A. DF Test Protocol

Performance Test Protocol for Dioxins/Furans

Group 1 Aluminum Furnace

MI Metals, Inc.

301 Commerce Blvd
Oldsmar, Florida 34677

Air Permit Facility 1030114 – Emission Unit ID 001

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Section 1 – Introduction

This performance test plan and protocol for Dioxins/Furans (DF) has been prepared for the MI Metals, Inc. (MI) facility located at 301 Commerce Blvd., Oldsmar FL 34677. The plan is in accordance with the requirements of 40 CFR Part 63 Subpart RRR – National Emission Standard for Hazardous Air Pollutants (NESHAP) for Secondary Aluminum Production (MACT). The plan has been prepared based on specific requirements in 40 CFR 63.1511, as well as the requirements set forth in 40 CFR 63.7(c) for a quality assurance and quality control program.

This facility is classified as a Secondary Aluminum Production Facility with a primary Standard Industrial Classification Code (SIC) 3354 Aluminum Extruded Products, and secondary SIC 3365 Aluminum Foundries.

MI Metals operates a furnace with a dimensional capacity of 25 tons of aluminum and an actual holding capacity of 22.5 tons. The furnace processes scrap aluminum containing painted or unpainted metal from any grades or Institute of Scrap and Recycling Industries (ISRI) codes listed in the Description of Scrap Aluminum (Appendix C) up to a maximum permitted charge feed amount based on operating cycle of 21.6 tons Al, up to a maximum permitted reactive flux rate based on operating cycle of 0.885 pounds of chlorine per ton aluminum charged (refer to **Appendix E** for Chlorine Flux Emissions Calculations), and lime feed rate of 10.4 pounds per hour. A batch operating cycle is defined in accordance with 40 CFR 63.1503 as the period beginning when the feed material is first charged and ending when the casting process is completed.

This facility is a non-major area source, since the potential emissions are less than 10 tons per year of any Hazardous Air Pollutant (HAP), less than 25 tons per year of any combination of HAPs, and less than 100 tons per year of any regulated air pollutant. As an area source it is required to comply with the USEPA's MACT emission limit for DF only. This facility is not subject to the USEPA's MACT emission limits for Particulate Matter (PM) and hydrogen chloride (HCl).

This performance test plan for DF will provide the strategy and the basis for furnace compliance demonstrations with the USEPA's DF standards of 2.1×10^{-4} grain DF per ton aluminum = 3.00×10^{-8} pound DF/ton aluminum and 2.89×10^{-7} ton DF/year as set forth in 40 CFR 63.1505(d)(iii) and 63.1505(i)(3).

A separate Performance Test Protocol for Particulate Matter (PM) and Visible Emissions (VE) has been prepared to comply with FDEP's PM emission limits in accordance with FDEP F.A.C. Rule 62-296.320(4)(a) and Rule 62-296.320(4)(b).

It is MI's intent to use results of this and future tests as documentation of compliance with FDEP's permit issued to Facility 1030114 to allow operation of the furnace with scrap aluminum listed in Description of Scrap Aluminum (**Appendix C**) up to a combined maximum of 60% by weight Tutu plus Toto, up to a maximum permitted charge feed amount based on operating cycle 21.6 tons aluminum, up to a maximum permitted reactive flux rate based on operating cycle of 0.885 pounds chlorine/ton aluminum charged, and lime feed rate of 10.4 pounds/hour at a 3 hour block average baghouse inlet temperature. Permit conditions and calculations are based on a batch operating cycle.

Section 2 – Source Descriptions

2.1 Introduction

This section provides a description of the facility source subject to the Secondary Aluminum NESHAPs including design specifications, operating information, and source-specific operating parameters to be monitored and recorded during source operation. Some of these parameters will be correlated to the regulated emissions and used to verify compliance with the standard on an ongoing basis. Typical Operating Cycles for Charges are summarized in **Appendix D**.

2.2 Remelt Furnace

MI operates a furnace with a dimensional capacity of 25 tons of aluminum and an actual holding capacity of 22.5 tons. The furnace processes scrap aluminum containing painted or unpainted metal from any grades or ISRI codes listed in the Description of Scrap Aluminum (**Appendix C**) up to a combined maximum permitted limit of 60% by weight Tutu plus Toto, up to a maximum permitted charge feed amount based on operating cycles of 21.6 tons Al, up to a maximum permitted reactive flux rate based on operating cycle of 0.885 pounds of chlorine per ton aluminum charged (refer to **Appendix E** for Chlorine Flux Emissions Calculations), and lime feed rate of 10.4 pounds per hour. The furnace is never emptied during casting since there is always a heel left for the next charge. This heel accounts for the difference between the actual holding capacity and the charge feed amount. Essentially, the furnace is continually alternating between being charged and tapped and is never emptied. The furnace also experiences holding phases during which the level of molten aluminum is simply being maintained and aluminum is neither being added or removed.

This melting/holding furnace has no charging side wells and is classified as a Group 1 furnace because it processes coated and non-coated aluminum. The furnace is equipped with a baghouse air pollution control device that includes lime coated fabric filters with an intermittent lime injection feeder. Lime addition is monitored daily to ensure that the lime feed rate is set at 10.4 pounds per hour and that a total count of five (5) 50 pound bags of lime per day are used as established by the DF test.

The only fuel is natural gas that is fired through a set of two 10 million British thermal units per hour (mmBTU/hr) burners for a total of 20 mmBTU/hr. Process and combustion emissions from the furnace are vented through a single flue stack. The furnace processes coated and uncoated aluminum scrap alloy listed in Description of Scrap Aluminum (**Appendix C**).

The furnace operates as a continuous batch process, with aluminum scrap being placed on the deck of the charging tabled by means of forklifts or bobcats. There is a maximum of 3 charges during the course of the day. An alloying metal may be added to the molten aluminum depending upon the type of product being manufactured. The front door of the furnace is opened immediately before placing the charging table into position and is closed as soon as the charging is finished.

Reactive chlorine flux is injected into the furnace molten metal bath with a degassing wand during a 15 minute period just prior to casting. The furnace bath is fluxed as needed with a maximum of 30 pounds Amlox 72F or equivalent per 21.6 tons aluminum or a maximum of 60 pounds Amlox 72F (or equivalent) per day. This equates to a maximum of 0.885 pounds chlorine per ton of aluminum charged based on operating cycle. The maximum potential stoichiometric amounts of HAP produced from these fluxes are 7.17 tons HCl per year and 7.17 tons total HAPs per year. Refer to **Appendix E** for Chlorine Flux Emissions Calculations.

Section 3 – Objectives

A Group 1 aluminum furnace charging other than "clean charge" at area sources is required to meet a DF emissions limit. A Group 1 furnace is subject to a limit of 2.1×10^{-4} grain DF per ton aluminum charged in accordance with 40 CFR 63.1505(i).

This emission test methodology is designed to establish the highest level of DF emissions possible from the furnace under normal operating conditions from each source at a 3-hour block average baghouse inlet temperature.

The Emission Capture/Collection & Closed Vent Systems Annual Inspection form (**Appendix G**) will be completed prior to this performance test to ensure systems compliance with 40 CFR 60.1506 (c).

Section 4 – Performance Test Conditions and Furnace Operation

4.1 Introduction

This section provides the rationale used in establishing performance test conditions and for determining the number of test runs to be performed. In addition, it defines operating parameters proposed for the furnace during testing, sampling and monitoring methods, and how the data gathered during the performance test will define the furnace's operating limits and demonstrate ongoing compliance with the emission limit.

4.2 Testing Rationale

This performance test for DF will be conducted while operating at the highest charge feed amount of 60% by weight of ISRI Code Tutu (highest potential emission), and the greatest reactive flux rate. Refer to **Appendix F** for summary of Operating Cycle Comparison for DF Testing. Daily operation at equal or lower operation levels will ensure ongoing compliance since performance test results would have passed regulatory standards. The performance test will be conducted as much as possible during daylight hours to provide safe working conditions and to obtain accurate measurements/readings.

The USEPA's DF performance test sampling will be conducted during an operating cycle when the feed charge amount will be at the maximum of 21.6 tons aluminum based on operating cycle, and include the maximum flux rate of 30 pounds Amlox 72F or equivalent. The 30 pounds Amlox 72F/21.6 tons aluminum is equivalent to 0.885 pounds chlorine/ton aluminum charged. There will be 3 separate DF performance test runs on 3 different work days. The DF test runs will be approximately 10 hours each in duration to cover an entire DF test operating cycle. Refer to **Appendix F** for summary of Operating Cycle Comparison for DF Testing. Actual start/stop times and charge weights may vary depending on the process operations of the day. Operating limits for the furnace's charge feed amount, reactive flux feed rate, lime feed rate, and 3-hour block average baghouse inlet temperature will be established by averaging the results of the 3 DF performance test runs.

The tons aluminum of charge feed amount based on operating cycle, pounds chlorine/ton aluminum of reactive flux rate based on operating cycle, % by weight of Tutu, pounds lime/hour, and 3 hour block average baghouse inlet temperature will be calculated for all three DF performance test runs based on the following recorded information:

- The total quantity (in tons) of all scrap aluminum charged
- The total duration (in hours) of the *operating cycle*
- The total quantity (in tons) of Tutu material charged
- The quantity (in pounds) of flux added to charge
- The quantity (in pounds) of lime added per day
- The 3-hour block average baghouse inlet temperature (in °F)

A calibrated scale accurate to 1% or better will be used to weigh charge material. Equivalent potential amount of chlorine from fluxes will be calculated from stoichiometric equations. The weight of fluxes and lime will be based on manufacturer's pre-weighed packages.

4.3 Stack Parameters

Baghouse stack gas emission parameters will be measured using USEPA Reference Methods for Sampling of Stationary Sources. Specifically, USEPA Reference Method 1 will be used to establish the sample and velocity traverse points. USEPA Reference Method 2 will be used to determine the stack gas differential pressure (from which the stack gas velocity can be calculated). USEPA Reference Method 3 will be used to determine the stack gas composition by assigning a value of 30.0 for dry molecular weight, in lieu of actual measurements for processes burning natural gas, while USEPA Reference Method 4 will be used to measure the stack gas moisture content. The baghouse vertical emission stack has a 4 feet diameter with a combination permanent/temporary sampling platform in accordance with 62-297, F.A.C. (Refer to drawing in **Appendix B**).

4.4 Dioxins/Furans

Baghouse stack gas emissions will be sampled and analyzed for polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDF) utilizing an USEPA Reference Method 23 sampling train. Therefore, the performance test for each batch process will consist of three separate runs for approximately 10 hours each in order to test an entire operating cycle. 12 sample points will be located and sampled per traverse for each sample port for DF. Each traverse point will be sampled for 25 minutes as the sample probe is started all the way out and pushed all the way into the stack (total 300 minutes per port). One sample port will be tested at a time. A diagram showing the testing port locations is included as **Appendix B**. A batch operating cycle is defined in accordance with 40 CFR 63.1503 as the period beginning when the feed material is first charged and ending when the casting process is completed.

Note: *MI requested approval from the USEPA/FDEP/PDEM to modify EPA Method 23 – Dioxins and Furans (Refer to **Appendix I**) to allow the laboratory to combine the toluene rinse with the methylene chloride/acetone rinse for analysis of each DF test run. This will result in only 3 lab analyses for DF (1 combined test run for each test run x 3 test runs). MI will implement this modification to EPA Method 23 upon USEPA/FDEP/PDEM approval.*

4.5 Baghouse Operating Conditions

Baghouse inlet temperatures will be recorded to establish the 3-hour block average, lime addition will be recorded, and baghouse pressure drop will be monitored to establish the required conditions parameters for the Operation Monitoring and Maintenance (OM&M) Plan.

4.6 Ongoing Compliance Demonstration

Following demonstrated compliance with the DF emission limits requirements of 40 CFR 63.1505(i), the operating conditions of the performance test will become the revised furnace operating limits in accordance with the FDEP permit issued to Facility 1030114. The facility OM&M Plan will be revised as necessary to incorporate these operating limit changes. The OM&M Plan will establish the monitoring parameters and recordkeeping requirements to demonstrate ongoing compliance.

Section 5 – Compliance Test Summary and Schedule

A summary of the performance test compliance testing purpose and proposed schedule are as follows:

- Testing is being performed to satisfy requirements of 40 CFR 63, Subpart RRR (Secondary Aluminum Production NESHAPs).
- Testing is being conducted to demonstrate compliance with the DF emission limits specified for the remelt furnace as well as set operating parameters to demonstrate ongoing compliance.
- The testing program will be conducted in accordance with FDEPs permit issued to facility 1030114. A daily schedule is provided in Table 1. FDEP and PDEM will receive notification from MI of actual test dates at least 15 days prior to testing.
- Test results will be submitted by MI to the FDEP and PDEM within 45 days of last test completion.

Table 1
Proposed Compliance Testing Schedule (DF and PM/VE Testing)

Sequence of Events		Tasks
First Week	1st Day	Arrive on the site, set up equipment, and prepare DF Test Run #1
	2nd Day	Perform DF Test Run #1 on the furnace
	3rd Day	Process DF Test Run #1 sample and Perform DF Test Run #2 on the furnace
	4th Day	Process DF Test Run #2 sample and Perform DF Test Run #3 on the furnace
	5th Day	Process DF Test Run #3 sample
Second Week	1st Day	Arrive on the site, set up equipment, and prepare PM Test Run #1
	2nd Day	Perform PM test run #1 and VE test on furnace
	3rd Day	Perform PM test run #2
	4th Day	Perform PM test run #3 and dismantle test equipment and depart

Note: In the event of a malfunction or mishap, variance to the above schedule may be granted at the discretion of the EPA, FDEP, or PDEM.

Section 6 – Quality Assurance

6.1 Internal Quality Assurance

Internal quality procedures will be used to review and control data gathered by MI personnel and contractors during the testing events. These procedures will cover such information as emission tests, data parameters for process and emission control units, raw material samples, record keeping, and reporting. Specific Quality Control (QC) procedures will be followed to ensure the continuous production of valid data throughout the course of this test program. The QC checks and procedures describe in this section represent an integral part of the overall sampling and analytical scheme. Strict adherence to prescribed procedures is quite often the most applicable QC check. A discussion of both the sampling and analytical QC checks that will be utilized during this program is represented below.

6.1.1 Chain-Of-Custody (COC) Procedures

The environmental testing firm's field personnel will be responsible for labeling each individual sample and completing a COC sheet to track samples through the analysis process.

6.1.2 Source Test Preparation

MI will provide or, as required, make necessary facilities available as follows:

- Sampling ports located as required by the regulations for the applicable test methods
- Safe sampling platform(s)
- Safe access to sampling platform(s)
- Utilities for sampling and testing equipment

6.1.3 Source Test Analysis

All source testing analysis will be completed per the requirements of the referenced test methods. The applicable test methods are identified in Section 4.

6.1.4 Leak Check Procedures

All leak check procedures will be completed per the requirements of the referenced test methods.

6.1.5 Equipment Calibration

All process equipment calibration will be completed in accordance with the OM&M Plan.

6.1.6 Analytical Instrumentation

All analytical instrumentation will be as identified in the requirements of the referenced test methods.

6.1.7 Methods Validation

Performance materials (samples blanks and spikes) will be requested at least 30 days prior to the test date. Contacts for obtaining these materials are listed at 40 CFR 63.7(c)(4)(i). All method validation will be completed per the requirements of the referenced test methods.

6.1.8 Record Keeping

All record keeping will be done in accordance with the OM&M Plan.

6.1.9 Reporting

All reporting will be done in accordance with FDEPs permit issued to Facility 1030114. The "Initial Notification of Compliance Status Report" will be submitted within 60 days following the compliance date for the affected source. This report will summarize all of the affected data and establish the monitoring parameters values that will be tracked to demonstrate continuous compliance with the standard.

6.2 External Quality Assurance

External quality assurance (QA) procedures will be established and used by outside testing firms and laboratories. All contractors will comply with requirements of their QA programs during the testing event. The environmental testing firm will follow the QA methods published in the *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume III (EPA600/4-77-0276).*

Information or data generated by outside testing firms or laboratories will be handled and maintained at a minimum per the previously described internal quality procedures.

6.3 Data Control Objectives

The test plan is to identify data quality objectives that are associated with the monitoring of process parameters, the measurement of direct process emissions, and other process observations that are made to demonstrate compliance with the NESHAPs.

Operation of the remelt furnace requires that specific operating parameters be monitored during the performance test. The data collected must be evaluated to address the data quality objectives that are associated with the measurement, collection, and data processing activities.

6.3.1 Continuous Monitoring System

The systems that are operated to collect and monitor the affected source or emission unit to demonstrate compliance are classified as Continuous Monitoring Systems (CMS). A CMS is defined as a comprehensive term that may incorporate, but is not limited to, continuous emission monitoring instruments, continuous opacity monitoring systems, continuous parametric monitoring systems, or other manual or automatic monitoring devices that are used to demonstrate compliance on a continuous basis as defined by the regulations. The following CMSs will be operated to demonstrate compliance with the NESHAPs operational requirements for the MI facility.

- Charge amount will be recorded on the Furnace Charge Log (**Appendix H**)
- Baghouse inlet temperature will be recorded every 15 minutes and the average temperature over a 3 hour period will be calculated.
- Lime addition monitoring procedures will include reading the lime feed rate setting and counting the total number of 50 pound bags of lime that have been used per day. Results of lime addition will be recorded on the Lime Feed Inspection/Maintenance Completion Log (**Appendix H**).
- Baghouse pressure drop will be recorded on the Baghouse Inspection/Maintenance Completion Log (**Appendix H**)
- Reactive flux feed will be recorded on the Daily Operation Log – Reactive Flux Feed Rate (**Appendix H**).

The operating parameters for this aluminum furnace based on the Performance Test results will be established in the OM&M Plan.

Appendix A
CMS Performance Evaluation Test Plan

CMS Performance Evaluation Test Plan

Facilities that are subject to NESHAPs that have operational requirements that must be monitored using CMSs are required to prepare this additional plan. The CMSs that are associated with this plan are as follows:

- Furnace charge feed amount
- Baghouse inlet temperature
- Baghouse lime addition
- Baghouse pressure drop
- Reactive flux feed rate

The operating parameters for this aluminum furnace based on the Performance Test results will be established in the OM&M Plan.

Scope of the plan as specified by 40 CFR Part 63.8(e).

This plan covers the performance evaluation of multiple CMSs as specified for this source in the NESHAPs for Secondary Aluminum Production (40 CFR Part 63 Subpart RRR). The types of systems installed to address these CMSs have been listed above.

The issues that affect the evaluation of the CMS devices will be observed and recorded as specifically identified in this plan. USEPA guidance documents (e.g. Compliance Assurance Monitoring (CAM) Technical Guidance) and the manufacturers' specifications of the selected monitoring devices are being used to establish this plan.

General Operation Description

Furnace Charge Log, Lime Feed Inspection/Maintenance Completion Log, Baghouse Inspection/Maintenance Completion Log, and the Daily Operation Log – Reactive Flux Feed Rate (**Appendix H**) are to be completed in accordance with the OM&M Plan.

CMS Evaluation Program Objectives

The furnace charge feed amount based on the operating cycle is to be at the maximum of 21.6 tons aluminum, the percent Tutu is to be at the maximum 60% by weight, the reactive flux feed rate is to be at the maximum 0.885 pounds chlorine/ton of aluminum, and the lime feed rate is to be 10.4 pounds per hour during the CMS evaluation program.

CMS Evaluation Program Summary

The CMS system will be checked and/or calibrated as required in accordance with the OM&M Plan.

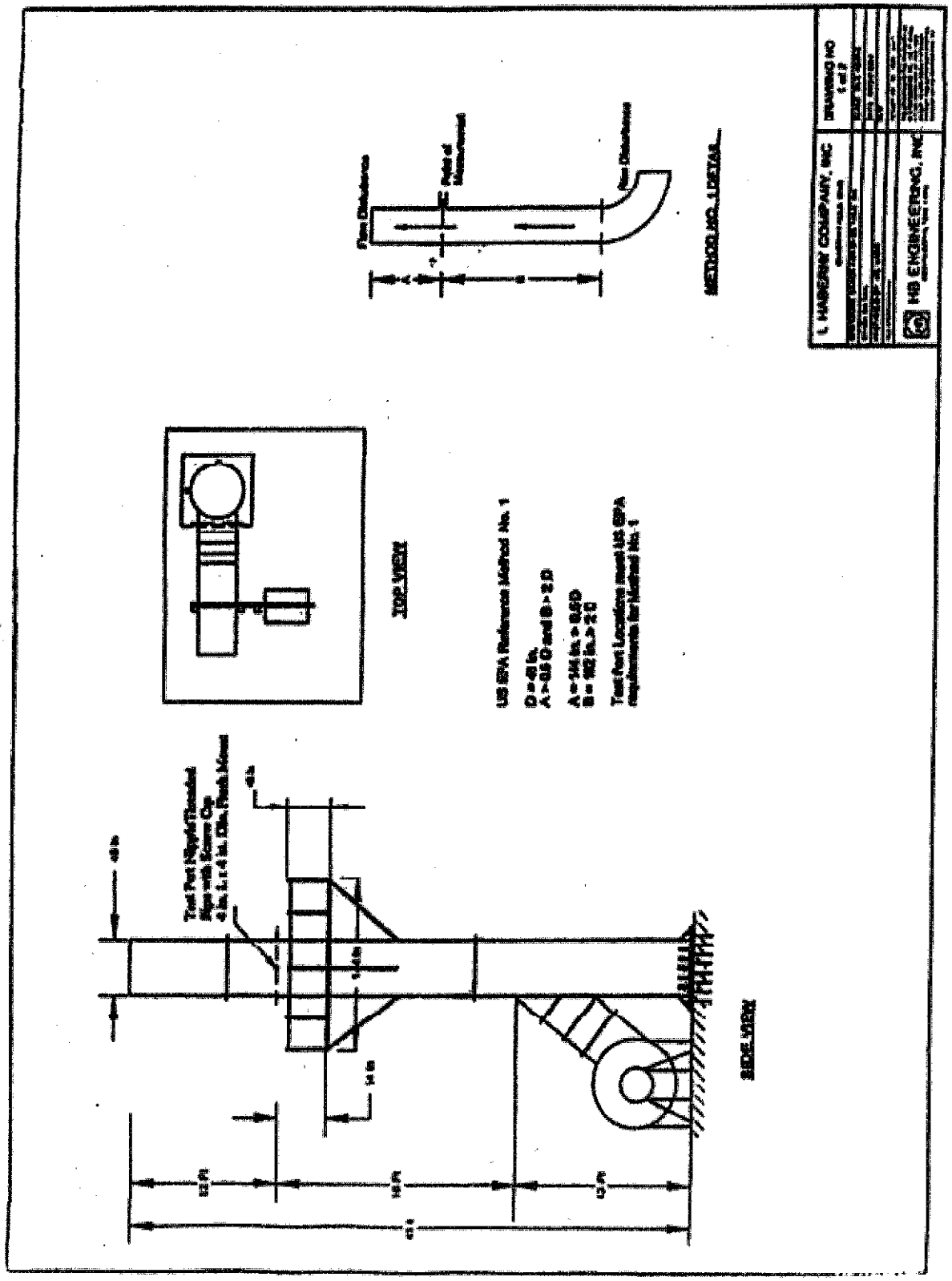
CMS Data Quality Objectives

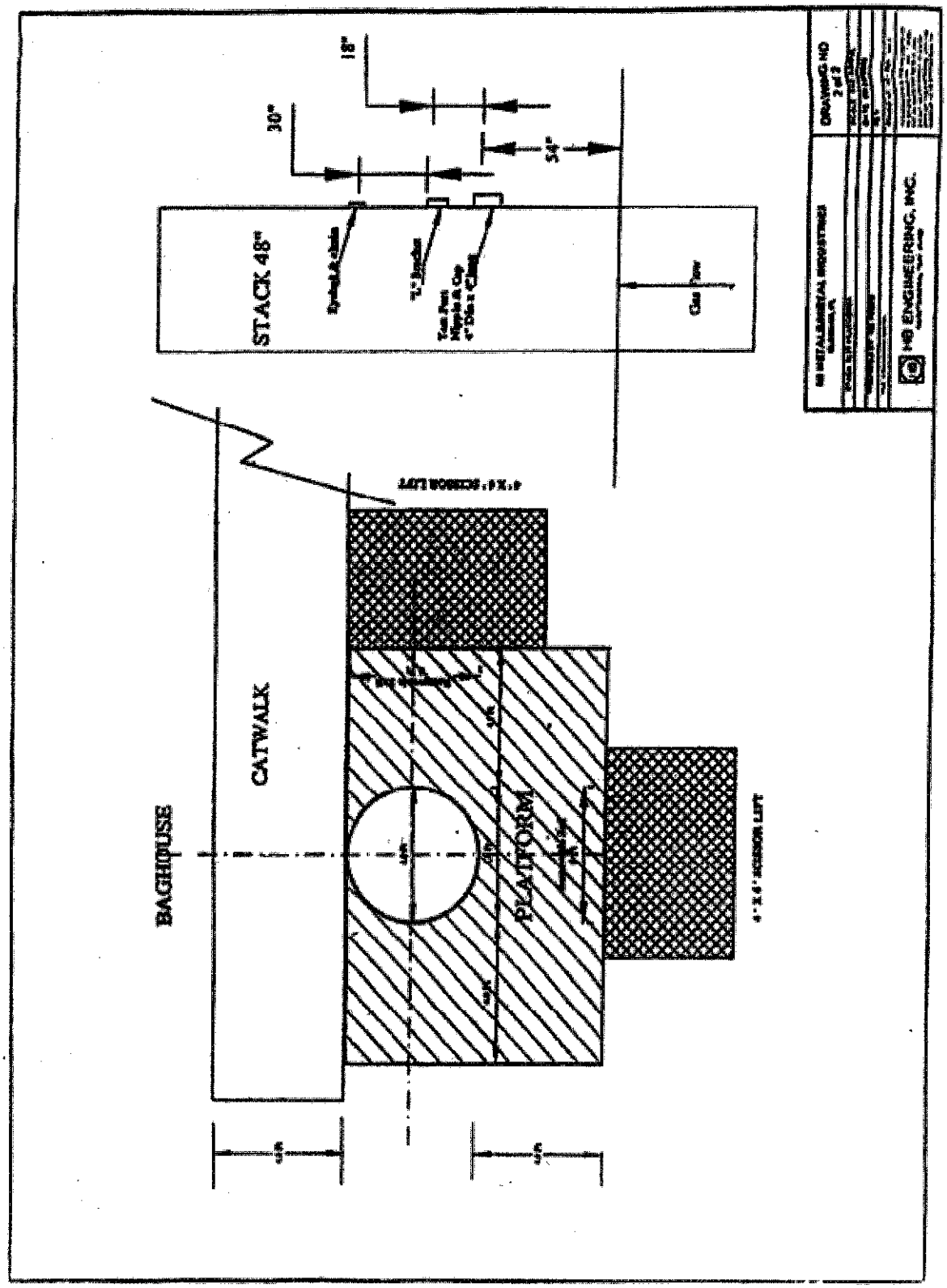
The observations that result from this plan will be recorded assigning each record with the name of the device being monitored, the time of the observation, the initials of the individual making the observation, and the description of the observation (numeric readings will be accompanied with appropriate units).

If applicable, regulatory personnel will be offered a briefing of the critical systems location and the planned schedule of events on the day of the actual performance testing.

The environmental testing contractor will be provided all relevant information regarding the monitoring devices during the setup period for the performance test.

Appendix B
Stack Test Port / Platform Diagram


TOP VIEW
SIDE VIEW
METHOD NO. 1 DETAIL
US EPA Reference Method No. 1
L. HANSONY COMPANY, INC
HB ENGINEERING, INC


STACK 48"
30"
18"
54"
CATWALK
BAGHOUSE
PLATFORM
HB ENGINEERING, INC.

Appendix C
Description of Scrap Aluminum

Grades

Aluminum Extrusions (includes bales, bin, bag, shreds and butt ends) – shall consist of clean aluminum extrusions including window & door frames. Must be free of iron inserts, screw, plastic, rubber or other foreign materials.

Low Copper Aluminum – shall consist of clean, uncoated aluminum plate, may include clips or punching. ISRI grade Taboo may be included in this grade.

New Beverage Can Stock – shall consist of new clean pre-consumer aluminum can stock (printed or unprinted) and may include clips or punching skeletons, & cans in various states of production but may not include whole cans from packaging lines. Equivalent to ISRI code Take.

Remelt Aluminum Ingot – shall consist of remelted aluminum scrap from a sweat furnace operation & poured into a uniform pig or ingot block with a minimum weight of 25 pounds, and a maximum weight of 75 pounds. Must be free of slag or dross materials and prepared in a uniform material handleable form. Similar to ISRI code Throb.

Remelt Aluminum Sows – shall consist of remelted aluminum scrap for a sweat furnace operation & poured into a uniform slabs or sow blocks with a minimum weight of 500 pounds, and a maximum weight of 2,200 pounds. Must be free of slag or dross materials and prepared in a uniform material handleable form. Similar to ISRI code Throb.

Bare Aluminum Wire – Shall consist of clean aluminum wire free of iron or insulation. ISRI code Tassel, Taste, Talon, and Tann may be included in this grade.

Aluminum Nodules – shall consist of clean aluminum wire recovered from a chopping operation and must be free of iron, copper, & brass wire, aluminum hair wires and free of dirt, oil, and foreign materials. Equivelant to ISRI code Tall.

ISRI (Institute if Scrap and Recycling Industries) Codes

Taint/Tabor – Clean Mixed Old Alloy Sheet Aluminum – shall consist of clean old alloy aluminum sheet of two or more alloys, free of foil, venetian blinds, casting, hair wire, screen wire, food, or beverage containers, radiator shells, airplane sheet, bottle caps, plastic, dirt and other non-metallic items. Oil and grease not to total more than 1%. Up to 10%Tale permitted.

Take – New Aluminum Can Stock – shall consist of new low copper aluminum can stock and clippings, clean lithographed or not lithographed, and coated with clear lacquer but free of lids with sealers, iron, dirt and other foreign contamination. Oil not to exceed 1%.

Tall – E.C. Aluminum Nodules – shall consist of clean E.C. aluminum, chopped or shredded, free of screening, hair-wire, iron, copper, insulation, and other non-metallic items. Must be free of minus 20 mesh material. Must contain 99.45% aluminum content.

Talon - New Pure Aluminum Wire & Cable – shall consist of new, clean, unalloyed aluminum wire or cable free from hair wire, ACSR, wire screen, iron, insulation and other non-metallic items.

Tann – New Mixed Aluminum Wire & Cable - shall consist of ne, clean, un-alloyed aluminum wire or cable free from hair wire, ACSR, wire screen, iron, insulation and other non-metallic items.

Tata – New Production Aluminum Extrusions – shall consist of one allow (typically 6063). Material (includes bales, bins, bags and shreds) may contain "butt ends" from the extrusion process but must be free of any foreign contamination. Anodized material is acceptable. Painted material or other alloys other than 6063 must be agreed upon by buyer and seller.

Toto – Aluminum Extrusion "10/10" – shall consist of new production and old/used 6063 extrusions (includes bales, bins, bags and shreds) that may contain up to (but not exceed) 10% painted extrusions and 10% 6061 alloy extrusions. Must not contain other alloys of aluminum. Material should be free of zinc corners, iron attachments, felt, plastic, paper, cardboard, thermo break, dirt and other contaminants.

Tutu – Aluminum Extrusion Dealer Grade – shall consist of old aluminum extrusion typically of alloy 6063, 6061, or 7075 that contain more than 10% painted extrusions (includes bales, bins, bags and shreds). Material must be free of of iron, thero break, saw chips, zinc corners, dirt, paper, cardboard, and other foreign contamination.

Appendix D
Typical Operating Cycles for Charges

Typical Operating Cycles for Charges

Shorter Operating Cycle

1. Operating cycle begins when aluminum scrap is initially added into furnace.
2. A maximum of 8.8 – 17.3 tons charge feed amount of scrap is added into the furnace.
3. Charge feed consists of approximately 40 -60% by weight of baled, binned, bagged and/or shredded extrusion from ISRI Codes Toto/Tutu (includes painted material).
4. Balance of charge material is mill finish, primary ingot, and billet butt (unpainted materials) from Grades and ISRI Codes listed in the Description of Scrap Aluminum (Appendix A).
5. A maximum of ten pounds of Amlox 72F or equivalent flux is added during the 15 minutes before the casting. This is equivalent to 6.37 pounds of chlorine or approximate flux rate of 0.368 to 0.741 pounds of chlorine/ton charge.
6. Casting begins at approximately 2 – 6 hours after cycle begins.
7. Operating cycle ends when casting ends at approximately 4 – 10 hours after operating cycle begins.

Longer Operating Cycle

1. Operating cycle begins when aluminum scrap is initially added into furnace.
2. A maximum of 21.6 tons charge feed amount of scrap is added into the furnace.
3. Charge feed consists of approximately 40 -60% by weight of baled, binned, bagged and/or shredded extrusion from ISRI Codes Toto/Tutu (includes painted material).
4. Balance of charge material is mill finish, primary ingot, and billet butt (unpainted materials) from Grades and ISRI Codes listed in the Description of Scrap Aluminum (Appendix A).
5. A maximum of twenty pounds of Amlox 72F or equivalent flux is added during the 15 minutes before the casting. This is equivalent to 12.74 pounds of chlorine or approximate flux rate of 0.590 pounds of chlorine/ton charge.
6. Total aluminum melting time is approximately 8 – 10 hours.
7. The furnace is placed on "hold mode" for approximately 0 – 14 hours before casting. No charge or flux is added during this hold period.
8. Casting begins at approximately 8 – 20 hours after cycle begins.
9. Operating cycle ends when casting ends at approximately 10 – 20 hours after operating cycle begins.

Appendix E
Air Emission Calculations

Air Emission Calculations

Refer to Safety Data Sheet: Amlox 72F is maximum 60% Magnesium Chloride + 40% Potassium Chloride.

Chemistry:

Magnesium Chloride	$MgCl_2$	Atomic Weight (g/mol)
	Magnesium	1 x 24.305 = 24.305
	2 x Chloride	2 x 35.453 = 70.906
	Total	**95.211 g/mol**

Weight Fraction ($Cl_2/MgCL_2$) = 70.906 ÷ 95.211 = **0.7447**

Potassium Chloride	KCl	Atomic Weight (g/mol)
	Potassium	1 x 39.0983 = 39.0983
	Chloride	1 x 35.453 = 35.453
	Total	**74.5513 g/mol**

Weight Fraction (Cl/KCl) = 35.453 ÷ 74.5513 = **0.4756**

Conversion Factor Ratio:

$$\frac{\text{lbs Cl}}{\text{lb Amlox 72F}} = [\%\ MgCl_2 \times \text{Weight Fraction}(Cl_2/MgCl_2)] + [\%\ KCl \times \text{Weight Fraction}(Cl/KCl)]$$

= [0.6 x 0.7447] + [0.4 x 0.4756]

= **0.637** lbs Cl per lb Amlox 72F

$$\frac{\text{Max lbs Cl}}{\text{ton Al}} = [30\ (\text{lbs Amlox 72F}) \times 0.637\ (\text{lbs Cl/lb Amlox 72 F})] \div [21.6\ (\text{ton Al/day})]$$

= **0.885** Max lbs Cl per ton Al charged

Appendix F
Operating Cycle Comparison

OPERATING CYCLE COMPARISON FOR DIOXINS/FURANS (DF) TESTING

Parameter	Typical *Shorter* Operating Cycle	Typical *Longer* Operating Cycle	DF Performance Test Operating Cycle
Total Scrap Aluminum Charge Feed Amount (ton)	≤ 8.8 to 17.3	≤ 21.6	* ~ 21.6
Charge Type	~ 40-60% by weight of baled, bin, bag, and shredded extrusion material from ISRI Codes Toto/Tutu. Remainder material is mill finished, ingot, and butt (unpainted material) from Grades and ISRI Codes listed in the Description of Scrap Aluminum	~ 40-60% by weight of baled, bin, bag, and shredded extrusion material from ISRI Codes Toto/Tutu. Remainder material is mill finished, ingot, and butt (unpainted material) from Grades and ISRI Codes listed in the Description of Scrap Aluminum	** 60% by weight of baled, bin, bag, and shredded extrusion material from ISRI Codes Toto/Tutu. Remainder material is mill finished, ingot, and butt (unpainted material) from Grades and ISRI Codes listed in the Description of Scrap Aluminum
Amlox Flux / Equiv. (lb/operating cycle)	**≤ 10**	**≤ 20**	**30**
Equiv. Amount of Chlorine (lb Cl/operating cycle)	**~6.37** (6.37 = 10 x 0.637)	**~12.74** (12.74 = 20 x 0.637)	**19.11** (19.11 = 30 x 0.637)
Flux Rate (lb Cl/ton Al charged)	**~0.724** (0.724 = 6.37/8.8) **~0.368** (0.368 = 6.37/17.3)	**~0.590** (0.590 = 12.74/21.6)	*** **~0.885** (0.885 = 19.11/21.6) (Testing rate of 0.885 is the permitted maximum)
Flux addition	During 15 minutes before casting begins	During 15 minutes before casting begins	During 15 minutes before casting begins
Melt Process (hrs)	~2-4	~8-10	~8-10
Holding Mode (hrs)	0	~0-10	0
Operating Cycle (hrs)	~4-10	~10-24	~10
Process Rate (ton Al/hr)	~1.23 – 2.2	~0.9 - 2.16	~2.16 (2.16 = 21.6/10) (Testing rate of 2.16 is within 10% of the permitted maximum (2.2))

Comments: * - Highest charge feed amount (generates the permitted maximum process rate based on a ten hour operating cycle)

** - Highest potential emissions (maximum permitted rate during testing)

*** - Highest flux rate (maximum permitted rate during testing)

Operating cycle is defined in accordance with 40 CFR 63.1503 as the period beginning when the feed material is first charged and ending when the casting process is completed.

No charge or flux is added during any holding period.

Maximum potential Dioxin and Furans emissions occur from paint on the extrusions and chlorine flux.

Daily operation will not exceed permitted limits.

Appendix G
Emission Capture/Collection & Closed Vent System
Annual Inspection

MI Metals – Oldsmar – Permit 1030114
Emission Capture/Collection & Closed Vent System
Annual Inspection

Print Inspector Name_____Signature_____Date_____

Emission Unit: Reverberatory Furnace_____ Emission Unit ID: 001_____

Type of Capture Collection System: Enclosing Hood and Baghouse Collection System__

Inspect all sides of the capture/collection system hood/vestibule to ensure all sides are intact and free of any holes.

Inspection Results: _____

_____

Verify that emissions are being drawn into the hood of the capture/collection system. Make note of any visible emissions escaping from the hood.

Inspection Results: _____

_____

Inspect all sides of the ductwork of the capture/collection system for any holes that need to be repaired.

Inspection Results: _____

_____

Inspect the length of the ductwork of the capture/collection system for any discontinuities that need to be repaired.

Inspection Results: _____

_____

Verify that there are no visible emissions escaping from the ductwork of the capture/collection system.

Inspection Results: _____

_____

Verify air flow rate of capture/collection system using EPA Reference Methods 1 and 2. Record results and compare to ACGIH minimum flow rate calculations.

Inspection Results: _____

_____

Capture/Collection System Repair Summary

Print Inspectors Name: _____ Inspection Date: _____

Area to be repaired	Repair to be made	Schedule Repair Date	Repair Complete Date	Initial When Complete

Appendix H
Log Forms

MI Metals – Oldsmar
Permit 103011 EU ID 001
Daily Operation Log – Operating Cycle Process Rate

Month_____ **Year**_____

Operating Max of 1.35 tons aluminum processed/hour based on operating cycle.

Day	First Charge					Second Charge					Third Charge					total/day	Initial
	Tons Al process	Cycle begin am pm	Cycle end am pm	Cycle hours	Ton Al \ hr	Tons Al process	Cycle begin am pm	Cycle end am pm	Cycle hours	Ton Al \ hr	Tons Al process	Cycle begin am pm	Cycle end am pm	Cycle hours	Ton Al \ hr	Amlox max 60 lb	
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2																	
3																	
4																	
5																	
6																	
7																	
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31																	

Conversion Factor: 1 lbs Amlox 72F = 0.655 lbs HCl

	Hours	Tons Al	Lbs Amlox	Tons HCl	Tons HAP	Tons PM	Tons DF
Month							
12 Month							
Max Limit	8760	19,272	N/A	7.17	7.17	25.6	2.89×10^{-7}

MI Metals – Oldsmar
Permit 103011 EU ID 001
Furnace Charge Log

Date Charged [ ] 1st/2nd/3rd [ ] Alloy [ ] Batch# [ ]

Weight Pounds Al	Bale			Ingot	Tote Bin/Bag			
	Painted Tutu	Painted Toto	Mill Finish	Primary Ingot	Billet Butt	Painted Tutu	Painted Toto	Mill Finish
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3								
4								
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20								
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22								
23								
24								
25								
Total Tons Al								

Tons Al Charge Feed Amount Based on Operating Cycle [ ]

Max Allowed Charge Feed Amount Based on Operating Cycle = 21.6 tons Al

% Tutu [ ] %Toto [ ] Max Allowed Tutu + Toto = 60%

Total Hours Operating Cycle [ ]

Tons Al/Hour Process Rate Based on Operating Cycle [ ]

Max Allowed Process Rate Based on Operating Cycle = 1.35 Tons Al/Hour

Sign _____

MI Metals – Oldsmar
Permit 103011 EU ID 001
Daily Operation Log – Reactive Flux Rate

Month_____ Year_____

Amlox 72F or equivalent is reactive chlorine flux injected over 15 minute period; Conversion factor 0.637 lbs Cl/lbs Amlox 72F.
Operating Max of 0.815 lbs Cl/ton Al based on operating cycle.

Day	First Charge							Second Charge							Initial
	Charge Begin	Flux Begin am pm	Flux End Cast Begin am pm	Lbs Amlox 15 Min	Lbs Cl X 0.637	Tons Al	Lbs Cl Ton Al	Charge Begin	Flux Begin am pm	Flux End Cast Begin am pm	Lbs Amlox 15 Min	Lbs Cl X 0.637	Tons Al	Lbs Cl Ton Al	
1															
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MI Metals – Oldsmar
Permit 103011 EU ID 001
Daily Operation Log – Reactive Flux Rate

Month_____ Year_____

Amlox 72F or equivalent is reactive chlorine flux injected over 15 minute period; Conversion factor 0.637 lbs Cl/lbs Amlox 72F. Operating Max of 0.815 lbs Cl/ton Al based on operating cycle.

Day	Third Charge (if necessary)							Initial
	Charge Begin	Flux Begin am pm	Flux End Cast Begin am pm	Lbs Amlox 15 Min	Lbs Cl X 0.637	Tons Al	Lbs Cl Ton Al	
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MI Metals – Oldsmar
Permit 103011 EU ID 001
Lime Feed Inspection/Maintenance Completion Log

Month_____ **Year**_____

Monitor sittings/Inspect Feeder at the beginning of each shift

Day	First Shift			Second Shift			Third Shift			50 Lbs Bags Used (5/Day)	Total Lime Used (250 lb/day)	Deviation/Blockage, Cause, Corrective Action Taken. *(inspect every 4 hours for 3 days after blockage)*
	Lbs/Hr 10.4	Free Flow	Initial	Lbs/Hr 10.4	Free Flow	Initial	Lbs/Hr 10.4	Free Flow	Initial			
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MI Metals – Oldsmar
Permit 103011 EU ID 001
Lime Feed Inspection *After Blockage* Completion Log

Date Blockage Occurred_____

Monitor sittings/Inspect Feeder Every 4 Hours for 3 Days After Blockage

Time	Day 1			Day 2			Day 3		
	Lbs/Hr 10.4	Free Flow	Initial	Lbs/Hr 10.4	Free Flow	Initial	Lbs/Hr 10.4	Free Flow	Initial
12 am									
4 am									
8 am									
12 pm									
4 pm									
8 pm									

MI Metals – Oldsmar
Permit 103011 EU ID 001
Process Inspection/Maintenance Completion Log

Month_____ Year_____

Sign after work completed per OM&M Plan

Day	Dailyt			Weekly				Monthly			Initial
	Check/Refill Water	Check Al/Gas Leaks	Check Visible Emissions	Add Algaecide Scale Chem	Check Refractory	Clean Air Filter	Cleanup Area	Remove Sludge/Dross	Grease Motor/Pumps	Check Unit Labeling	
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MI Metals – Oldsmar
Permit 103011 EU ID 001
Baghouse Inspection/Maintenance Completion Log

Month_____ Year_____

Day	Daily								Monthly			Annual			3 Year	Initial
	Pressure < 8" W.C.			Temperature ≤ 186° F			Mal-function	Equip Operation	Buildup/ Leaks	Oil / Grease	Detector/ Alarm	Bag Condition	Shaker	Fan / Housing	Replace Worn Bags	
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Appendix I
EPA Method 23
Dioxin and Furans

Step 1 METHOD 23—DETERMINATION OF POLYCHLORINATED DIBENZO-P-DIOXINS AND POLYCHLORINATED DIBENZOFURANS FROM STATIONARY SOURCES

Step 2 1. Applicability and Principle

1.1 Applicability. This method is applicable to the determination of polychlorinated dibenzo-p-dioxins (PCDD's) and polychlorinated dibenzofurans (PCDF's) from stationary sources.

1.2 Principle. A sample is withdrawn from the gas stream isokinetically and collected in the sample probe, on a glass fiber filter, and on a packed column of adsorbent material. The sample cannot be separated into a particle vapor fraction. The PCDD's and PCDF's are extracted from the sample, separated by high resolution gas chromatography, and measured by high resolution mass spectrometry.

Step 3 2. Apparatus

2.1 Sampling. A schematic of the sampling train used in this method is shown in Figure 23-1. Sealing greases may not be used in assembling the train. The train is identical to that described in section 2.1 of Method 5 of this appendix with the following additions:

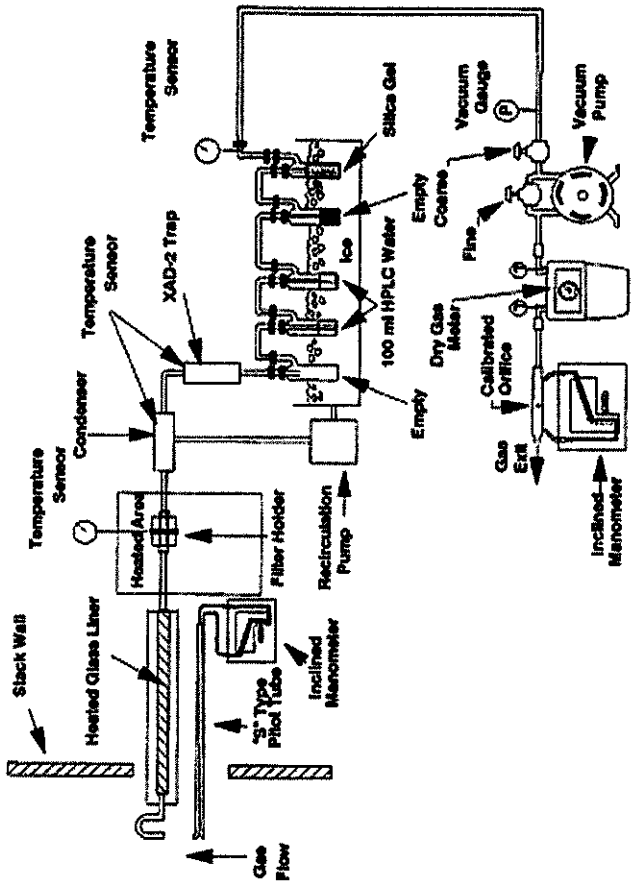

Figure 23.1 Sampling train

2.1.1 Nozzle. The nozzle shall be made of nickel, nickel-plated stainless steel, quartz, or borosilicate glass.

2.1.2 Sample Transfer Lines. The sample transfer lines, if needed, shall be heat traced, heavy walled TFE (½ in. OD with ⅛ in. wall) with connecting fittings that are capable of forming leak-free, vacuum-tight connections without using sealing greases. The line shall be as short as possible and must be maintained at 120 °C.

2.1.1 Filter Support. Teflon or Teflon-coated wire.

2.1.2 Condenser. Glass, coil type with compatible fittings. A schematic diagram is shown in Figure 23-2.

2.1.3 Water Bath. Thermostatically controlled to maintain the gas temperature exiting the condenser at <20 °C (68 °F).

2.1.4 Adsorbent Module. Glass container to hold the solid adsorbent. A shematic diagram is shown in Figure 23-2. Other physical configurations of the resin trap/condenser assembly are acceptable. The connecting fittings shall form leak-free, vacuum tight seals. No sealant greases shall be used in the sampling train. A coarse glass frit is included to retain the adsorbent.

2.2 Sample Recovery.

2.2.1 Fitting Caps. Ground glass, Teflon tape, or aluminum foil (Section 2.2.6) to cap off the sample exposed sections of the train.

2.2.2 Wash Bottles. Teflon, 500-ml.

2.2.3 Probe-Liner Probe-Nozzle, and Filter-Holder Brushes. Inert bristle brushes with precleaned stainless steel or Teflon handles. The probe brush shall have extensions of stainless steel or Teflon, at least as long as the probe. The brushes shall be properly sized and shaped to brush out the nozzle, probe liner, and transfer line, if used.

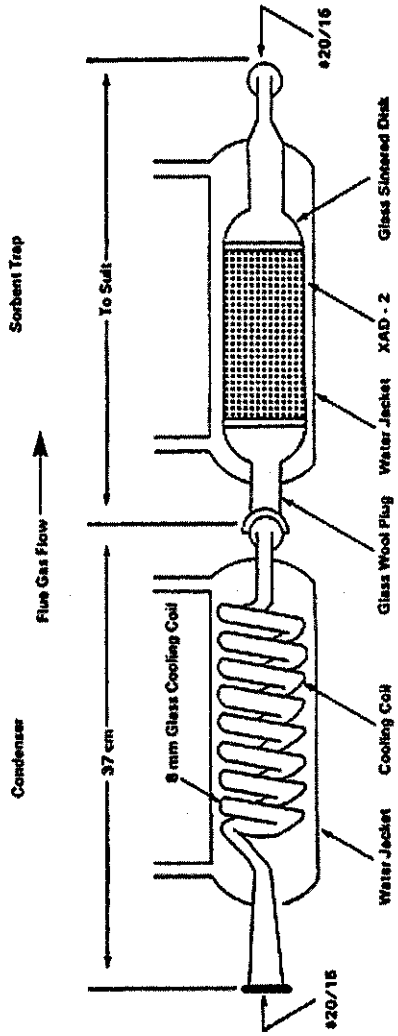

Figure 23.2. Condenser and adsorbent trap

2.2.4 Filter Storage Container. Sealed filter holder, wide-mouth amber glass jar with Teflon-lined cap, or glass petri dish.

2.2.5 Balance. Triple beam.

2.2.6 Aluminum Foil. Heavy duty, hexane-rinsed.

2.2.7 Storage Container. Air-tight container to store silica gel.

2.2.8 Graduated Cylinder. Glass, 250-ml with 2-ml graduation.

2.2.9 Glass Sample Storage Container. Amber glass bottle for sample glassware washes, 500- or 1000-ml, with leak free Teflon-lined caps.

2.3 Analysis.

2.3.1 Sample Container. 125- and 250-ml flint glass bottles with Teflon-lined caps.

2.3.2 Test Tube. Glass.

2.3.3 Soxhlet Extraction Apparatus. Capable of holding 43×123 mm extraction thimbles.

2.3.4 Extraction Thimble. Glass, precleaned cellulosic, or glass fiber.

2.3.5 Pasteur Pipettes. For preparing liquid chromatographic columns.

2.3.6 Reacti-vials. Amber glass, 2-ml, silanized prior to use.

2.3.7 Rotary Evaporator. Buchi/Brinkman RF-121 or equivalent.

2.3.8 Nitrogen Evaporative Concentrator. N-Evap Analytical Evaporator Model III or equivalent.

2.3.9 Separatory Funnels. Glass, 2-liter.

2.3.10 Gas Chromatograph. Consisting of the following components:

2.3.10.1 Oven. Capable of maintaining the separation column at the proper operating temperature ±°C and performing programmed increases in temperature at rates of at least 40 °C/min.

2.3.10.2 Temperature Gauge. To monitor column oven, detector, and exhaust temperatures ±1 °C.

2.3.10.3 Flow System. Gas metering system to measure sample, fuel, combustion gas, and carrier gas flows.

2.3.10.4 Capillary Columns. A fused silica column, 60 × 0.25 mm inside diameter (ID), coated with DB-5 and a fused silica column, 30 m × 0.25 mm ID coated with DB-225. Other column systems may be used provided that the user is able to demonstrate using calibration and performance checks that the column system is able to meet the specifications of section 6.1.2.2.

2.3.11 Mass Spectrometer. Capable of routine operation at a resolution of 1:10000 with a stability of ±5 ppm.

2.3.12 Data System. Compatible with the mass spectrometer and capable of monitoring at least five groups of 25 ions.

2.3.13 Analytical Balance. To measure within 0.1 mg.

Step 4 3. Reagents

3.1 Sampling.

3.1.1 Filters. Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3-micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM Standard Method D 2986-71 (Reapproved 1978) (incorporated by reference—see §60.17).

3.1.1.1 Precleaning. All filters shall be cleaned before their initial use. Place a glass extraction thimble and 1 g of silica gel and a plug of glass wool into a Soxhlet apparatus, charge the apparatus with toluene, and reflux for a minimum of 3 hours. Remove the toluene and discard it, but retain the silica gel. Place no more than 50 filters in the thimble onto the silica gel bed and top with the cleaned glass wool. Charge the Soxhlet with toluene and reflux for 16 hours. After extraction, allow the Soxhlet to cool, remove the filters, and dry them under a clean N_2 stream. Store the filters in a glass petri dish sealed with Teflon tape.

3.1.2 Adsorbent Resin. Amberlite XAD-2 resin. Thoroughly cleaned before initial use.

3.1.2.1 Cleaning Procedure. This procedure may be carried out in a giant Soxhlet extractor. An all-glass filter thimble containing an extra-course frit is used for extraction of XAD-2. The frit is recessed 10-15 mm above a crenelated ring at the bottom of the thimble to facilitate drainage. The resin must be carefully retained in the extractor cup with a glass wool plug and a stainless steel ring because it floats on methylene chloride. This process involves sequential extraction in the following order.

Solvent	Procedure
Water	Initial rinse: Place resin in a beaker, rinse once with water, and discard. Fill with water a second time, let stand overnight, and discard.
Water	Extract with water for 8 hours.
Methanol	Extract for 22 hours.
Methylene Chloride	Extract for 22 hours.
Toluene	Extract for 22 hours.

3.1.2.2 Drying.

3.1.2.2.1 Drying Column. Pyrex pipe, 10.2 cm ID by 0.6 m long, with suitable retainers.

3.1.2.2.2 Procedure. The adsorbent must be dried with clean inert gas. Liquid nitrogen from a standard commercial liquid nitrogen cylinder has proven to be a reliable source of large volumes of gas free from organic contaminants. Connect the liquid nitrogen cylinder to the column by a length of cleaned copper tubing, 0.95 cm ID, coiled to pass through a heat source. A convenient heat source is a water-bath heated from a steam line. The final nitrogen temperature should only be warm to the touch and not over 40 °C. Continue flowing nitrogen through the adsorbent until all the residual solvent is removed. The flow rate should be sufficient to gently agitate the particles but not so excessive as the cause the particles to fracture.

3.1.2.3 Quality Control Check. The adsorbent must be checked for residual toluene.

3.1.2.3.1 Extraction. Weigh 1.0 g sample of dried resin into a small vial, add 3 ml of toluene, cap the vial, and shake it well.

3.1.2.3.2 Analysis. Inject a 2 µl sample of the extract into a gas chromatograph operated under the following conditions:

Column: 6 ft × ⅛ in stainless steel containing 10 percent OV-101 on 100/120 Supelcoport.

Carrier Gas: Helium at a rate of 30 ml/min.

Detector: Flame ionization detector operated at a sensitivity of 4×10^{-11} A/mV.

Injection Port Temperature: 250 °C.

Detector Temperature: 305 °C.

Oven Temperature: 30 °C for 4 min; programmed to rise at 40 °C/min until it reaches 250 °C; return to 30 °C after 17 minutes.

Compare the results of the analysis to the results from the reference solution. Prepare the reference solution by injection 2.5 µl of methylene chloride into 100 ml of toluene. This corresponds to 100 µg of methylene chloride per g of adsorbent. The maximum acceptable concentration is 1000 µg/g of adsorbent. If the adsorbent exceeds this level, drying must be continued until the excess methylene chloride is removed.

3.1.2.4 Storage. The adsorbent must be used within 4 weeks of cleaning. After cleaning, it may be stored in a wide mouth amber glass container with a Teflon-lined cap or placed in one of the glass adsorbent modules tightly sealed with glass stoppers. If precleaned adsorbent is purchased in sealed containers, it must be used within 4 weeks after the seal is broken.

3.1.3 Glass Wool. Cleaned by sequential immersion in three aliquots of methylene chloride, dried in a 110 °C oven, and stored in a methylene chloride-washed glass jar with a Teflon-lined screw cap.

3.1.4 Water. Deionized distilled and stored in a methylene chloride-rinsed glass container with a Teflon-lined screw cap.

3.1.5 Silica Gel. Indicating type, 6 to 16 mesh. If previously used, dry at 175 °C (350 °F) for two hours. New silica gel may be used as received. Alternately other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.

3.1.6 Chromic Acid Cleaning Solution. Dissolve 20 g of sodium dichromate in 15 ml of water, and then carefully add 400 ml of concentrated sulfuric acid.

3.2 Sample Recovery.

3.2.2 Acetone. Pesticide quality.

3.2.2 Methylene Chloride. Pesticide qualtity.

3.2.3 Toluene. Pesticide quality.

3.3 Analysis.

3.3.1 Potassium Hydroxide. ACS grade, 2-percent (weight/volume) in water.

3.3.2 Sodium Sulfate. Granulated, reagent grade. Purify prior to use by rinsing with methylene chloride and oven drying. Store the cleaned material in a glass container with a Teflon-lined screw cap.

3.3.3 Sulfuric Acid. Reagent grade.

3.3.4 Sodium Hydroxide. 1.0 N. Weigh 40 g of sodium hydroxide into a 1-liter volumetric flask. Dilute to 1 liter with water.

3.3.5 Hexane. Pesticide grade.

3.3.6 Methylene Chloride. Pesticide grade.

3.3.7 Benzene. Pesticide Grade.

3.3.8 Ethyl Acetate.

3.3.9 Methanol. Pesticide Grade.

3.3.10 Toluene. Pesticide Grade.

3.3.11 Nonane. Pesticide Grade.

3.3.12 Cyclohexane. Pesticide Grade.

3.3.13 Basic Alumina. Activity grade 1, 100-200 mesh. Prior to use, activate the alumina by heating for 16 hours at 130 °C before use. Store in a desiccator. Pre-activated alumina may be purchased from a supplier and may be used as received.

3.3.14 Silica Gel. Bio-Sil A, 100-200 mesh. Prior to use, activate the silica gel by heating for at least 30 minutes at 180 °C. After cooling, rinse the silica gel sequentially with methanol and methylene chloride. Heat the rinsed silica gel at 50 °C for 10 minutes, then increase the temperature gradually to 180 °C over 25 minutes and maintain it at this temperature for 90 minutes. Cool at room temperature and store in a glass container with a Teflon-lined screw cap.

3.3.15 Silica Gel Impregnated with Sulfuric Acid. Combine 100 g of silica gel with 44 g of concentrated sulfuric acid in a screw capped glass bottle and agitate thoroughly. Disperse the solids with

a stirring rod until a uniform mixture is obtained. Store the mixture in a glass container with a Teflon-lined screw cap.

3.3.16 Silica Gel Impregnated with Sodium Hydroxide. Combine 39 g of 1 N sodium hydroxide with 100 g of silica gel in a screw capped glass bottle and agitate thoroughly. Disperse solids with a stirring rod until a uniform mixture is obtained. Store the mixture in glass container with a Teflon-lined screw cap.

3.3.17 Carbon/Celite. Combine 10.7 g of AX-21 carbon with 124 g of Celite 545 in a 250-ml glass bottle with a Teflon-lined screw cap. Agitate the mixture thoroughly until a uniform mixture is obtained. Store in the glass container.

3.3.18 Nitrogen. Ultra high purity.

3.3.19 Hydrogen. Ultra high purity.

3.3.20 Internal Standard Solution. Prepare a stock standard solution containing the isotopically labelled PCDD's and PCDF's at the concentrations shown in Table 1 under the heading "Internal Standards" in 10 ml of nonane.

3.3.21 Surrogate Standard Solution. Prepare a stock standard solution containing the isotopically labelled PCDD's and PCDF's at the concentrations shown in Table 1 under the heading "Surrogate Standards" in 10 ml of nonane.

3.3.22 Recovery Standard Solution. Prepare a stock standard solution containing the isotopically labelled PCDD's and PCDF's at the concentrations shown in Table 1 under the heading "Recovery Standards" in 10 ml of nonane.

Step 5 4. Procedure

4.1 Sampling. The complexity of this method is such that, in order to obtain reliable results, testers should be trained and experienced with the test procedures.

4.1.1 Pretest Preparation.

4.1.1.1 Cleaning Glassware. All glass components of the train upstream of and including the adsorbent module, shall be cleaned as described in section 3A of the "Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples." Special care shall be devoted to the removal of residual silicone grease sealants on ground glass connections of used glassware. Any residue shall be removed by soaking the glassware for several hours in a chromic acid cleaning solution prior to cleaning as described above.

4.1.1.2 Adsorbent Trap. The traps must be loaded in a clean area to avoid contamination. They may not be loaded in the field. Fill a trap with 20 to 40 g of XAD-2. Follow the XAD-2 with glass wool and tightly cap both ends of the trap. Add 100 µl of the surrogate standard solution (section 3.3.21) to each trap.

4.1.1.3 Sample Train. It is suggested that all components be maintained according to the procedure described in APTD-0576. Alternative mercury-free thermometers may be used if the thermometers are, at a minimum, equivalent in terms of performance or suitably effective for the specific temperature measurement application.

4.1.1.4 Silica Gel. Weigh several 200 to 300 g portions of silica gel in an air tight container to the nearest 0.5 g. Record the total weight of the silica gel plus container, on each container. As an alternative, the silica gel may be weighed directly in its impinger or sampling holder just prior to sampling.

4.1.1.5 Filter. Check each filter against light for irregularities and flaws or pinhole leaks. Pack the filters flat in a clean glass container.

4.1.2 Preliminary Determinations. Same as section 4.1.2 of Method 5.

4.1.3 Preparation of Collection Train.

4.1.3.1 During preparation and assembly of the sampling train, keep all train openings where contamination can enter, sealed until just prior to assembly or until sampling is about to begin.

NOTE: Do not use sealant grease in assembling the train.

4.1.3.2 Place approximately 100 ml of water in the second and third impingers, leave the first and fourth impingers empty, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fifth impinger.

4.1.3.3 Place the silica gel container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded.

4.1.3.4 Assemble the train as shown in Figure 23-1.

4.1.3.5 Turn on the adsorbent module and condenser coil recirculating pump and begin monitoring the adsorbent module gas entry temperature. Ensure proper sorbent temperature gas entry temperature before proceeding and before sampling is initiated. It is extremely important that the XAD-2 adsorbent resin temperature never exceed 50 °C because thermal decomposition will occur. During testing, the XAD-2 temperature must not exceed 20 °C for efficient capture of the PCDD's and PCDF's.

4.1.4 Leak-Check Procedure. Same as Method 5, section 4.1.4.

4.1.5 Sample Train Operation. Same as Method 5, section 4.1.5.

4.2 Sample Recovery. Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Seal the nozzle end of the sampling probe with Teflon tape or aluminum foil.

When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe. Remove the probe from the train and close off both ends with aluminum foil. Seal off the inlet to the train with Teflon tape, a ground glass cap, or aluminum foil.

Transfer the probe and impinger assembly to the cleanup area. This area shall be clean and enclosed so that the chances of losing or contaminating the sample are minimized. Smoking, which could contaminate the sample, shall not be allowed in the cleanup area.

Inspect the train prior to and during disassembly and note any abnormal conditions, e.g., broken filters, colored impinger liquid, etc. Treat the samples as follows:

4.2.1 Container No. 1. Either seal the filter holder or carefully remove the filter from the filter holder and place it in its identified container. Use a pair of cleaned tweezers to handle the filter. If it is necessary to fold the filter, do so such that the particulate cake is inside the fold. Carefully transfer to the container any particulate matter and filter fibers which adhere to the filter holder gasket, by using a dry inert bristle brush and a sharp-edged blade. Seal the container.

4.2.2 Adsorbent Module. Remove the module from the train, tightly cap both ends, label it, cover with aluminum foil, and store it on ice for transport to the laboratory.

4.2.3 Container No. 2. Quantitatively recover material deposited in the nozzle, probe transfer lines, the front half of the filter holder, and the cyclone, if used, first, by brushing while rinsing three times each with acetone and then, by rinsing the probe three times with methylene chloride. Collect all the rinses in Container No. 2.

Rinse the back half of the filter holder three times with acetone. Rinse the connecting line between the filter and the condenser three times with acetone. Soak the connecting line with three separate portions of methylene chloride for 5 minutes each. If using a separate condenser and adsorbent trap, rinse the condenser in the same manner as the connecting line. Collect all the rinses in Container No. 2 and mark the level of the liquid on the container.

4.2.4 Container No. 3. Repeat the methylene chloride-rinsing described in section 4.2.3 using toluene as the rinse solvent. Collect the rinses in Container No. 3 and mark the level of the liquid on the container.

4.2.5 Impinger Water. Measure the liquid in the first three impingers to within ±1 ml by using a graduated cylinder or by weighing it to within ±0.5 g by using a balance. Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas.

Discard the liquid after measuring and recording the volume or weight.

4.2.7 Silica Gel. Note the color of the indicating silica gel to determine if it has been completely spent and make a mention of its condition. Transfer the silica gel from the fifth impinger to its original container and seal. If a moisture determination is made, follow the applicable procedures in sections 8.7.6.3 and 11.2.3 of Method 5 to handle and weigh the silica gel. If moisture is not measured, the silica gel may be disposed.

Step 6 5. Analysis

All glassware shall be cleaned as described in section 3A of the "Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples." All samples must be extracted within 30 days of collection and analyzed within 45 days of extraction.

5.1 Sample Extraction.

5.1.1 Extraction System. Place an extraction thimble (section 2.3.4), 1 g of silica gel, and a plug of glass wool into the Soxhlet apparatus, charge the apparatus with toluene, and reflux for a minimum of 3 hours. Remove the toluene and discard it, but retain the silica gel. Remove the extraction thimble from the extraction system and place it in a glass beaker to catch the solvent rinses.

5.1.2 Container No. 1 (Filter). Transfer the contents directly to the glass thimble of the extraction system and extract them simultaneously with the XAD-2 resin.

5.1.3 Adsorbent Cartridge. Suspend the adsorbent module directly over the extraction thimble in the beaker (See section 5.1.1). The glass frit of the module should be in the up position. Using a Teflon squeeze bottle containing toluene, flush the XAD-2 into the thimble onto the bed of cleaned silica gel. Thoroughly rinse the glass module catching the rinsings in the beaker containing the thimble. If the resin is wet, effective extraction can be accomplished by loosely packing the resin in the thimble. Add the XAD-2 glass wool plug into the thimble.

5.1.4 Container No. 2 (Acetone and Methylene Chloride). Concentrate the sample to a volume of about 1-5 ml using the rotary evaporator apparatus, at a temperature of less than 37 °C. Rinse the sample container three times with small portions of methylene chloride and add these to the concentrated solution and concentrate further to near dryness. This residue contains particulate matter removed in the rinse of the train probe and nozzle. Add the concentrate to the filter and the XAD-2 resin in the Soxhlet apparatus described in section 5.1.1.

5.1.5 Extraction. Add 100 µl of the internal standard solution (Section 3.3.20) to the extraction thimble containing the contents of the adsorbent cartridge, the contents of Container No. 1, and the concentrate from section 5.1.4. Cover the contents of the extraction thimble with the cleaned glass wool plug to prevent the XAD-2 resin from floating into the solvent reservoir of the extractor. Place the thimble in the extractor, and add the toluene contained in the beaker to the solvent reservoir. Pour additional toluene to fill the reservoir approximately ⅔ full. Add Teflon boiling chips and assemble the apparatus. Adjust the heat source to cause the extractor to cycle three times per hour. Extract the sample for 16 hours. After extraction, allow the Soxhlet to cool. Transfer the toluene extract and three 10-ml rinses to the rotary evaporator. Concentrate the extract to approximately 10 ml. At this point the analyst may choose to split the sample in half. If so, split the sample, store one half for future use, and analyze the other according to the procedures in sections 5.2 and 5.3. In either case, use a nitrogen evaporative concentrator to reduce the volume of the sample being analyzed to near dryness. Dissolve the residue in 5 ml of hexane.

5.1.6 Container No. 3 (Toluene Rinse). Add 100 µl of the Internal Standard solution (section 3.3.2) to the contents of the container. Concentrate the sample to a volume of about 1-5 ml using the rotary evaporator apparatus at a temperature of less than 37 °C. Rinse the sample container apparatus at a temperature of less than 37 °C. Rinse the sample container three times with small portions of toluene and add these to the concentrated solution and concentrate further to near dryness. Analyze the extract separately according to the procedures in sections 5.2 and 5.3, but concentrate the solution in a rotary evaporator apparatus rather than a nitrogen evaporative concentrator.

5.2 Sample Cleanup and Fractionation.

5.2.1 Silica Gel Column. Pack one end of a glass column, 20 mm×230 mm, with glass wool. Add in sequence, 1 g silica gel, 2 g of sodium hydroxide impregnated silica gel, 1 g silica gel, 4 g of acid-modified silica gel, and 1 g of silica gel. Wash the column with 30 ml of hexane and discard it. Add the sample extract, dissolved in 5 ml of hexane to the column with two additional 5-ml rinses. Elute the column with an additional 90 ml of hexane and retain the entire eluate. Concentrate this solution to a volume of about 1 ml using the nitrogen evaporative concentrator (section 2.3.7).

5.2.2 Basic Alumina Column. Shorten a 25-ml disposable Pasteur pipette to about 16 ml. Pack the lower section with glass wool and 12 g of basic alumina. Transfer the concentrated extract from the silica gel column to the top of the basic alumina column and elute the column sequentially with 120 ml of 0.5 percent methylene chloride in hexane followed by 120 ml of 35 percent methylene chloride in hexane. Discard the first 120 ml of eluate. Collect the second 120 ml of eluate and concentrate it to about 0.5 ml using the nitrogen evaporative concentrator.

5.2.3 AX-21 Carbon/Celite 545 Column. Remove the botton 0.5 in. from the tip of a 9-ml disposable Pasteur pipette. Insert a glass fiber filter disk in the top of the pipette 2.5 cm from the constriction. Add sufficient carbon/celite mixture to form a 2 cm column. Top with a glass wool plug. In some cases AX-21 carbon fines may wash through the glass wool plug and enter the sample. This may be prevented by adding a celite plug to the exit end of the column. Rinse the column in sequence with 2 ml of 50 percent benzene in ethyl acetate, 1 ml of 50 percent methylene chloride in cyclohexane, and 2 ml of hexane. Discard these rinses. Transfer the concentrate in 1 ml of hexane from the basic alumina column to the carbon/celite column along with 1 ml of hexane rinse. Elute the column sequentially with 2 ml of 50 percent methylene chloride in hexane and 2 ml of 50 percent benzene in ethyl acetate and discard these eluates. Invert the column and elute in the reverse direction with 13 ml of toluene. Collect this eluate. Concentrate the eluate in a rotary evaporator at 50 °C to about 1 ml. Transfer the concentrate to a Reacti-vial using a toluene rinse and concentrate to a volume of 200 µl using a stream of N_2. Store extracts at room temperature, shielded from light, until the analysis is performed.

5.3 Analysis. Analyze the sample with a gas chromatograph coupled to a mass spectrometer (GC/MS) using the instrumental parameters in sections 5.3.1 and 5.3.2. Immediately prior to analysis, add a 20 µl aliquot of the Recovery Standard solution from Table 1 to each sample. A 2 µl aliquot of the extract is injected into the GC. Sample extracts are first analyzed using the DB-5 capillary column to determine the concentration of each isomer of PCDD's and PCDF's (tetra-through octa-). If tetra-chlorinated dibenzofurans are detected in this analysis, then analyze another aliquot of the sample in a separate run, using the DB-225 column to measure the 2,3,7,8 tetra-chloro dibenzofuran isomer. Other column systems may be used, provided that the user is able to demonstrate using calibration and performance checks that the column system is able to meet the specifications of section 6.1.2.2.

5.3.1 Gas Chromatograph Operating Conditions.

5.3.1.1 Injector. Configured for capillary column, splitless, 250 °C.

5.3.1.2 Carrier Gas. Helium, 1-2 ml/min.

5.3.1.3 Oven. Initially at 150 °C. Raise by at least 40 °C/min to 190 °C and then at 3 °C/min up to 300 °C.

5.3.2 High Resolution Mass Spectrometer.

5.3.2.1 Resolution. 10000 m/e.

5.3.2.2 Ionization Mode. Electron impact.

5.3.2.3 Source Temperature 250 °C.

5.3.2.4 Monitoring Mode. Selected ion monitoring. A list of the various ions to be monitored is summarized in Table 3.

5.3.2.5 Identification Criteria. The following identification criteria shall be used for the characterization of polychlorinated dibenzodioxins and dibenzofurans.

1. The integrated ion-abundance ratio (M/M+2 or M+2/M+4) shall be within 15 percent of the theoretical value. The acceptable ion-abundance ratio ranges for the identification of chlorine-containing compounds are given in Table 4.

2. The retention time for the analytes must be within 3 seconds of the corresponding ^{13}C-labeled internal standard, surrogate or alternate standard.

3. The monitored ions, shown in Table 3 for a given analyte, shall reach their maximum within 2 seconds of each other.

4. The identification of specific isomers that do not have corresponding ^{13}C-labeled standards is done by comparison of the relative retention time (RRT) of the analyte to the nearest internal standard retention time with reference (i.e., within 0.005 RRT units) to the comparable RRT's found in the continuing calibration.

5. The signal to noise ratio for all monitored ions must be greater than 2.5.

6. The confirmation of 2, 3, 7, 8-TCDD and 2, 3, 7, 8-TCDF shall satisfy all of the above identification criteria.

7. For the identification of PCDF's, no signal may be found in the corresponding PCDPE channels.

5.3.2.6 Quantification. The peak areas for the two ions monitored for each analyte are summed to yield the total response for each analyte. Each internal standard is used to quantify the indigenous PCDD's or PCDF's in its homologous series. For example, the $^{13}C_{12}$-2,3,7,8-tetra chlorinated dibenzodioxin is used to calculate the concentrations of all other tetra chlorinated isomers. Recoveries of the tetra- and penta- internal standards are calculated using the $^{13}C_{12}$-1,2,3,4-TCDD. Recoveries of the hexa- through octa- internal standards are calculated using $^{13}C_{12}$-1,2,3,7,8,9-HxCDD. Recoveries of the surrogate standards are calculated using the corresponding homolog from the internal standard.

Step 7 6. Calibration

Same as Method 5 with the following additions.

6.1 GC/MS System.

6.1.1 Initial Calibration. Calibrate the GC/MS system using the set of five standards shown in Table 2. The relative standard deviation for the mean response factor from each of the unlabeled analytes (Table 2) and of the internal, surrogate, and alternate standards shall be less than or equal to the values in Table 5. The signal to noise ratio for the GC signal present in every selected ion current profile shall be greater than or equal to 2.5. The ion abundance ratios shall be within the control limits in Table 4.

6.1.2 Daily Performance Check.

6.1.2.1 Calibration Check. Inject on µl of solution Number 3 from Table 2. Calculate the relative response factor (RRF) for each compound and compare each RRF to the corresponding mean RRF obtained during the initial calibration. The analyzer performance is acceptable if the measured RRF's for the labeled and unlabeled compounds for the daily run are within the limits of the mean values shown in Table 5. In addition, the ion-abundance ratios shall be within the allowable control limits shown in Table 4.

6.1.2.2 Column Separation Check. Inject a solution of a mixture of PCDD's and PCDF's that documents resolution between 2,3,7,8-TCDD and other TCDD isomers. Resolution is defined as a valley between peaks that is less than 25 percent of the lower of the two peaks. Identify and record the retention time windows for each homologous series.

Perform a similar resolution check on the confirmation column to document the resolution between 2,3,7,8 TCDF and other TCDF isomers.

6.2 Lock Channels. Set mass spectrometer lock channels as specified in Table 3. Monitor the quality control check channels specified in Table 3 to verify instrument stability during the analysis.

Step 8 7. Quality Control

7.1 Sampling Train Collection Efficiency Check. Add 100 µl of the surrogate standards in Table 1 to the absorbent cartridge of each train before collecting the field samples.

7.2 Internal Standard Percent Recoveries. A group of nine carbon labeled PCDD's and PCDF's representing, the tetra-through octachlorinated homologues, is added to every sample prior to extraction. The role of the internal standards is to quantify the native PCDD's and PCDF's present in the sample as well as to determine the overall method efficiency. Recoveries of the internal standards must be between 40 to 130 percent for the tetra-through hexachlorinated compounds while the range is 25 to 130 percent for the higher hepta- and octachlorinated homologues.

7.3 Surrogate Recoveries. The five surrogate compounds in Table 2 are added to the resin in the adsorbent sampling cartridge before the sample is collected. The surrogate recoveries are measured relative to the internal standards and are a measure of collection efficiency. They are not used to measure native PCDD's and PCDF's. All recoveries shall be between 70 and 130 percent. Poor recoveries for all the surrogates may be an indication of breakthrough in the sampling train. If the recovery of all standards is below 70 percent, the sampling runs must be repeated. As an alternative, the sampling runs do not have to be repeated if the final results are divided by the fraction of surrogate recovery. Poor recoveries of isolated surrogate compounds should not be grounds for rejecting an entire set of the samples.

7.4 Toluene QA Rinse. Report the results of the toluene QA rinse separately from the total sample catch. Do not add it to the total sample.

Step 9 8.0 [Reserved]

Step 10 9. Calculations

Same as Method 5, section 6 with the following additions.

9.1 Nomenclature.

A_{ni}=Integrated ion current of the noise at the retention time of the analyte.

A^*_{ci}=Integrated ion current of the two ions characteristic of the internal standard i in the calibration standard.

A_{cij}=Integrated ion current of the two ions characteristic of compound i in the jth calibration standard.

A^*_{cij}=Integrated ion current of the two ions characteristic of the internal standard i in the jth calibration standard.

A_{csi}=Integrated ion current of the two ions characteristic of surrogate compound i in the calibration standard.

A_i=Integrated ion current of the two ions characteristic of compound i in the sample.

A^*_i=Integrated ion current of the two ions characteristic of internal standard i in the sample.

A_{rs}=Integrated ion current of the two ions characteristic of the recovery standard.

A_{si}=Integrated ion current of the two ions characteristic of surrogate compound i in the sample.

C_i=Concentration of PCDD or PCDF i in the sample, pg/M^3.

C_T=Total concentration of PCDD's or PCDF's in the sample, pg/M^3.

m_{ci}=Mass of compound i in the calibration standard injected into the analyzer, pg.

m_{rs}=Mass of recovery standard in the calibration standard injected into the analyzer, pg.

m_{si}=Mass of surrogate compound in the calibration standard, pg.

RRF_i=Relative response factor.

RRF_{rs}=Recovery standard response factor.

RRF_s=Surrogate compound response factor.

9.2 Average Relative Response Factor.

$$RRF_i = \frac{1}{n}\sum_{j=1}^{n}\frac{A_{dij}\, m^*_{di}}{A^*_{dij}\, m_{di}} \qquad Eq.\ 23\text{-}1$$

9.3 Concentration of the PCDD's and PCDF's.

$$C_i = \frac{m_i^* A_i}{A_i^* RRF_i V_{mstd}} \qquad Eq.\ 23\text{-}2$$

9.4 Recovery Standard Response Factor.

$$RRF_{rs} = \frac{A_{di}^* m_{rs}}{A_{rs} m_{di}^*} \qquad Eq.\ 23\text{-}3$$

9.5 Recovery of Internal Standards (R*).

$$R^* = \frac{A_i^* m_{rs}}{A_{rs} RF_{rs} m_i^*} \times 100\% \qquad Eq.\ 23\text{-}4$$

9.6 Surrogate Compound Response Factor.

$$RRF_s = \frac{A_{di}^* m_s}{A_{dis} m_{di}^*} \qquad Eq.\ 23\text{-}5$$

9.7 Recovery of Surrogate Compounds (R_s).

$$R_s = \frac{A_s m_i^*}{A_i^* RRF_s m_s} \times 100\% \qquad Eq.\ 23\text{-}6$$

9.8 Minimum Detectable Limit (MDL).

$$MDL = \frac{2.5\, A_{di} m_i^*}{A_{di}^* RRF_i} \qquad Eq.\ 23\text{-}7$$

9.9 Total Concentration of PCDD's and PCDF's in the Sample.

$$C_{TT} = \sum_{i=1}^{n} C_i \qquad Eq.\ 23\text{-}8$$

Any PCDD's or PCDF's that are reported as nondetected (below the MDL) shall be counted as zero for the purpose of calculating the total concentration of PCDD's and PCDF's in the sample.

Step 11 10. Bibliography

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3. Thompson, J. R. (ed.). Analysis of Pesticide Residues in Human and Environmental Samples. U.S. Environmental Protection Agency. Research Triangle Park, NC. 1974.

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TABLE 1—COMPOSITION OF THE SAMPLE FORTIFICATION AND RECOVERY STANDARDS SOLUTIONS

Analyte	Concentration (pg/µl)
Internal Standards:	
$^{13}C_{12}$-2,3,7,8-TCDD	100
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100
$^{13}C_{12}$-OCDD	100
$^{13}C_{12}$-2,3,7,8-TCDF	100
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100
Surrogate Standards:	
$^{37}Cl_4$-2,3,7,8-TCDD	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100
Recovery Standards:	
$^{13}C_{12}$-1,2,3,4-TCDD	500
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	500

TABLE 2—COMPOSITION OF THE INITIAL CALIBRATION SOLUTIONS

Compound	Concentrations (pg/µL)				
	Solution No.				
	1	2	3	4	5
Alternate Standard:					
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	2.5	5	25	250	500
Recovery Standards:					
$^{13}C_{12}$-1,2,3,4-TCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100

TABLE 3—ELEMENTAL COMPOSITIONS AND EXACT MASSES OF THE IONS MONITORED BY HIGH RESOLUTION MASS SPECTROMETRY FOR PCDD'S AND PCDF'S

Descriptor No.	Accurate mass	Ion type	Elemental composition	Analyte
2	292.9825	LOCK	C_7F_{11}	PFK
	303.9016	M	$C_{12}H_4{}^{35}Cl_4O$	TCDF
	305.8987	M+2	$C_{12}H_4{}^{35}Cl^{37}O$	TCDF
	315.9419	M	$^{13}C_{12}H_4{}^{35}Cl_4O$	TCDF (S)
	317.9389	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF (S)
	319.8965	M	$C_{12}H_4{}^{35}ClO_2$	TCDD
	321.8936	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD
	327.8847	M	$C_{12}H_4{}^{37}Cl_4O_2$	TCDD (S)
	330.9792	QC	C_7F_{13}	PFK
	331.9368	M	$^{13}C_{12}H_4{}^{35}Cl_4O_2$	TCDD (S)
	333.9339	M+2	$^{13}C_{12}H_4{}^{35}Cl^{37}ClO_2$	TCDD (S)
	339.8597	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PECDF
	341.8567	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF
	351.9000	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF (S)
	353.8970	M+4	$^{13}C_{12}H_3{}^{35}Cl^{3537}Cl_2O$	PeCDF (S)
	355.8546	M+2	$C_{12}H_3{}^{35}Cl_3 37ClO_2$	PeCDD
	357.8516	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD
	367.8949	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD (S)
	369.8919	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}\ Cl_2O_2$	PeCDD (S)
	375.8364	M+2	$C_{12}H_4{}^{35}Cl_5{}^{37}ClO$	HxCDPE
	409.7974	M+2	$C_{12}H_3{}^{35}Cl_6{}^{37}ClO$	HpCPDE
3	373.8208	M+2	$C_{12}H_2 35Cl_5{}^{37}ClO$	HxCDF
	375.8178	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDF
	383.8639	M	$^{13}C_{12}H_2{}^{35}Cl_6O$	HxCDF (S)
	385.8610	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF (S)
	389.8157	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD
	391.8127	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD
	392.9760	LOCK	C_9F_{15}	PFK
	401.8559	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD (S)
	403.8529	M+4	$^{13}C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDD (S)
	445.7555	M+4	$C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2O$	OCDPE

	430.9729	QC	C_9F_{17}	PFK
4	407.7818	M+2	$C_{12}H^{35}Cl_5{}^{37}ClO$	HpCDF
	409.7789	M+4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O$	HpCDF
	417.8253	M	$^{13}C_{12}H^{35}Cl_7O$	HpCDF (S)
	419.8220	M+2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF (S)
	423.7766	M+2	$C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD
	425.7737	M+4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD
	435.8169	M+2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD (S)
	437.8140	M+4	$^{13}C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD (S)
	479.7165	M+4	$C_{12}H^{35}Cl_7{}^{37}Cl_2O$	NCPDE
	430.9729	LOCK	C_9F_{17}	PFK
	441.7428	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO$	OCDF
	443.7399	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O$	OCDF
	457.7377	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD
	459.7348	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD
	469.7779	M+2	$^{13}C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD (S)
	471.7750	M+4	$^{13}C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD (S)
	513.6775	M+4	$C_{12}{}^{35}Cl_8{}^{37}Cl_2O_2$	DCDPE
	442.9728	QC	$C_{10}F_{17}$	PFK

(a) The following nuclidic masses were used:

H=1.007825

C=12.000000

^{13}C=13.003355

F=18.9984

O=15.994915

^{35}Cl=34.968853

^{37}Cl=36.965903

S=Labeled Standard

QC=Ion selected for monitoring instrument stability during the GC/MS analysis.

TABLE 4—ACCEPTABLE RANGES FOR ION-ABUNDANCE RATIOS OF PCDD'S AND PCDF'S

No. of chlorine atoms	Ion type	Theoretical ratio	Control limits	
			Lower	Upper
4	M/M+2	0.77	0.65	0.89
5	M+2/M+4	1.55	1.32	1.78

6	M+2/M+4	1.24	1.05	1.43
6[a]	M/M+2	0.51	0.43	0.59
7[b]	M/M+2	0.44	0.37	0.51
7	M+2/M+4	1.04	0.88	1.20
8	M+2/M+4	0.89	0.76	1.02

[a]Used only for ^{13}C-HxCDF.

[b]Used only for ^{13}C-HpCDF.

TABLE 5—MINIMUM REQUIREMENTS FOR INITIAL AND DAILY CALIBRATION RESPONSE FACTORS

Compound	Relative response factors	
	Initial calibration RSD	Daily calibration % difference
Unlabeled Analytes:		
2,3,7,8-TCDD	25	25
2,3,7,8-TCDF	25	25
1,2,3,7,8-PeCDD	25	25
1,2,3,7,8-PeCDF	25	25
2,3,4,7,8-PeCDF	25	25
1,2,4,5,7,8-HxCDD	25	25
1,2,3,6,7,8-HxCDD	25	25
1,2,3,7,8,9-HxCDD	25	25
1,2,3,4,7,8-HxCDF	25	25
1,2,3,6,7,8-HxCDF	25	25
1,2,3,7,8,9-HxCDF	25	25
2,3,4,6,7,8-HxCDF	25	25
1,2,3,4,6,7,8-HpCDD	25	25
1,2,3,4,6,7,8-HpCDF	25	25
OCDD	25	25
OCDF	30	30
Internal Standards:		
$^{13}C_{12}$-2,3,7,8-TCDD	25	25
$^{13}C_{12}$-1,2,3,7,8-PeCDD	30	30
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	25	25
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	30	30
$^{13}C_{12}$-OCDD	30	30

$^{13}C_{12}$-2,3,7,8-TCDF	30	30
$^{13}C_{12}$-1,2,3,7,8-PeCDF	30	30
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	30	30
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	30	30
Surrogate Standards:		
$^{37}Cl_4$-2,3,7,8-TCDD	25	25
$^{13}C_{12}$-2,3,4,7,8-PeCDF	25	25
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	25	25
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	25	25
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	25	25
Alternate Standard:		
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	25	25