DEVELOPMENT AND IMPLEMENTATION OF A FAST ANALYSIS FOR THE DETERMINATION OF PCDD/F TO DELIVER RESULTS IN 48 HOURS – PART II – PROCEDURE AND QUALITY ASSURANCE/ QUALITY CONTROL

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Introduction

The Dow Chemical Company conducted an investigation of the floodplain along the first 6.5 river miles of the Tittabawassee River, in Midland, Michigan as required by Dow's Midland, Michigan site's Hazardous Waste License. The sampling was conducted by Ann Arbor Technical Services (ATS) and was based on ATS' GeoMorph® site characterization process. It was anticipated to analyze more than 3500 samples in less than 6 months. In order to carry out this investigation, data about PCDD/F as the primary constituents of concern needed to be available in a time frame which is significantly shorter than the typical 2 -3 weeks turn-around-time. To meet the above needs, a PCDD/F analysis method was developed that was optimized to analyze for only a selected number of 2378-substituted PCDD/F, with a quantification level below the Michigan Department of Environmental Quality 90 ppt direct contact cleanup criteria. By determining a selected number of 2378-substituted PCDD/F, an estimated TEQ value could be determined (E-TEQ) which was based upon the 2005 data [1,2]. For a five month period that involved about 3700 samples, this optimization led to a method that consistently delivered results within 48 hours at 30% the cost of the traditional dioxin analysis.

Materials and Methods

Extraction

The samples were prepared by weighing approximately 30g of homogenized soil into a 30mm x 100mm glass microfibre thimble. To the soil, 10 µL of ^{13}C-labeled standard solution was added that contained between 1000 ng/mL to 2000 ng/mL of each 2378-congeners. The thimble was placed into a Soxhlet/Dean Stark (SDS) extractor filled with benzene. The samples were extracted for a total of 16-24 hours. After the extraction period, the samples were concentrated in the round bottom flask until the level of benzene was at or below 40 mL. The extract was then transferred into a 40mL vial and the extract volume was adjusted to 40 mL with benzene. A 20 mL aliquot was removed from this total extract for sample clean-up and analysis. The remaining crude extract was retained for future analysis if necessary.

Extract Cleanup

The above benzene extract was processed through a dual column system to remove interferences. The column system was comprised of an acid silica column that drained into a carbon column. The acid silica column contained, from top to bottom, 0.2 g of dried silica, 0.5 g of acid silica (44% concentrated sulfuric acid by weight), and 0.5 g of dried silica. The carbon column contained 0.5 g of 18% w/w mixture of Carbopak B/Celite 545.

Prior to the sample addition, both columns were pre-eluted by adding 5 mL of benzene with the carbon column receiving an additional 5 mL wash with hexane/methylene chloride (50/50). After pre-elution, half of the sample extract (20 mL) was applied to the acid silica column. When the sample extract passed through the acid silica column, 5 mL of hexane was added to the column to serve as a rinse. After the hexane rinse was complete, the acid column was discarded. Next, the carbon column was inverted and washed with 10 mL of hexane/methylene chloride (50/50). To elute the PCDDs/PCDFs, 10 mL of toluene was added to the carbon column and then collected in a culture tube. The toluene extract was blown to dryness under a stream of nitrogen on a Turbo-

Vap®. The dried extract was transferred, using hexane, to a 0.3mL conical vial. The hexane extract was blown to dryness and 20 µL of injection standard (50 ng/mL ^{13}C-1278-TCDF in nonane) was added to the vial.

HRGC/LRMS Analysis
The selected PCDD/F congeners, which were 2378-TCDD, 2378-TCDF, 12378-PeCDF, 23478-PeCDF, and 1234(6)78-HxCDF, and their stable isotopes were identified and quantified by 6890 gas chromatograph coupled with a 5973N mass selective detector (GC/MSD by Agilent Technologies Palo Alta, CA, USA). The instrument was equipped with an electron ionization (EI) ion source operating in the positive ionization mode. Typical ionization conditions were: electron energy of 70 eV, ion source temperature of 250°C and quadrupole temperature of 150°C. The mass spectrometer data were obtained by quadrupole analyzer operating in the selected ion monitoring (SIM) mode at essentially unit mass resolution. The ions were acquired using a 50 milliseconds dwell time for TCDD/TCDF and 100 millisecond dwell time for all other analytes.

For GC analysis, a DB-5MS (J&W Scientific, Folsom, CA) fused-silica capillary column of 30 m x 0.25 mm i.d. x 0.25 µm film thickness with a 10m guard column was used. The oven temperature was programmed from 100°C 1 min hold, to 240°C at 40°C/min, to 295°C at 5°C/min, to 325°C at 30°C/min and held for 6.5 min at 325°C. The inlet was operated at pulsed splitless injection mode at 32 psi pulsed pressure over 1 min. After the pulse, the pressure was 20 psi for 13 minutes, to 32 psi at 12 psi/min, and held at 32 psi for 8 min. The injection port and transfer line were operated at 250°C and at 280°C, respectively.

Results and Discussion

In most dioxin analyses, there are four basic steps: extraction, extract cleanup, instrumental analysis, and data reduction/calculation. To expedite and simplify the dioxin analysis process, each step was examined and potentially altered. To demonstrate that these changes did not adversely affect the analysis, a series of quality control measures were instituted. The quality control measures involved method blanks, on-going precision and recovery (OPR) samples, calibration curve verification standards, detection level standards, and method duplicates.

Method blanks (reagent sand spiked with isotopic standards and processed as a normal sample) were run with each batch of samples. For the fast analysis, many of the suggested cleaning steps in the EPA methods 8280, 8290, and 1613b were removed to save time, such as pre-extraction of glassware.[3,4,5] These changes, as seen in Table I, did not adversely affect the sample data.

Table I: E-TEQ Values in ppt of the Fast Analysis Method Blanks

	ETEQ (ND=0)*	ETEQ (ND=0.5 LoQ)**	ETEQ (ND=LoQ)***
Average	0.84	1.34	1.83
Median	0.67	1.07	1.48
Std Dev	0.91	0.83	1.28
Minimum	0.00	0.34	0.39
Maximum	5.07	5.07	6.46

* non detect given a value of zero
** non detect given a value of half the value of the limit of quantitation
*** non detect given a value of limit of quantitation

The ability to accept lower than usual ^{13}C-standard recovery levels had to be allowed in order to make significant changes to the cleanup procedure by defining column elution parameters that emphasized collection of a relatively narrow analyte elution window to remove the greatest amount of interfering compounds. The allowable ^{13}C-standard recovery levels for all analytes were lowered to between 5-10%. To demonstrate that lowering the recovery limits would have no effect on the native calculations, an on-going precision and recovery

sample, just as described in 1613b, was analyzed with each batch of samples. Tables II and III display a summary of the results from OPR samples run with each batch of samples during the 5 month study.

Table II: OPR recovery results

	2378-TCDD % recovery	2378-TCDF % recovery	12378-PeCDF % recovery	23478-PeCDF % recovery	1234(6)78-HxCDF % recovery
Average	100	102	103	102	102
% RSD	6	6	5	5	5
Minimum	87	88	89	89	89
Maximum	116	119	120	118	119

Table III: OPR ^{13}C-standard recovery results

	^{13}C-2378-TCDD % recovery	^{13}C-2378-TCDF % recovery	^{13}C-12378-PeCDF % recovery	^{13}C-23478-PeCDF % recovery	^{13}C-1234(6)78-HxCDF % recovery
Average	46	27	46	43	39
% RSD	30	28	27	26	33
Minimum	18	12	22	20	10
Maximum	74	43	73	67	69

The data from these OPR samples clearly demonstrate the ability of the ^{13}C-standard to correct for native analyte loss throughout the analysis process. For example, the minimum recovery values reported in Table III would have been below the acceptable level as defined in the EPA methods 8280, 8290, and 1613b. However, at no time was the OPR value greater than +/-20% of the true value.

For EPA method 8280, the low resolution mass spectrometer PCDD/F method, the quantification level per analyte ranges from 1-5 ppb. Unfortunately, this is much higher than the 50 ppt TEQ quantification level needed for this study. To demonstrate the fast analysis method was capable of lower detection levels than EPA method 8280, a method detection level (MDL) study was performed. This study demonstrated that the detection level, on a concentration basis, for each analyte was 10 ppt or less. However there are two major problems with a MDL study for this method. First, the ability of the ^{13}C-isotopic standards to provide accurate and precise results close to the noise level leads to, that the MDL methodology determines artificially low detection levels. This is due to the MDL-methodology using statistical variation to determine the Limit of Detection (LoD) whereas the LoD when using ^{13}C-standards is based on the signal to noise ratio. Secondly, the MDL is only a “snapshot” in time and is not representative of an instrument’s performance throughout a study. For these reasons, a detection level standard was run every day to verify the instrument’s performance. This standard had to have a height greater than 10 times signal to noise and was used to mark concentrations below the quantification level.

To test the calibration curve used in every analysis, a calibration verification standard was analyzed. This step is very typical in many EPA methods. The test involves injecting a standard at the middle point of the calibration curve and determining the standard’s concentration from the calibration curve. If the concentration varied by less than 20 percent when compared to the true value for all analytes, the curve was used. If it varied by more than 20 percent, a new curve was built.

A duplicate sample was run with each batch of samples to obtain an understanding of the performance of the homogenization procedure and the samples consistency. The duplicate sample’s purpose is different than the OPR sample, which is a better method to test the variation of the analytical method excluding the

homogenization process. The table below details the results from the duplicate sample analyzed with each batch of samples.

Table IV: Duplicate Analyses

Concentration	Average % Difference	% Difference Std Dev	# of Samples
>50 ppt ETEQ	27	39	36
>100 ppt ETEQ	29	43	29
>250 ppt ETEQ	22	19	24
>1000 ppt ETEQ	21	17	13
>5000 ppt ETEQ	15	10	5

The duplicate samples show that as you increase the concentration the better the precision is between the samples. The reason for this phenomenon is suspected to be due to sample inhomogeneities which we observe quite frequently in soil and sediment samples from the floodplains.

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References

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