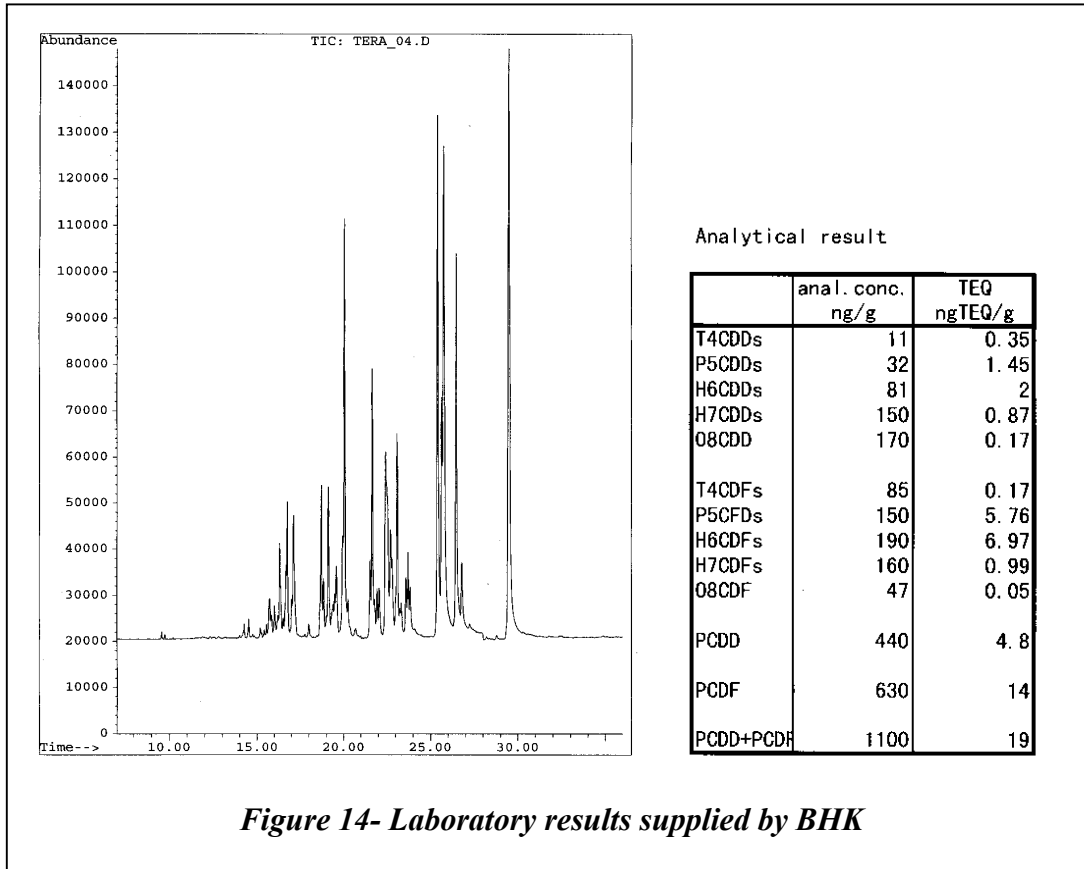


Figure 13 Increased resolution with slower ramp and lower temperature.

	Measured pg	Flyash ng/g
Tetra DF	171	14
Penta DF	-	-
Hexa DF	282	23
Hepta DF	123	10
Octa DF	-	-
total DF	576	46

Comparison with Laboratory Results

Independent laboratory results of GC/MS analysis upon the flyash samples was supplied by JAPANESE COMPANY and a sample chromatogram as well as the analytical results are shown in Figure 14. The concentration of furan/dioxin isomers detected ranged from 96 to as high as 1100 ng/g. These results are quite similar to that reported with the GC/SAW, however the analysis time is approximately 30 minutes. In this case a much longer column was used and the resolution is greatly improved.



Comparing the average of GC/SAW measurements with the JAPANESE COMPANY laboratory results provides an estimate of the recovery of the simple extraction method as follows.

	Measured ng/g	Laboratory ng/g	Estimated Recovery %
Di/Tri DF	29	-	-
Tetra DF	75	96	78%
Penta DF	57	182	31%
Hexa DF	63	271	23%
Hepta DF	103	210	49%
Octa DF	101	217	46%
total DF	427	1100	39%

Recommendations

The simple extraction method used in these preliminary evaluations was designed to provide an initial field method for quickly screening flyash samples. There is a need to perform accurate recovery and MDL testing on this method. A Soxhlet extraction will be used as a baseline measurement for comparison. To accomplish this the Soxhlet extraction apparatus pictured in Figure 15 was purchased and is available.

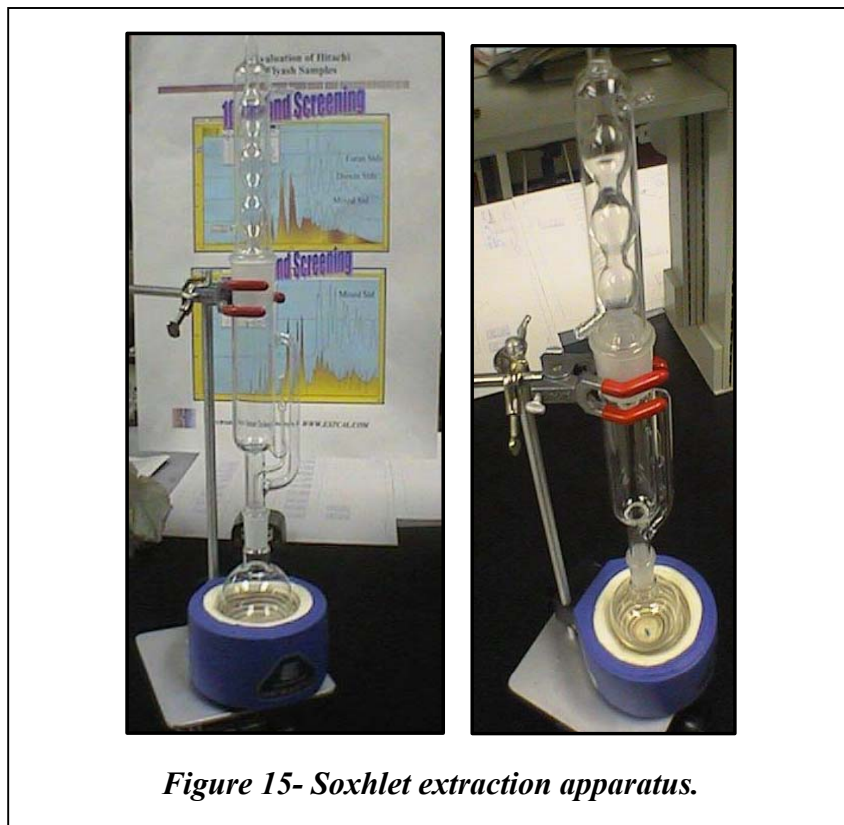


Figure 15- Soxhlet extraction apparatus.

The preliminary results demonstrated that there is significant amount of background compounds which might create false alarms. To reduce this probability there needs to be an application of some cleanup method. Also, an evaluation of solid phase extraction (SPE) and solid phase micro extraction SPME as a means for filtering and reducing the number of compounds which might interfere with dioxin/furan detection will be tested in the future.