INTERNATIONAL SEMATECH

Guidelines for Environmental Characterization of Semiconductor Equipment

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Abstract: This document provides guidelines for suppliers of semiconductor processing and abatement equipment to characterize their equipment to meet environmental performance goals. The characterization must include quantification of both air and water emissions. Results must be presented in a final report that includes measurements on both the centerline process recipe and set of design of experiments (DOE) involving the key parameters for that particular process. Forms for recording characterization results and recommended measurement protocols are included.

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1 INTRODUCTION

1.1 Introduction

The semiconductor industry believes in the highest level of environmental performance for its operations. As an end user, the industry has a responsibility to its employees and the community to minimize the environmental impact of its process and operations. To fulfill this responsibility, environmental performance goals have been set for its processes and operations. Equipment suppliers are required to assist the semiconductor industry in achieving these goals. Consequently, equipment suppliers are expected to minimize the consumption of chemicals, production of waste emissions, and usage of utilities.

This document has been designed to provide guidance to equipment and abatement suppliers on how to characterize the environmental performance of their semiconductor processes. The characterization must include quantification of both air and water emissions. Results must be presented in a final report that includes measurements on both the centerline process recipe and set of design of experiments (DOE) involving the key parameters for that particular process.

1.2 Expectations

Table 1 describes what types of emissions information are required for each tool type.

Table 1   Required Tool Emissions Information

Tool Type	Air Testing	Water/Waste Testing	Parts Clean/PMs/ Wipedowns
Diffusion Furnaces	X		X
Wet Hoods	X	X	X
Tracks	X		X
CVD	X		X
Dry Etch	X		X
Implanters	X		X
CMP		X	X
Plating		X	X
Metrology			X
PVD			X

To satisfy the Air Testing requirements, complete the General Info., Recipe Info., and Emissions Info. sections of the Air Emissions Measurements Report.

To satisfy the Water/Wastewater Testing requirements for wet benches, complete the Emissions form Process Tools Using "Open" Tanks/Bath section and the following Recipe Info., Emissions Info., and IPA Dryer sections.

To satisfy the Water/Wastewater Testing requirements for the rest of the tool types, complete the General Information, Connection Hookup Diagram, Chemical/Water Connections and Discharges, and Solid Waste Generated during Wafer Processing and PMs sections.

To satisfy the Parts Clean/PMs/Wipedownsrequirements, complete the Preventive Maintenance and Parts Cleans sections.

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For each process application that the supplier plans to offer for manufacturing, the following information must be provided:

A. Chemical/Water Mass Balance

A chemical mass balance must show the composition and quantity of each chemical used in the supplier's equipment and the composition and quantity of each waste stream discharged to each exhaust, wastewater, and separate chemical drain.

The mass balance must
- Be on a per-wafer processed basis
- Include chemicals used for maintenance and parts cleaning
- Be based on actual measurements
- Be >90%

B. Air Emission Measurements

Emissions testing methods must
- Follow an approved method (Fourier transform infrared [FTIR] or quadrupole mass spectroscopy [QMS])
- Be reported on the Standard Format for Reporting Emissions Testing Results as outlined in section 4
- Include emissions from maintenance and parts cleaning operations in the emissions results
- Include a volume balance that accounts for >90% of fluorine, chlorine, and bromine

1.3 Roles and Responsibilities of Suppliers for Selection Activity

1. The supplier has a responsibility to assist the end user in achieving the customer's environmental emission goals.

2. Suppliers can perform the engineering analysis and emission measurements using approved in-house analytical resources or the supplier can use a qualified third party.

3. The supplier is encouraged to contact a third party for establishing test methodologies based on the latest revision of methods specified in this document.

4. The supplier must fill out the emissions report form completely.

5. The supplier must provide a written engineering analysis and emission measurement report with supporting data.

1.4 Items to be Reviewed With a Third Party

It is suggested that the following actions be included when requesting quotes from potential third-party consultants. Preparation time in the process will help control costs and schedule issues. Suppliers need to match their concerns to the capabilities of an outside third-party resource. While many third parties are available, not all have the same capabilities.

To determine the appropriate third party, consider asking questions like the following during the request for quotes to ensure the best fit between you and your third party:

1. Can the third party provide a full emissions analysis and emissions report for each process application you plan to offer?
2. Does the third party have the internal expertise and analytical equipment required?
3. What are the strengths of the third party?
4. What are the weaknesses and how will the third party compensate?
5. What engineering resources can the third party provide to assist in determining solutions for any improvements that may be identified to meet emission goals?
6. Will the third party review the equipment after completion of potential improvements and issue a final report?
7. What is their previous experience in conducting these types of characterization studies?
8. Is the supplier using calibration standards to quantify the results?

Be sure to request at least three competitive quotes.

2 TARGET EMISSIONS

The following list and table show which emission compounds should be quantified for a particular process chemical. Table 2 was designed to be a **guide** for equipment suppliers. If a process chemical is not listed, consult one of the technical contacts (Section 5.1).

2.1 Special Instructions

The following target compounds must be quantitated using calibration standards: NF_3, C_3F_8, C_2F_6, CF_4, C_4F_8, SF_6, CHF_3, C_5F_8, CH_3OH (methanol), C_2H_5OH (ethanol), CH_3COCH_3 (acetone), $(CH_3)_2CHOH$ (isopropanol), $NH(Si(CH_3)_3)_2$ (HMDS), $C_2H_5OOCCC(OH)CH_3$ (Ethyl lactate), $C_4H_6ON(CH_3)$ (NMP), $CH_3O(CH_2)_3OOCCH_3$ (PGMEA), $C_4H_8SO_2$ (Sulfolane), $CH_3(CO)C_5H_{11}$ (2-Heptanone), HF, Cl_2, HCl, F_2, SiF_4, OF_2, CO, NO, NO_2, N_2O, SO_2

– BrCl should be measured when Br- and Cl-containing compounds are present in the process recipe
– During emissions testing, a survey scan must be acquired. If any unidentified intensities are 10% of the height of the most intense peak attributed to a process gas, then the source of that peak needs to be identified and quantified.
– If FTIR analysis is ineffective in determining NO or NO_2 emissions, then chemiluminescence methods can be used to quantitate the emissions.

Table 2   Target Compounds

Process Chemicals	Target Compounds to Quantify
AsH_3	AsH_3
BCl_3	Cl_2, BCl_3, HCl, $SiCl_4$, CCl_4, $CHCl_3$
Br_2	Br_2, HBr, $SiBr_4$
CF_4	C_2F_6, CF_4, CHF_3, HF, F_2, SiF_4, OF_2, COF_2, CO
C_2F_6	C_2F_6, CF_4, CHF_3, HF, F_2, SiF_4, OF_2, COF_2, C_2F_4, CO
C_3F_8	C_2F_6, CF_4, C_3F_8, CHF_3, HF, F_2, SiF_4, OF_2, COF_2, C_2F_4, CO
C_4F_8	C_2F_6, CF_4, C_4F_8, C_3F_8, CHF_3, HF, F_2, SiF_4, OF_2, COF_2, C_2F_4, CO
C_5F_8	C_2F_6, CF_4, C_5F_8, C_4F_8, C_3F_8, CHF_3, HF, F_2, SiF_4, OF_2, COF_2, C_2F_4, CO
CHF_3	C_2F_6, CF_4, CHF_3, HF, F_2, SiF_4, OF_2, COF_2, C_2F_4, CO
CH_3COCH_3 (Acetone)	CH_3COCH_3
CH_3OH (Methanol)	CH_3OH (Methanol)
C_2H_5OH (Ethanol)	C_2H_5OH (Ethanol)
$(CH_3)_2CHOH$ (Isopropanol)	$(CH_3)_2CHOH$ (Isopropanol)
$CH_3O(CH_2)_3OOCCH_3$ (PGMEA)	$CH_3O(CH_2)_3OOCCH_3$ (PGMEA)
$C_2H_5OOCCC(OH)CH_3$ (Ethyl lactate)	$C_2H_5OOCCC(OH)CH_3$ (Ethyl lactate)
$C_4H_6ON(CH_3)$ (NMP)	$C_4H_6ON(CH_3)$ (NMP)
$C_4H_8SO_2$ (Sulfolane)	$C_4H_8SO_2$ (Sulfolane)
$CH_3(CO)C_5H_{11}$ (2-Heptanone)	$CH_3(CO)C_5H_{11}$ (2-Heptanone)
Cl_2	Cl_2, HCl, $SiCl_4$, CCl_4, $CHCl_3$
HBr	HBr, Br_2, $SiBr_4$
HCl	Cl_2, HCl, $SiCl_4$, CCl_4, $CHCl_3$
HF	HF, F_2, SiF_4, OF_2, COF_2
NF_3	NF_3, HF, F_2, SiF_4, OF_2, COF_2, NO, NO_2, N_2O
NH_3	NH_3
$NH(Si(CH_3)_3)_2$ (HMDS)	$NH(Si(CH_3)_3)_2$ (HMDS)
N_2O	N_2O, NO, NO_2
O_3	O_3
PH_3	PH_3
SiF_4	HF, F_2, SiF_4, OF_2, COF_2
SiH_4	SiH_4
SF_6	SF_6, HF, F_2, SiF_4, OF_2, COF_2, SOF_2, SO_2F_2, SO_2
$Si(OC_2H_5)_4$ (TEOS)	$Si(OC_2H_5)_4$, CH_3OH, HCOOH, C_2H_5OH, CO, CO_2
$PO(C_2H_5O)_3$ (TEPO)	$PO(C_2H_5O)_3$ (TEPO)
$TiCl_4$	$TiCl_4$
WF_6	WF_6, HF, F_2, SiF_4, OF_2, COF_2

3 EMISSIONS REPORT FORMAT

3.1 Air Emissions Measurements Report

This section outlines the instructions for completing the emissions forms in Section 4, Table 3 and Table 4. Please refer to the table in Section 1.1 to determine which parts of the form to fill out.

3.2 General Information

The first section of the report must include
1. Type of tool tested
   - Name of baseline process, name of tool, description of process function (e.g., "deposits 1000 Å of an oxide film")
2. The specific methodology used to determine the emissions
   - who performed the testing (in house vs. contractor), contact number for technical questions
3. Instrumentation Parameters
   - mass or wavenumber range, detection limits of instrumentation for each of the analyte compounds
   - model name and type
   - sampling conditions for calibration and wafer monitoring (source pressure, electron energy, sampling frequency, detection method and settings [faraday or multiplier], etc.)

3.3 Recipe/Emissions Information

1. A template (emissions form) will be provided on which to fill in the results of the testing.

2. Experiments to be conducted (figures must be included for each of these experiments).
   a. Calibrations. Calibrate those compounds denoted by an asterisk in the emissions compound matrix.
   b. Run process gas recipe with no radio frequency (RF). Must be repeated three times. (This step is applicable to only those process tools that use plasma sources.)
   c. Monitor wafer processing. So that semiconductor companies can relate the emissions values from the equipment supplier to the individual semiconductor process, conduct a statistical design of experiments (DOE) for chemical flow, RF power (if applicable), and plasma pressure (if applicable). For process tools that use spin coaters, spin speed should be one of the variables used in the DOE. If the DOE cannot be completed (i.e., insufficient time), then the baseline recipe should be tested. All baseline emission values should be the average of at least five wafers. The average and the standard deviation should be reported.

3. All values on the template that have an asterisk (*) must have an error associated with them. The contributions to the error reported must be explained. All values should have three significant digits.

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4. In general, the data needed are as follows:

  a. Process Recipes – The equipment supplier's baseline process recipe must include flows, times, RF power, plasma pressure, and spin speed. All substeps to the process should be included. For example, most etching recipes consist of a stabilization, etch, and over-etch step. The process parameters (flows, times, etc.) listed previously should be determined for each of the substeps of the overall process.

  b. Pump Purge Estimation – The pump purge rate on the process tool must be determined when sampling the process exhaust post pump. Accepted methods of determining pump purge rates can be found in the mass spectrometry methodology. Note: The pump purge rate estimation methodology can be done with an FTIR also.

  c. Calibration Curves – Plots of signal intensity vs. analyte concentration must be provided for each of the compounds. The slope (with error), y intercept, and correlation coefficients must be provided with each plot. Figure 1 shows an example of a typical calibration curve. The error associated with the slope must not exceed 5%. The calibration curve should consist of at least 1 point per factor of 10 and no less than 5 points.

  d. Emission Values – If the process tool uses a plasma, then both the concentration (ppmv) vs. time plots for the no RF and wafer processing experiments must be included. Figure 1 illustrates how the concentration (ppmv) vs. time plots should plotted. All final emission values must be expressed in lbs./wafer. The equation used to derive the lbs./wafer value from the raw signal intensities must be included. **To allow a semiconductor company to relate the emission values obtained from the tool supplier to its particular process, conduct a statistical design of experiments (DOE) for chemical flow, RF power (if applicable), and plasma pressure (if applicable). For process tools that use spin coaters, spin speed should be one of the variables used in the DOE**. If the DOE cannot be completed (i.e., insufficient time), then the baseline recipe should be tested. All baseline emission values should be the average of at least five wafers. The average as well as the standard deviation should be reported. The error in the average must not exceed 10%. If a specific compound is not detected, then the detection limit of the instrumentation for that compound must be given. How the detection limit was determined must also be clearly explained.

  e. Volume Closure – From the equivalent halide inlet and outlet amounts, a volume closure on the halogens (F, Cl, Br) must be calculated. Equivalent Halide Outlet (EHO) is calculated by the following equation:

  EHO (x) = Volume emitted of compound X * number of halides in compound X

Similarly the Equivalent Halide Inlet (EHI) is calculated by the following equation:

  EHI (x) = Volume of process compound used for compound X (from recipe) * number of halides present in compound X

The volume closure is then calculated by the following equation:

Volume closure = (total amount of EHO/Total amount of EHI) * 100.

(Note: The total amount of EHO or EHI is merely the sum of the EH for all compounds that are either emitted (outlet) or used (inlet) in the process.)

Example: A process recipe of 50 sccm (0.05 slpm) of CF_4 for 60 sec emits 30 scc (0.03 std. liters) of HF and 40 scc (0.04 std. liters) of CF_4.

Total EHI = 0.05 slpm * 1 Min. * 4 Fluorine equivalents in CF_4 = 0.20

Total EHO = (0.03 * 1 Fluorine equivalent in HF) + (0.04 * 4 Fluorine equivalents in CF_4) = 0.03 + 0.16 = 0.19

Fluorine Volume closure = 0.19/0.20 *100 = 95%

The success criterion for volume closure is to be greater than 90%. If the volume closure for volatile emissions is less than 90%, a plausible explanation and supporting data must accompany the report. Some possible reasons for a low volume closure are (1) solids formation, (2) unquantitated volatile emissions, and (3) liquid emissions. For example, if the equipment supplier gets a 60% volume closure for a specific process and believes it is due to solids formation, then the supplier must identify the composition of the solids.

slope = 0.00052 $\pm$ 0.00001
y-int. = 0.10 $\pm$ 0.06
R^2 = 0.9988
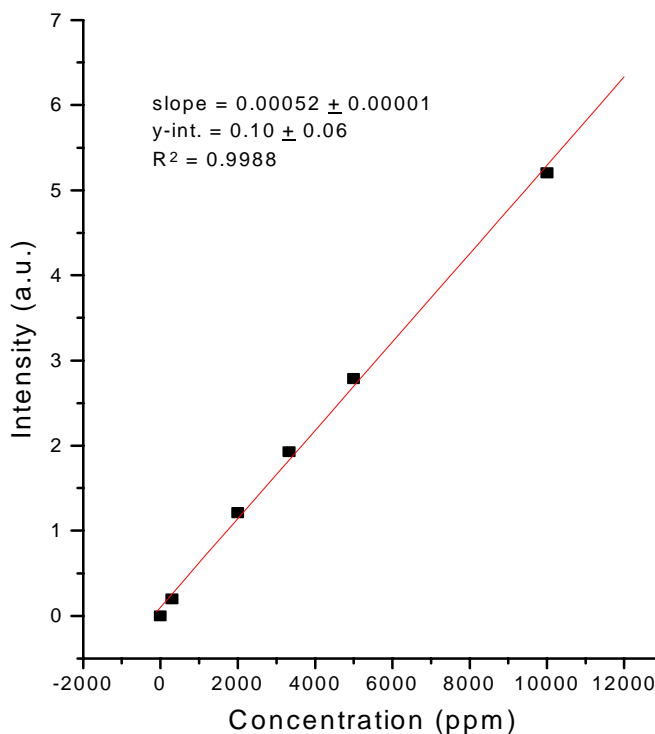
Figure 1   Sample Calibration Curve
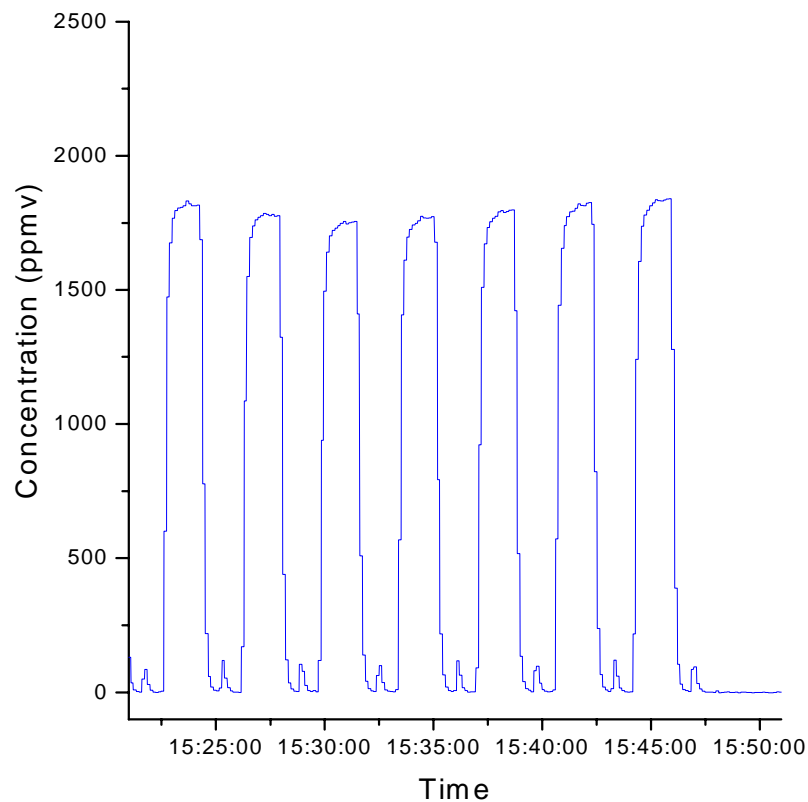
Figure 2   Example of Process Emission Plots

     f.   Utilization Efficiencies - If the process tool uses a plasma, the utilization efficiency (UE) must be calculated by two methods. If the process tool does not use a plasma source, then only method #2 needs to be used. The first method of calculation is given by the equation:

3.3.1   Method #1 (Plasma)

Utilization Efficiency = 1 – [integrated area of process compound emitted[1]/integrated area of process compound input[2]] * 100

  [1]   This value is the integrated emissions for a single wafer for the emitted process compound from the "wafer processing" concentration vs. time plot (Figure 2).

  [2]   This value is the integrated emissions for a single wafer for the emitted process compound from the "no RF experiment" concentration vs. time plot (Figure 2).

This first method uses the values from concentration vs. time plots (i.e., the raw intensities have not been converted into lbs./wafer).

3.3.2 Method #2 (Plasma and No Plasma)

Utilization Efficiency = 1 – [integrated area of process compound emitted[3]/mass of process compound used[4]] * 100

[3] This value is the mass of emitted process compound for a single wafer (lbs./wafer), which is calculated by integrating the area under the curve of process compound emitted for each wafer.

[4] This value is the mass of process compound used as calculated from the process recipe.

3.4 Preventive Maintenance (PM) Procedures

This section is designed to provide information about the specific preventive maintenance (PM) procedures that are required for a given process/process tool. Since it is assumed that usage equals emissions, only usage data will be required for this section.

Tool Identity: Enter the name and description of the process and process tool.

Description of Procedure: Briefly describe each PM procedure. For example, a wet clean is a procedure used during a PM. Other procedures that are routinely conducted during PMs that use chemicals must also be included in this section. Examples are mass flow controller (MFC) calibration procedures and plasma cleans associated with PMs.

Frequency of Procedure: Indicate how often the specific procedure is conducted on a per wafer basis.

Method: Explain how the procedure is conducted. Example: wiping the chamber clean with a saturated wipe, using a chamber plasma clean with 500 sccm of O2 for 30 seconds, etc.

Chemical Used: Identify which chemicals are used by the specific PM procedure and its concentration (e.g., 10% or 100%). Example: 100% Isopropanol (IPA)

Chemical (Vol./Procedure): Identify how much of each chemical is used in the procedure on a per procedure basis. Example: 100 mls of IPA

Water Purity: If water is used in the PM, tell what type of water is needed. Example: ultrapure water (UPW), etc.

Water (Vol./Procedure): Indicate the amount of water used on a per procedure basis. Example: 5 gallons of UPW/procedure

3.5 Parts Clean

Note: Even if the parts clean is outsourced, it must still be included.

This section is designed to provide the details of the parts clean procedures required for a given process/process tool. Since it is assumed that usage equals emissions, only usage data are required.

Frequency of Parts Clean: Indicate how often the parts clean is conducted on a per wafer basis.

Cleaning Method: Explain how the parts clean is carried out. Examples: by bead blasting for 10 minutes, by etching in a 50:50 HF:water bath for 10 minutes, etc.

Chemical Used: Identify which chemicals are used in the parts clean process. Example: HF.

Chemical (Vol./Clean): Explain how much of each chemical is used in the procedure on a per procedure basis. Example: 50 ml of HF/clean

Water Purity: If water is used in the parts clean process, identify what type of water is needed. Example: ultrapure water (UPW), etc.

Water (Vol./Clean): Indicate the amount of water used on a per clean basis. Example: 5 gallons of UPW/clean

3.6 Emissions from Process Tools Using "Open" Tanks/Baths

3.6.1 General Testing Procedures

There are additional testing concerns when characterizing the emissions of process tools that contain open bath/tanks. The sampling point for the emissions characterizations should be downstream of the process tool (i.e., somewhere on the exhaust manifold of the tool). Because the emissions from these types of tools are continuous, testing must be completed during wafer processing and when the tool is idle. During testing, factory conditions must be used whenever possible. For example, the emissions testing should be conducted while the tool is processing wafers. Furthermore, because data suggest the emissions from these tools depend on how may wafers are on the rack, these test must be conducted using FULL racks of wafers. The emissions should be reported in terms of liters/rack and lbs./rack. The emission values should be the average of at least five racks of wafers. The equipment supplier must also clearly indicate how many wafers are in a rack (25 wafers, 50 wafers, etc.).

3.6.2 Correction for Dragout

Dragout is defined as the chemical residue on the wafers or chemical dripped on the surface of the process tool as the wafers leave the baths (i.e., anything that does not go down the open tank/bath drain). This residue ultimately evaporates into the air or is rinsed off in the UPW baths (depending upon the specific process). Dragout can become significant as the number of wafers processed increases. To determine dragout, the volume of liquid that is liberated during wafer lot transfer must be measured. This volume should then be converted into lbs./wafer. This experiment should be run at least five times. The final dragout number (in lbs./wafer) should be reported as an average of these experiments with a standard deviation.

3.6.3 IPA Dryers

Because the emissions from these types of tools are continuous, testing must be completed during wafer processing and when the tool is idle. During emissions testing, factory conditions must be used whenever possible. For example, emissions should be tested while the tool is processing wafers. Furthermore, because data suggest the emissions from this tool depend on how may wafers are on the rack, these test must be conducted using FULL racks of wafers. The emissions should be reported in terms of liters/rack and lbs./rack. The emission values should be the average of at least five racks of wafers. The equipment supplier must also clearly indicate how many wafers are in a rack (25 wafers, 50 wafers, etc.).

3.7 Chemical/Water Mass Balance

3.7.1 General Information

The purpose of the following sections is to provide guidance in correctly completing the chemical usage and wastewater emissions form to fulfill the wastewater emissions requirement for process tool selection. This applies to all process tools that have a drain in which liquid chemicals (i.e., pure or combined with water) are emitted from the process tool.

This General Information section should contain general information about the process tool. It should contain the name of the process tool and company, the function of the process tool (e.g., deposits oxide film, etches a silicon nitride film, etc.), the run rate (in wafers/hour), and the total number of drains for the process tool.

3.8 Connection Hookup Diagram

The equipment supplier should provide a detailed block diagram that clearly shows all the points of connection to the process tool (both input chemicals and the output liquid chemicals and wastewater [drains]). The drains should be labeled by type (i.e., solvent drain, acid drain, wastewater drain, etc.). Also the identity and concentrations of the primary constituents of the outputs (drains) should be included.

Example: A process tool with four connection points (three inputs [chemicals] and one output [drain]), as shown in Figure 3.

Input   Output

UPW $\longrightarrow$

H_2SO_4 $\longrightarrow$ | Process Tool | $\longrightarrow$ Acid drain (100 ppm H_2SO_4, 50 ppm HC1)

HC1 $\longrightarrow$
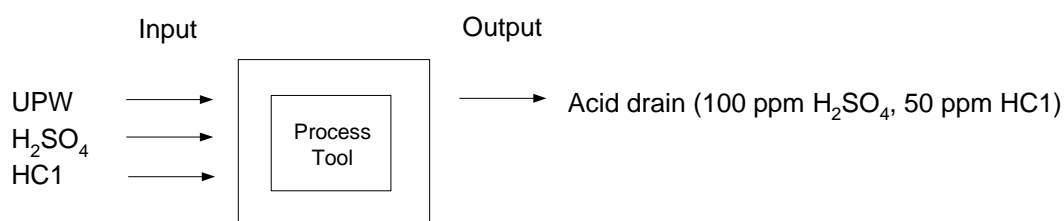
Figure 3   Connection Hookup Diagram

3.9 Chemical/Water Connections and Discharges

More specific information is required for each point of connection (whether it be an input chemical/water or an output chemical/wastewater/water). Each point of connection should be assigned a number and purpose. Example: Connection point #1 is the input process chilled water (UPW). Its purpose is to supply UPW to the process tool for cooling.

Next, the volume associated with each connection point must be included. If the chemical/water flows through the tool, then the volume should be quantified in gallons per minute. For the constant flowrates, a high flowrate and low flowrate along with an associated time per wafer for each of the flows are required. If the chemical/water is used in a static bath, then the volume should be expressed in gallons and the dump frequency included. If the connection point is a drain, then the outlet flowrate of the chemicals/wastewater should be included. Finally, the primary constituents should be identified and quantified for each of the output connection points (drains). All concentrations should be the average of at least five cycles. Both the average and standard deviation should be included. National standard testing methods should be used for the testing procedures.

3.10 Solid Waste Generated During Wafer Processing and PMs

Information about the amount of solids emitted from the process tool is required. The equipment supplier must identify any solid material that is emitted from the process tool and the quantity of solid emissions in lbs./wafer through the tool. All emissions should be the average of at least five cycles. Both the average and standard deviation should be included.

4 STANDARD FORMATS FOR REPORTING EMISSIONS TESTING RESULTS

Table 3   Air Emissions Measurements Report

General Info.					
Process No.:	Tool Tested:	Process Step Name:			
Test Date:	Tool Model:	No. Wafers Tested:			
Pump Purge rate*:	Thickness of Film Deposited/Etched/ Cleaned:	Type of Film Deposited/Etched/ Cleaned:			
Recipe Info.					
Input (Process) Compound	Process Step	Flow, sccm	Time, sec.	RF Power^2,	Plasma Press.^{2}
				W	millitorr
Emissions Info.					
Input Compound	Volume In	Equivalent Inlet Halide*	Mass In*,		
	Std. liters/wafer		lbs./wafer		
Emissions Compound	Volume Out Std.	Equivalent Outlet Halide *	Mass Out*,	Util. Eff.^{1} *	Vol. Closure*
	liters/wafer		lbs./wafer	%	(F, Cl, Br)
1 – Utilization efficiencies must be calculated by two methods as described in the emissions report criteria.					
* These values must have error bars associated with them					
2 – If applicable.					

Preventive Maintenance (PMs)						
Tool Identity:						
Description of Procedure	Frequency of Procedure (# of wafer passes)	Method Details	Chemical Used	Chemical Vol./Procedure	Water Purity	Water Vol./Procedure
Parts Cleans						
* Include usage even if outsourcing of cleaning is suggested						
Frequency of Clean (# of wafer passes)	Cleaning Method	Chemical Used	Chemical Vol./Clean	Water Purity	Water Vol./Clean	

Emissions from Process Tools Using "Open" Tanks/Baths					
Examples of Process Tools using open Tanks/Baths - Acid Wet Stations, Acid Wet Benches					
Tool Identity:					
Description of Process:					
Recipe Info.					
(Should be filled out for each open tank/bath in process tool.)					
Chemicals Used in Tank/Bath	% Composition	Total Volume of Tank	# of Bath/Tanks per Tool	Time Bath/Tank is Open (per rack)	Air Velocity Across Open Tank
		liters		sec.	ft^3/min
Emissions Info.					
(Should be filled out for the entire process tool.)					
Emissions Compound	Volume Out Std. liters/rack	Mass Out*, lbs./rack	Dragout[1] lbs./rack		
IPA Dryer[2]					
Input Compound	Volume In Std. liters/rack	Mass In*, lbs./rack	Emissions Compound	Volume Out Std. liters/rack	Mass Out*, lbs./rack
1 – See Emissions Report Criteria.					
2 – If applicable.					
* These values must have error bars associated with them					

Table 4   Chemical/Water Mass Balance

General Information					
Equipment Name/Company:					
Function of Process Tool:					
Run rate (wafers/hour):					
Total # Connections/Tool:					
Connection Hookup Diagram					
Attach a block diagram showing points of connection for chemical/water inputs and chemical/water discharges.					
Chemical/Water Connections *and Discharges*[2]					
Connection #					
Purpose:					
Volume[1]	Time	Dump Frequency	Constituents	Concentration[3]	
	per wafer	(wafer based)		(mg/L)	
Solid Waste Generated during Wafer Processing and PMs					
Identification	Emissions				
	(lbs./wafer pass)				
1 – If the chemical/water flows through the tool, then the volume should be quantified in gpm. For constant flowrates, a high flowrate and low flowrate along with an associated time per wafer for each of the flows is required. If the chemical/water used is in the form of a static bath, then the volume should be expressed in gallons and the dump frequency included.					
2 – This section should be filled out for every connection in the process tool.					
3 – Flows and concentrations must be based on measurements averaged over at least 5 wafer cycles					

5   CONTACT INFORMATION

Listed below are technical contacts for the mass spectrometry and infrared spectroscopy protocols:

Name	Area of Expertise	Telephone #
David Green (NIST)	MS and FTIR	(301) 975-4869
Pete Maroulis (APCI)	MS	(610) 481-6242
Bill Reagen (3M)	FTIR	(612) 778-6565
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APPENDIX – TECHNICAL PROTOCOLS

This section explains the best known methods for conducting process tool emissions experiments. While other analytical methods may be applied to emissions characterization, most of these techniques have severe limitations. If other analytical techniques are used to characterize process tool emissions, more supporting data must be provided to guarantee the quality of the data. These additional supporting data will have to be defined case by case given the considerable number of analytical techniques that could be used. The two recommended techniques for conducting the air emissions studies are mass spectrometry (MS) and FTIR. The MS protocol was written by Air Products and Chemicals Inc.; the FTIR protocol was written by 3M Corporation.

A.1 Mass Spectrometry Protocol

Standard Quantitative Analytical Method for the Determination of CF_4, C_2F_6, C_3F_8, CHF_3, NF_3, and SF_6 in Process Tool Exhaust Streams

A.1.1 Introduction

This procedure was developed to determine CF_4, C_2F_6, C_3F_8, CHF_3, NF_3, and SF_6 found in semiconductor processing effluent streams. These compounds are primarily found in the effluent of chemical vapor deposition (CVD) and plasma etch applications. The method is based on using QMS. In QMS, the sample is ionized using electron impact ionization. The quadrupole mass filter separates the ions based on their mass-to-charge ratio (m/e). A secondary electron multiplier or a Faraday plate is used as a detector for these mass separated ions. Concentrations of the individual components in the sample are determined from QMS response factors, which are determined from direct calibration of the QMS response to the compounds listed above.

Basic Quadrupole Mass Spectrometer Configuration: The basic components of a quadrupole mass spectrometer system are an ionizer, a quadrupole mass filter, and a detector such as an electron multiplier.

Ionizer: Here the molecules in the sample gas are ionized. Thermionic emission from tungsten or thoriated iridium filaments are used to produce 70 eV electrons. These electrons can ionize the molecules by the following interaction:

$$e^- + ABC \rightarrow ABC^{+*} + 2e\text{-}$$

$$ABC^{+*} \rightarrow A + C + B^+$$
$$\rightarrow AB^+ + C$$
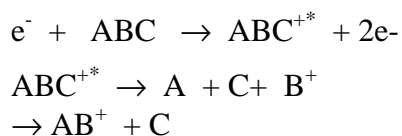
The molecule ABC is first ionized into an excited ionic state. Depending upon the structure of the molecule the excited ionic state will produce different fragment ions of the type AB^+, B^+, AC^+, etc.

The ions produced in the ionizer are extracted using an electrostatic lens. A series of electrostatic lenses are used to focus the extracted ions into the entrance of the quadrupole mass filter.

Quadrupole Mass Filter: The quadrupole mass filter consists of four cylindrical rods to which both RF and DC voltages are applied. The rods opposite each other are connected together. The voltage U + Vcoswt is applied to one set of rods, whereas the voltage -(U + Vcosωt) is applied to the other set of rods. The typical operating frequency of the RF voltage is 1.2 MHz. Under the

influence of this quadrupolar field, the equation of motion for the ions is represented by Matheiu's equation:

$$\frac{d^2u}{d\zeta^2} + \left(a_u - 2q_q \cos 2\zeta\right) u = 0$$

where $\quad \zeta = \dfrac{\omega t}{2}$

and $\quad a_u = \dfrac{4eU}{m\omega^2 r^2}$

where U is the DC voltage, m is mass, ω is angular frequency, and r is the radius of the quadrupole and

$$q_u = \frac{2eV}{m\omega^2 r^2}$$

where V is the peak amplitude of the RF voltage of angular frequency ω.

The solutions to the Matheiu equation fall into either stable or unstable regions, depending upon the mass-to-charge ratio of the ion. The ions for which the solution is stable exit the quadrupole, whereas all other ions have unstable trajectories and hit the rods of the quadrupole. By changing the amplitude of the RF field, V, different ions can be made to have stable trajectories. Thus by changing the RF field, the quadrupole mass spectrometer can be tuned to transmit different masses. The resolution of the quadrupole mass filter is determined by the ratio U/V. For constant resolution, the ratio U/V is kept constant when the RF voltage is adjusted to change the transmitted mass.

Detection System: The ions transmitted by the quadrupole mass filter are detected using either a Faraday plate or an electron multiplier. The Faraday plate is a metal plate placed at the end of the quadrupole filter. A sensitive electrometer connected to this plate records the current produced when a charged ion hits the Faraday plate. Typically, the electrometer is sensitive enough to detect current in the pico ampere range.

For currents smaller than a few pico amperes, an electron multiplier is used instead of the Faraday plate. In most QMSs, a continuous dynode electron multiplier is used although a discrete dynode electron multiplier could also be used. The entrance of the electron multiplier is biased at about -2000 V whereas the other end is connected to a ground-referenced amplifier. The positive ions exiting the quadrupole are accelerated towards the -1500 V potential on the entrance of the electron multiplier. When the ions strike the electron multiplier, they generate a few secondary electrons. These secondary electrons, under the influence of the gradient in the electron multiplier, strike a different part of the electron multiplier. Each electron produces a few secondary electrons. These electrons will cascade down the electron multiplier. This cascading effect generates about a million electrons for every ion that strikes the entrance of the electron multiplier. This enhanced signal is measured by the preamplifier.

Quadrupole Mass Spectrometer Resolution: A QMS is normally operated in a unit mass resolution mode meaning masses are separated by one atomic mass unit. The resolution of a quadrupole mass filter is defined by the equation:

$$m/\Delta m = (0.126)(0.1678 - U/V)^{-1}$$

For infinite resolution, U and V are given by the equations:

$$U \text{ (volts)} = 1.212 \text{ mf}^2\text{r}^2$$
$$V \text{ (volts)} = 7.219 \text{ mf}^2\text{r}^2$$

where f is frequency. Resolution (m/Δm) can be empirically determined by dividing the center point mass by the full width at half height of the peak for each mass of interest.

Detection Limits: The mass spectrometer chosen for this application should have the necessary sensitivity to detect the selected effluent species at a predetermined level. The typical detection limit of each component determined with the QMS used for this study was 1 to 10 ppmv. System detection limits can be calculated using the SEMI guideline, which describes the calculation of a regression-based limit of detection. Two regression-based means for determination of a limit of detection (LOD), ordinary least squares (OLS) and weighted least squares (WLS) are often used. OLS analyses implicitly assume that signal variability is the same everywhere within the calibration window. WLS analyses allow signal variability to vary over the calibration window, but require an appropriate set of weights to complete the analysis. The LOD is calculated to obtain a 3-sigma equivalent (in probability) upper confidence limit. PC-based software is available from Air Products to help calculate statistical LODs based on the SEMI guideline.

A.1.2 Sampling Conditions

Sampling Location: The sample is taken downstream of the process tool and pump package (see Figure 4). The exact location will be determined by the specific tool and piping configuration associated with the process. The sample exhaust is vented back into the corrosive house ventilation system at a point downstream of the sample inlet location.
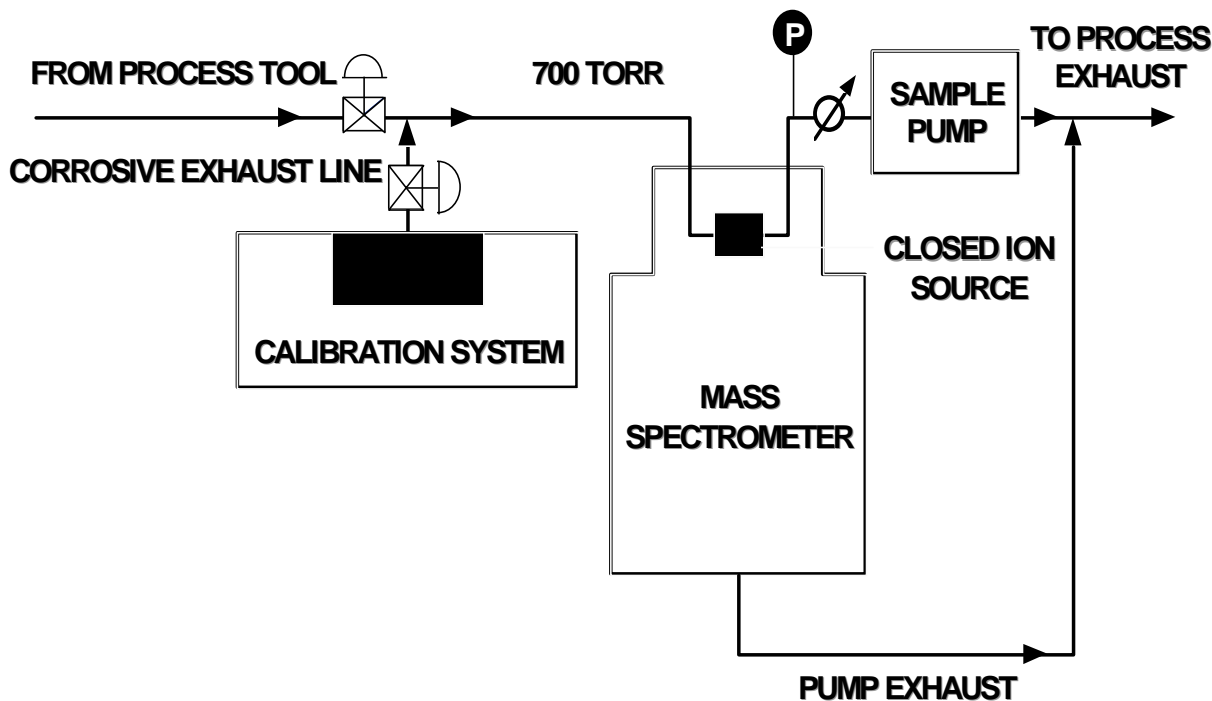

Figure 4   Process Tool Exhaust Sampling System

Sampling Conditions: Perfluorocompound (PFC) utilization efficiencies should be determined during actual wafer processing. For etch applications, efficiencies should be determined while etching a wafer (WIP, dummy, or test). For CVD applications, efficiencies should be determined during a chamber clean after deposition (efficiencies should not be determined in a clean chamber). All sampling is performed non-intrusively during wafer processing. Samples are drawn through the mass spectrometer source by an external sample pump. The pressure in the exhaust is slightly below 1 atm. (~ 750 torr). The pressure of the sample inlet is maintained at a lower pressure (approximately 700 to 740 torr) by throttling the sample pump. Because of the inertness of CF_4, C_2F_6, C_3F_8, CHF_3, NF_3, and SF_6, the sample lines do not need to be heated.

Mass Spectrometer Parameters: Choice of specific QMS operating conditions such as electron energy, secondary electron multiplier voltage, emission current, and ion focusing voltage are left to the discretion of the analyst provided the QMS responses to analytes are calibrated under the same conditions. These parameters are systems-specific and will need to be determined by the analyst. To address questions in this area, analysts should consult the QMS manufacturer, the system manual, basic mass spectrometer textbook, and other such sources.

Data Acquisition Mode: For this application, the mass spectrometer is operated in the selective ion monitoring (SIM) mode. The ions chosen depend on the PFC(s) used in the process and the byproducts being monitored. Listed below are the fragment ions used to determine the perfluorocompounds typically in CVD and etch tool exhausts.

Compound	Monitored Fragment Ion	m/e
CF_4	CF_3^+	69
C_2F_6	$C_2F_5^+$	119
C_3F_8	$C_3F_7^+$	169
CHF_3	CHF_2^+	51
NF_3	NF_2^+/NF_3^+	52/71
SF_6	SF_5^+	127

To identify unknown and known components in the sample, a complete mass spectrum is obtained by operating the mass spectrometer in the full spectrum scan mode. Standard mass spectra for each of the compounds listed above are include as part of this document (see Figure 5 through Figure 10). The spectra were obtained from the National Institute of Standards and Technology's website (http://webbook.nist.gov/).

Flowrates: A sample flowrate of approximately 0.5 to 1.5 slm is drawn from the process tool exhaust stream under study. This typical flowrate is needed to purge the sample manifold and obtain a temporally representative sample of the process. The flowrate into the mass spectrometer source is approximately 10 to 20 sccm.

Sample Frequency: The required sample frequency depends on the process being monitored. The software of the mass spectrometer should be capable of capturing the data at the required sample frequency. Fast processes, such as etch processes, require rapid sampling frequencies. Typical etch sampling frequencies should be on the order of 0.33 to 1 Hz. Chemical vapor deposition processes are longer and can tolerate sampling frequencies of 0.1 to 0.33 Hz.

Dynamic Dilution Calibration Parameters: The QMS must be calibrated for both mass location and response to analytes. A dynamic dilution calibration system is used to perform both types of mass spectrometer system calibrations. The simplest type of dynamic calibration system includes appropriate tubing, fittings, and two mass flow meters. One mass flow meter regulates the flowrate of the standard component used to calibrate the system. The second mass flow meter regulates the amount of diluent gas used to mix with the standard. The flowrates of the mass flow meters are adjusted to the appropriate settings to obtain the required concentrations for calibrating the MS. These data are used to generate a calibration curve for each compound of interest.

Mass flow controllers are used to accurately regulate the flowrates of the diluent and calibration gases. They should be calibrated using the single component gas being used with them. MFCs used with calibration mixtures should be calibrated with the calibration mixture balance gas if the individual components are approximately 2% or less. They should be calibrated over their range of use and operated in their experimentally determined dynamic linear range.

Mass Location Calibration: A mixture containing 1% He, Ar, Kr, and Xe in a balance gas of nitrogen is used to assure the alignment of the quadrupole mass filter. This mixture covers both low and high mass ranges. The mass spectrometer should be chosen so that the mass range is sufficient to detect the predominant peaks of the components under study.

QMS Response Calibration: The response of the QMS to the compounds listed above is determined by calibrating the system with test atmospheres containing the compounds of interest. These test atmospheres are created using dynamic phase dilution techniques as described above. A calibration curve should be generated for each compound.

Calibration Frequency: The mass spectrometer is calibrated before performing the first analysis of the day and after it is completed at the end of the day. This will enable the analysis to determine the drift of the instrument throughout the day.

Calibration Range: The mass spectrometer is quantitatively calibrated over the concentration range of the analysis for each gas to be analyzed. A multi-level calibration is performed using a minimum of five different concentrations including a zero. The zero point is defined as diluent containing no added analyte. The system should be calibrated over the concentration range of the samples.

Operating Procedures

1. Perform a qualitative mass calibration by running a standard containing stable components that provide predominant signals at m/e values distributed throughout the mass range to be used. This will ensure the mass locations are properly identified and that the m/e values of the mass fragments are correctly identified.

2. Quantitatively calibrate the mass spectrometer system over the concentration range of each component in the sample that will be analyzed. The sample concentration should fall in the linear dynamic range of the mass spectrometer signal response. The calibration should be performed at the same mass spectrometer inlet pressure as when obtaining an effluent sample for analysis. One way to do this is to carefully regulate the inlet pressure using a throttle valve and monitor the pressure using a capacitance manometer. If this is not done, then the relationship between inlet pressure and signal response should be empirically determined on the mass spectrometer being used.

3. To determine the response time of the instrument to changes in a process, a process gas such as C_2F_6 should be turned on at the process tool for a fixed period of time. This should be a relatively short period (e.g., 20 seconds). Then the amount of time it takes for the mass spectrometer to respond to this process gas should be recorded. This should be done at the beginning of each tool evaluation.

4. Pass the sample gas through the mass spectrometer, and acquire data for the required amount of time to track the process. The sample frequency is set to monitor the changes in the process. Repeat this for at least five wafers on the same process to obtain an average and standard deviation of process efficiencies and emission concentrations.

5. Repeat 1.5.2 at the end of the day and more frequently if necessary.

A.1.3   Calculations

Calibration: Plot ion intensity vs. analyte concentration for a given compound obtained during the calibration of the analytical system. Determine the slope and intercept for each calibrated species to obtain response factors with which to calculate concentrations in the sample. For an acceptable calibration, the R^2 value of the calibration curve should be at least 0.98.

Sample Analysis: To determine the concentration of a specific component in the sample, divide the ion intensity of the sample response by the calibrated response factor. Repeat this for each component.

Deconvolution of Interfering Peaks: It is necessary to deconvolute interfering peaks to obtain accurate results. As an example of this, C_2F_6 and CF_4 have common fragments in their mass spectra (CF_3^+, CF_2^+, CF^+, and F^+). CF_4 does not produce a fragment that is not observed in the mass spectra for C_2F_6. Thus it is necessary to deconvolute the contribution of ions attributable to C_2F_6 from the ions attributable to CF_4 at a common mass. Deconvolution can be achieved by using a prominent peak, such as $C_2F_5^+$, which is not common to both molecules. Contributions to m/e 69 from C_2F_6 can be subtracted by using the m/e 69/ m/e 119 ion intensity ratio obtained when C_2F_6 is present alone. For example, to determine the CF_4 concentration in the presence of C_2F_6, the following expression can be used:

$$S_{CF4}^{69} \;=\; S_{\text{Total}}^{69} - \left(S_{C2F6}^{119}\right)(B)$$

$$C_{CF4}^{69} \;=\; \left(S_{CF4}^{69}\right)\left(R_{CF4}^{69}\right)$$

where S is QMS signal, C is concentration, R is the response factor determine from the calibration curve, superscripts are amu values, and B is the branching ratio defined by:

$$B_{C2F6} \;=\; \frac{S_{C2F6}^{69}}{S_{C2F6}^{119}}$$

If other compounds are presents that contribute to the signal at m/e=69, they must also be included in the calculation.

Pump Purge Dilution: To calculate the exhaust dilution factor, determine the concentration of the PFC in the effluent by turning the RF power in the chamber off and flowing the PFC at the process flowrate. Divide the process flowrate specified in slm by this determined concentration (specified as liter of analyte) to yield the pump purge dilution. This information can be used to

estimate the emissions on a mass or volume bases (e.g., pounds per year or liters per years). Other ways to determine this value is by using a mass flow controller or a velometer.

The calculation below shows an example of how to determine pump purge dilution. Assume 50 sccm of CF_4 in the process tool yielded 500 ppmv average CF_4 effluent concentration with the RF power off.

$$\frac{0.050 \text{ L}_{CF4}(\text{min})^{-1}}{5 \times 10^{-6} \text{ L}_{CF4}(L_{Total\ Flow})^{-1}} = 100 \text{ L}_{Total\ Flow}(\text{min})^{-1}$$

Note that it is necessary to ensure RF power is off and that the compound chosen is thermally stable at the chamber temperature.
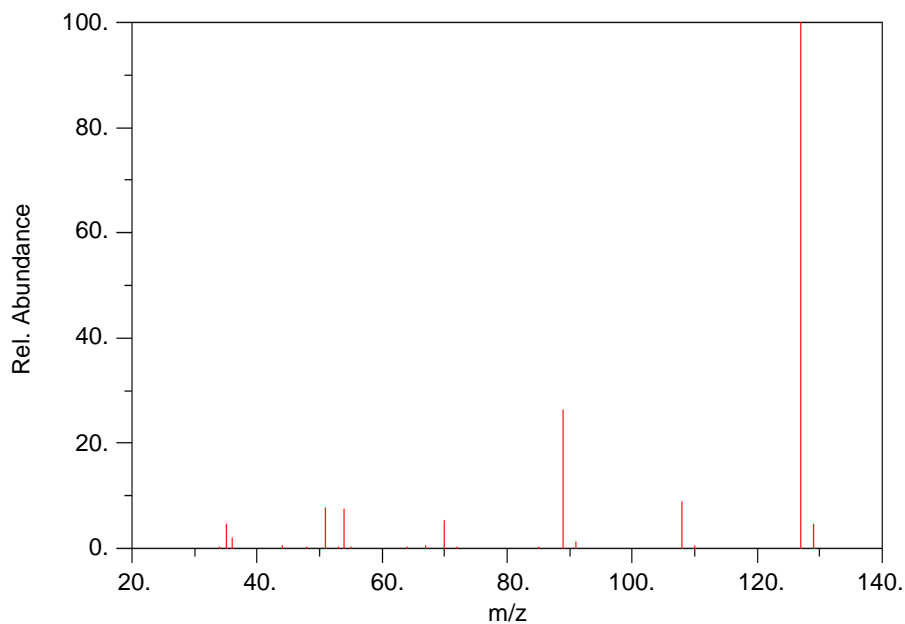

Figure 5   Mass Spectrum for Sulfur Hexafluoride (SF$_6$)
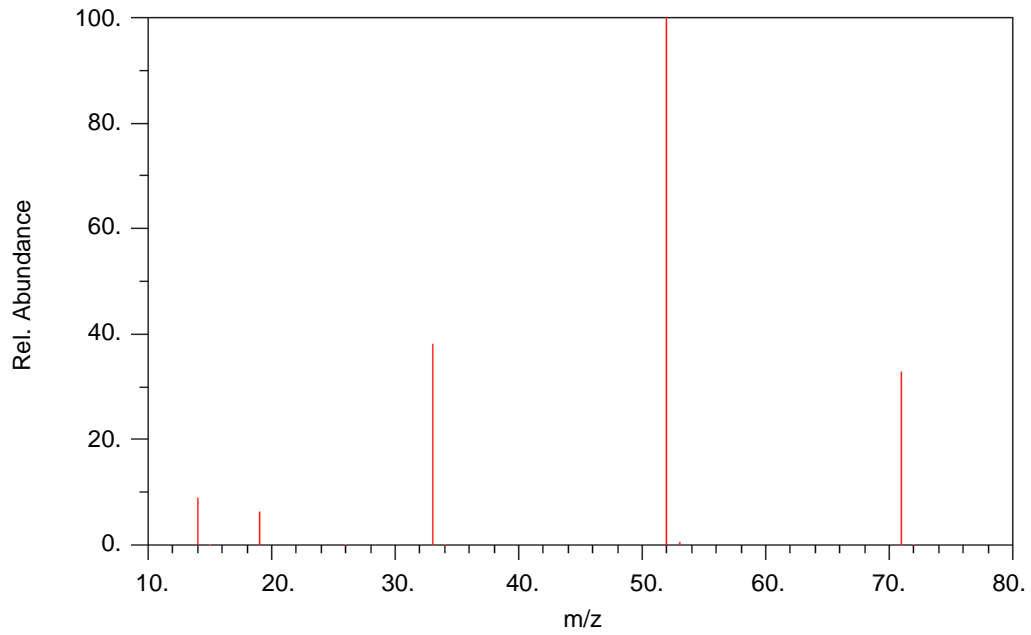
Figure 6   Mass Spectrum for Nitrogen Trifluoride (NF₃)
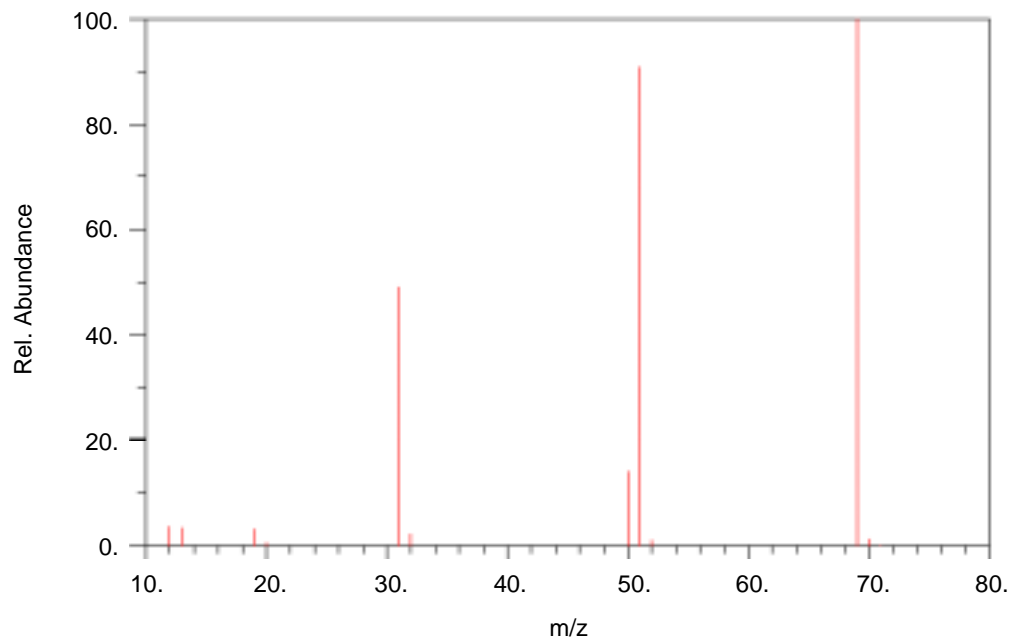

Figure 7   Mass Spectrum for Trifluoromethane (CHF₃)
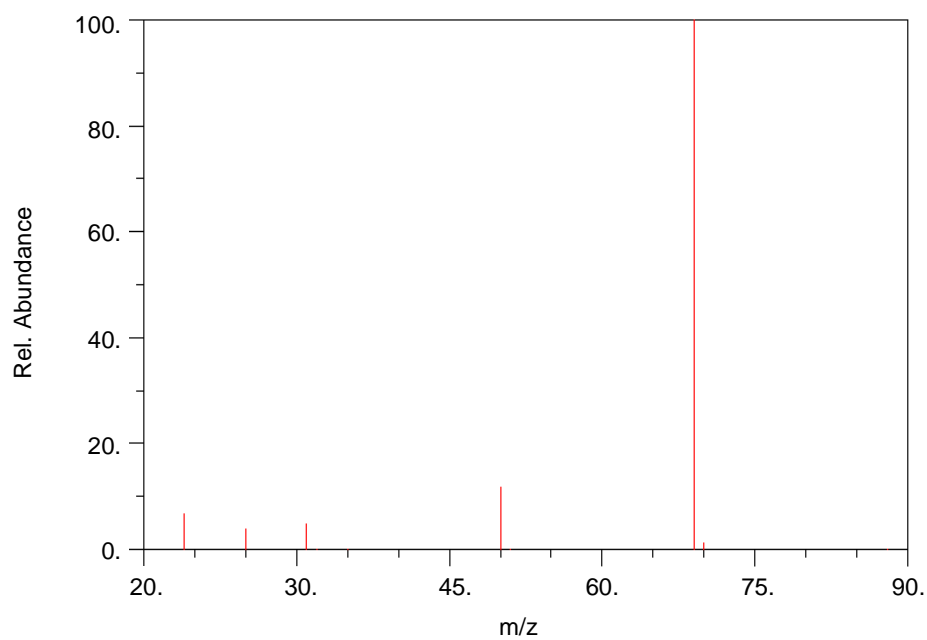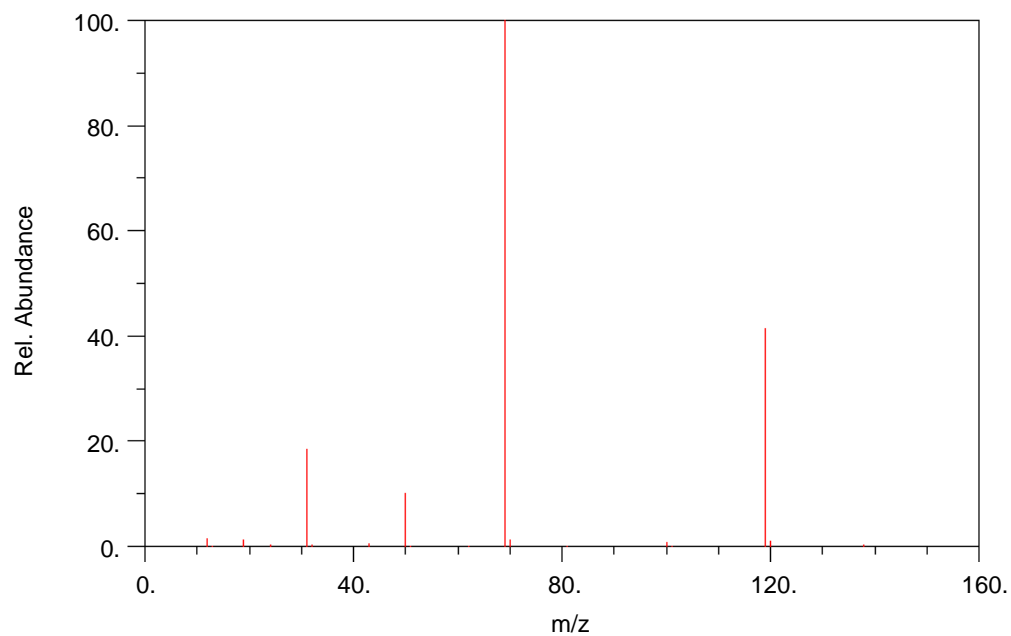
Figure 8   Mass Spectrum for Carbon Tetrafluoride (CF₄)

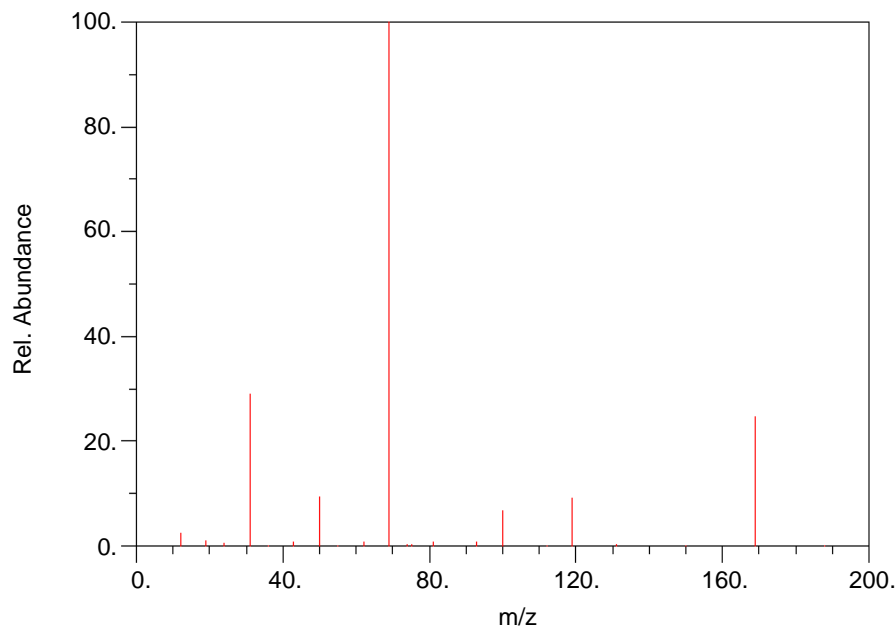**Figure 9   Mass Spectrum for Hexafluoro-ethane (C₂F₆)**

Figure 10   Mass Spectrum for Octafluoropropane (C$_3$F$_8$)

A.2   Fourier Transform Infrared (FTIR) Spectroscopy Protocol

Protocol for FTIR Measurements of Fluorinated Compounds in Semiconductor Process Tool Exhaust

A.2.1   Introduction

The intent of this document is to provide procedural and Quality Assurance and Quality Control (QA/QC) bases for gaseous concentration measurements of fluorinated compounds by extractive Fourier transform infrared (FTIR) spectrometry. The compounds of interest are Sulfur Hexafluoride (SF$_6$), Nitrogen Trifluoride (NF$_3$), Perfluoroethane (C$_2$F$_6$), Perfluoropropane (C$_3$F$_8$), Perfluoromethane (CF$_4$), and Trifluoromethane(CHF$_3$). They are to be measured in enclosed samples extracted from the effluent of semiconductor plasma tools; the analytes are typically in a mixture of oxygen and nitrogen with low moisture content (less than 0.1% by volume). Typical concentrations of the six analytes are in the 100 to 50,000 part-per-million volume (ppmv) range. Because the tool effluent concentrations can change rapidly, measurements must be made at least twice per minute, and several times per minute if possible. This requirement places special emphasis on the sampling and data acquisition operations for this application.

Substantial field experience in the use FTIR spectroscopy was gained in previous SEMATECH studies and described in reference 1, and has been used in the preparation of this protocol. The nomenclature employed in this document is adopted from reference 2, the guideline publication "Protocol for the Use of Extractive Fourier Transform Infrared Spectrometry for the Analyses of Gaseous Emissions From Stationary Sources." Appendix A (below) lists a number of the salient definitions. The intended audience of the current document is the technical community familiar with plasma tool operation and standard emission testing methodologies. However, because

FTIR spectrometry is a relatively new emissions testing technique, it is briefly described in Appendix B. Additional mathematical details of the technique are provided in Appendices C and D. Sections 2.0 and 3.0 outline procedures for the development and application of FTIR spectrometry to the application of interest. Existing documents employed in the development of this protocol are listed in Section 4.0.

A.2.2   Method Development

This section outlines a general procedure for the development and documentation of an extractive, FTIR-based analysis of the effluent from semiconductor plasma tools. This development has been largely accomplished in studies carried out by SEMATECH and 3M Corporation. The procedural outline below therefore serves as a means of summarizing and organizing the techniques employed in those studies within a common terminology and operational approach.

Within this procedural framework, FTIR Method development is seen to consist of two distinct phases, which are 1) a laboratory study phase and 2) a field study phase. In practice, portions of these developmental phases may occur simultaneously, and the results of some later portions of the procedural outline may necessitate adjustment and/or repetition of some activities appearing before them in the outline.

A.2.3   Laboratory Studies

Proposed Spectroscopic Conditions. Propose a set of spectroscopic conditions under which the field studies and subsequent field applications are to be carried out. These include the minimum instrumental linewidth (MIL), spectrometer wavenumber range, sample gas temperature, sample gas pressure, absorption pathlength, maximum sampling system volume (including the absorption cell), minimum sample flowrate, and maximum allowable time between consecutive infrared analyses of the effluent.

Criteria for Reference Spectral Libraries. On the basis of previous emissions test results and/or process knowledge, estimate the maximum concentrations of the six analytes in the effluent and their minimum concentrations of interest (those concentrations below which the measurement of the compounds is of no importance to the analysis). Values between the maximum expected concentration and the minimum concentration of interest are referred to below as the "expected concentration range." Calculate the expected maximum absorbance level for each compound under the proposed spectroscopic conditions.

A minimum of four reference spectra must be available for each analyte. When the set of spectra is ordered according to absorbance, the absorbance levels of adjacent reference spectra should not differ by more than a factor of six. Optimally, reference spectra for each analyte should be available at absorbance levels which bracket the analyte's expected concentration range; minimally, the spectrum must be available whose absorbance exceeds each analyte's expected maximum concentration.

If reference spectral libraries meeting these criteria do not exist for all the analytes and interferants, or cannot be accurately generated from existing libraries exhibiting lower MIL values than that proposed for the testing, prepare the required spectra according to the procedures below.

Preparation of Reference Spectra. When practical, pairs of reference spectra at the same absorbance level (to within 10%) should be recorded of independently prepared samples. The reference samples should be prepared from neat forms of the analyte or from gas standards of the highest quality commonly available from commercial sources. Either barometric or volumetric methods may be used to dilute the reference samples to the required concentrations, and the equipment used should be periodically calibrated in some independent fashion to ensure suitable accuracy. Dynamic and static reference sample preparation methods are acceptable, but dynamic preparations are more likely than static methods to give consistent results for reactive analytes. Any well-characterized absorption pathlength may be employed in recording reference spectra, but the temperature and pressure of the reference samples should match as closely as possible those of the proposed spectroscopic conditions.

If an MCT or other potentially non-linear detector (that is, a detector whose response versus total infrared power is not a linear function over the range of response employed) is used for recording the reference spectra, the effects of this type of response on the resulting concentration values should be examined and corrected for. Spectra of a calibration transfer standard (CTS) should also be recorded periodically with the laboratory spectrometer system to verify the absorption pathlength and other aspects of the system performance. All reference spectral data should be recorded in interferometric form and stored digitally.

Sampling System Preparation. Construct a sampling system suitable for delivering the proposed sample flowrate from the effluent source to the infrared absorption cell. For the compounds of interest, the surfaces of the system exposed to the effluent stream should be limited to stainless steel and Teflon; because of the potential for generation of inorganic automated gases, glass surfaces within the sampling system and absorption cell should be Teflon coated. Demonstrate that the system, when sampling from a simulated source at the estimated effluent source pressure, delivers a volume of sample at least four times the maximum sampling system volume in a time shorter than the proposed minimum time between consecutive infrared analyses.

Preliminary Analytical Routines. For the proposed absorption pathlength to be used in actual emissions testing, prepare a simulated spectrum of all the effluent compounds at their expected maximum concentrations plus the field CTS compound at 20% of its full concentration. Prepare a computer program or analytical routine for calculation of the six analyte concentrations plus the CTS compound (and their uncertainties) from a sample spectrum using a subset of the analyte and interferant reference spectra. Apply the program to all reference spectra and to the simulated (maximum expected concentration) spectrum. For each single analyte reference spectrum, ensure that the calculated concentrations and uncertainties of the other five analyte compounds are lower than the minimum concentrations of interest. For each analyte, plot the calculated concentrations versus the known reference spectrum concentrations, and ensure that the degree of linearity of this plot is suitable for the application. For the simulated spectrum, ensure that the calculated concentrations match the known reference and CTS spectrum concentrations to within the calculated uncertainty, and that the uncertainties are suitably low for the application.

Documentation. The laboratory and mathematical techniques used to generate reference spectra and to convert sample spectral information to compound concentrations should be thoroughly documented. The required level of detail for the documentation is that which allows an independent analyst to reproduce the results from the documentation and the stored interferometric data.

A.2.4 Field Studies

The performance of the proposed spectroscopic system, sampling system, and analytical method should be rigorously examined in a field study. During the field study, all the sampling and analytical procedures envisioned for future field applications should be demonstrated. Additional procedures not to be required during routine field applications, notably thorough dynamic spiking studies of the analyte gases, should be performed during the field study. The field study need be performed only once if the results are acceptable and if the effluent sources in future field applications prove suitably similar to those chosen for the field study. If significant changes in the effluent sources in future applications are noted and require substantial changes to the analytical equipment and/or procedures, a separate field study should be performed for the new set of effluent source conditions. Ideally, all data taken during the study should be carefully stored and documented, and all spectral information should be permanently stored in interferometric form.

System Installation. The spectroscopic and sampling sub-systems should be assembled and installed according to the manufacturers' recommendations and as used in section B.1.4. For the field study, the length of the sample lines used should exceed the maximum length envisioned for future field applications. The system should be given sufficient time to stabilize before testing begins.

Pre-Test Calibration. Record a suitable background spectrum using pure nitrogen gas. Introduce a sample of the CTS gas directly into the absorption cell at the expected sample pressure and record its absorbance spectrum (the "initial field CTS spectrum"). Compare it to the laboratory CTS spectra to determine the effective absorption pathlength. If possible, record spectra of field calibration gas standards (single component standards of the analyte compounds) and determine their concentrations using the reference spectra and analytical routines developed in sections 2.1.3 and 2.1.5; these spectra may be used instead of the reference spectra in actual concentration and uncertainty calculations.

Reactivity and Response Time Checks. While sampling ambient air and continuously recording absorbance spectra, suddenly replace the ambient air flow with CTS gas introduced as close as possible to the probe tip. Examine the subsequent spectra to determine whether the flowrate and sample volume allow the system to respond quickly enough to changes in the sampled gas. Substitute the field calibration standards for the CTS gas and repeat the process for each reactive analyte. Examine the subsequent spectra to ensure that the reactivities of the analytes with the exposed surfaces of the sampling system do not limit the time response of the analytical system. Monitor the absorption cell temperature and pressure; verify that the (absolute) pressure remains within 2% of the pressure specified in the proposed system conditions.

Sampling System Integrity Checks. While sampling ambient air, and using a mass flow meter or controller, introduce a known flowrate of CTS gas into the sample stream as close as possible to the probe tip. Measure and monitor the total sample flowrate during this process. Verify from the observed CTS concentration and the two flowrates that the sampling system has no leaks and that the flowrate measurements are accurate. During this process, monitor the absorption cell temperature and pressure; verify that the pressure remains within 2% of the pressure specified in the proposed system conditions.

Analyte Spiking. While sampling actual source effluent, introduce a known flowrate of CTS gas into the sample stream as close as possible to the probe tip. Measure and monitor the total sample flowrate during this process, and adjust the spike flowrate until it represents between 10% and

20% of the total flowrate. After waiting until at least four absorption cell volumes have been sampled, record four spectra of the spiked effluent, terminate the CTS spike flow, pause again until at least four cell volumes are sampled, and then record four (un-spiked) spectra. Repeat this process until 12 spiked and 12 un-spiked spectra have been obtained. During this process, monitor the absorption cell temperature and pressure; verify that the pressure remains within 2% of the pressure specified in the proposed system conditions. Calculate the expected CTS compound concentrations in the spectra and compare them to the values observed in the spectrum.

Repeat this spiking process with all effluent compounds which are potentially reactive with either the sampling system components or with other effluent compounds.

Post-Test Calibration. At the completion of a sampling run and at the end of the field study, record the spectrum of the CTS gas as described in Section 2.2.2. The resulting "final field CTS spectrum" should be compared to the initial field CTS spectrum to verify suitable stability of the spectroscopic system throughout the course of the field study.

Amendment of Analytical Routines. The presence of unanticipated interferant compounds and/or the observation of compounds at concentrations outside their expected concentration ranges may necessitate the repetition of portions of the Appendix B procedures. Such amendments are allowable before final analysis of the data, but must be represented in the documentation required in Section 2.1.6.

Documentation. The sampling and spiking techniques used to generate the field study spectra and to convert sample spectral information to concentrations should be thoroughly documented. The required level of detail for the documentation is that which allows an independent analyst to reproduce the results from the documentation and the stored interferometric data.

A.2.5   Method Application

When the required laboratory and field studies have been completed, and if the results indicate a suitable degree of accuracy, the methods developed may be applied to practical field measurement tasks. During field applications, the procedures demonstrated in the field study (see Section 2.0) should be adhered to as closely as possible, with the following exceptions:

1. Ideally, the sampling lines employed should be as short as practically possible and not longer than those used in the field study.
2. Variations from field study conditions, equipment, and analytical techniques must be noted and included in reports of the field application results.
3. Analyte spiking (Section 2.2.5) and reactivity checks (Section 2.2.3) are required only immediately following the installation of or major repair to the sampling system. Four samples spiked with CTS or a surrogate analyte should be compared to four un-spiked samples recorded under the same conditions.
4. Sampling and other operational data should be recorded and documented as during the field study, but not all the interferometric data need be stored permanently. It is sufficient to store only that amount interferometric data to sufficient reproduce and verify some portion of the reported data; typically, less than 5% of the interferometric data (including interferograms for related background and sample single-beam spectra) are required for this purpose.

A.2.6   References

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5.   D.M. Haaland and R.G. Easterling, "Improved Sensitivity of Infrared Spectroscopy by the Application of Least Squares Methods," *Appl. Spectrosc*. 34(5):539-548 (1980).

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7.   D.M. Haaland, R.G. Easterling and D.A. Vopicka, "Multivariate Least-Squares Methods Applied to the Quantitative Spectral Analysis of Multicomponent Samples," *Appl. Spectrosc*. 39(1):73-84 (1985).

8.   W.C. Hamilton, *Statistics in Physical Science*, Ronald Press Co., New York, 1964, Chapter 4.

A.2.7   Definitions of Symbols and Terms

A, absorbance – the logarithm to the base 10 of the reciprocal of the transmittance (T).

$$A \ = \ \log_{10}\left(\frac{1}{T}\right) \ = \ \text{-}\log_{10}T$$

absorption band – A contiguous wavenumber region of a spectrum (equivalently, a contiguous set of absorbance spectrum data points) in which the absorbance passes through a maximum or a series of maxima.

absorption pathlength – In a spectrophotometer, the distance, measured in the direction of propagation of the beam of radiant energy, between the surface of the specimen on which the radiant energy is incident and the surface of the specimen from which it is emergent.

apodization – Modification of the instrument line shape function (ILS) by multiplying the interferogram by a weighing function whose magnitude varies with retardation.

background spectrum – The single beam spectrum obtained with all system components without sample present.

baseline – Any line drawn on an absorption spectrum to establish a reference point that represents a function of the radiant power incident on a sample at a given wavelength.

Beer's law – The direct proportionality of the absorbance of a sample to the concentrations of its constituent compounds (see Equation 3).

calibration transfer standard (CTS) gas – A gas standard of a compound used to achieve and/or demonstrate suitable quantitative agreement between sample spectra and the reference spectral library.

compound – A substance possessing a distinct, unique molecular structure.

concentration (c) – The quantity of a compound contained in a unit quantity of sample. The unit "ppmv" (part-per-million volume) is employed in this document, and is equivalent under the assumption of ideal gases to the same quantity expressed on a number, or molar, basis.

double beam spectrum – A transmission or absorbance spectrum derived by dividing the sample single beam spectrum by the background spectrum.

Note: The term "double-beam" is used elsewhere to denote a spectrum in which the sample and background interferograms are collected simultaneously along physically distinct absorption paths. Here, the term denotes a spectrum in which the sample and background interferograms are collected at different times along the same absorption path.

fast Fourier transform (FFT) – A method of speeding up the computation of a discrete FT by factoring the data into sparse matrices containing mostly zeros.

Fourier transform (FT) – The mathematical process for converting an amplitude-time spectrum to an amplitude-frequency spectrum, or vice versa.

Fourier transform infrared (FTIR) spectrometer – An analytical system that employs a source of mid-infrared radiation, an interferometer, an enclosed sample cell of known absorption pathlength, an infrared detector, optical elements that transfer infrared radiation between components, and a computer system. The time-domain detector response (interferogram) is processed by a Fourier transform to yield a representation of the detector response vs. infrared frequency.

Note: When FTIR spectrometers are interfaced with other instruments, a slash should be used to denote the interface; e.g., GC/FTIR; HPCL/FTIR, and the use of FTIR should be explicit; i.e., FTIR not IR.

frequency, v – The number of cycles per unit time.

infrared – The portion of the electromagnetic spectrum containing wavelengths from approximately 0.78 to 800 microns.

interferogram, I(σ) – A record of the modulated component of the interference signal measured as a function of retardation by the detector.

interferometer – A device that divides a beam of radiant energy into two or more paths, generates an optical path difference between the beams, and recombines them to produce repetitive interference maxima and minima as the optical retardation is varied.

linewidth – The full width at half maximum of an absorption band in units of wavenumbers (cm^{-1}).

MIL, minimum instrumental linewidth – The minimum linewidth (observed in absorbance spectra) exhibited by the FTIR , in wavenumbers.

Note: The MIL of a system may be determined by observing an absorption band known (through higher resolution examinations) to be narrower than indicated by the system. The MIL is

fundamentally limited by the retardation of the interferometer, but is also affected by other operational parameters (e.g., the choice of apodization function).

mid-infrared – The region of the electromagnetic spectrum from approximately 400 to 5000 cm^{-1}.

reference spectra – Absorption spectra of gases with known chemical compositions, recorded at a known absorption pathlength, which are used in the quantitative analysis of gas samples.

retardation, σ – Optical path difference between two beams in an interferometer; also known as "optical path difference" or "optical retardation."

scan – Digital representation of the detector output obtained during one complete motion of the interferometer's moving assembly or assemblies.

single beam spectrum – Fourier-transformed interferogram, representing the detector response vs. wavenumber.

Note: The term "single-beam" is used elsewhere to denote any spectrum in which the sample and background interferograms are recorded on the same physical absorption path; such usage differentiates such spectra from those generated using interferograms recorded along two physically distinct absorption paths (see "double-beam spectrum" above). Here, the term applies (for example) to the two spectra used directly in the calculation of transmission and absorbance spectra of a sample.

T$_R$ – Absolute temperature of gases used in recording reference spectra.

T$_S$ – Absolute temperature of sample gas as sample spectra are recorded.

transmittance, T – The ratio of radiant power transmitted by the sample to the radiant power incident on the sample. Estimated in FTIR spectroscopy by forming the ratio of the single-beam sample and background spectra.

wavenumber, $\overline{\nu}$ – tThe number of waves per unit length.

Note: The usual unit of wavenumber is the reciprocal centimeter, cm^{-1}. The wavenumber is the reciprocal of the wavelength, λ, when λ is expressed in centimeters.

A.2.8   Description of Extractive FTIR Spectrometry

Molecular Rotation-Vibration Absorption and Beer's Law

The energy of a molecule associated with its vibrational and rotational motions is quantized, that is, may take on only particular, discrete values. The allowed values are determined by the molecular structure, the atomic masses, and certain other internal molecular interactions. A molecule can (but need not) absorb light when the energy of an incident photon closely matches the energy spacing between two of its allowed energy levels. For most molecular structures, the allowed vibrational/rotational energy level spacings correspond to the energies of photons in the mid-infrared range, so most molecules exhibit some degree of absorption in that spectral range. The probability of an absorption occurring in a bulk sample containing a large number of similar molecules is dependent on several factors besides the incident infrared photon energy, including (but not limited to) the number of absorbing molecules, the total gas pressure, the gas temperature, and the distance the photon is allowed to travel through the sample.

The energy of a photon is proportional to its frequency; mathematically, the energy is given by $E = h\nu$, where h is Planck's constant and ν is the frequency of the photon; ν is related to the speed of light c and the photon wavelength λ through the relation $c = \lambda\nu$. It is customary in infrared spectroscopy to describe radiation by its wavenumber $\bar{\nu}$, defined by the relation $\bar{\nu} = 1/\lambda$; when λ is expressed in centimeters, the units of $\bar{\nu}$ are cm^{-1}. These units, which are proportional to the frequency and to the energy of the photon, are used almost exclusively in the remainder of this document. The spectral range of interest, namely the mid-infrared region, is usually taken to lie between 400 and 5000 cm^{-1}.

FTIR spectrometers rapidly provide accurate estimates to the total energy in an infrared beam at hundreds to tens of thousands of particular wavenumber values across the mid-infrared region. These estimates are arranged in wavenumber order to form a "single beam spectrum" of the infrared power versus wavenumber. In extractive spectroscopy, two such spectra are used to determine molecular concentrations. The first spectrum, recorded using a non-absorbing gas as the sample, is called the "background" spectrum; its value at the ith wavenumber value is referred to here as B_i. The second, or "sample," spectrum is recorded under the same conditions using the sample gas of interest; its value at the ith wavenumber value is referred to here as S_i. It is the direct availability of the quantities B_i, measured under the same conditions as the quantities S_i, which most clearly differentiates extractive FTIR spectroscopy from other types described in the literature (e.g., "remote" or "open path" FTIR spectroscopy).

The "transmittance" spectrum of the sample, representing the fraction of the incident infrared power transmitted by the sample at each wavenumber value, is calculated point-by-point from the sample and background single-beam spectra according to

$$T_i = \frac{S_i}{B_i}. \qquad \textbf{(Eq. 1)}$$

The "absorbance" of the sample at each wavenumber value, A_i, is calculated according to the definition

$$A_i = -\log_{10} T_i. \qquad \textbf{(Eq. 2)}$$

The absorbance of the sample is the quantity of greatest interest in quantitative analyses because it is linearly related to the gaseous concentrations of the absorbing species. The following equation, often referred to as Beer's Law, relates several FTIR experimental parameters to the concentrations in a gaseous mixture of compounds:

$$A_i = \sum_{j=1}^{M} a_{ij} L C_j, \qquad \textbf{(Eq. 3)}$$

where

       i = an index labeling the wavenumber values represented in an FTIR spectrum.

       j = an index labeling the absorbing compounds in the mixture.

      M = the number of absorbing compounds in the mixture.

      a_{ij} = the absorptivity of the jth compound at the ith wavenumber value.

      L = the absorption pathlength (length of interaction of radiation and sample).

      C_j = the volumetric concentration of the jth compound in the mixture.

Instrumentation and techniques for determining the quantities in Equation 3 are found in the following three sections. A modern and more complete description of the molecular physics related to qualitative and quantitative molecular spectroscopy is found in reference 3.

Spectroscopic Instrumentation

Modern FTIR spectrometers are available from many manufacturers and in many configurations. However, most spectrometers for gas phase analysis consist of the several standard components illustrated in Figure 11. Broad-band, collimated infrared (IR) radiation is produced in a glowbar or other thermal source and directed into an interferometer. The interferometer optically processes the infrared beam, which consists of radiation containing all wavenumbers (wavelengths) across the mid-infrared region, in such a way that the exiting beam is amplitude modulated at an audio frequency which is proportional to the radiation's infrared frequency. The modulated IR beam is directed through one or more enclosed sample volumes; Figure 11 shows a series combination of a multiple-pass (White) sample cell and two single-pass sample cells. After interacting with the sample, the infrared beam exits the sample region and illuminates a square-law infrared detector.

The interferometer contains at least one moving element; the motion is responsible for the amplitude modulation of the infrared radiation, and a computer records the detector response as a function of the position of the moving element. The resulting plot of the detector response (total infrared power) versus position (more accurately, the optical retardation) is referred to as an "interferogram." Through appropriate mathematical manipulations and a fast Fourier transform (FFT), the same computer (effectively) digitally de-modulates the interferogram, and the resulting single-beam spectrum accurately represents the power in the beam versus wavenumber. Note that, as is characteristic of the Fourier transform, the independent variable in the original function (position, in units of cm) is the inverse of the independent variable in the transformed function (wavenumber, in units of cm^{-1}). As described in section B.1, two single beam spectra (recorded with and without the sample present in the cell) yield the absorbance of the sample in a straightforward calculation.

Many operational parameters are available to the analyst for adjustment and optimization of the spectrometer system, and play important roles in any practical application. Discussions of most of these parameters are beyond the scope of this work, but are available in reference 4 and from many other sources. Of greatest importance to the current application are the choices of integration time, absorption pathlength and spectral resolution; these parameters are discussed in turn below.

Integration time. Under optimal conditions (i.e., when "white" noise in the detector limits the system performance), the signal-to-noise ratio (S/N) in a single beam spectrum is proportional to the square root of the time spent averaging the detector signal during collection of the interferogram, referred to here as the "integration time." In typical systems, the integration time is proportional to the number of "scans" (results of a single motion of the interferometer's moving element) which are co-added to form a complete interferogram. The time required for a single scan depends on details of the detector response speed and the chosen spectral resolution (see below), but is typically between 0.1 and 3.0 seconds. As long as composition of the sample gas changes slowly on the time scale of a single scan, the result of an integration over multiple scans represents a time-average (over the integration time) of the sample composition. Because the generation of absorbance spectra requires two single beam spectra, it is important that the integration time used in collecting both the background and sample interferograms are suitably

long; in practice, the background integration is usually carried out over at least twice as many scans as the subsequent sample interferograms, so that the noise in the background spectrum is not dominant.

Absorption pathlength. As stated in Equation 3, the absorbance of a given sample is proportional to the length (the "absorption pathlength") over which the infrared beam is allowed to interact with the sample. If all other spectral properties are held constant, including the S/N, the lowest concentration of a single gaseous component at which its absorbance is detectable in the spectral noise is inversely proportional to the absorption pathlength. For samples containing multiple analytes over a large range of concentrations, a single absorption pathlength may not allow optimal measurement of all the components. In typical systems, the absorption pathlength cannot be quickly and easily varied; the optical series configuration of absorption cells depicted in Figure 11 represents an approach to the problem of optimizing the absorption pathlength for various sample constituents and/or sample concentrations. Rather than changing the pathlength of a single absorption cell, the operator can choose to direct the sample stream through one of three cells while the others are purged with a non-absorbing gas. This allows relatively rapid adjustment of the absorption pathlength, limited only by the rate at which the sample and purge gases can be replaced in each cell.

Minimum instrumental linewidth. For a given set of operating parameters pertaining to the interferometer and FFT, an FTIR spectrometer exhibits a lower limit to the full width at half-maximum (FWHM) of absorption features present in an absorbance spectrum. This lower limit is referred to here as the "minimum instrumental linewidth," or MIL. Significantly lowering the MIL, or "improving the spectral resolution" of the system, is possible only by increasing the physical length over which a given interferometer's moving element is displaced during a single scan. For a given interferometer, there is always an upper limit to this physical length, and therefore a lower limit to the MIL. Careful consideration must be given to the choice of MIL for a given application, since decreasing the MIL introduces severe costs in both interferometer fragility and S/N achieved per integration time. It is generally accepted that 0.5 cm^{-1} is currently the lowest practical MIL value for gas phase spectroscopic field applications. However, if the spectrometer hardware allows both use of a larger MIL and optimization of the effective infrared source size (usually by adjustment of an aperture, or "Jacquinot stop" located somewhere in the beam path), significant improvements in the achievable S/N per integration time can be made.

Sampling of Effluent Gases

As state above, the direct availability of a background spectrum B_i, measured under the same conditions as the sample single beam spectrum S_i, is an advantage of extractive spectroscopy. However, this advantage comes at the sometimes considerable cost of extracting a truly *representative* sample. Interactions between the components of the gas and the sampling system, as well as interactions of the sample gases themselves, can change the composition of some samples and lead to inaccurate results. The rate at which gas is extracted from the effluent source, relative to the volume of sample required for the analysis, must also be taken into account when the concentrations of the components change over time.

The gas matrix of current interest consists mainly of compounds which are reactive neither with each other nor with the materials used in standard gas extraction systems. However, because of the possibility of reactions between these and other, unanticipated sample constituents or with water vapor, demonstrations of both suitable delivery efficiency and integrity of the sampling system should be performed.

Figure 11 illustrates the standard components of a gas sampling system suitable for the application addressed in this document. It consists of a stainless steel sample probe, Teflon sample lines, calibration gas source, and a pump (not shown). The pump attaches to the outlet of the infrared absorption cell (in this case, the cell with 1 cm absorption pathlength), maintains a slight negative pressure (< 10″ H_2O below ambient) throughout the absorption cell, sample lines, and probe, and provides a sample gas flowrate of approximately one liter per minute (lpm). With a suitably calibrated mass flow controller or meter, the operator can introduce known rates of both nitrogen-balance calibration and "spike" gases into the sample stream through the calibration line, which feeds into the probe through a standard "tee" fitting. This allows replacement of any desired fraction of the actual sample flow with known concentrations of analytes or other compounds. Procedures for calibrating and dynamically spiking analytes into the sample stream are discussed in sections 2 and 3 above.

Data Acquisition and Analysis

Equation B 3 (Beer's Law) represents the basis for nearly all quantitative analyses of mid-infrared spectra recorded with a known absorption pathlength. The literature (for example, references 4, 5, and 6) contains substantial discussion and comparison of several types of algorithms used to derive estimates of multi-component gas sample concentrations from a sample spectrum using libraries of reference spectra. These spectral libraries are also referred to in the literature as "training sets." Examples of techniques described in the literature are the "P-matrix," "K-matrix" (or "classical least squares"), "principal component regression," and "partial least squares" algorithms. A simplified classical least squares analysis is described below in Appendix C. Experienced analysts can also employ visual subtraction techniques to obtain accurate concentration data and uncertainties.

In most cases, the choice of an appropriate technique for determining sample concentrations is a matter of both trial and error and of convenience. Important features of an acceptable method of spectral analysis include:

1. Careful preparation of multiple reference spectra for each compound of interest, and mathematical characterization of the extent to which the quality of the reference spectral data may limit the overall accuracy and uncertainty from sample spectrum analyses.

2. Generation of both concentration data and an estimate of the associated error or uncertainty in the determined values for each individual spectrum analyzed and for every concentration quoted.

3. Complete documentation of the mathematical processing of the acquired field data, at the level of detail allowing an independent analyst to reproduce quoted concentration results and uncertainties from the interferometric data.

Procedures related to these desired qualities of the spectral analysis routine are presented above in sections 2 and 3.

A.2.9   Mathematical Description of Beer's Law

Direct calculation of the probability of absorption for a particular molecular structure is complex, but can be characterized for a bulk sample and radiation at a particular wavenumber $\overline{v}$ by the absorption coefficient $\alpha_{\overline{v}}$, defined through the relation

$$\alpha_{\overline{v}} = -\left(\frac{1}{P_o}\right)\left(\frac{dP(z)}{dz}\right). \qquad \textbf{(Eq. 4)}$$

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Here, the radiation is traveling in the z-direction, is incident on the sample with power P_O at $z = 0$, and has power $P(z)$ as a function of location along the z axis. If the sample includes a single molecule with non-zero absorption coefficient $\alpha_{\bar{v}}$, integration of Equation 1 from $z = 0$ to $z = L$ leads to the following expression for the fraction of the incident power left in the incident radiation after the "absorption pathlength" L, defined as the transmittance $T_{\bar{v}}$:

$$T_{\bar{v}} = \left(\frac{P(z)}{P_o} \right) = e^{-L\,\alpha_{\bar{v}}} \tag{Eq. 5}$$

If two species (1 and 2) in the sample *both* absorb radiation at the wavenumber $\bar{v}$, with absorption coefficients α_1 and α_2, the fraction of power transmitted after distance L, can be seen from Equation C-2 to be

$$T_{\bar{v}} = \left(e^{-L\,\alpha_1} \right)\left(e^{-L\,\alpha_2} \right) = e^{-L\left(\alpha_1 + \alpha_2\right)}. \tag{Eq. 6}$$

This relation represents the efficacy of measuring $T_{\bar{v}}$ for a sample containing a mixture of compounds, since contributions to the logarithm of $T_{\bar{v}}$ from the different compounds are additive.

It can be shown from first principles[3,4] that the quantities α_j in gaseous samples are proportional to the average concentrations (per unit volume) of the absorbing species, labeled here by the index j. By defining the "absorbance" at some discrete (i^{th}) wavenumber through $A_i = -\log_{10} T_i$, we can write the following simple relation for the absorbance of a mixture of M compounds with concentrations C_j:

$$A_i = \sum_{j=1}^{M} a_{ij} L C_j \tag{Eq. 7}$$

Here, the absorption coefficients for the jth compound at the ith wavenumber have been replaced by the "absorptivity" a_{ij}, to which it is proportional. Equation C-4 is often referred to as the "Beer-Lambert Relation,", or simply as "Beer's Law." It is rigorously true for gas samples only when all its quantities are perfectly measured at a given sample (equilibrium) pressure, and when the effects of spontaneous emission are small enough to be neglected.

A useful practical strategy, and one often used in conjunction with FTIR spectrometry, is to determine the absorptivities a_{ij} for single components at a large number of wavenumber values under well-characterized experimental conditions. Beer's Law can then be used to determine the concentrations C_j for a gaseous mixture from the absorption pathlength L and the mixture's observed absorbance A_i. As described in section B.2, FTIR spectrometers rapidly estimate several thousand values of A_i (at various wavenumber values), providing a statistically powerful means for determining a large number of gaseous concentrations from a single sample spectrum.

A.2.10   Mathematical Description of a Least Squares Analysis

Virtually all quantitative analyses of FTIR absorption spectra are based Beer's Law (Equation 3), or on some physically reasonable adaptation of Beer's Law indicated by the pertinent experimental constraints. For the reader's convenience, this equation and the definitions of its quantities are re-stated here:

$$A_i = \sum_{j=1}^{M} a_{ij} L C_j \quad , i = 1, 2, \dots N \qquad \textbf{(Eq. 8)}$$

where

M = the number of compounds assumed to absorb in the spectral region analyzed (with index j);

N = the number of infrared frequencies used in the analysis (with index i);

A_i = the observed sample absorbance at the ith infrared frequency;

C_j = the (unknown) volumetric concentration of the jth component of the mixture;

L = the absorption path length used in recording the sample spectrum;

a_{ij} = the absorptivity of the jth compound at the ith infrared frequency.

Once the absorbance of a sample gas (A_i) and the absorptivities are determined, many mathematical techniques are suitable for an inversion of Equation 8. The technique described here is a simple least-squares analysis using a single reference spectrum for each component in the mixture.

The following approach to estimating the quantities C_j in Equation 8 is similar in most respects to one described in a series of papers written by David Haaland and co-workers.[5, 6,7] The following treatment follows the notation of reference 8. We rewrite Beer's law as

$$A_i^S = \alpha + \beta \bar{v}_i + \varepsilon_i + \sum_{j=1}^{M} \gamma_{ij} S_j . \qquad \textbf{(Eq. 9)}$$

where

- the measurements of the sample absorbances A_i^S are made at absolute temperature T, absorption path length L (meters), and pressure p (atm);

- $\bar{v}_i$ is the wavenumber value of the ith absorbance point;

- $\alpha + \beta \bar{v}_i$ represents a linear baseline error in Beer's Law for the selected (contiguous) data points;

- ε_i represents the non-baseline error in Beer's law at v_i ;

- S_j is a "scaling factor" for the jth compound included in the analysis.

We define the quantity γ_{ij} in Equation 9 as the "reduced absorptivity" of the jth compound at the frequency v_i . For the purposes of the present calculation, it may be estimated by

$$\gamma_{ij} = \frac{T_j}{L_j p_j C_j^R} A_{ij}^R \qquad \textbf{(Eq. 10)}$$

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where

A_{ij}^R = the absorbance of a single reference spectrum of the (pure) j^{th} compound, recorded with absorption path length L_j (meters) at absolute temperature T_j and pressure p_j (atm), and concentration C_j^R (ppmv).

If we can use Equation 9 to form least squares estimates of α, β, and the scaling factors S_j, denoted by $\overline{\alpha}$, $\overline{\beta}$, and $\overline{S}_j$, then the desired least squares estimates of the concentrations C_j are given by

$$\overline{C}_j = \frac{T}{Lp} \overline{S}_j \, . \tag{Eq. 11}$$

The least squares estimates $\overline{\alpha}$, $\overline{\beta}$, and $\overline{S}_j$ can be formulated from the linear model of Equation 9 as follows.[8] We form the "design matrix" $\mathbf{D}$ of with M+2 columns and N rows; each the first M columns of $\mathbf{D}$ corresponds to the jth compound, and consists of the N values γ_{ij}. The $(M+1)^{th}$ column consists of N entries of any non-zero constant, representing the constant baseline offset term α, the $(M+2)^{th}$ column consists of the N values v_i. If we define similar vectors $\mathbf{A}$ to represent the values A_i, $\mathbf{X}$ to represent the M+2 unknown quantities $\{S_1, S_2,...S_M, \alpha, \beta\}$, and $\mathbf{E}$ to represent the errors ε_i, the linear model in Equation (D-2) takes the form

$$\mathbf{A} = \mathbf{DX} + \mathbf{E} \, . \tag{Eq. 12}$$

In the over-determined case of interest to us (N>>M+2), we may proceed by assuming the errors ε_i posses a joint distribution with zero means, and a variance-covariance matrix of the form

$$\mathbf{M}_f = \begin{pmatrix} \sigma_1^2 & \sigma_1\sigma_2\rho_{12} & \cdot & \sigma_1\sigma_N\rho_{1N} \\ \sigma_1\sigma_2\rho_{12} & \sigma_2^2 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \sigma_1\sigma_N\rho_{1N} & \cdot & \cdot & \sigma_N^2 \end{pmatrix} \tag{Eq. 13}$$

We assume further that $\mathbf{M}_f$ is known only to within a scaling factor σ^2, that is,

$$\mathbf{M}_f = \sigma^2\mathbf{N} \, . \tag{Eq. 14}$$

Denoting the matrix transpose with the superscript "t" and the matrix inverse with superscript "-1," the least squares estimate to the desired quantity $\mathbf{X}$ is given simply by

$$\overline{\mathbf{X}} = \left(\mathbf{D^t N^{-1} D}\right)^{-1} \mathbf{D^t N^{-1} A} \, . \tag{Eq. 15}$$

The matrix $\mathbf{N^{-1}}$ is the "weight matrix." In the simplest case where all the observed quantities A_i have equal variances σ^2, $\mathbf{N^{-1}}$ is the identity matrix $\mathbf{I}$, and $\mathbf{M}_f = \sigma^2\mathbf{I}$.

Least squares estimates of several other important quantities are available from $\overline{\mathbf{X}}$, including the errors in the components of $\overline{\mathbf{X}}$ itself, that is, the errors in the scaling factor estimates. We can immediately calculate the residual vector

$$\mathbf{V} = \mathbf{A} - \mathbf{D}\overline{\mathbf{X}} \, , \tag{Eq. 16}$$

which gives the point-by-point difference between the measured A_i^S and its least squares estimate according to our linear model; from **V**, the parameter moment matrix $\mathbf{M_X}$ can be estimated according to

$$\mathbf{M_X} = \left(\frac{\mathbf{V^t N^{-1} V}}{N - M - 3} \right) \left(\mathbf{D^t N^{-1} D} \right)^{-1} , \qquad \textbf{(Eq. 17)}$$

and the uncertainty Δ_i in the parameter estimate $\overline{X}_i$ is given by

$$\Delta_i = \sqrt{\left(\mathbf{M_X} \right)_{ii}} . \qquad \textbf{(Eq. 18)}$$

The least squares estimates of the concentrations and the uncertainties in these estimates are obtained by combining Equations 11, 15, and 18 for the appropriate elements of the set $\{S_1, S_2,...S_M, \alpha, \beta\}$.

A.3   Modifications to QMS/FTIR Protocols to Quantitate Corrosive Air Emissions

The two technical protocols specifically address the quantification of emissions of perfluorinated carbon compounds. Several issues must be addressed for these protocols to be effective for quantifying corrosive air emissions. The two main issues are material compatibilities and passivation of the analytical system. The three main corrosive air emissions of interest are HF, HCl, and Cl_2. Due to the corrosiveness and reactivity of these compounds, special precautions must be taken to ensure the quality of the emissions data. The first issue is material compatibility with these three compounds. All of the parts of the analytical equipment (i.e., sample lines, roughing and turbo pumps, exhaust lines, etc.) must be compatible with these three gases. It is recommended that stainless steel and ceramic parts be used whenever possible and that Teflon and Viton parts be minimized. The second issue concerns the passivation of the analytical system with each of these compounds. The solution is to allow these gases to run through the analytical system until a stable signal is achieved (i.e., the system is "passivated"). This can be accomplished by either running the corrosive compounds through the system without running wafers (if the compounds are used in the process) or by running wafers through the system until the signals are stable (if the compounds are byproducts).

It is also recommended that all parts of the instrumentation that will be in contact with these compounds be heated. The heating will accomplish two tasks:

1.   Drive out any water from the system
2.   Limit the reactivity of the corrosive compounds with the analytical system

The first item is extremely important since HF is very reactive with water. It should not be assumed that if the system is passivated with one of the compounds that it is passivated with the other two compounds. Passivation times can range from 15 minutes to 2 hours depending on the condition of the sample lines, temperature of the sample lines, and nature of the compound. In general, the passivation time of the analytical system is longest for HF and shortest for Cl_2. During emissions testing, extreme care must be taken to ensure that the temperature of the heated sample lines is the same during the calibration steps as it is during the wafer processing steps.

A.4 Point of Use (POU) Abatement Protocol

Depending on the specific characteristics of the gas stream analyzed, the sampling technique can be as important as the analytical instrument used. In many cases, traditional sampling methods fail and custom designed techniques are needed to minimize analyte loss or distorted results. The following are some techniques used to characterize specific, problematic tool effluent streams. They will serve as the first of a compilation of different, application-specific analytical sampling methods used to characterize semiconductor processing effluent streams. As additional methods are reviewed and qualified, they will be added to this document.

- *Representative Sampling:* Collecting gas samples from pipes, specially those with laminar flow characteristics, requires special attention. Sampling from a fitting bored into a pipe can result in wall effects that cause false or inaccurate results. This is especially true when sampling the outlet of wet scrubbers as moisture tends to condensate on the inner walls of exhaust pipes; disproportionate levels of moisture and dissolved gases are drawn into analyzers leading to incorrect gas phase composition characterization. One way to minimize these effects is to introduce a probe bent at 90° to collect samples concentrically and concurrent with respect to the direction of the gas flow from the center of the pipe (see Figure 11).

- *Acid Gas Analyses:* This can include measurement of acid gases at the exhaust of a metal etch tool (BCl_3, HCl, and Cl_2) using a QMS and in water vapor saturated conditions (HF, HCl, Cl_2) (i.e., after a water scrubber) using FTIR spectrometers and QMS. In acid gas sampling and analysis, materials compatibility can be a dominant concern. The two main materials used for sampling are heated stainless steel and Teflon. The disadvantage with heated stainless steel is evidence of reactions between Cl_2 and HF with the walls of the sampling lines when water is present. The disadvantage with Teflon lines is evidence of an interaction of HF with Teflon. Ensure that the choice of sampling lines does not affect the accuracy or reproducibility of the emissions measurements. In extreme wet conditions, it is recommended that an inline permeation dryer (PERMA-PURE) be used, which can eliminate 90% of the moisture in the gas stream. Studies of analyzer responses (QMS and FTIR spectroscopy) with and without the dryer in line have shown no analyte was lost in the water removal process (i.e., the dryer is selective and does not remove any acids). This technique proved effective for measuring the acid gases at the outlets of wet scrubbers and for characterizing SiF_4 and HF emissions during a wet HF clean of an atmospheric pressure (AP) CVD tool. Note, however, that before implementing any of these sample conditioning techniques, a specific effluent stream needs to be thoroughly tested. For instance, further tests have determined that some polar organic compounds, ammonia, and TEOS permeate out of the dryer.

- *Sequentially Varied Effluent Streams:* In performing mixed effluent characterization studies, it is helpful to install three-way valves at the sampling ports. One end is connected to the tool exhaust duct, the other is connected to purging dry nitrogen, and the common port is directed to the analyzer. This setup allows either the purging nitrogen or sample stream to be transferred to the FTIR or QMS. Dry nitrogen is used to collect background or baseline spectra or to clean the lines and spectrometer between runs. Whenever the port is remote or inaccessible, the three-way valve can include a pneumatic actuator to switch between the sample or nitrogen stream collection. This can be useful when characterizing varied exhaust streams (e.g., measurements inside an ion implanter processing arsine, phosphine, boron trifluoride, and silicon tetrafluoride).

- *Solid Particulates Clogging:* Many processes in the semiconductor industry release solid particulates. For example, silicon-containing reactants often generate silica, boron-containing species boric acid, aluminum etch aluminum chloride, and tungsten CVD tungsten trioxide. These solids not only hinder material balance calculations but can also obstruct sampling lines, analytical tools, and sampling valves. To allow continuous analysis, a sampling system has been designed to minimize particle (SiO_2) interference with the analysis. This system has been shown to be very effective in the characterization of the tool effluent composition and concentration of species released during a APCVD TEOS/ozone process. The setup (see Figure 11) includes a ¼-inch Teflon-lined stainless steel probe bent at 90° to collect samples concentrically and concurrent with respect to the direction of the gas flow. Interference from solid particles is further minimized using a filter setup (2 µm pore size). Solid particulates within the gas stream are removed by filter #1 before entering the analyzer. When filter #1 becomes saturated with solids, two pneumatically actuated three-way valves direct the sample stream to filter #2, allowing the replacement of the clogged filter. This setup can result in trouble-free analysis of particulate-laden streams throughout an extended testing period.
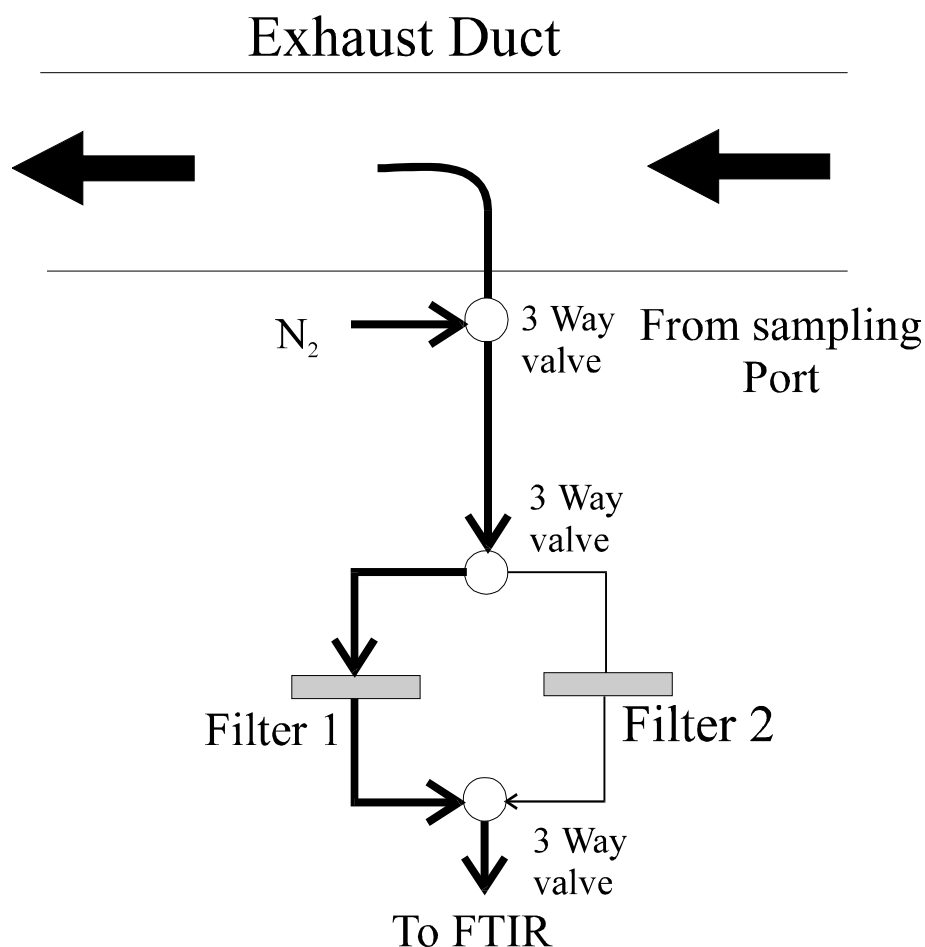

Figure 11   Sampling Setup to Minimize Particle Clogging