Electronic Sensor Technology GC/SAW Performance Evaluation Report

For

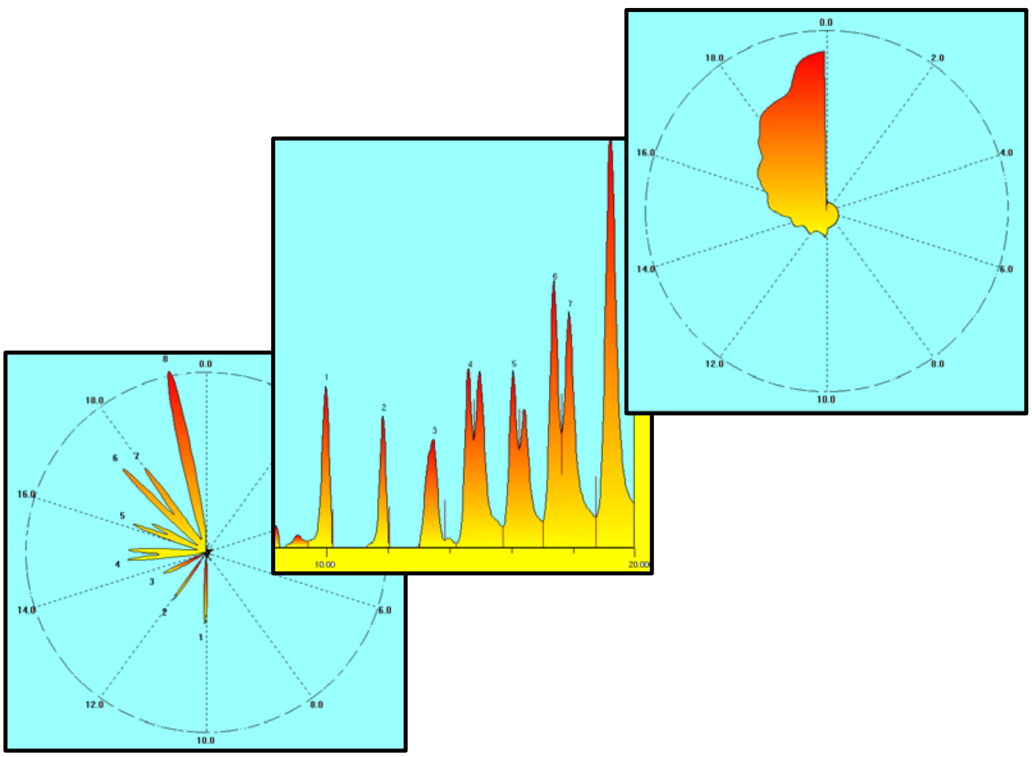
CEMS Dioxin Monitor Testing Program

Prepared for:

MSE Technology Applications Inc.

Butte, Montana

Speed of an Electronic Nose



and the Precision and Accuracy of a GC !!

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Purpose and Scope:

The United States Department of Energy (DOE) has identified the need to measure dioxin/furans in real or near real time in stack gases to meet the Environmental Protection Agency's (EPA) Maximum Achievable Control Technology (MACT) Standard. As part of a preliminary evaluation of promising technologies such as fast chromatography a mixture of various dioxin/furans was 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 evaluation sample contained a mixture of dioxins and furans at 1-10 nanogram per microliter levels in nonane. Evaluation was performed by injecting microliter quantities of undiluted sample, 1:50 diluted sample, and a 1:1000 diluted sample 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.

Description of GC/SAW Technology

Electronic Sensor Technology currently manufactures fast chromatographs in two different models and both use surface acoustic wave (SAW) integrating detectors. One system, the model 7100, 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.

These instruments can be configured to quickly analyze a wide range of volatile

Figure 2- Benchtop Model 7100 GC/SAW Vapor Analyzer.

Figure 1- Handheld Model 4100 GC/SAW vapor Analyzer.

and semi-volatile compounds using the patented integrating SAW detector. Using a temperature ramped DB-6 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 MSE 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.

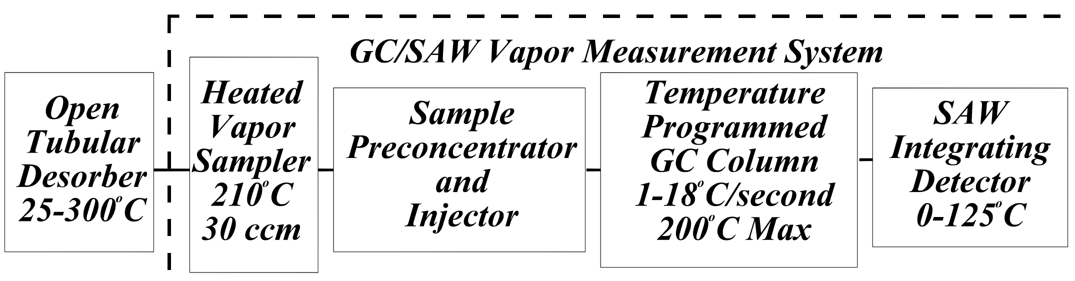

Figure 3- block diagram of GC/SAW vapor measurement system.

Sample Preparation and Injection

Stock solution was obtained from MSE and two dilutions were carried out in hexane. A 50 to 1 dilution was prepared by injecting 20 μliters of stock solution into 1 milliliter of hexane. A 1000 to 1 dilution was prepared by injecting 1 μliter of stock into 1 milliliter of hexane.

Figure 40 Attachment of Open-Tubular sample desorber attached in inlet of GC/SAW Vapor Analyzer.

All samples and calibration standards were injected using a 10 μliter glass syringe. Sample injection and measurement was carried out in two steps:

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

Step 2- A desorbtion tube heater (280^{o}C) is placed over the glass desorbtion 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 µliter of toluene. A 10-to-1 dilution was used as a calibration level of 0.5 ng/µliter. 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 5- Analyte Standards Used in Sample Evaluation.

No other standards were available for comparison with the MSE 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.

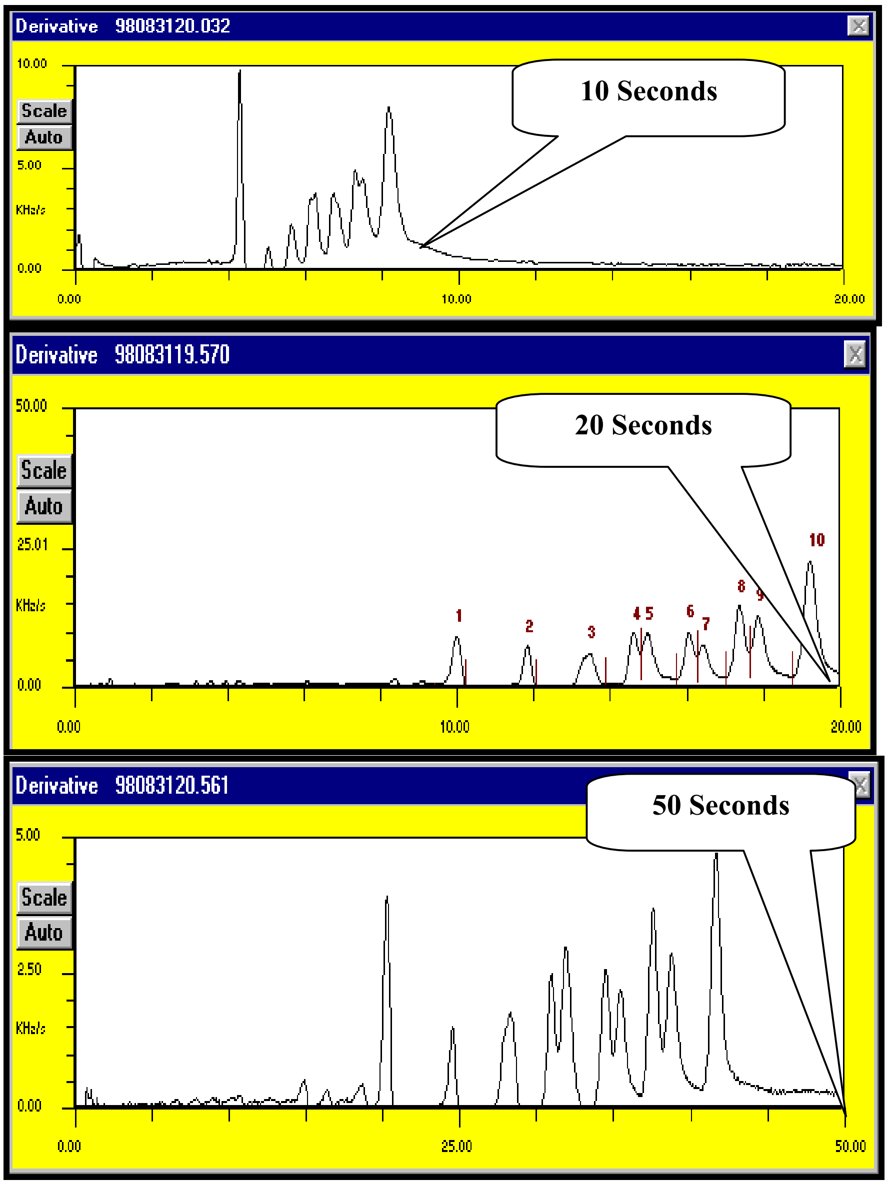

Figure 6- Resolution vs speed displayed for 18^{o}C/sec, 7^{o}C/sec, and 3^{o}C/sec column ramping rates.

For quantification of the MSE sample a 20 second chromatogram was achieved with a linear increase of column temperature from 60^{o}C to 200^{o}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^{o}C..

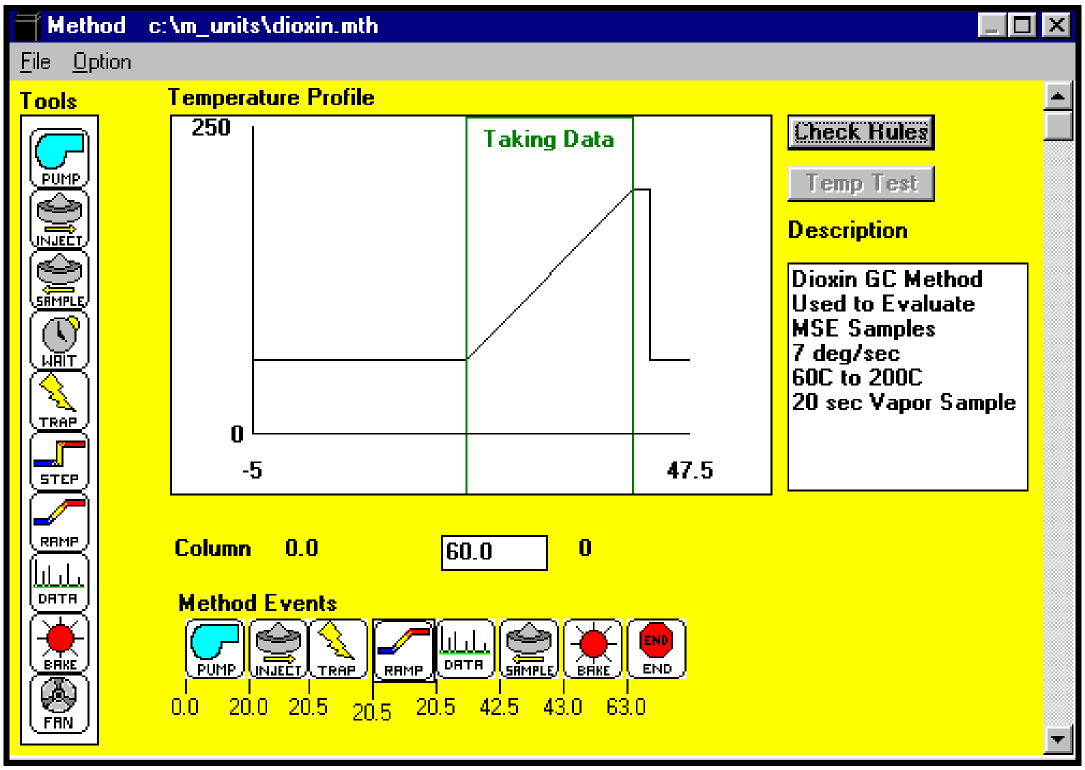

Figure 7- GC Method dialog screen showing method used to evaluate MSE samples.

Analysis Time Requirements

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

	Minimum (Sec)	MSE 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**

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

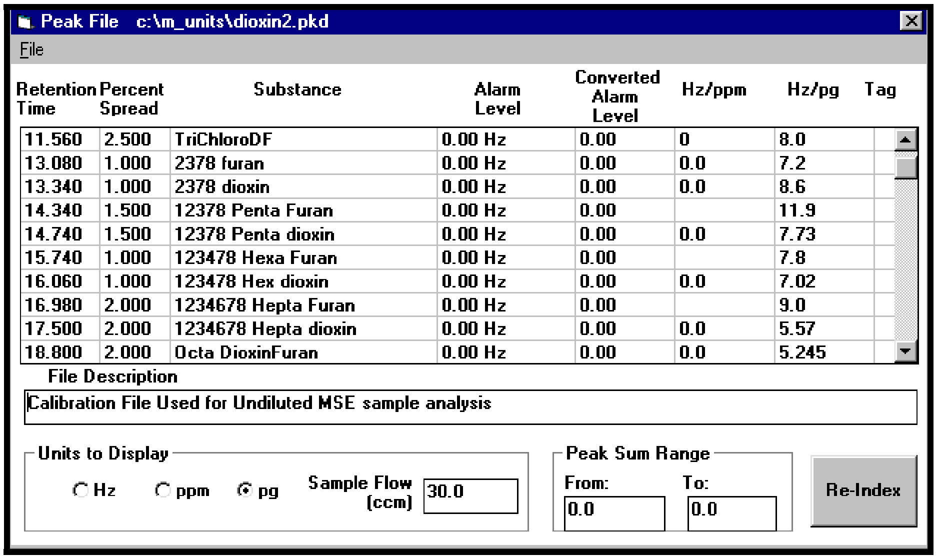

Figure 9- Operator entry of retention time windows, peak labels, and response factors completes system software calibration.

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.

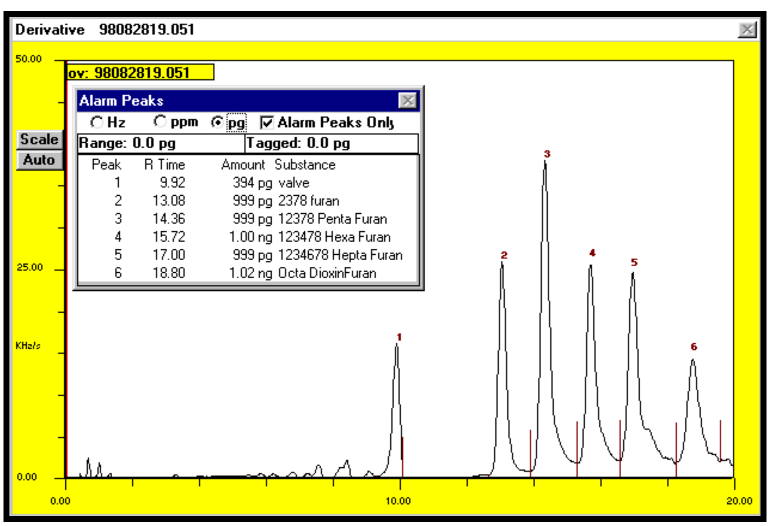

Figure 8- Chromatogram of furan standards after entry of proper response factors and retention times into peak identification file.

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.

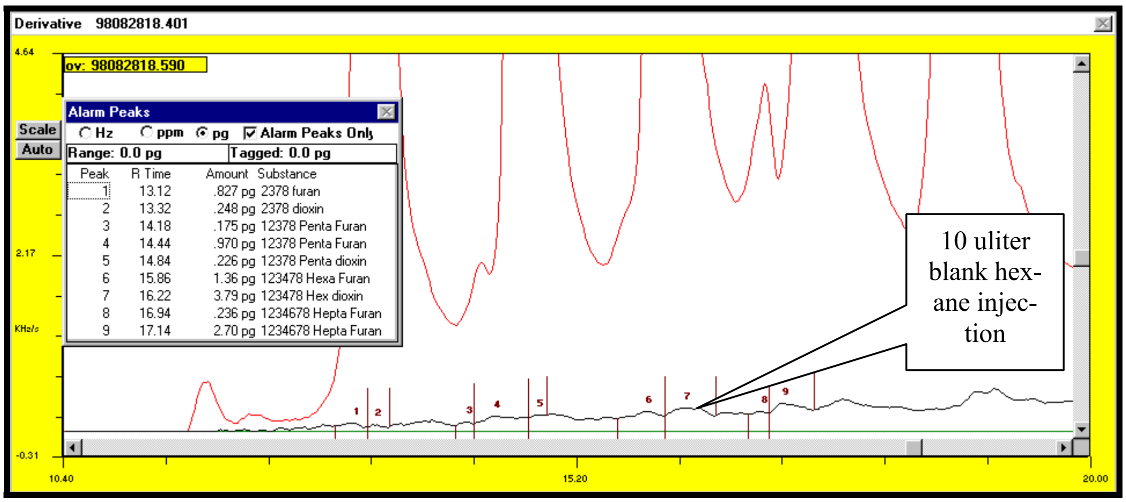

Figure 9- Blank injection chromatogram of 10 uliters of hexane compared with 2 uliter dioxin standard (0.5 ng/uliter).

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 MSE 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 MSE samples. All GC data taken on the MSE 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.

Evaluation Results – Undiluted MSE Sample

An average of three 1 µliter injection-measurements (See Excel spreadsheet in appendix) were used to arrive at the following analyte concentrations:

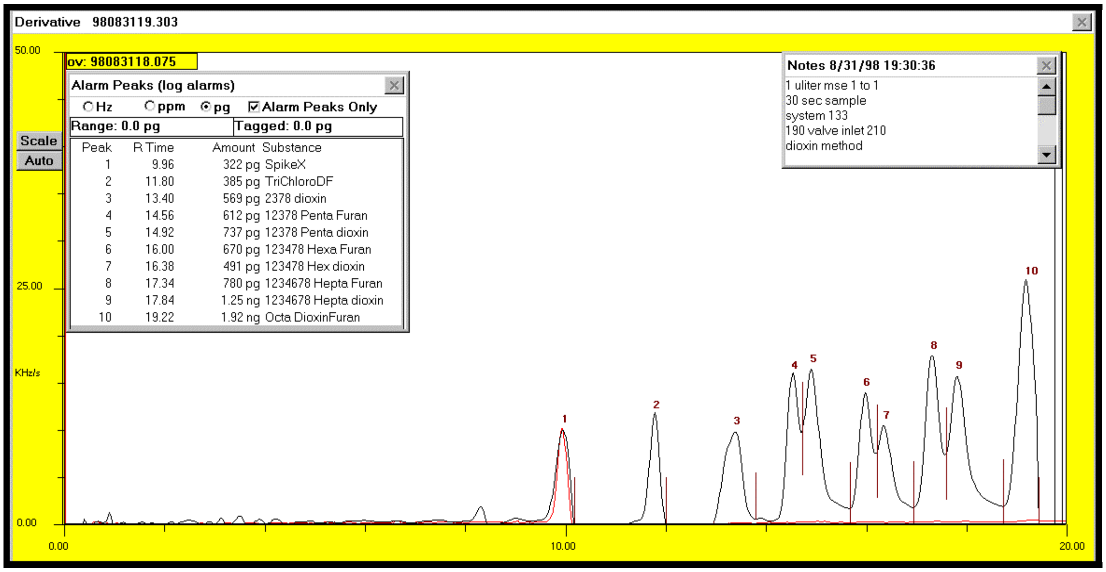

Figure 10- Chromatogram from 1 uliter injection of undiluted MSE sample.

Tri-chloro furan/dioxin	308 pg/µliter	Uncalibrated estimate
2378 TetraFuran	0	Unresolved from group
2378 TetraDioxin	478.7 pg/µliter	At least one other Tetra present
12378 PentaFuran	478.7 pg/µliter	Good retention time match
12378 PentaDioxin	598.7 pg/µliter	Poor retention time match
123478 HexaFuran	549.3 pg/µliter	Good retention time match
123478 HexaDioxin	429.0 pg/µliter	Good retention time match
1234678 HeptaFuran	681.7 pg/µliter	Good retention time match
1234678 HeptaDioxin	1133.3 pg/µliter	Good retention time match
OctaFuran/Dioxin	2200 pg/µliter	Octa Furan & dioxin not resolved

Evaluation of 50 to 1 MSE Sample

An average of three 5 µliter injection-measurements (See Excel spreadsheet in appendix) were used to arrive at the following analyte concentrations:

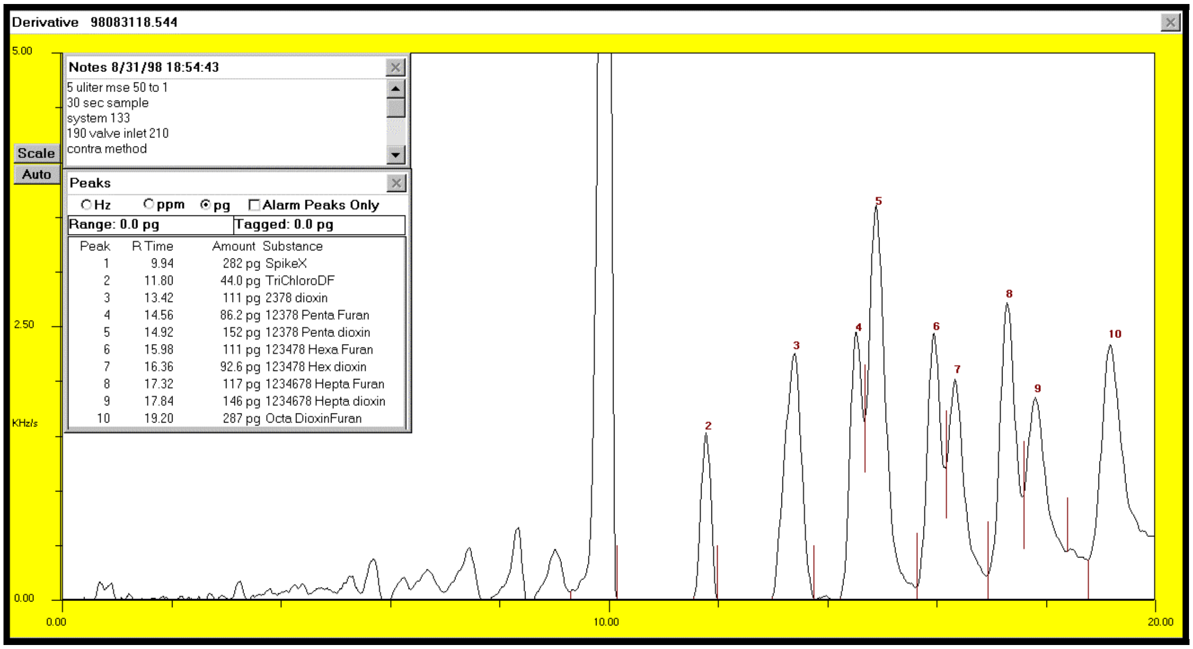

Figure 11- Injection of 10 µliter of MSE sample diluted 50 to 1. Inset table shows measured amounts for each analyte.

Tri-chloro furan/dioxin	9.44 pg/µliter	Uncalibrated estimate
2378 TetraFuran	0	Unresolved from group
2378 TetraDioxin	22.8 pg/µliter	At least one other Tetra present
12378 PentaFuran	17.8 pg/µliter	Good retention time match
12378 PentaDioxin	29.8 pg/µliter	Poor retention time match
123478 HexaFuran	22.7 pg/µliter	Good retention time match
123478 HexaDioxin	19 pg/µliter	Good retention time match
1234678 HeptaFuran	24.3 pg/µliter	Good retention time match
1234678 HeptaDioxin	33.5 pg/µliter	Good retention time match
OctaFuran/Dioxin	54.9 pg/µliter	Octa Furan & dioxin not resolved

Evaluation of 1000 to 1 MSE Sample

An average of three 10 μliter injection-measurements (See Excel spreadsheet in appendix) were used to arrive at the following analyte concentrations:

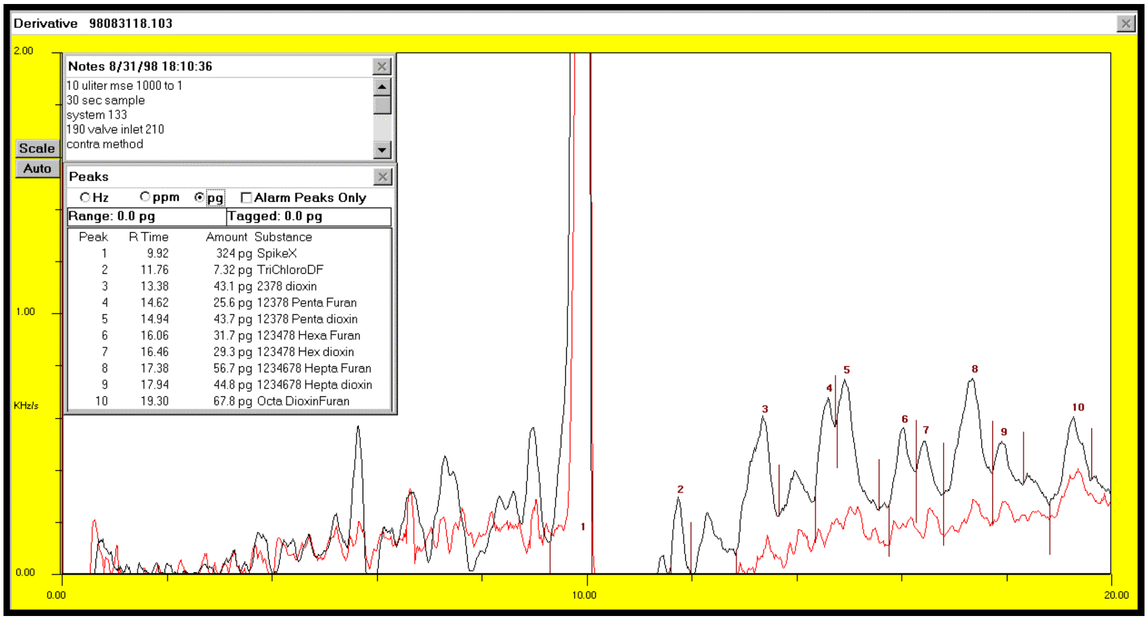

Figure 12- Injection of 10 μliter of MSE sample diluted 1000 to 1. Inset table records measured amounts for each chromatogram.

Tri-chloro furan/dioxin	0.732 pg/μliter	Uncalibrated estimate
2378 TetraFuran	0	Unresolved from group
2378 TetraDioxin	4.31 pg/μliter	At least one other Tetra present
12378 PentaFuran	2.56 pg/μliter	Good retention time match
12378 PentaDioxin	4.37 pg/μliter	Poor retention time match
123478 HexaFuran	3.17 pg/μliter	Good retention time match
123478 HexaDioxin	2.93 pg/μliter	Good retention time match
1234678 HeptaFuran	5.67 pg/μliter	Good retention time match
1234678 HeptaDioxin	4.48 pg/μliter	Good retention time match
OctaFuran/Dioxin	6.78 pg/μliter	Octa Furan & dioxin not resolved

Peak Identification

Individual furan and dioxin isomers can be identified by retention time matching with known standards. An MSE sample chromatogram with overlays (in red) 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.

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/µliter of 2368 Furan present in the previously identified 478.7 pg/µliter 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.

The software also reported 12378 Penta dioxin (598.7 pg/µliter) in the undiluted sample and this is a mis-identification since the retention time does not match the standard. The actual isomer is probably 12347 or 12478 Penta dioxin.

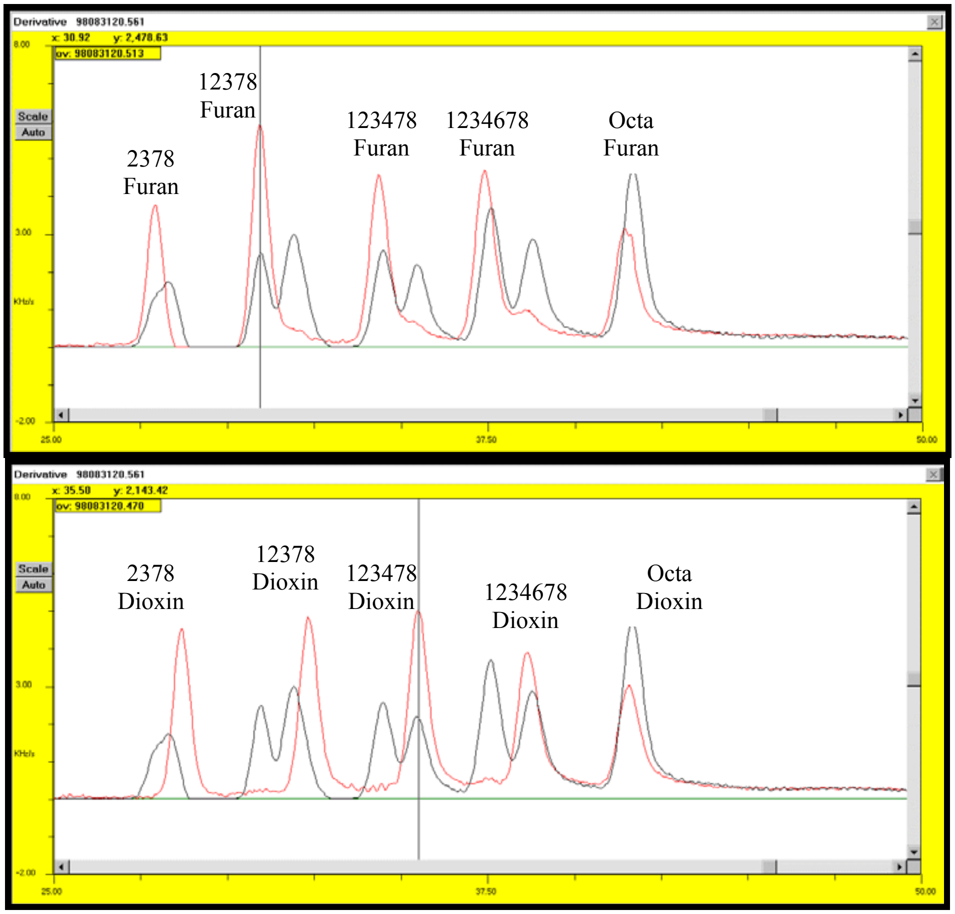

Figure 13- Comparison of 50 second chromatogram r3sults with furan and dioxin standards.

Summary of Results

In summarizing our findings we have listed 2378 dioxin is 0 although it may be much lower concentration than other tetra dioxins detected. Also 12378 Penta-dioxin is listed as zero because the Penta-dioxin peak detected did not match the retention time of standards.

Summary of Results

Tri-chloro furan/dioxin	308 pg/μliter	Uncalibrated estimate
2378 TetraFuran	200 pg/μliter	Unresolved estimate
2378 TetraDioxin	0	Other Tetra dioxins present
12378 PentaFuran	478.7 pg/μliter	Good retention time match
12378 PentaDioxin	0	Other Penta dioxins present
123478 HexaFuran	549.3 pg/μliter	Good retention time match
123478 HexaDioxin	429.0 pg/μliter	Good retention time match
1234678 HeptaFuran	681.7 pg/μliter	Good retention time match
1234678 HeptaDioxin	1133.3 pg/μliter	Good retention time match
OctaFuran/Dioxin	2200 pg/μliter	Octa Furan & dioxin not resolved

Appendix

On the following pages are detailed data logged results together with detected amounts and timestamps. These pages are contained in a separate Excel Spreadsheet file and are listed for those interested in details of measurements and calibration standards.