QUALITY ASSURANCE PROJECT PLAN

for the

DIOXIN EXPOSURE INITIATIVE:
NATIONAL DIOXIN AIR MONITORING NETWORK

ANALYTICAL METHODs for the DETERMINATION of TOTAL & INDIVIDUAL PCDDs/PCDFs and INDIVIDUAL CO-PLANAR PCBs COMPOUNDS in AIR

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07/20/01

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ANALYTICAL METHOD for the DETERMINATION of TOTAL & INDIVIDUAL PCDDs/PCDFs and INDIVIDUAL CO-PLANAR PCBs CONGENERS in AIR AND DEPOSITION SAMPLES

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C **METHOD 1613**
Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS
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USEPA/Office of Water Regulations & Standards
Industrial Technology Division
Office of Water/ April, 1990

D **METHOD TO-9A**
Sampling and Analysis Method for the Determination of Polychlorinated, Polybrominated, and Brominated/Chlorinated Dibenzo-p-Dioxins and Dibenzofurans in Ambient Air
USEPA 600/4-89-018
Compendium of Methods for Organic Air Pollutants,
Atmospheric Exposures Assessment Research Laboratory,
Research Triangle Park, N.C.
September, 1995

E References - Ferrario, J.B., Byrne, C., McDaniel, D., Dupuy,A.
Determination of 2,3,7,8-Chlorine-substituted Dibenzo-p-dioxins and -furans at the Part-per-Trillion Level in United States Beef Fat Using High Resolution Gas Chromatography High Resolution Mass Spectroscopy. Analytical Chemistry, Vol68, #4, pp.647-652, 1996.

Ferrario, J.B., Byrne,.C., Dupuy,A. Background Contamination by Coplanar PCBs in Trace Level High Resolution GC/MS Analytical Procedures.Chemosphere, Vol. 34, #11, pp. 2451-2465.1997

FIGURES

3.0 PROJECT DESCRIPTION

The United States Environmental Protection Agency (EPA) is conducting a reassessment of the health and environmental effects of dioxins and dioxin-like compounds. This reassessment began in 1991 and is being coordinated by EPA's Office of Research and Development. First drafts of the health and exposure documents were released in August of 1992. The second drafts of these documents were released in September of 1994. In September of 1994, the EPA announced a program known as the Dioxin Exposure Initiative (DEI). It was created with the intended purpose of providing source, exposure, and environmental trend information to address the critical data needs identified during the reassessment program as well as providing information to the Agency in its emerging dioxin strategy.

A key result of the exposure portion was that 90% of the human exposure to dioxins occurs via food ingestion, primarily through animal food products of high fat content including meats, dairy products, and fish. The exposure portion also concluded that there is a need for further data on quantifiable levels of specific dioxin congeners in the general food supply.

This project, National Dioxin Air Monitoring Network (NDAMN) Project is intended to concurrently serve four purposes: 1) provide data useful for calibrating long -range transport models used to estimate air concentrations of these compounds; 2) provide air monitoring capability for the occurrences and levels of dioxin-like compounds in primary areas where animal feeds used to feed livestock are grown; 3) provide for the air monitoring of dioxin-like compounds in different regions of the United States; and 4) provide results that can be used for the calculation of depositional flux.

This project will involve the sampling and analysis of ambient air and atmospheric deposition samples and will be performed by the United States Environmental Protection Agency (USEPA). Battelle, a private contractor, will sample selected sites during designed periods and ship the samples to the designated EPA laboratory for analysis.

As part of the dioxin reassessment, a Memorandum of Understanding (MOU) had been established between EPA's Office of Research and Development (ORD) and EPA's Office of Prevention, Pesticides, and Toxic Substances (OPPTS). Under this MOU, the Environmental Chemistry Laboratory (ECL) of the Office of Pesticide Programs (OPP) would prepare and analyze these environmental samples for the presence of specific 2,3,7,8-substituted

polychlorinated dibenzodioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and selected co-planar polychlorinated biphenyls (PCBs). The NDAMN involves the analyses of air and deposition samples for several years for the presence of these compounds. Appropriate quantities of each sample will be shipped for analysis.

The analytes to be determined are:

PCDDs
2,3,7,8-TCDD
Total TCDD
1,2,3,7,8-PeCDD

Total PeCDD
1,2,3,4,7,8-HxCDD
1,2,3,6,7,8-HxCDD
1,2,3,7,8,9-HxCDD
Total HxCDD
1,2,3,4,6,7,8-HpCDD
Total HpCDD
OCDD

PCDFs
2,3,7,8-TCDF
Total TCDF
1,2,3,7,8-PeCDF
2,3,4,7,8-PeCDF
Total PeCDF
1,2,3,4,7,8-HxCDF
1,2,3,6,7,8-HxCDF
1,2,3,7,8,9-HxCDF
2,3,4,6,7,8-HxCDF
Total HxCDF
1,2,3,4,6,7,8-HpCDF
1,2,3,4,7,8,9-HpCDF
Total HpCDF
OCDF

Co-Planar PCBs
PCB-77
PCB-105
PCB-118
PCB-126
PCB-156
PCB-157
PCB-169

Analytical responsibilities for this study were delegated to the EPA OPP/Environmental Chemistry Laboratory (ECL), John C. Stennis Space Center, Mississippi.

The OPP ECL will perform all sample preparations and, will perform high resolution gas chromatographic/high resolution mass spectrometric (HRGC/HRMS) analysis for PCDDs, PCDFs, and co-planar PCBs in samples from this study. Sample analysis are anticipated to begin in the summer of 1998 and it is anticipated that the analysis of the samples for the targeted dioxins, furans, and PCBs will extend for several years.

4.0 PROJECT ORGANIZATION AND RESPONSIBILITIES

The Survey of Dioxin-Like Compounds in Air and Deposition Project is a joint project among the USEPA ORD and OPPTS. The project co-manager for the study is David Cleverly of the USEPA Office of Research and Development and his telephone number is
(202)564-3238.

Figure 4-1 displays the overall organization structure of the USEPA/USDA Survey of Dioxin-Like Compounds in Air and Deposition Project.

Principal laboratory responsibilities for the Survey of Dioxin-Like Compounds in Air and Deposition (NDAMN) Project will be carried out by OPP/Environmental Chemistry Section (ECL), which is managed by Dr. Aubry Dupuy Jr., Section Chief. Mr. Joseph Ferrario, chemist at ECL, will serve as Project Leader and will be responsible for the day-to-day management of NDAMN analytical activities. He will also provide high resolution gas chromatographic/high resolution mass spectrometric (HRGC/HRMS) analysis together with data compilation and reporting. Dr. Christian Byrne will provide QA oversight.

The Sample Custodian for ECL and the NDAMN is Mr. Stanley Mecomber. Mr. Stanley Mecomber, and Mr. Ray Shaw, will handle sample preparation, extraction, and isolation. Ms. Elizabeth Flynt will assist in the computer software interfacing.

Upon the completion of the analyses of the air/deposition samples, the data will be reviewed by the NDAMN/QAO and the results reported to the USEPA/ORD .Problems that arise during the course of the project will be discussed with Mr. Cleverly. Periodic telephone conference calls will be held among OPPTS and ORD personnel to discuss the progress of the project.

The EPA telephone number for the Project Leader for NDAMN is: Mr. Joseph Ferrario, (601) 688-3171.

Figure 4-2 presents the organizational sub-structure of the project as it relates to the responsibilities of ECL.

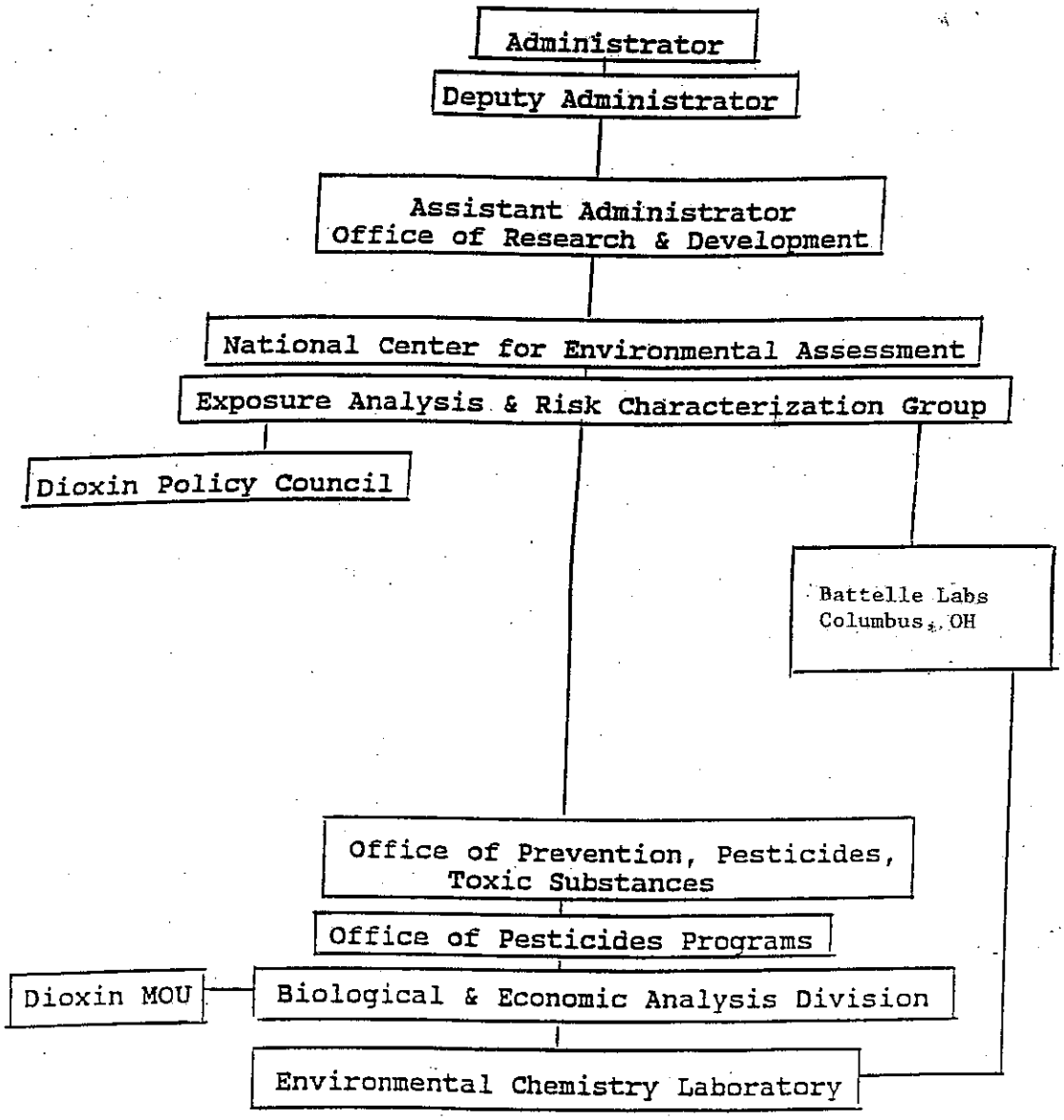


Figure 4-1: Overall Organizational Structure of the NDAMN - USEPA/ORD/Battelle/OPPTS/ECL

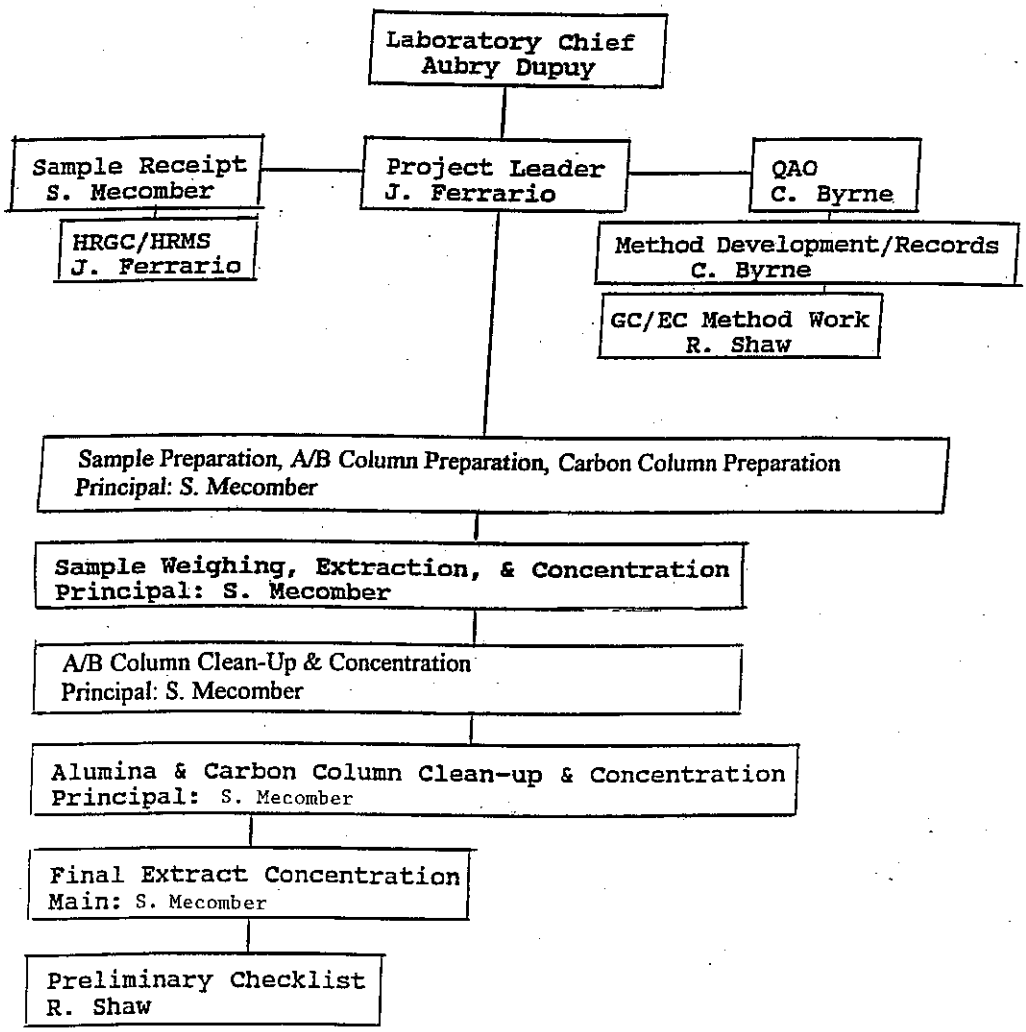


Figure 4-2: Organization Sub-Structure of NDAMN/ECL.

5.0 QA OBJECTIVES FOR MEASUREMENT DATA

5.1 Descriptions of the Native Analytes, (^{13}C) Labeled Recovery Surrogates, and the Internal Standards

1. The "native" analytes:

Dibenzofurans	Dibenzodioxins	Co-Planar PCBs
2,3,7,8- TCDF	2,3,7,8- TCDD	PCB-77
1,2,3,7,8-PeCDF	1,2,3,7,8-PeCDD	PCB-105
2,3,4,7,8-PeCDF	1,2,3,4,7,8-HxCDD	PCB-118
1,2,3,4,7,8-HxCDF	1,2,3,6,7,8-HxCDD	PCB-126
1,2,3,6,7,8-HxCDF	1,2,3,7,8,9-HxCDD	PCB-156
1,2,3,7,8,9-HxCDF	1,2,3,4,6,7,8-HpCDD	PCB-157
2,3,4,6,7,8-HxCDF	OCDD	PCB-169
1,2,3,4,6,7,8-HpCDF		
1,2,3,4,7,8,9-HpCDF		
OCDF		

2. The (^{13}C) labeled recovery surrogates:

Dibenzofurans	Dibenzodioxins	Co-Planar PCBs
2,3,7,8- TCDF	2,3,7,8- TCDD	PCB-77
1,2,3,7,8-PeCDF	1,2,3,7,8-PeCDD	PCB-105
2,3,4,7,8-PeCDF	1,2,3,4,7,8-HxCDD	PCB-118
1,2,3,4,7,8-HxCDF	1,2,3,6,7,8-HxCDD	PCB-126
1,2,3,6,7,8-HxCDF	1,2,3,7,8,9-HxCDD	PCB-156
1,2,3,7,8,9-HxCDF	1,2,3,4,6,7,8-HpCDD	PCB-169
2,3,4,6,7,8-HxCDF	OCDD	
1,2,3,4,6,7,8-HpCDF		
1,2,3,4,7,8,9-HpCDF		

3. The internal standards are the ^{13}C labeled 1,2,3,4-TCDD, 1,2,3,7,8,9-HxCDD, PCB-111, and PCB-128.

5.2 Initial Determination of Capabilities

1. Replicates of the air/deposition matrices will be spiked at approximately the lowest expected method quantitation limits for the various groups of dioxins, furans, and PCBs to ensure that this concentration can be reliably detected and quantitated. A demonstration of capability will performed at no greater than 3-5 times the Limit of Quantitation (LOQ) to establish precision and accuracy thresholds for the laboratory control sample (LCS).

2. From an examination of the resulting data, the mean recoveries, standard deviations, and %RSDs will be calculated. The accuracy and precision of the resulting recoveries must agree within +/-25% of the expected concentrations for 94% of the native analytes (with the exception of OCDF). From these data, the target limits of detection and quantitation will be established.

5.3 Laboratory QC Requirement for Primary Analyses

1. A laboratory control sample (LCS), containing all of the native and labeled PCDDs, PCDFs, and PCBs will be analyzed with each set of samples. The native spike concentrations used for the demonstration of capability and the continuing LSC will be at no greater than 3-5 times the LOQ.

2. The continuing calibration standard, analyzed at the beginning of each work day, must be compared to the existing calibration curve and the observed concentration must agree within +/- 25% of the expected concentration for 94% of the analytes.

3. The recoveries of the ^{13}C labeled surrogates of the PCDDs, PCDFs, and PCBs of all standards, laboratory control spiked samples, and field samples must fall between 25-150%.

4. A set of samples is defined as all samples, blanks, spiked samples, etc., on which similar analytical operations are performed at the same time and during a single analytical run.

5. The measurement system is to be evaluated whenever any analyte is observed in the System Blank or Matrix Blank, at a concentration greater than or equal to the lowest calibration standard or greater than amounts known to be present in the unspiked matrix. The significance of any background concentrations of the analytes in the System Blanks and Matrix Blanks will be assessed on a sample set basis.

6. System Blanks and Matrix Blanks are to be analyzed with each set of samples. The Matrix Blanks will consist of precleaned PUF and QFFs.

7. The criteria for monitoring instrument control standards will be utilized as stated in the method (see Section 9).

8. The requirements for monitoring calibration responses will be followed as written in the method (see Section 9).

9. Samples failing the QC criteria and not receiving an exception variance from the Project Leader will be reanalyzed.

10. Any deviation from the analytical procedures or QC requirements, must be approved by the Project Leader and documented in writing.

5.3 Sample Management.

1. Samples must arrive at the laboratory with refrigerant remaining in the shipping container. If the sample container arrives without sufficient refrigeration, the Sample Custodian should contact the Project Leader. One of them will notify the contractor responsible for sample collection.

6.0 SAMPLING PROCEDURES

Battelle Inc. has responsibility for the collection and shipment of samples from the designated sites to ECL. The samples are to be shipped in pre-cleaned and tested glass containers or wrapped in pre-cleaned aluminum foil. The samples, once taken, will be refrigerated or frozen dependent on matrix and shipped as such to ECL. ECL will record the condition of the sample upon receipt, assign an internal laboratory number, and properly store the samples until analysis. The ECL sample custodian will consult with Tony Wisbeth or Patty Hallowicky (Field Program Coordinators) for problem resolution, including needs for resampling, if specimens are lost in transit, arrive thawed or spoiled or in damaged containers, or were not analyzed for any other reason. he samples will be shipped directly to Mr. Stanley Mecomber, the NDAMN Sample Custodian at ECL.

7.0 SAMPLE CUSTODY

7.1 Sample Requirements Following Receipt at Laboratory

Tracking of all samples arriving at the laboratory will begin upon the receipt of any sample and will continue through each phase of the analysis. Copies of all Forms and Logbooks can be found in Appendix A.

o Upon receipt of the samples, each is identified according to its Battelle Sample Number and the matrix type, logged in, and stored at either 4°C or -70°C. This information is documented on the "NDAMN LOGGING FORM", (Appendix A).

o The Project Leader will compile "sets" of samples comprised of samples with appropriate controls as covered in Section 9 of the QAPP. At this time the samples, which had previously been designated by their "Battelle Sample Number", will be reassigned an ECL sample number. The new number will contain five (5) letters followed by four (4) numerals. The five letters will be NDAMN (National Dioxin Air Monitoring Network) Project, which identifies the project. The first three (3) numerals will identify the analysis set number and the second two (2) numerals will identify the specific sample of that set. For example, the first sample in the first set will be NDAMN###-##. The composition of each set is documented on a "NDAMN SET COMPOSITION/QA DATA FORM", (Appendix A).

o Transfer of samples into and out of storage will be documented on an INTERNAL CHAIN-OF-CUSTODY LOGBOOK (Appendix A). Only those samples in the "set" on which analytical work will be done will be removed. The extraction technician(s) will sign and date this logbook when removing and returning samples to storage.

o After removal from storage, samples are tracked through extraction and HRGC/HRMS analysis via a "NDAMN SET COMPOSITION/QA DATA FORM." The unused quantities of the samples will be returned to storage at 4°C or -70°C. Samples will be extracted within 24 hours after thawing.

o Following extraction, sample extracts are stored in a refrigerator at 4°C until analyses are completed (within 45 days). Following analysis, a 10 ul aliquot of the sample is transferred to a capillary transfer tube and sealed for storage at -

5°C. Upon completion of the entire project, the unused quantities of air and deposition samples will be disposed of upon notification by USEPA ORD.

7.2 Storage Conditions

Upon receipt at the laboratory, the samples will be stored under ultra-refrigeration at 4°C or -70°C and protected from light.

7.3 Holding Times

Frozen samples may be kept up to one year, **but extracts need to be analyzed within 45 days.**

7.4 Disposal

Upon completion of the project all unused portions of the samples will be disposed of. The sample extracts and the associated standards will be disposed of as hazardous waste by an EPA-approved hazardous waste disposal firm. The date of disposal of the extracts is listed on the SET COMPOSITION/QA DATA FORM.

7.5 Internal Practices Concerning Sample Storage

The temperature of coolers, refrigerators, and freezers where samples and/or extracts are stored are monitored each working day, and this activity and the temperature are recorded in a logbook maintained for this purpose.

The ECL Sample Custodian, Stanley Mecomber, or the Assistant Sample Custodian are responsible for monitoring these storage areas. ECL has an agreement with the facility contractor to provide weekly preventive maintenance and emergency repair service on the large systems where samples will be stored.

8.0 CALIBRATION PROCEDURES AND FREQUENCY

8.1 HRGC/HRMS System Performance

All analysis are performed on a KRATOS CONCEPT high resolution mass spectrometer (HRMS). The HRMS is operated in the electron impact ionization mode using the Selected Ion Monitoring (SIM) technique at a resolution of 10,000.

Separations are achieved using a Hewlett-Packard 5890 Series 2 gas chromatograph employing a 60 meter x 0.32 mm DB-5 MS capillary column. The gas chromatographic conditions employed will be optimized to completely separate the various 2,3,7,8-substituted dioxins, furans, and co-planar PCBs. These conditions are listed on the bottom right-hand corner of Figure 8-1. The MS conditions are described on the top left-hand corner of the same figure. The GCMS system is calibrated and the analyte concentrations determined using an isotope dilution technique.

The MS is tuned to a minimum resolution of 10,000 (10% valley) atm/z = 330.9792. The instrument is then mass calibrated and the results of the calibration hardcopied. This printout shows the intensity, the resolution, and the calibration error in parts-per-million for a range of the perfluorokerosene (PFK) ions that bracket the mass range of interest (Resolution/Mass Calibration MS, Figure 8-2). The error can not exceed 10% for any calibration peak and the average resolution must exceed 10,000.

The level of PFK metered into the ion source during the analysis is adjusted, so that the most intense selected lock-mass ion signal does not exceed 10% of full scale deflection. All mass spectrometer operational, acquisitional, and data processing parameters that are relevant to interpreting the data or assessing the system performance are listed on Figure 8-1.

If totals are to be done for the dioxins and furans, a gas chromatographic window defining mixture will be periodically analyzed to ensure that the chromatographic conditions employed are sufficient for the desired separations.

The standard operating procedures for the GC/MS are included in **Instruction and Operating Manual for KRATOS Concept Mach 3 Data System Users Guide,**
Issue 3: December 1990, Reference: 39-159 and **Concept**

H Series Mass Spectrometer Operating Instrument
Issue 4: January 1991, Reference 39-138.

8.2 Standard Solutions

The standards are purchased as solutions from Cambridge Isotope Laboratories with certification to their purity, concentration, and authenticity. All pertinent information involving standard preparation is entered into a "STANDARD SOLUTION LOGBOOK" (Appendix A). Dilutions of stock solutions are made using nonane and a mark placed on the vial at the level of the solution, so that solvent evaporation can be detected and corrected. The spiking solutions will always contain all of the 2,3,7,8 isomers and native PCBs as prepared from the solutions from Cambridge Isotope Laboratories. All standards will be stored out of the light in a freezer at -20°C until use.

8.3 Instrument Calibration

At least three-five calibration standards with native analyte concentrations bracketing the expected analyte concentrations will be analyzed prior to analyzing samples. The calibration standard solutions will also contain the labeled ^{13}C recovery standards and the two labeled ^{13}C internal standards at the appropriate concentrations. The four labeled ^{13}C internal standards (^{13}C-1,2,3,4,-TCDD, ^{13}C-1,2,3,7,8,9-HxCDD, ^{13}C-PCB-111 & ^{13}C-PCB-128) together with the ^{13}C labeled analytes and the native (unlabeled) analytes are included on the TARGET COMPOUND LIBRARY LIST (Appendix B). The labeled analytes are designed as standards, native analytes as analytes, and the internal standards as surrogates. In addition, for the dioxins/furans the quantities of the compounds of CAL STD #1 are listed on the TARGET COMPOUND LIBRARY LIST. The analyte quantities in the other calibration standards are multiples of CAL STD #1 as follows: factors 1x, 2.5x, 5x, 10x, & 50x. For the PCBs the quantities of the compounds of CAL STD #3 are listed on the TARGET COMPOUND LIBRARY LIST. The analyte quantities in the other calibration standards are multiples of CAL STD #3 as follows: factors 0.25x, 0.5x, 1x, 5x and 10x. These quantities will be adjusted based on the expected sample concentrations.

The analysis of these calibration solutions permit the relative response factors (RRFs) (unlabeled to labeled analytes) and the response factors (RFs) (labeled analytes to internal standards) to be determined as a function of the concentration using linear regression. The RRF is determined for each native analyte at each concentration using the isotope dilution technique. The RSD of the RRFs for each native analyte must be less than 25%. The RF will be determined using an internal standard method and will be calculated for each

labeled recovery standard in each of the calibration solutions. The RSD of the RF for each labeled standard must be less than 35%. The RSDs and other control
limits approximate those described in EPA Method 1613.

The calibration curves are considered to be linear under these conditions and the analytical system will be considered calibrated when these conditions have been satisfied. The average response factors will be used for subsequent quantitations. If these conditions are not satisfied for 94% of the analytes, the mass spectrometer will be re-tuned and/or new calibration standards prepared and re-analyzed.

On the days samples are to be analyzed, the linearity of the calibration curve will be verified by analyzing the calibration solution of intermediate concentration and determining the response factors. The percent difference between the new RRFs and the average determined during the initial calibration must be less than or equal to 25% for the native analytes and the percent difference for the new RFs for the labeled analytes must be less than or equal to 35%. If these conditions are not satisfied for 94% of the analytes by a second injection of the calibration solution, the mass spectrometer will be re-tuned and the initial calibration procedure repeated.

The selected ion current profiles for each of the specified ions [see TARGET COMPOUNDS LIBRARY LIST (Appendix B)] will be obtained and the ion abundance determined. The areas of the peaks representing both unlabeled and labeled analytes in the calibration standards must have a signal to noise ratio of, at least, 5, which is automatically calculated by the system software. The observed ion abundance ratios must be within +/- 15% of the theoretical ratio. (See attached TARGET COMPOUND LIBRARY LIST for theoretical values). If expected analyte concentrations require the MS to be calibrated at the 50 femtogram level, the control limits for the abundance ratios for this calibration standard will be expanded to +/- 25%. If 10% of the ion abundance ratios for any of the calibration standards exceed the limits, the MS will be adjusted and the standard reanalyzed until the ratios fall within the specified control limits.

The mass chromatograms from the continuing calibration check will also be examined to ensure that all the 2,3,7,8-substituted isomers are clearly separated and to verify the expected retention times for each labeled and native analyte. If the S/N ratios, ion abundance ratios, response factors, and isomer separations are within specified limits, then sample analysis can proceed. Corrective action will be initiated, if specified control limits are exceeded.

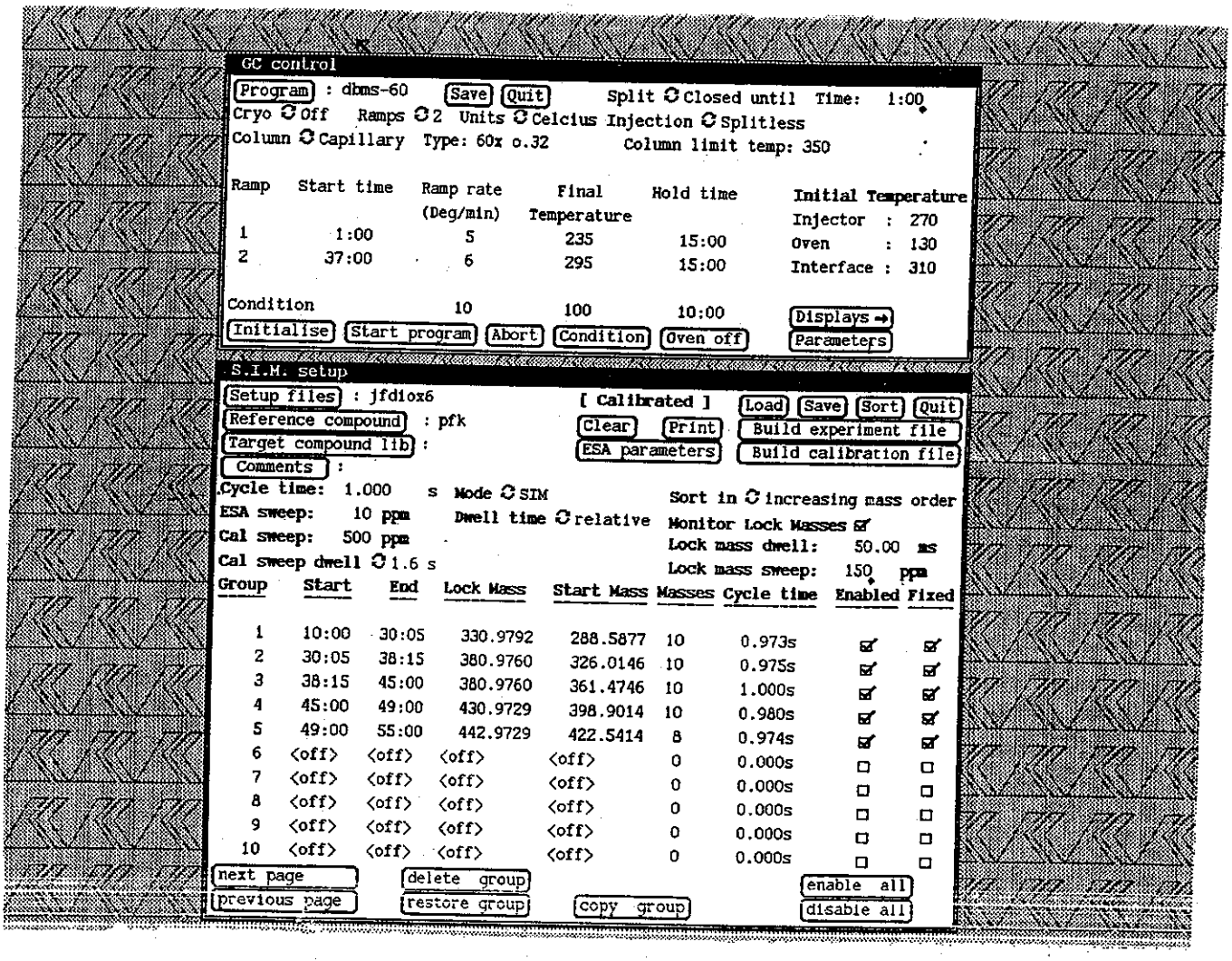


Figure 8-1: HRGC/HRMS conditions

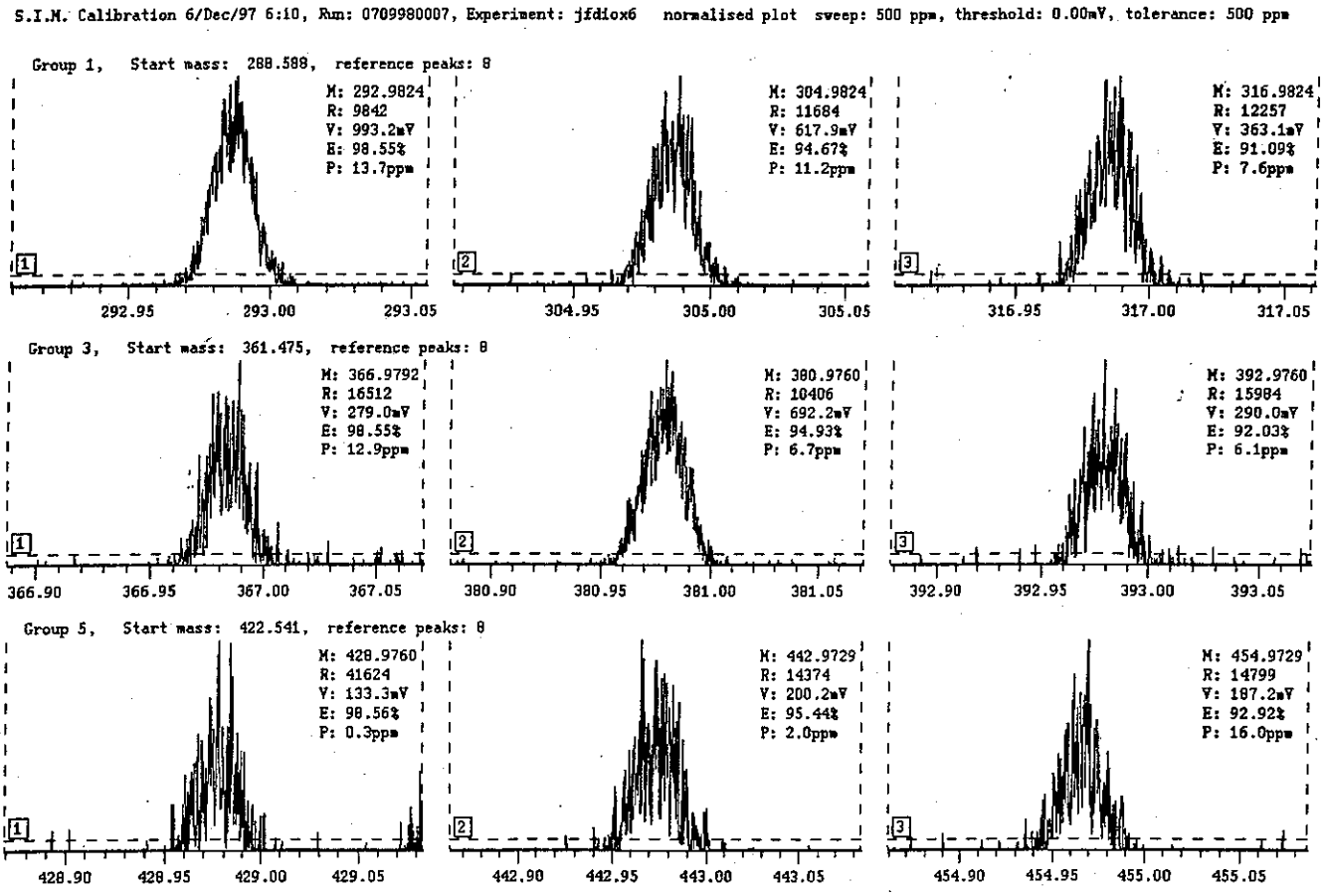


Figure 8-2 Resolution/Mass Calibration for MS

9.0 ANALYTICAL PROCEDURES

The analytical procedure to be used in this study follow the analytical procedures of the Dioxin Exposure Initiative - National Dioxin Air Monitoring Project. The procedure is listed below.

Procedures for the Extraction of Air and Deposition Samples

The night before they are to be processed, remove the individual samples from the refrigeration and transfer them to the refrigerator in the PCB control laboratory trailer. All of the sample extractions and clean-up will be performed in this trailer to limit sample exposure to ambient PCB, PCDD, and PCDF levels. Make certain that the number on the sample jar agrees with the number on the extraction sheet.

Extraction Procedure for Polyurethane Foam Plugs (PUFs) (Vapor phase)

Note : **Vapor and Particulate Phase**. In most cases the PUF and QFFs from a particular sample will be analyzed together. Accordingly, they are added to the same Soxhlet extractor and treated as described below.

Per **Section 12. METHOD TO-9A: Sampling and Analysis Method for the Determination of Polychlorinated, Polybrominated, and Brominated/Chlorinated Dibenzo-p-Dioxins and Dibenzofurans in Ambient Air (1995), USEPA 600/4-89-018**
Take the PUF out of the glass cartridge contained in the shipping container and place it in a 50 mm Soxhlet extractor (also add the QFFs if both phases are to be analyzed together). Add 20 µl of ^{13}C-labeled sample fortification solution. Assemble the Soxhlet extractor fitted with a 500 ml Erlenmeyer flask containing 275 ml of benzene.

Place a small funnel in the top of the Soxhlet extractor, making sure that the top of the funnel is inside the extractor. Rinse the inside of the corresponding glass cylinder into the extractor using approximately 25 ml of benzene. Place the extractor on a heating mantle. Adjust the heat until the benzene drips at approximately 2 drops per second and allow to flow for 16 hours. Allow the apparatus to cool.

Remove the extractor and place a 3-bulb Snyder column onto the flask containing the benzene extract. Place on a heating mantel and concentrate the

benzene to 25 ml (**DO NOT LET GO TO DRYNESS**). Add 100 ml of hexane and again concentrate to 25 ml. Add a second 100 ml portion of hexane and again concentrate to 25 ml.

Let cool and add 25 ml of hexane. The extract is ready to proceed to the acid/base silica gel cleanup.

Extraction Procedure for the Quartz Fiber Filters (Particulate Phase)

Per **Section 12. Sample Preparation of TO-9A (1995)**: Take the quartz fiber filters out of the glass cartridge contained in the shipping container and place it in a 43 x 150 mm pre-ashed glass fiber thimble. Add 20 µl of ^{13}C-labeled sample fortification solution. Assemble the 50 mm Soxhlet extractor fitted with a 500 ml Erlenmeyer flask containing 275 ml of benzene. Place the thimble into the Soxhlet extractor fitted with a 500 ml Erlenmeyer flask containing 275 ml of benzene. Place the extractor on a heating mantle. Adjust the heat until the benzene drips at approximately 2 drops per second and allow to flow for 16 hours. Allow the apparatus to cool.

Remove the extractor and place a 3-bulb Snyder column onto the flask containing the benzene extract. Place on a heating mantel and concentrate the benzene to 25 ml (**DO NOT LET GO TO DRYNESS**). Add 100 ml of hexane and again concentrate to 25 ml. Add a second 100 ml portion of hexane and again concentrate to 25 ml.

Let cool and add 25 ml of hexane. The extract is ready to proceed to the acid/base silica gel cleanup.

Preparation of Acid/Base Silica Gel Chromatography Column

Equipment (Glassware/Chemicals)

a) Chromatography column - column 11 mm i.d. x 300 mm length with a 250 ml reservoir, Teflon stopcock and glass tip.
b) Glass wool - Pyrex Fiberglass Sliver 8 µm
Prewash with acetone, hexane, air dry in trailer, and then heat @ 425°C for at least 8 hours in Building 1105. Remove while hot and take to trailer.
c) Sodium sulfate, anhydrous (ACS grade) -

Place 600-800 g in an oven @ 425°C for a minimum of eight hours. Remove hot (100°C) and cool in trailer. Store in an air-tight container until use.

d) Silica gel (Davisil) 35-60 mesh, Type 60 Å -
Heated @ 175°C at least 8 hours. Store in an air-tight container.

1) Acid Form Silica Gel - 35/60 mesh
Weigh out 28 g of pre-baked silica gel into a 250 ml Erlenmeyer flask and then add 12 ml of concentrated high-purity sulfuric acid (Ultrex Grade). Add acid slowly, drop-wise, mixing after each addition. The silica gel is then put on a vortex shaker at high speed and mixed for 10 minutes. The acidified silica gel is then stored in a desiccator. Make only enough for 1 sample set, discard any remaining silica.

2) Base Form Silica Gel - 100-200 mesh
Weight out 34 g of pre-baked silica gel into a 250 ml Erlenmeyer flask and then add 8 ml of 2N sodium hydroxide solution. Add base slowly, dropwise, mixing after each addition. The silica gel is then put on a vortex shaker at high speed for 10 minutes. The basic silica gel is then stored in a desiccator. Make only enough for 1 sample set, discarding any remaining silica.

Acid/Base Silica Gel Chromatography Preparation

A small plug of glass wool and a stopcock to control flow is place into the chromatographic column. **CAUTION**: Enough glass wool must be used to prevent silica gel from falling into the receiving tube. The following series of materials are added:
0.25 g of sodium sulfate, anhydrous
4 g of basic silica gel (100-200 mesh)
8.0 g acidic silica gel (35/60 mesh)
1.0 g of sodium sulfate, anhydrous.

The sodium sulfate, anhydrous, should be the final compound added to the column. The column should be gently tapped from bottom to top to settle the contents to reduce possible solvent channeling.

Procedure for Silica Gel Chromatography

Remove the sample extracts from the refrigerator before preparing the columns and allow them to come to room temperature. After columns are packed, pre-rinse columns with 50 ml of hexane, place carbon filter on the column and leave on at all times. Close the stopcocks while there is about a one inch head of

hexane. Place a 200 ml Turbovap II tube under each column and wrap a piece of baked aluminum foil around the top of each tube to minimize contamination from air and position glass tip against receiver wall. Pour the <100 ml of sample onto the top of the column. Rinse the flask with 2-5 ml of hexane and add to the column. Repeat this step a second time and replace carbon filter.

Open the stopcock. After the sample and final rinses have reached the top of the sodium sulfate, remove the carbon filter, add 100 ml of hexane to the top of the column, replace the carbon filter, and allow the entire volume to elute from the column into the 200 ml Turbovap II tube. Proceed to carbon column clean up. If time does not permit, cap Teflon seal and refrigerate the sample extract.

Add 5 µl of tetradecane. Concentrate the extract to 0.5 ml using TurboVap II. The water temperature is set at 45°C and the nitrogen is opened to produce a gentle vortex. The tubes should be washed several times with small aliquots of hexane to insure that the residues are concentrated into the final volume of extract. It takes approximately one hour to concentrate six samples.

NOTE. Samples that are suspected of being particularly "dirty"or that are not suitably clean after the acid/base column may be subjected to additional clean-up procedures involving an "acid stir" step as described in Method 1613. Samples undergoing additional procedures will be identified on the sample set sheet.

DO NOT ALLOW THE EXTRACTS TO GO TO DRYNESS!

Transfer the 0.5 ml of hexane from the Turbovap II tube to a 15 ml centrifuge tube with two 2 ml rinses of hexane. Concentrate to ½ ml. Cap and refrigerate. Proceed with carbon column chromatography the next day.

Procedure for the Preparation of Carbon Column Chromatography

Equipment (Glassware/Chemicals)

a) 2.0 ml Disposable Pipette
b) Glass wool - Pyrex Fiberglass Sliver 8 µm
Prewash with acetone, hexane, air dry in trailer, and
then heat @ 425°C for at least 8 hours in Building 1105. Remove while hot and take to trailer.
c) Amoco PX-21 Carbon

1) Isolation Mixture -
Weigh out 9.5 g of the BioSilA (100-200 mesh) silica gel into a 50 ml screw cap container. Weigh 0.50 g of the Amoco PX-21 carbon onto the silica gel, cap, and shake the container vigorously for two hour. Prior to immediate use, rotate the container by hand for at least one minute.

Disposable Pipette Preparation

Etch @ 0.2, 0.6, 0.7 ml marks. Break a glass graduated 2.0 ml disposable pipette at the 1.9 ml mark and fire polish the end. Bake the pipettes @ 425°C to remove all ink markings before preparing the column.

Carbon Chromatography Preparation

Place a small plug of glass wool in the pipette and pack it at the 0.7 ml mark using two small solid glass rods. Add 0.1 ml of Bio-Sil A 100-200 mesh silica gel. If more than one column is to be made at one time, it is best to add the silica gel to all the columns and then add the carbon-silica gel mixture to all columns. Add 0.40 ml of the carbon-silica gel mixture to the column; the top of the mixture will be at the 0.2 ml mark on the pipette. Top the column with a small plug of glass wool, clean the glass column with a cotton swab to remove any carbon and add an additional plug of glass wool.

Procedure for Carbon Column Chromatography

If refrigerated, remove the sample extracts from the refrigerator.

Carbon Column Procedure

Before starting the procedure, clean column ends to remove any loose carbon particles. **Examine the carbon columns for channels and tighten the packing if necessary. Replace with new columns if cracking cannot be eliminated or if flow is irregular. Place the columns in a suitable clamp with the silica gel up.** Fit a 10 ml disposable pipette on top of the carbon column with a short piece of extruded Teflon® tubing. Add 10 ml of 50% benzene-methylene chloride (v/v) to the reservoir and tap gently to make a one inch head on the column. When all of this solution has gone through the carbon column, add 10 ml toluene to reservoir and tap gently to make a solvent head. After all the toluene has gone through the carbon column, add 5 ml of hexane to the reservoir and tap to make

a head.

NOTE: During the rinse, again check for channeling and correct any problems or replace with new column if flow is not consistent.

When all of the hexane has gone into the silica , remove the reservoir and transfer
the extract in the 15 ml centrifuge tube (approximately 0.5 ml) onto the column with a Pasteur pipette. Rinse the centrifuge tube with two separate 0.5 ml portion of hexane and transfer them to the column. Allow the top of the sample and each of the rinse solvents to enter the top of the silica before adding the next. When the last rinse has entered the top of the silica , replace the reservoir and add 5.0 ml of 25%/75% methylene chloride-hexane (v/v) solution and top to make a head. **This fraction is saved until the next collected PCB fractions have been analyzed and the recoveries of C13- 118 and C13-105 have been verified to be within control limits.** If recoveries are below control limits , this fraction is re-fractioned on another carbon col.

NOTE: Do not use any mixed solvents from the squirt bottles unless they have just been transferred from an air-tight container.

When all of the 25%/75% solution has eluted, ensure that all eluent has been removed from the tip of the column. Carefully rinse the tip of the column with hexane (inside and out) and then place a 50 ml catch tube under the carbon column and check to ensure that the tip of the column is touching the side of the catch tube.

Seal the tube to the column with a piece of aluminum foil. Add 5.0 ml of methylene chloride to the reservoir and tap to form a head. When all of the solvent has gone into the carbon column, add 13.0 ml of 75%/25% benzene-methylene chloride (v/v) solution to the reservoir and tap to make a head. Catch the methylene chloride and the 75%/25% benzene-methylene chloride solution in the same tube. Ensure that all eluent is removed from the column(gently tap the column and let remaining eluent flow into the catch tube),and rinse the tip with a touch of solvent(into the catch tube).If this fraction is not to be concentrated directly, cap, Teflon seal and store in the refrigerator.
When all of the above solvents have eluted, remove the reservoirs, take the column out of the holders, and rinse each end with toluene, turn the columns over, and put them back into the holders. Place a 15 ml receiving catch tube under the column, replace the reservoir, and add 13.0 ml of toluene and tap to

make a head.

When all of the toluene has been eluted,(ensure that all eluent has been removed from column) rinse the tip of column with a touch of solvent and transfer the toluene fraction to a 50 ml TurboVap II® tube with two 5 ml rinses of hexane and add 5 µl of tetradecane.(add 5 ml of hexane to the carbon column as a rinse, elute and store the column in the designated container.) Concentrate the toluene to approximately 50 µl using the TurboVap II® Concentrator equipped with a pre-purified nitrogen vortex stream. Rinse the TurboVap tube walls with hexane while concentration proceeds. Add 0.5 ml of hexane and concentrate to approximately 25 µl. Add 0.5 ml of hexane and proceed with the Alumina Column Cleanup.

Concentrating PCB Fraction

Add 2 µl of tetradecane to the combined methylene chloride and the 75%/25 benzene-methylene chloride fraction and concentrate to 0.5 ml using a water bath at 45°C and a stream of pre-purified nitrogen. Transfer the extract to a Chromoflex® tube with two 0.5 ml rinses of hexane and concentrate to a little less than 10 µl, cap and Teflon seal. This fraction will contain all of the dioxin-like PCBs. This procedure takes approximately three hours. Store the extract in a freezer until ready for analysis.

NOTE:
• Rinse the sides of the catch tube and the sides of the Chromoflex tube each at least twice while concentration proceeds.
• Position aluminum foil in front of the concentration to block air flow. CAUTION: Do not allow foil to extend over tubes as water vapor may condense on foil and enter sample.

Procedure for the Preparation of Alumina Column Chromatography

Equipment (Glassware/Chemicals)

a) 2.0 ml Disposable Pasteur Pipette
b) Glass wool - Pyrex Fiberglass Sliver 8 µm
   Bake @ 425°C for at least 8 hours.
c) Sodium sulfate, anhydrous (ACS grade) -
   Use as is.
d) Neutral Alumina - Activity Grade 1

Alumina Column Chromatography Preparation

A small plug of glass wool is gently tampered into the bottom of a 5¾ inch disposable Pasteur Pipette. Pour the neutral alumina into the pipette while tapping the column with a pencil until a height of approximately 4.5 cm of alumina is packed into the column. Top the alumina with 0.5 cm of anhydrous granular sodium sulfate. Prewash the column with 3 ml dichloromethane. Allow the solvent to drain and then force the remaining solvent from the column with a gentle stream of nitrogen. Place the columns in the oven @ 225°C ± 4°C until ready for use, at least overnight. Remove the columns needed and place them in a desiccator over Drierite® until they have equilibrated to room temperature. Use immediately.

Procedure for Alumina Column Chromatography

Pre-wet the alumina column with 1 ml of hexane. Transfer the 0.5 ml of the hexane eluant from the carbon cleanup chromatography onto the column. Rinse the sample tube that contains the eluant with two separate 0.5 ml portions of hexane and transfer each rinse onto the column. Wash the column with 6 ml of carbon tetrachloride and discard. Add 4 ml of dichloromethane and collect in a 12 ml concentration tube.

Add 2 µl of tetradecane and concentrate the methylene chloride to 0.5 ml using a combination of pre-purified nitrogen and a water bath @ 50°C. Reduce twice more with 2 1 ml portions of hexane. Transfer the concentrated extract to Chromoflex® tube with two 0.5 ml rinses of hexane. Concentrate the extract to a little less than 10 µl with nitrogen on a water bath at 60°C. Rinse down the sides of the Chromoflex tube while the concentration procedure proceeds.

DO NOT ALLOW THE EXTRACTS TO GO TO DRYNESS!

The extract is then transferred to the HRGC/HRMS operator for storage in the freezer in the HRGC/HRMS laboratory until analysis. These extracts will contain the PCDDs/PCDFs.

Preparation Glassware and Equipment

All glassware and equipment utilized in the DEI will be ordered specifically for this project. Upon receipt, they will be transferred to the PCB control laboratory

trailer. All glassware will undergo standard cleaning for trace organic analysis (laboratory grade aqueous glassware cleaner, multiple rinses with warm water, multiple solvent rinses [acetone and hexane]). The glassware will be oven baked at approximately 425°C for a minimum of 8 hours. Glassware should be washed with soap and thoroughly rinsed with water **AS SOON AS PRACTICAL** after use. Glassware should be rinsed immediately prior to being baked in the oven (bake at 425°C for 6-8 hr.).Glassware is to be removed and covered while still hot, 100°C, (use insulated gloves) and transferred to the trailer. All sample containers should be closed as soon as they have cooled. Any glassware that is to come into contact with solvent should be rinsed with that solvent **IMMEDIATELY** before use. Glassware should not be air dried but rather used immediately. Glassware destined for the oven should be baked ASAP after the solvent rinse has evaporated.

HRGC/HRMS Sample Analysis

Samples expected to contain dioxins and furans at the low parts-per-trillion level are spiked with known amounts of ^{13}C labeled recovery surrogates. The amount of surrogate added to the samples is determined based on the sample size and the concentration desired in the pre-determined final extract volume and will be equal to the concentration of labeled surrogate in the calibration solutions (e.g. 5 pg/μl). (For specific concentrations, see **TARGET COMPOUND LIBRARY LIST**). In most cases 1ul of sample is analyzed from a final sample vol. of 20ul and therefore the total amount of each recovery surrogate added is 100 picograms (Note: samples may be concentrated to 10ul and 2.0/10 injected to increase the number of detects or enhance the S/N ratio.) The degree of native analyte loss during sample preparation is reflected in the percentage recovered of the spiked recovery surrogates. Recoveries in the range between 25-150% will be acceptable. On the day samples are to be analyzed, an appropriate amount of the internal standard solution containing two internal standards is added to each of the sample extracts and the sample volume adjusted to a predetermined volume with nonane. The amount of internal standard added will be determined based on the final volume and will be equal to the concentration of the internal standards in the calibration solutions. The final volume will be 20 μl and the internal standard concentration will be 10 pg/μl. Samples containing relatively high concentrations of co-planar PCBs which exceed the calibration range will be quantitated using the internal standard method.

Prior to analysis, mass spectral resolution and mass calibration will be verified as described in the following section B7.1. Subsequently, the calibration standard of

intermediate concentration is analyzed and all QA/QC control parameters will be verified to be within the specified limits. Once these conditions have been established, sample analysis will proceed. The mass spectrometer is operated in a mass drift correction mode using perfluorokerosene to provide lock masses. All calibration standards, QA/QC check samples, blanks, and authentic samples will be processed and analyzed under identical conditions as described in this document.

The selected ion current profile (SICP) areas for the characteristic ions for each native and labeled analyte will be measured. Each homologous group is monitored in succession as a function of GC retention times to ensure that all co-planar PCBs are detected.
In addition, the ion current generated by each lock mass ion will also be monitored throughout its respective RT window. Variations of the lock mass ion signal by more than 10% indicates the presence of coeluting interferences that may significantly reduce sensitivity.

10.0 DATA REDUCTION, VALIDATION, & REPORTING

10.1 Quantitation and Data Reduction

The HRGC/HRMS Analyst will be responsible for the quantitation and data reduction of the raw data generated from the HRMS. The calibration and quantitation of all
samples and standards associated with this study will follow the equations presented in **EPA Method 1613: Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS** - specifically Section 7. Calibration (parts 7.1 through 7.8.2), Section 14. System and Laboratory Performance (parts 14.1 through 14.5.4), and Section 16. Quantitative Determination (parts 16.1 through 16.6.3).

Native analyte concentrations will be determined by isotope dilution. Peak areas from the characteristic ions for each native analyte and its corresponding ^{13}C label are used in conjunction with RFFs and the initial calibration data to determine concentrations directly. Labeled surrogate concentrations (expressed as percent recovery) are calculated using the internal standard method. The peak areas from the characteristic ions for each labeled surrogate and the appropriate internal standard are used in conjunction with RFs and the initial calibration data to determine the amounts. The equations used for these

calculations are identical to those used in EPA Method 1613. These calculations are performed automatically by the data processing software of the GC/MS system; the results of which will be included in each sample data package. Blanks and spiked results will not be used in the calculations, but will be considered as described in Section 11.

The analyst will select some random results from previous analyses and recalculate them using an independent calculating procedure to validate the KRATOS software. If a new version of an existing software or new software is used, a similar check will be performed.

10.2 Peak Identification Criteria

Sample components are identified, quantitated, and reported only after having satisfied the following criteria:

1) Peak areas for each of the two selected molecular cluster ions must be at least 3-5 times the background noise level (S/N = 3-5).

2) the chlorine isotope ratio for the two molecular cluster ions must be within +/- 15% of the theoretical value. For amounts less than 100 femtogram, the control limits will be increased to 25%.

3) The peak maxima for the molecular cluster ions must coincide within two seconds.

4) Native and the corresponding labeled surrogate peak maxima must elute within three seconds.

5) The method blank must not contain interfering compounds and will be examined for the presence of the analyte of concern.

6) The ion chromatogram for the chlorinated diphenyl ether ion will be examined to ensure that it does not interfere with the analyte of concern (USEPA Method 1613, Table 3).

The HRGC/HRMS Analyst will inform the Project Leader when the data for a set does not meet the QA criteria (Section 9.8). The Project Leader will inform the QAO and the data in question will be reviewed.

10.3 Data Reporting

The amount (automatically corrected for recovery) of any native analyte detected will be listed on the quantitation report. The recovery of its labeled analog will also be listed on the quantitation report. The recovery of its labeled analog should fall between 25-150%.

For all analytes detected, documentation of the peak areas used for quantitations of all native analytes, labeled recovery surrogates, and labeled internal standards, as well as their corresponding isotope abundance ratios, S/N ratios, and retention times will be provided. Ion chromatograms of characteristic ions will be provided when necessary and/or requested.

Accompanying each set of samples will be the initial calibration report listing the response factors (RFs) used for quantitations and the relative standard deviation (RSD) of the RFs for each native and labeled analyte. In addition, a quantitation report of the calibration standard documenting the linearity of the calibration curve on the day of sample analysis will be included. This report will list the percent difference between the RFs generated during the initial calibration and the new RFs for all native and labeled analytes. Additionally, a quantitation report for the continuing calibration standard, which lists the amounts of all native analytes and the percent recovery of the labeled analogs, will be provided so that the accuracy of the quantitations can be assessed (Figure 10-1).

A hardcopy of the results from the KRATOS calibration procedure demonstrating the instrument resolution and error associated with the mass calibration will be provided for each day of sample analysis.

A final report listing the sample designation, analytes, concentrations detected, and detection limits will be forwarded to USEPA/Battelle for use and dissemination (Figure 10-2).

KRATOS MACH3 PEAK AREA QUANTITATION:- CONCENTRATION REPORT:

Date: 31 Jan 1 Internal Standard method.
Sample: 0201010005 Library: total1 - Ion data Quantitation

Run Title: 1/20ul of QFF 832 269-06
Average response factor calibration method

COMPOUND	C.A.S.	Concentration / pg	
___ Analytes and surrogates ___		Conc	MDL
2,3,7,8-TCDF	51207-31-9	0.0571	0.0016
2,3,7,8-TCDD	76523-40-5	0.0208	0.0021
1,2,3,7,8-PeCDF	57117-41-6	0.1042	0.0019
2,3,4,7,8-PeCDF	57117-31-6	0.2011	0.0019
1,2,3,7,8-PeCDD	40321-76-4	0.1992	0.0041
1,2,3,4,7,8-HxCDF	70648-26-9	0.3562	0.0028
1,2,3,6,7,8-HxCDF	57117-44-9	0.3566	0.0027
2,3,4,6,7,8-HxCDF	60851-34-5	0.5199	0.0032
1,2,3,4,7,8-HxCDD	39227-28-6	0.4898	0.0031
1,2,3,6,7,8-HxCDD	57653-85-7	1.0718	0.0036
1,2,3,7,8,9-HxCDD	19408.74-3	1.1336	0.0031
1,2,3,7,8,9-HxCDF	72918-21-9	0.0579	0.0046
1,2,3,4,6,7,8-HpCDF	67562-39-4	2.8820	0.0077
1,2,3,4,6,7,8-HpCDD	35822-46-9	24.0929	0.0043
1,2,3,4,7,8,9-HpCDF	55673-89-7	0.4002	0.0130
OCDD	3268-87-9	169.8747	0.0147
OCDF	39001-02-0	3.4816	0.0121
___ Internal standards	% recovery___		
13C-1,2,3,4-TCDF		0.2942 %	
C13-2,3,7,8-TCDF	89059-46-1	65.7543 %	
13C-2,3,7,8-TCDD	76523-40-5	68.1452 %	
13C-1,2,3,7,8-PeCDF	109719-77-9	94.7882 %	
13C-2,3,4,7,8-PeCDF	116843-02-8	95.0702 %	
13C-1,2,3,7,8-PeCDD	109719-79-1	89.3335 %	
13C-1,2,3,4,7,8-HxCDF	114423-98-2	86.1796 %	
13C-1,2,3,6,7,8-HxCDF	116843-03-9	86.2855 %	
13C-2,3,4,6,7,8-HxCDF	116843-05-1	76.5025 %	
13C-1,2,3,4,7,8-HxCDD	109719-80-4	77.3367 %	
13C-1,2,3,6,7,8-HxCDD	109719-81-5	75.3720 %	
13C-1,2,3,7,8,9-HxCDF	116843-04-0	80.7284 %	
13C-1,2,3,4,6,7,8-HpCDF	109719-84-8	73.8462 %	
13C-1,2,3,4,6,7,8-HpCDD	109719-83-7	77.6902 %	
13C-1,2,3,4,7,8,9-HpCDF	109719-94-0	77.5064 %	
13C-OCDD	114423-97-1	60.6082 %	

___ Totals entries ___

Total-TCDF 60851-34-5 (MDL 0.0012)

Peaks within Isotope ratio limits: Concentration / pg

Figure 10-1 Quantitation Report of MS Analysis

USEPA/OPPTS/OPP/BEAD/ECL **Final Data** **06/15/01**
Sample Results from National Dioxin Air Monitoring Network (PCDDs/PCDFs, & PCBs)
Project (NDAMN) **File: NDAM-FY00-3f**

Sample Amount (pg)

Description of Sample	Air	Air	Air	Air	Air
Set #/Sample #	267-01	266-03	266-04	266-05	266-06
ORD Identification	Method Blank	P/F01-003-S	P/F02-003-S	P/F03-003-S	P/F05-003-S
Concentration	(pg)	(pg)	(pg)	(pg)	(pg)
Congener					
PCBs					
PCB 77	16.83	554.71	344.37	296.36	464.09
PCB 118	379.98	7621.96	5030.38	3609.15	5768.41
PCB 105	197.86	2377.10	1536.97	1212.26	1840.41
PCB 126	-	43.96	26.85	24.51	21.94
PCB 156	53.90	341.67	216.58	200.38	253.79
PCB 157	11.65	78.07	50.11	46.34	58.08
PCB 169	-	4.20	2.77	3.61	1.88
13C-PCB 81 % Recovery	n/a	112.64	106.84	105.78	106.84
PCDDs/PCDFs					
2,3,7,8-TCDF	-	17.05	11.19	7.29	10.35
2,3,7,8-TCDD	-	8.92	5.11	1.23	2.38
1,2,3,7,8-PeCDF	-	15.89	9.94	10.35	6.08
2,3,4,7,8-PeCDF	-	23.42	13.94	18.83	9.83
1,2,3,7,8-PeCDD	-	36.56	22.89	6.33	5.97
1,2,3,4,7,8-HxCDF	-	27.59	18.74	23.51	12.82
1,2,3,6,7,8-HxCDF	-	32.69	21.66	22.59	12.27
2,3,4,6,7,8-HxCDF	0.77	33.36	19.11	35.50	14.49
1,2,3,4,7,8-HxCDD	-	21.29	13.78	5.56	9.11
1,2,3,6,7,8-HxCDD	-	45.52	26.21	12.01	19.56
1,2,3,7,8,9-HxCDD	-	34.55	19.36	8.80	17.89
1,2,3,7,8,9-HxCDF	-	3.72	2.55	4.08	2.02
1,2,3,4,6,7,8-HpCDF	2.55	173.22	114.98	132.84	73.02
1,2,3,4,6,7,8-HpCDD	2.07	443.50	253.52	126.98	338.05
1,2,3,4,7,8,9-HpCDF	-	10.55	7.12	15.84	8.51
OCDD	24.02	2191.23	1292.60	496.36	1469.73
OCDF	12.31	131.79	84.09	115.14	96.83
13C-1,2,3,4-TCDF (%Recovery)	n/a	99.80	94.57	106.15	95.88
Totals					
TCDFs	n/a	748.19	422.41	527.39	402.10
TCDDs	n/a	77.96	44.87	49.70	34.85
PeCDF	n/a	488.25	283.43	314.78	153.20
PeCDD	n/a	120.32	84.95	75.25	57.95
HxCDF	n/a	653.63	417.82	334.95	155.27
HxCDD	n/a	513.89	300.24	217.11	219.25
HpCDF	n/a	277.68	179.38	195.15	117.56
HpCDD	n/a	1827.56	788.35	349.03	762.86

Values underlined indicate that the ion ratio of the quantitative ions are outside of the QA/QC limits

11.0 INTERNAL QUALITY CONTROL CHECKS

11.1 Quality Control

Prior to the analysis of authentic samples, a demonstration of the method performance capabilities will be conducted. After the method detection/quantitation limits have been estimated, replicate samples (4 -7) will be fortified at 3-5 times the LOD with all of the 2,3,7,8-substituted dioxins, furans, co-planar PCBs and the ^{13}C recovery surrogates to verify the precision and accuracy. The target LODs/LOQs for the dioxins, furans, and co-planar PCBs will be based on the minimum amount that can be detected based on the acceptance criteria and the volume of sampled air.(Which will vary depending on the sample.) For the tetra -dioxins/furans and PCB 126 and 169 the instrumental detection limit is 50 femtograms. For the penta-, hexa-, and hepta-chlorinated dioxins and furans the detection limit is 150 fg, and for the octa-chlorinated dioxins and furans the detection limit is 1 pg. These estimates are based on the S/N ratios of the quantitation ions from the native congeners from a 1ul injection of the lowest calibration standard. For the remaining PCBS and the dioxins and furans (i.e., heptadioxin, OCDD and OCDF) for which detectable amounts are present in the method blanks, the detection limits are based on the minimum amount that can be reliably detected above background as described in Ferrario et. al., 1997. The target LODs are one half of the concentrations of the LOQs. The spiking level for the ^{13}C labeled surrogates will be 100 pg for each label, which will give 5.0 pg/μl at the final extract volume of 20 μl. For the demonstration of capability, replicate cleaned PUFs and QFFs will be spiked at a level 3- 5 times the LOQ with all of the 2,3,7,8-substituted dioxins, furans, and co-planar PCBS and the ^{13}C recovery surrogates. Each set of samples will also contain a method blank and the appropriate matrix blank. The samples will be processed and analyzed according to the method detailed in this document.

The target instrumental detection limits for the analyses based on a 2/10ul injection of a sample extract and considering the background amounts for several of the congeners normally present in method blanks ,the detection limits for the analytical procedure expressed as total picograms for each congener are as follows.

TCDD/CDF	0.5 pg	PCB 77	20 pg
PeCDD/CDF & HxCDD/CDF	1.5	PCB 118	500
HpCDF	1.5	PCB 105	300
HpCDD	2.5	PCB 126	2.0
OCDF	4.0	PCB 156	80.0
OCDD	20.0	PCB 157	20.0
		PCB 169	1.0

NOTE: The congener specific detection limits on a per sample basis can be derived by dividing the total picograms tabulated above by the volume of air sampled.

The analytical procedure will be considered to be in statistical control if the mean value determined for the replicates for 94% of the native analytes (with the exception of OCDF) is within 25% of the true value, and the RSD (Relative Standard Deviation) of the replicates do not exceed 25%. The concentration of the native OCDF cannot be accurately corrected for by the recovery of ^{13}C labeled OCDD, but this possible decrease of accuracy is not considered significant because of the low toxicity of this compound. These conditions will be verified by checking the actual values determined for each analyte on the quantitation report and examining the RSDs for the response factors calculated for each native analyte. In addition, the percent recovery of the ^{13}C labeled analytes must be between 25-150%.

The method and matrix blanks will be examined to ensure that there are no contaminants that might interfere with the analysis. Method blanks containing native analytes at levels that would preclude achieving the detection limits stated previously is cause for corrective action to eliminate the contamination. Sample results from a set that contains a method blank considered to have elevated background that may have compromised the data may not be reported at the discretion of the Team Leader and the QAO.

For each sample set containing authentic samples, one control sample matrix (Laboratory Control Spike, LCS) spiked as described above will be processed and analyzed along with the samples. The actual values determined for 94% of the native analytes (with the exception of OCDF) must be within ± 25% of the actual value. Alternately, one duplicate sample will be processed and analyzed and the values for the native analytes determined. The percent difference for the native analytes detected in the duplicates must be less than 25%. Recoveries of all ^{13}C labeled surrogates must be within 25-150%. Other quality control measures taken to ensure the integrity of the data are described in the appropriate section.

The HRGC/HRMS Analyst will be responsible for the quantitation and data reduction of the raw data generated from the HRMS. The calibration and quantitation of all samples and standards associated with this study will follow the equations presented in **EPA Method 1613: Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS** - specifically Section 7.

Calibration (parts 7.1 through 7.8.2), Section 14. System and Laboratory Performance (parts 14.1 through 14.5.4), and Section 16. Quantitative Determination (parts 16.1 through 16.6.3).

Native analyte concentrations will be determined by isotope dilution. Peak areas from the characteristic ions for each native analyte and its corresponding ^{13}C label are used in conjunction with RFFs and the initial calibration data to determine concentrations directly. Labeled surrogate concentrations (expressed as percent recovery) are calculated using the internal standard method. The peak areas from the characteristic ions for each labeled surrogate and the appropriate internal standard are used in conjunction with RFs and the initial calibration data to determine the amounts. The equations used for these calculations are identical to those used in EPA Method 1613. These calculations are performed automatically by the data processing software of the GC/MS system; the results of which will be included in each sample data package. Blanks and spiked results will not be used in the calculations, but will be considered as described in Section 5.2.2.

The analyst will select some random results from previous analyses and recalculate them using an independent calculating procedure to validate the KRATOS software. If a new version of an existing software or new software is used, a similar check will be performed.

11.2 Other QC Checks Performed at ECL

11.21 Quality Control Data Sheet

Information on all solvents, reagents, and solutions used during each DRP set extraction and cleanup is kept in the "NDAMN SOLVENT/CHEMICAL LOGBOOK" and "NDAMN STANDARD SOLUTION LOGBOOK".

11.22 NDAMN Quality Assurance Data Form

Before any work is begun on a sample set, a "NDAMN SET COMPOSITION/QA DATA FORM" initiated. After extraction, cleanup, concentration, and analysis, all pertinent set information is recorded on this form.

A copy of this form is presented in Appendix A.

11.3 Qualitative/Quantitative Limitations as Determined by Initial Demonstration of Capability Determinations

After the completion of the Demonstration of Capabilities for the analytes, the NDAMN HRGC/HRMS Analyst, NDAMN QAO, NDAMN Project Leader, and the Laboratory Section Chief will meet and finalize all project qualitative/quantitative thresholds (e.g. limits of detection (LODs), limits of quantitation (LOQs), etc.). This will serve as the guidelines for all future QA/QC internal audits, project result tabulations, and qualitative discussions. If, as a result of future data, these thresholds need to be re-calculated, then it will be done only with the joint agreement among the NDAMN QAO, NDAMN Project Leader, and Laboratory Section Chief.

11.4 Data Review, Tabulation, and Archiving

With the completion of the results of each defined sample set by the HRGC/HRMS Analyst, the completed sample set file (i.e. QA/QC set form, sample weight information form, individual sample data files, reference forms, exceptions to the QAPP, updated RFFs, HRMS spectra, etc.) will be passed to the NDAMN Project Leader for review and approval. At no time may more than three completed sample set files be allowed in the possession of the Project Leader without the concurrence of the NDAMN QAO. If this situation does occur, then the HRGC/HRMS Analyst will stop all present and future preparative and analytical work until this problem has been resolved.

Upon his review of the completed sample set file, the Project Leader will pass the file to the QAO for his possible review and comment. The QAO will return the completed sample set file to the Project Leader. The Project Leader will tabulate the final data for that sample set into the computer within one week of the completion of the QAO review. The QAO willcheck after that week to insure the tabulation of the data of that individual set.

Upon completion of the project, the NDAMN QAO and Project Leader will meet and review the final tabulation of the data.

11.5 Exceptions to the QAPP

11.5.1 Request for Approval

Occasionally, it may become necessary for personnel assigned to the NDAMN to request approval for exceptions or deviations from this QAPP. This approval

must come from the NDAMN Project Leader and may be initially requested verbally or in writing, but in either case, the request must be supported by a clear rationale, laboratory data, and documentation.

11.5.2 Documentation and Following Requirements

The NDAMN Project Leader will enter into the data set the exception requested and the information and documentation required to support approval of the exception to the QAPP.

2.0 AUDITS

12.1 Requirements

Technical Systems and Data Quality Audits shall be conducted by NDAMN QAO on the analytical work to assess the adherence to the QA Project Plan and to assess the quality of data generated by the analytical systems.

12.2 Frequency

12.21 Technical Services and Data Quality

These audits shall be conducted at the beginning of the project after 10 samples have been analyzed and at the end of the project, exclusive of external audits.

12.3 Nature of Audits

12.31 Technical Systems Audits shall include the following:

12.311 Project Management System

12.3111 Personnel - Qualifications

12.3112 Documentation - QAPP & SOPs

12.3113 Communications about Changes in Requirements

12.3114 Analyst Feedback

12.312 Sample Tracking System

12.313 System for Sample Preparation

12.314 Systems for Analytical Operations

12.3141 Standards

12.3142 Calibrations

12.3143 Documentation of Analytical Operations

12.3144 Corrective Action Loop

12.3145 Instrument Maintenance

12.315 Data Management Systems

12.3151 Collections

12.3152 Reduction

12.3153 Verifications

12.3154 Internal Review

12.3155 Reporting

12.3156 Use of QC Data at Bench Level

12.3157 Data Storage & Retrieval

12.316 Laboratory Management Systems

12.3161 Major Equipment Purchases

12.3162 Services and Supplies

12.3163 Maintenance of Ancillary Equipment

12.3164 General Physical Facilities

12.3165 Cold Storage Facilities

12.32 Data Quality Audits shall include tracking two samples from log-in through preparation, isolation, and HRGC/HRMS analysis, data handling, and disposal.

12.33 Reporting and Use of Audit Results

Following any of the above audits, the NDAMN QAO shall report the results in writing to both the NDAMN Project Leader and the Laboratory Branch Chief. If deficiencies are found, each shall specifically be identified along with the cause, if known. The QAO will provide a written plan or suggestion for corrective action to the NDAMN Project Leader with a copy to the ECL Chief. The QAO shall also follow up with a limited audit to verify that deficiencies were resolved by the proposed corrective action.

13.0 PREVENTIVE MAINTENANCE

13.1 HRGC/HRMS

The following schedule of maintenance tasks and spare parts applies to the KRATOS CONCEPT.

Routine maintenance will be performed on the HRGC/HRMS in accordance with the following schedule:

Tasks	Frequency
Clean source	Monthly or as required
Bake out magnetic sector	Monthly or as required
Bake out GC column	Daily or as required
Change pump oil	Every six months or as required
Change GC column	As required by performance
Change injector port septa	Weekly or as required
Clean injector port liner	Monthly or as required

Most maintenance is done in-house. When a problem is encountered which cannot be resolved, KRATOS is contacted and service is arranged. Critical spare parts are also available to minimize downtime and the following list of replacement parts and consumable spares is maintained within the laboratory:

1) Columns, 2) Ferrules for columns, 3) Syringes,
4) Filaments, 5) Gold gaskets, 6) Injector port septa,
7) Vacuum pump oil.

14.0 CORRECTIVE ACTIONS

Corrective action is required when out-of-control situations develop regarding QC criteria, procedure, or specific project requirements and is delineated in Section 11.3. Sections 5 contain specific QC objectives and criteria for this project, and Section 7 contains specific sampling and tracking requirements. All of these elements are evaluated as required by established EPA guidelines and notations of the changes within the data set are maintained as documentation.

An analyst, team member, or Sample Custodian experienced with this project and involved in the its day-to-day activities will be the first to be aware of a problem, inconsistency, or QC parameter outside acceptance limits. It is his/her responsibility to note the nature and significance of the problem and to bring it to the attention of the NDAMN Project Leader. Such problems shall be properly documented through the use of the "NDAMN LOGGING FORM" and related logbooks in Sample Receiving and by the use of the "SET COMPOSITION /QUALITY ASSURANCE DATA FORM".

The following areas should be addressed:

o specific exceptions to the QC requirement

o when the problem was first noted and by whom

o who was notified

o corrective or remedial action required

o action taken

o the date and verification that a QC exception or problem was resolved

o sample set number and specific sample/s involved.

If the NDAMN Project Leader cannot readily resolve the problem or provide guidance for corrective action, the NDAMN Quality Assurance Officer (NDAMN QAO) must be notified. The QAO will take a lead role in developing a strategy to resolve the problem. Verification that the problem has been resolved must also

be provided before analytical work continue.
All QC exceptions, problems, corrective actions, and verification documentation must be reported monthly to the NDAMN Project Leader. For any problems requiring involvement of the NDAMN QAO, the NDAMN Project Leader must be immediately informed.

15. QA REPORTS TO MANAGEMENT

The NDAMN Project Leader will interact daily with the analyst performing the bench work and data generation. The analyst will inform the Project Leader immediately when any QA problem or unusual situation develops. The analyst will follow the verbal notification with a written explanation of the problem. The NDAMN Project Leader will keep the NDAMN QA Officer informed and will discuss unresolved problems with him. The Project Leader will inform the ECL Branch Chief of major problems.

The Project Leader will complete an "EPA NDAMN LABORATORY PROGRESS - QA REPORT FORM" (Figure 15-1). Copies of this report will be submitted monthly to the Branch Chief and the NDAMN QA Officer.

The Project Leader will submit supplemental information regarding status of samples, ambiguity in reported concentrations, etc. to the USDA as the situation requires.

EPA NDAMN LABORATORY PROGRESS - QA REPORT

Date: _____

Report Period: _____

Analyst: _____

1. Progress:

    # Samples analyzed: _____

    # Samples invalidated: _____

    # No of data sets archived: ____

2. Bench Level Corrective Action (s)

    Date: _____

    Sample Set: _____

    Problem: _____

    Action Taken: _____

    Verification of Correction: _____

3. Problems (Project-Related): _____

4. Changes in Personnel: _____

5. Comments: _____

Figure 15-1. EPA NDAMN LABORATORY PROGRESS - QA REPORT

Appendix A

Date:

CHAIN OF CUSTODY & SAMPLE RECEIVING FORM

USEPA/Environmental Chemistry Laboratory

Investigations of the Presence of PCDDs/PCDFs/co-planar PCBs in National Dioxin Air Monitoring Network **(FYXX-Moment X)**

Sample No.	Site	Sample Battelle # T # Yr/M D	Sample ECL ID #	Description	Sample PUF	Sample GFF	Location	Date Collected	Date Shipped	Date Received	Condition

Signed : _____
ECL Quality Assurance Officer

Signed : _____
ECL Sample Custodian

SET COMPOSITION/QA DATA FORM

Date: _____ SET # _____

Freezer: _____

USEPA/ECL/ORD SURVEY OF DIOXIN-LIKE COMPOUNDS IN NATIONAL DIOXIN AIR MONITORING NETWORK/ MOMENT / 200_

#	ECL Sample	Description	Quantity Weighed (g)/(ml)	_____	_____ Spiking	_____ Solution	_____	GC/MS Date/Analyst/ Volume (µl) Dioxin	GC/MS Date/Analyst/ Volume (µl) PCBs	Date Archived Freezer #
1										
2										
3										
4										
5										
6										
7										
8										
9										
10										
11										
12										

SET # _____

Date of original sample ground/person _____/_____

Date homogenate returned to freezer/stored/person _____/_____

Date sample extracted/person _____/_____

Date sample extracted acid/silica washed/person _____/_____

Date extracts concentrated/person _____/_____

Date A/B Silica Gel Col Chrom/person _____/_____

Date SGC extracts concentrated/person _____/_____

Date Carbon Col Chrom/person _____/_____

Date CCC/PCBs extracts conced/person _____/_____

Date CCC/Dioxins extracts conced/person _____/_____

Date PCB fraction transfer to analyst/person from/person received by

_____/_____/_____

Date Alumina Col Chrom/person _____/_____

Date ACC extracts concentrated/person _____/_____

Date dioxin fraction transfer to analyst/person from/person received by

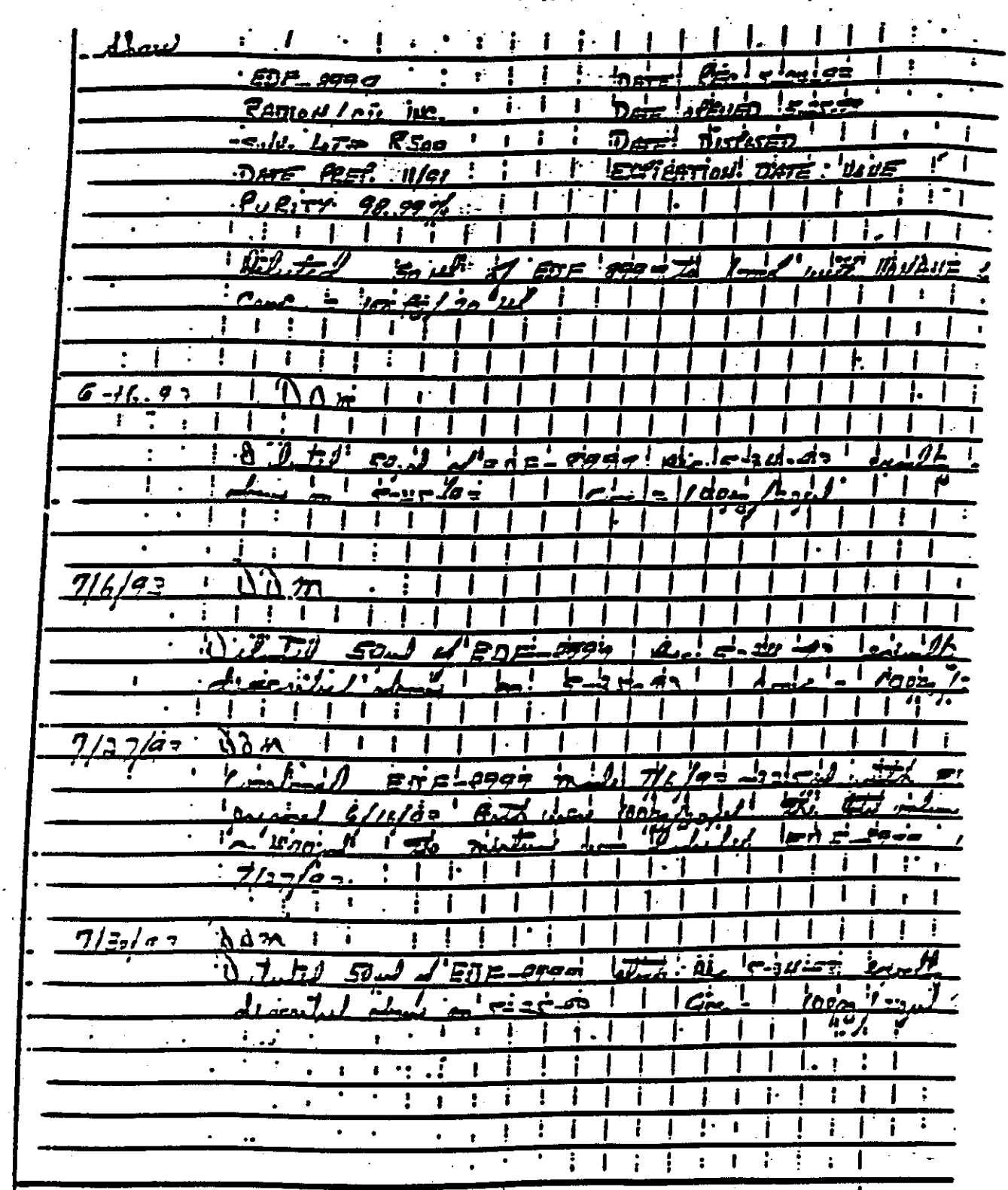
_____/_____/_____

GC/MS Analysis _____

_____

Archiving Data _____

_____



Witnessed & Understood by me.	Date	Invented by	Date
		Recorded by	

NDAMN STANDARD SOLUTION LOGBOOK

Date/Solvent/Vendor/Lot #	Date Received	Date Opened
[illegible] / Manganese / Mallinkr.-Jt / 3023KTLV-0	10-15-92	11-07-92
93 GC/GC-MS / Baxter	RE1CO	1-27-93

NDAMN SOLVENT/CHEMICAL LOGBOOK

KRATOS MACH3 PEAK AREA QUANTITATION:- CONCENTRATION REPORT:

Date: 31 Jan 1 Internal Standard method.
Sample: 0201010005 Library: totall - Ion data Quantitation

Run Title: 1/20ul of QFF 832 269-06
Average response factor calibration method

COMPOUND	C.A.S.	Concentration / pg	
___ Analytes and surrogates ___		Conc	MDL
2,3,7,8-TCDF	51207-31-9	0.0571	0.0016
2,3,7,8-TCDD	76523-40-5	0.0208	0.0021
1,2,3,7,8-PeCDF	57117-41-6	0.1042	0.0019
2,3,4,7,8-PeCDF	57117-31-6	0.2011	0.0019
1,2,3,7,8-PeCDD	40321-76-4	0.1992	0.0041
1,2,3,4,7,8-HxCDF	70648-26-9	0.3562	0.0028
1,2,3,6,7,8-HxCDF	57117-44-9	0.3566	0.0027
2,3,4,6,7,8-HxCDF	60851-34-5	0.5199	0.0032
1,2,3,4,7,8-HxCDD	39227-28-6	0.4898	0.0031
1,2,3,6,7,8-HxCDD	57653-85-7	1.0718	0.0036
1,2,3,7,8,9-HxCDD	19408.74-3	1.1336	0.0031
1,2,3,7,8,9-HxCDF	72918-21-9	0.0579	0.0046
1,2,3,4,6,7,8-HpCDF	67562-39-4	2.8820	0.0077
1,2,3,4,6,7,8-HpCDD	35822-46-9	24.0929	0.0043
1,2,3,4,7,8,9-HpCDF	55673-89-7	0.4002	0.0130
OCDD	3268-87-9	169.8747	0.0147
OCDF	39001-02-0	3.4816	0.0121
___ Internal standards % recovery___			
13C-1,2,3,4-TCDF		0.2942 %	
C13-2,3,7,8-TCDF	89059-46-1	65.7543 %	
13C-2,3,7,8-TCDD	76523-40-5	68.1452 %	
13C-1,2,3,7,8-PeCDF	109719-77-9	94.7882 %	
13C-2,3,4,7,8-PeCDF	116843-02-8	95.0702 %	
13C-1,2,3,7,8-PeCDD	109719-79-1	89.3335 %	
13C-1,2,3,4,7,8-HxCDF	114423-98-2	86.1796 %	
13C-1,2,3,6,7,8-HxCDF	116843-03-9	86.2855 %	
13C-2,3,4,6,7,8-HxCDF	116843-05-1	76.5025 %	
13C-1,2,3,4,7,8-HxCDD	109719-80-4	77.3367 %	
13C-1,2,3,6,7,8-HxCDD	109719-81-5	75.3720 %	
13C-1,2,3,7,8,9-HxCDF	116843-04-0	80.7284 %	
13C-1,2,3,4,6,7,8-HpCDF	109719-84-8	73.8462 %	
13C-1,2,3,4,6,7,8-HpCDD	109719-83-7	77.6902 %	
13C-1,2,3,4,7,8,9-HpCDF	109719-94-0	77.5064 %	
13C-OCDD	114423-97-1	60.6082 %	

___ Totals entries ___

Total-TCDF 60851-34-5 (MDL 0.0012)

Peaks within Isotope ratio limits: Concentration / pg

Quantitation Report of MS Analysis

EPA NDAMN LABORATORY PROGRESS - QA REPORT

Date: _____

Report Period: _____

Analyst: _____

1. Progress:

    # Samples analyzed: _____

    # Samples invalidated: _____

    # No of data sets archived: ____

2. Bench Level Corrective Action (s)

    Date: _____

    Sample Set: _____

    Problem: _____

    Action Taken: _____

    Verification of Correction: _____

3. Problems (Project-Related): _____

4. Changes in Personnel: _____

5. Comments: _____

USEPA/OPPTS/OPP/BEAD/ECL **Final Data** **06/15/01**

Sample Results from National Dioxin Air Monitoring Network (PCDDs/PCDFs, & PCBs) Project (NDAMN)

File: NDAM-FY00-3f

Sample Amount (pg)

Description of Sample	Air	Air	Air	Air	Air
Set #/Sample #	267-01	266-03	266-04	266-05	266-06
ORD Identification	Method Blank	P/F01-003-S	P/F02-003-S	P/F03-003-S	P/F05-003-S
Concentration	(pg)	(pg)	(pg)	(pg)	(pg)
Congener					
PCBs					
PCB 77	16.83	554.71	344.37	296.36	464.09
PCB 118	379.98	7621.96	5030.38	3609.15	5768.41
PCB 105	197.86	2377.10	1536.97	1212.26	1840.41
PCB 126	-	43.96	26.85	24.51	21.94
PCB 156	53.90	341.67	216.58	200.38	253.79
PCB 157	11.65	78.07	50.11	46.34	58.08
PCB 169	-	4.20	2.77	3.61	1.88
13C-PCB 81 % Recovery	n/a	112.64	106.84	105.78	106.84
PCDDs/PCDFs					
2,3,7,8-TCDF	-	17.05	11.19	7.29	10.35
2,3,7,8-TCDD	-	8.92	5.11	1.23	2.38
1,2,3,7,8-PeCDF	-	15.89	9.94	10.35	6.08
2,3,4,7,8-PeCDF	-	23.42	13.94	18.83	9.83
1,2,3,7,8-PeCDD	-	36.56	22.89	6.33	5.97
1,2,3,4,7,8-HxCDF	-	27.59	18.74	23.51	12.82
1,2,3,6,7,8-HxCDF	-	32.69	21.66	22.59	12.27
2,3,4,6,7,8-HxCDF	0.77	33.36	19.11	35.50	14.49
1,2,3,4,7,8-HxCDD	-	21.29	13.78	5.56	9.11
1,2,3,6,7,8-HxCDD	-	45.52	26.21	12.01	19.56
1,2,3,7,8,9-HxCDD	-	34.55	19.36	8.80	17.89
1,2,3,7,8,9-HxCDF	-	3.72	2.55	4.08	2.02
1,2,3,4,6,7,8-HpCDF	2.55	173.22	114.98	132.84	73.02
1,2,3,4,6,7,8-HpCDD	2.07	443.50	253.52	126.98	338.05
1,2,3,4,7,8,9-HpCDF	-	10.55	7.12	15.84	8.51
OCDD	24.02	2191.23	1292.60	496.36	1469.73
OCDF	12.31	131.79	84.09	115.14	96.83
13C-1,2,3,4-TCDF (%Recovery)	n/a	99.80	94.57	106.15	95.88
Totals					
TCDFs	n/a	748.19	422.41	527.39	402.10
TCDDs	n/a	77.96	44.87	49.70	34.85
PeCDF	n/a	488.25	283.43	314.78	153.20
PeCDD	n/a	120.32	84.95	75.25	57.95
HxCDF	n/a	653.63	417.82	334.95	155.27
HxCDD	n/a	513.89	300.24	217.11	219.25
HpCDF	n/a	277.68	179.38	195.15	117.56
HpCDD	n/a	1827.56	788.35	349.03	762.86

Values underlined indicate that the ion ratio of the quantitative ions are outside of the QA/QC limits

Appendix B

TARGET COMPOUND LIBRARY LIST

Library name - dioxjo

Entry	Type	Ref	Retention Time	Retention Window	Retention Offset	Masses	Isotope Ratios To	Isotope Ratios Theory	Isotope Ratios Tolera
1	std	3	27:48	0:10	0:00	315.9419 Q 317.9389 Q	2	77.00	15.00
Quantity		5.000 pg							
CAS	89059-46-1								
Name:	13C-2,3,7,8-TCDF								
2	ana	1	27:50	0:10	0:00	303.9016 Q 305.8987 Q	2	77.00	15.00
Quantity		0.100 pg							
Toxic Equiv. factor		0.10000							
CAS	51207-31-9								
Name:	2,3,7,8-TCDF								
3	sur	3	28:00	0:10	0:00	331.9368 Q 333.9339 Q	2	77.00	15.00
Quantity		10.000 pg							
CAS									
Name:	13C-1,2,3,4,-tcdd								
4	std	3	28:34	0:10	0:00	331.9368 Q 333.9339 Q	2	77.00	15.00
Quantity		5.000 pg							
CAS	76523-4C-5								
Name:	13C-2,3,7,8-TCDD								
5	ana	4	28:33	0:10	0:00	319.8965 Q 321.8936 Q	2	77.00	15.00
Quantity		0.100 pg							
Toxic Equiv. factor		1.00000							
CAS	1746-01-6								
Name:	2,3,7,8-TCDD								
6	std	3	33:20	0:10	0:00	351.9000 Q 353.8970 Q	2	155.00	15.00
Quantity		5.000 pg							
CAS	109719-77-9								
Name:	13C-1,2,3,7,8-PeCDF								
7	ana	6	33:22	0:10	0:00	339.8597 Q 341.8567 Q	2	155.00	15.00
Quantity		0.500 pg							
Toxic Equiv. factor		0.10000							
CAS	57117-41-6								
Name:	1,2,3,7,8-PeCDF								
8	ana	9	35:20	0:10	0:00	339.8597 Q 341.8567 Q	2	155.00	15.00
Quantity		0.500 pg							
Toxic Equiv. factor		0.10000							
CAS	57117-31-4								

TARGET COMPOUND LIBRARY LIST

Library name - dioxjo

Entry	Type	Ref	Retention Time	Retention Window	Retention Offset	Masses	Isotope Ratios To	Isotope Ratios Theory	Isotope Ratios Tolerance
Name: 2,3,4,7,8-PeCDF									
9	std	3	35:18	0:10	0:00	351.9000 Q	2	155.00	15.00
Quantity		5.000 pg				353.8970 Q			
CAS 116843-02-8									
Name: 13C-2,3,4,7,8-PeCDF									
10	std	3	35:55	0:10	0:00	367.8949 Q	2	155.00	15.00
Quantity		5.000 pg				369.8919 Q			
CAS 109719-79-1									
Name: 13C-1,2,3,7,8-PeCDD									
11	ana	10	36:01	0:10	0:00	355.8546 Q	2	155.00	15.00
Quantity		0.500 pg				357.8516 Q			
Toxic Equiv. factor 0.50000									
CAS 40321-76-4									
Name: 1,2,3,7,8-PeCDD									
12	std	23	41:15	0:10	0:00	383.8639 Q	2	51.00	15.00
Quantity		5.000 pg				385.8610 Q			
CAS 114423-98-2									
Name: 13C-1,2,3,4,7,8-HxCDF									
13	ana	12	41:16	0:10	0:00	373.8208 Q	2	124.00	15.00
Quantity		0.500 pg				375.8178 Q			
Toxic Equiv. factor 0.01000									
CAS 70648-26-9									
Name: 1,2,3,4,7,8-HxCDF									
14	ana	15	41:29	0:10	0:00	373.8208 Q	2	124.00	15.00
Quantity		0.500 pg				375.8178 Q			
Toxic Equiv. factor 0.01000									
CAS 57117-44-9									
Name: 1,2,3,6,7,8-HxCDF									
15	std	23	41:27	0:10	0:00	383.8639 Q	2	51.00	15.00
Quantity		5.000 pg				385.8610 Q			
CAS 116843-03-9									
Name: 13C-1,2,3,6,7,8-HxCDF									
16	ana	17	42:33	0:10	0:00	373.8208 Q	2	124.00	15.00
Quantity		0.500 pg				375.8178 Q			

TARGET COMPOUND LIBRARY LIST

Library name - dioxjc

Entry	Type	Ref	Retention Time	Retention Window	Retention Offset	Masses	To	Isotope Ratios Theory	Isotope Ratios Tolera
Toxic Equiv. factor 0.01000 CAS 72918-21-9 Name: 1,2,3,7,8,9-HxCDF									
17	std	23	42:30	0:10	0:00	383.8639 Q 385.8610 Q	2	51.00	15.00
Quantity 5.000 pg CAS 116843-04-0 Name: 13C-1,2,3,7,8,9-HxCDF									
18	std	23	42:46	0:09	0:00	401.8559 Q 403.8529 Q	2	-124.00	15.00
Quantity 5.000 pg CAS 109719-80-4 Name: 13C-1,2,3,4,7,8-HxCDD									
19	ana	18	42:47	0:09	0:00	389.8157 Q 391.8127 Q	2	124.00	15.00
Quantity 0.500 pg Toxic Equiv. factor 0.04000 CAS 39227-28-6 Name: 1,2,3,4,7,8-HxCDD									
20	std	23	42:58	0:09	0:00	401.8559 Q 403.8529 Q	2	124.00	15.00
Quantity 5.000 pg CAS 109719-81-5 Name: 13C-1,2,3,6,7,8-HxCDD									
21	ana	20	43:00	0:09	0:00	389.8157 Q 391.8127 Q	2	124.00	15.00
Quantity 0.500 pg Toxic Equiv. factor 0.04000 CAS 57653-85-7 Name: 1,2,3,6,7,8-HxCDD									
22	ana	20	43:20	0:10	0:00	389.8157 Q 391.8127 Q	2	124.00	15.00
Quantity 0.500 pg Toxic Equiv. factor 0.04000 CAS 19408-74-3 Name: 1,2,3,7,8,9-HxCDD									
23	sur	23	43:20	0:10	0:00	401.8559 Q 403.8529 Q	2	124.00	15.00
Quantity 10.000 pg CAS 109719-82-6 Name: 13C-1,2,3,7,8,9-HxCDD									

TARGET COMPOUND LIBRARY LIST

Library name - dioxjo

Entry	Type	Ref	Retention Time	Retention Window	Retention Offset	Masses		Isotope Ratios To	Isotope Ratios Theory	Isotope Ratios Toleran
24	std	23	43:49	0:10	0:00	383.8639	Q	2	51.00	15.00
Quantity		5.000 pg				385.8610	Q			
CAS 116843-05-1										
Name: 13C-2,3,4,6,7,8-HxCDF										
25	ana	24	43:51	0:10	0:00	373.8208	Q	2	124.00	15.00
Quantity		0.500 pg				375.8178	Q			
Toxic Equiv. factor 0.01000										
CAS 60851-34-5										
Name: 2,3,4,6,7,8-HxCDF										
26	ana	27	46:01	0:10	0:00	407.7818	Q	2	105.00	15.00
Quantity		0.500 pg				409.7789	Q			
Toxic Equiv. factor 0.00100										
CAS 67562-39-4										
Name: 1,2,3,4,6,7,8-HpCDF										
27.	std	23	45:59	0:10	0:00	417.8253	Q	2	44.00	15.00
Quantity		5.000 pg				419.8220	Q			
CAS 109719-84-3										
Name: 13C-1,2,3,4,6,7,8-HpCDF										
28	std	23	47:26	0:10	0:00	435.8169	Q	2	105.00	15.00
Quantity		5.000 pg				437.8140	Q			
CAS 109719-83-7										
Name: 13C-1,2,3,4,6,7,8-HpCDD										
29	ana	28	47:28	0:10	0:00	423.7766	Q	2	105.00	15.00
Quantity		0.500 pg				425.7737	Q			
Toxic Equiv. factor 0.00100										
CAS 35822-46-9										
Name: 1,2,3,4,6,7,8-HpCDD										
30	std	23	48:03	0:10	0:00	417.8253	Q	2	44.00	15.00
Quantity		5.000 pg				419.8220	Q			
CAS 109719-94-0										
Name: 13C-1,2,3,4,7,8,9-HpCDF										
31	ana	30	48:04	0:10	0:00	407.7818	Q	2	105.00	15.00
Quantity		0.500 pg				409.7789	Q			
Toxic Equiv. factor 0.00100										
CAS 55673-89-7										

TARGET COMPOUND LIBRARY LIST

Library name - dioxjo

Entry	Type	Ref	Retention Time	Retention Window	Retention Offset	Masses		Isotope Ratio To	Isotope Ratio Theory	Isotope Ratio Tole
Name: 1,2,3,4,7,8,9-HpCDF										
32	std	23	51:34	0:10	0:00	469.7779	Q	2	89.00	15.0
Quantity		10.000 pg				471.7750	Q			
CAS 114423-97-1										
Name: 13-OCDD										
33	ana	32	51:35	0:10	0:00	457.7377	Q	2	89.00	15.00
Quantity		1.000 pg				459.7348	Q			
CAS 3268-87-9										
Name: OCDD										
34	ana	32	51:48	0:10	0:00	441.7428	Q	2	89.00	15.00
Quantity		1.000 pg				443.7399	Q			
CAS 326828:59-87-9										
Name: OCDF										

TARGET COMPOUND LIBRARY LIST

Library name - pcb-cp

Entry	Type	Ref	Retention Time	Retention Window	Retention Offset	Masses	Isotope Ratios To	Isotope Ratios Theory	Isotope Ratios Tolerance
Name: C13-pcb105 penta									
9	ana	10	28:02	0:10	0:00	323.8834 Q	2	61.00	15.00
Quantity	2.000 pg					325.8805 Q			
CAS									
Name: pcb126 penta									
10	std	2	28:02	0:10	0:00	335.9237 Q	2	61.00	15.00
Quantity	5.000 pg					337.9207 Q			
CAS									
Name: C13-pcb126 penta									
11	sur	11	29:03	0:10	0:00	371.8817 Q	2	124.00	15.00
Quantity	10.000 pg					373.8788 Q			
CAS									
Name: C13-pcb128 hexa									
12	std	11	30:57	0:10	0:00	371.8817 Q	2	124.00	15.00
Quantity	5.000 pg					373.8788 Q			
CAS									
Name: C13-pcb156 hexa									
13	ana	12	30:59	0:10	0:00	359.8414 Q	2	124.00	15.00
Quantity	2.000 pg					361.8385 Q			
CAS									
Name: pcb156 hexa									
14	ana	12	31:22	0:10	0:00	359.8414 Q	2	124.00	15.00
Quantity	2.000 pg					361.8385 Q			
CAS									
Name: pcb157 hexa									
15	ana	16	34:26	0:10	0:00	359.8414 Q	2	124.00	15.00
Quantity	2.000 pg					361.8385 Q			
CAS									
Name: pcb169 hexa									
16	std	11	34:23	0:10	0:00	371.8817 Q	2	124.00	15.00
Quantity	5.000 pg					373.8788 Q			

TARGET COMPOUND LIBRARY LIST

Library name - pcb-cp

Entry	Type	Ref	Retention Time	Retention Window	Retention Offset	Masses	Isotope Ratios To	Isotope Ratios Theory	Isotope Ratios Tolerance
1	sur	1	18:45	0:10	0:00	301.9626 Q 303.9597 Q	2	77.00	15.00
Quantity		10.000 pg							
CAS Name: C13-pcb47 tetra									
2	sur	2	22:56	0:10	0:00	335.9237 Q 337.9207 Q	2	61.00	15.00
Quantity		10.000 pg							
CAS Name: C13-pcb111 penta									
3	ana	4	23:33	0:10	0:00	289.9240 Q 291.9194 Q	2	77.00	15.00
Quantity		2.000 pg							
CAS Name: pcb 77 tetra									
4	std	2	23:33	0:10	0:00	301.9626 Q 303.9597 Q	2	77.00	15.00
Quantity		5.000 pg							
CAS Name: C13-pcb77 tetra									
5	ana	6	24:41	0:10	0:00	323.8834 Q 325.8805 Q	2	61.00	15.00
Quantity		2.000 pg							
CAS Name: pcb118 penta									
6	std	2	24:41	0:10	0:00	335.9237 Q 337.9207 Q	2	61.00	15.00
Quantity		5.000 pg							
CAS Name: C13-pcb118 penta									
7	ana	8	26:00	0:10	0:00	323.8834 Q 325.8805 Q	2	61.00	15.00
Quantity		2.000 pg							
CAS Name: pcb105 penta									
8	std	2	26:00	0:10	0:00	335.9237 Q 337.9207 Q	2	61.00	15.00
Quantity		5.000 pg							
CAS									

TARGET COMPOUND LIBRARY LIST

Library name - pcb-cp

Entry Type	Ref	Retention Time	Retention Window	Retention Offset	Masses	Isotope Ratios To Theory	Isotope Ratios Tolerance
CAS Name: C13-pcb169 hexa							

Appendix C

METHOD 1613

Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS

Revision A
USEPA/Office of Water Regulations & Standards, Industrial Technology Division
Office of Water/ April, 1990

Appendix D

METHOD TO-9A

Sampling and Analysis Method for the Determination of Polychlorinated, Polybrominated, and Brominated /Chlorinated Dibenzo-p-Dioxins and Dibenzofurans in Ambient Air

USEPA 600/4-89-018
Compendium of Methods for Organic Air Pollutants,
Atmospheric Exposures Assessment Research Laboratory,
Research Triangle Park, N.C., September, 1995

Appendix E