EPA
United States Environmental Protection Agency

Version 1

Protocol for Measuring Destruction or Removal Efficiency (DRE) of Fluorinated Greenhouse Gas Abatement Equipment in Electronics Manufacturing

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PREFACE

The U. S. Environmental Protection Agency (EPA) initiated preparation of this Protocol as part of its commitment to assist the PFC Emissions Reduction/Climate Partnership for the Semiconductor Industry (the Partnership) to achieve its voluntary fluorinated greenhouse gas (F-GHG) emission reduction and reporting goals. F-GHGs include the most powerful and often persistent greenhouse gases such as perfluorocarbons (PFCs), hydrofluorocarbons (HFCs), sulfur hexafluoride (SF_6), and nitrogen trifluoride (NF_3). The Partnership's reduction goal is to decrease F-GHG emissions to 10 percent below the 1995 base-year amounts by 2010. Several F-GHG-reducing options are available, with reduction-efficiencies ranging from 10 to 99 percent or higher. Practical reduction strategies comprise modifying manufacturing processes—optimizing processes and switching to alternative gases with lower emissions potential—as well as installing point-of-use (POU) F-GHG abatement systems. Detailed methods for measuring F-GHG emissions from manufacturing processes were standardized in 1999 and are documented and continually updated in the industry's International Semiconductor Manufacturing Initiative (ISMI) Guidelines. Standard methods for measuring and documenting the destruction or removal efficiencies (DREs) from POU abatement systems have lagged those for measuring process emissions. One objective of this document (the Protocol) is to align measurement of emissions from manufacturing processes with those from abatement systems.

The Protocol builds on three DRE measurement studies of POU F-GHG thermal abatement systems conducted onsite at three U. S. semiconductor manufacturing facilities, each a member of the Partnership. Air Products performed and documented the measurements under subcontract to ICF International, who was contracted by EPA to support development of the Protocol. In total, four abatement systems were tested and all were connected to plasma-enhanced chemical vapor deposition (PECVD) or etch process equipment. During the studies, DRE measurements were made with the plasma on (during wafer processing) and with the plasma off. A key feature of these measurement studies was development and testing of a reliable method for measuring the dilution of F-GHGs during abatement.

This is the third version of the Protocol. It reflects two rounds of external reviews, one each for the first and second version. The first version, prepared after measurements were made at two facilities, was circulated to Semiconductor Industry Association (SIA), Japan Electronics and Information Technology Industries Association (JEITA), and Taiwan's Industrial Technology Research Institute (ITRI) as well as to abatement manufacturers and industry consultants experienced in measuring the DRE of F-GHG abatement systems. The comments and responses to those comments were documented and discussed with reviewers. This discussion led to the third and latest onsite measurement study, as well as to a second version of the Protocol. The second version of the Protocol was again circulated to a subset of the reviewers to the first version. The comments and responses to those comments were also documented and discussed with reviewers.

A consistent theme that emerged from EPA's testing and all the reviews of the Protocol is the diversity of manufacturing practices and conditions across the electronics manufacturing sector. Therefore experienced and resourceful metrologists are central to successful DRE measurements. This Protocol is aimed for use by experienced metrologists—experienced not only in the use of

advanced analytical measurement systems such as FTIR and QMS, but also in performing in-fab measurements of F-GHG emissions. Moreover, the Protocol does not constitute a recipe—a single approach for all circumstances—for making DRE in-fab measurements. Instead, properly construed, the Protocol permits flexibility in measurement practice provided the measurements achieve the performance standard that is integral to this Protocol

1. INTRODUCTION

Members of the U.S. Environmental Protection Agency's PFC Emissions Reduction/Climate Partnership for the Semiconductor Industry (the Partnership) operate under a voluntary agreement to reduce perfluorocompound (PFC, henceforth called fluorinated greenhouse gas, F-GHG) emissions to 10 percent below the 1995 base-year amounts by 2010. A variety of practical F-GHG-reducing options—with reduction-efficiencies that range from 10 to >99 percent—are available. These options include process optimization techniques, switching to alternative gases with lower emissions potentials, and point-of-use (POU) F-GHG abatement. While there are industry-standard guidelines that set forth methods for measuring and documenting process emissions (ISMI, 2006), that is not so for measuring the destruction-removal efficiencies (DRE) of POU F-GHG abatement systems, although published reports of DRE measurement studies are available (Beu et al., 1994; Li et al., 2001, 2002 and 2004; Lee et al., 2007).

The U.S. Environmental Protection Agency (EPA) initiated preparation of this document (the Protocol) as part of its commitment to assist the Partnership in achieving the F-GHG emission reduction and reporting goals. The development of this Protocol builds on three DRE measurement studies of POU F-GHG abatement systems conducted onsite at three U.S. semiconductor fabrication facilities (fabrication facilities are henceforth called fabs). (EPA 2008a, 2008b, and 2009)

1.1 Protocol Purpose

The purpose of the Protocol is to provide a practical and reliable method for measuring DREs of POU abatement systems of F-GHG gases used during the manufacture of electronics products, specifically semiconductor systems, micro-electro-mechanical systems (MEMS), thin film transistor (TFT) arrays and amorphous silicon (a-Si) and tandem amorphous silicon/ nanocrystaline silicon (a-Si/nc-Si) thin-film photovoltaic (PV) panels.[1]

The Protocol sets forth two specific methods for measuring abatement system inlet and outlet flows, and hence DREs, for single or multi-chamber process tools. These methods address measuring the mass or volume flows of F-GHGs entering and leaving the abatement system. Both methods account for the dilution that occurs in thermal abatement systems.[2]

The first and simplest, Method 1 - Dilution Adjusted Concentration Measurement, involves measuring DRE when the process tool is off. This approach will produce reliable results when F-GHG byproducts are not formed, for example, during chamber cleaning with CF_4, SF_6 or with NF_3 when carbon films are not present. A variation of Method 1 may be used that imitate byproducts formation. This involves taking appropriate steps to add proper amounts of byproduct F-GHG to the influent abatement-system flow of unutilized F-GHG(s).

The second method, Method 2 – Total Volume Flow Measurement, is the preferred method for measuring DRE when byproducts are formed. Method 2 measures abatement-system DRE under actual process conditions. One of two approaches may be used when applying Method 2, dependent upon if measurements are being taken sequentially or simultaneously.

Method 2, requires introducing a chemically stable material – a tracer or spiking agent that neither affects the performance of nor is affected by the abatement system—into the process line(s). Using this method will provide a reliable estimate of the effective dilution associated with in-fab thermal POU abatement systems[3] and, in turn, the DREs. This chemical-spiking approach is a special application of ASTM E 2029 – 99 (Re-approved 2004), which provides a method for measuring volumetric or mass flow rate of a gas in a duct, pipe, etc. using a tracer dilution technique (ASTM, 2004). ASTM E 2029-99, like this Protocol, addresses irregular and non-uniform flow conditions where conventional pitot tube or thermal anemometer velocity measurements are difficult or inappropriate due to the absence of a suitable run of duct/pipe upstream and downstream of the measurement location.

Establishing DREs based on this Protocol will (a) assure reliable comparisons of vendors' abatement systems; (b) assure third-parties of the reliability of reported emissions; (c) improve understanding of appropriate and necessary system maintenance; and (d) serve as a starting point

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[1] The electronics manufacturing sector includes, but is not limited to those industry sub-sectors that are listed. This Protocol is applicable to all electronics sectors; but it was developed based on work at a semiconductor manufacturing facilities. However EPA sees no limitation on why the Protocol may not be applied when measuring DREs at other electronics manufacturing facilities.

[2] Testing for the development of the Protocol focused on POU thermal abatement systems because dilution is greatest. It is expected the Kr tracer method is suited to POU plasma systems. However, EPA was not aware of fully operational plasma abatement systems in production fabs at the time of the Protocol's publication.

[3] See footnote 2.

for emerging carbon trading opportunities (i.e., measuring baseline and actual emission reductions).[4]

1.2 Protocol Objectives

The objectives of the Protocol are to specify:

- a method for measuring and reporting F-GHG-specific DREs of installed, in-fab abatement systems that are operating during normal production processing;
- a method for measuring and reporting F-GHG-specific DREs of abatement systems that are offered to manufacturers of electronic products that use F-GHGs during product manufacturing; and
- guidance to fab Environmental Safety &Health staff and to providers of POU abatement-testing services on best-practice procedures for measuring, documenting and reporting of in-fab determinations of F-GHG abatement system DREs.

1.3 Protocol Scope

The Protocol is applicable to measuring and reporting DREs of installed POU systems whose input flows may contain CF_4, CHF_3, CH_2F_2, C_2F_6, C_3F_6, C_3F_8, C_4F_6, c-C_4F_8, C_4F_8O, C_5F_8, NF_3 and SF_6. These high-GWP gases may be used directly in fab processes and, in some circumstances, may be formed during those processes.

The Protocol is intended to complement the guidance prepared by International SEMATECH Technology Transfer # 06124825A-ENG (December 2006); this Protocol adopts in its entirety Appendix A of SEMATECH TT # 06124825A-ENG (December 2006), which explains best known methods for measuring, among other things, F-GHG emissions. The principal difference between the 2006 updated SEMATECH guidance and this Protocol is the emphasis given here to POU abatement system DRE measurement and to measuring dilution across the abatement system.

The Protocol institutes two practices to establish the veracity of reported results. The first is adoption of a benchmark metric together with a performance standard for that metric. The benchmark metric is the relative error, which is a precision metric, in the reported true fraction emitted of which the DRE is its complement. The performance standard the relative error must meet is ±5 percent relative error.[5,6] The second practice is the requirement for metrologist

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[4] The Executive Board of the Clean Development Mechanism has final authority for approving methods for measuring emissions of greenhouse gases, for purposes of establishing a CDM project. However, CDM does not have authority in the United States..

[5] The fraction emitted is chosen as the performance metric rather than the DRE because the relative error of the measured DRE is a function of the true fraction emitted. As the true fraction emitted approaches one (DRE approaching zero), the relative error becomes very large even when the relative error in the true fraction is acceptably small. Similarly, when the true fraction approaches zero (DRE approaches one), the relative error in DRE can become small even when the relative error in the true fraction emitted is large. When the post-abatement concentration approaches or falls below minimum detection an alternative calculation is provided (vide infra).

[6] Experience demonstrates that ±5 percent or better is readily achievable in a fab environment. In three separate studies (EPA 2008a, 2008b, and 2009), the estimated relative error for the true fraction emitted for four POU

certification, certifying that the methods set forth in the Protocol were followed, including that the conditions under which the measurements were made (with the plasma off or actual process conditions).

EPA wishes to strike an appropriate balance between assuring reliable results and flexibility. In the remainder of the Protocol, where EPA anticipates the need for flexibility it has provided examples to demonstrate the nature and extent of the permitted flexibility. EPA will consider updating the Protocol given the availability of and access to additional testing experiences and well-documented results.

1.4 Development of the Protocol

The Protocol has gone through five stages of development: conceptualization, onsite tests, initial drafting, and two informal peer review processes. During the informal peer review processes EPA received comments from both national and international parties, including semiconductor manufacturers, equipment manufacturers, gas suppliers and analytic service providers. Appendix A discusses some of these comments, as well if and how the Protocol was revised to reflect them.

1.5 Expected Results

This Protocol results in an estimate for the DRE of F-GHG abatement systems, where the relative error of true fraction emitted estimate (the benchmark metric), measured under in-fab production processing circumstances and typical (in-fab, as-installed) POU system operating circumstances, is less than ±5 percent (the performance standard). The value of relative error of the true fraction emitted is determined by the methods outlined in the remainder of this Protocol.

2. MEASUREMENT PLAN, PREPARATION, METHODOLOGY, AND DATA ANALYSIS

2.1 Prepare Measurement Plan

A measurement plan serves two main purposes. First, it provides background on the tools, processes, and abatement systems to be tested; and second, it facilitates coordination between facility personnel and testing service providers. An understanding of the tools, processes, and abatement systems provides testing service providers with background on the experimental system in preparation for the study. Coordination with facility personnel reduces the likelihood of encountering unexpected problems of measurement execution during the study. Testing service providers should prepare a measurement plan and submit it to facility personnel at least two weeks prior to the measurement study. At a minimum, the measurement plan should contain detailed descriptions of the experimental system, the sampling configuration, required/expected

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systems attached to either etch or CVD process tools was below ±3 percent. Adoption of ±5 percent as a performance standard assures the *accuracy* of the measured true fraction emitted will be ±5 percent or better, under the reasonable assumptions that the accuracy of calibration gases and mass flow controllers are each ±3 percent or better.

resources/support from the fab, a measurement schedule, address safety and a quality control/quality assurance plan (QA/QC) as described in the following sections. In preparing the plan, attention to Appendix A of the 2006 ISMI Guidelines is essential to assuring best in-fab FTIR and QMS measurement practice is achieved.

2.1.1 Description of Experimental System

An understanding of the tools, processes, and abatement systems to be tested prepares the testing service provider for the onsite measurement study. For example, the experimental system setup informs the study's sampling configuration, whereas the expected dilution, flows, and DRE inform the type of analytical tools for data treatment needed for the study. To ensure that testing service providers are adequately prepared for conducting onsite measurements, information on the following aspects of the experimental system should be included in the measurement plan:

- Description of the process tool and abatement system;
- Configuration of the process tool and abatement system;
- Presence of vacuum pump purges and additional purges;
- Process operating conditions;
- Measurement conditions (i.e., plasma off or actual process conditions);
- Gases/flow rates (when measuring with the plasma off) and/or process recipe (when measuring during actual conditions);
- Number of process chambers served by abatement system;
- Nominal abatement system reactor temperature;
- Nominal abatement system exhaust flows;
- Nominal process exhaust flows;
- Nominal dilution factor (Note: Nominal dilution factor is defined as the ratio of the nominal abatement system exhaust flow to the nominal process exhaust flow); and
- Nominal DRE(s) for F-GHG(s) being tested.

2.1.2 Sampling Configuration

An example schematic of the sampling configuration, which illustrates the configuration of the process tool and abatement system, should be developed by testing service providers prior to onsite measurements. In the schematic the planned/proposed sampling and measurement layout in relation to the process tool and abatement systems, the process tool and abatement system effluent sampling locations, and the type of sampling port (e.g., tie-in type) should be clearly labeled (see Figure 1).

2.1.3 Required Resources

One of the primary purposes of the measurement plan is to facilitate coordination between the testing service providers and the facility personnel. The plan should include a sufficiently detailed description of all resources needed from the facility including sampling ports and fittings, gas supplies, electrical outlets, and assistance of facility personnel including roles, responsibility, and an anticipated schedule. Advance preparation by facility personnel is essential for maximizing the utility of testing service providers' time at the facility.
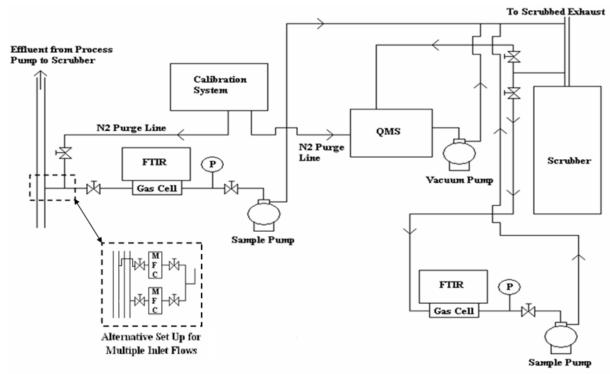
Figure 1. Sampling Schematic for Single and Multiple Chamber Inlet Flow(s) Source: EPA, 2009.
Note: Metrologists need to be mindful of recirculation issues when returning the sampled gas flows to exhaust lines.

2.1.4 Measurement Schedule

In order to minimize any interference with facility production, a measurement schedule should be agreed upon prior to conducting the onsite study. The measurement schedule should clearly indicate the sampling start and end times. Additionally, the tool operator should approve and be familiar with the measurement plan and experimental system including the process tools/chambers and abatement systems, the process conditions during sampling (i.e., plasma off versus actual process conditions), and the gas flow rates/process recipe to be supplied to the tool.

2.1.5 Safety

Safety of the measurement study participants is of highest priority. Prior to conducting any work onsite, testing service providers will be instructed by appropriate fab personnel about all pertinent safety requirements and practices. For example, appropriate personal protective equipment (PPE) should be worn while conducting measurements in a fabrication environment (e.g., head protection, hearing protection, eye protection, and foot protection). Additionally, testing service providers are responsible for acquainting themselves with the hazards that exist in the IC fabrication environment (e.g., hazardous gases, chemical spills, and heavy objects) and taking all steps to avoid adverse impacts. Special consideration should be given to the benefits and risks of mixing pyrophoric/flammable and oxidizing gases. Most abatement systems are

designed to prevent such mixing prior to combustion and measurement methodologies that defeat manfuacturers' design goal should be thoroughly considered.

2.1.6   Quality Assurance/Quality Control

In preparation for the measurement study, testing service providers should gather information on the experimental system and its expected characteristics, such as expected reactor temperature, exhaust flows, etc (see Section 2.1.1). This information serves as a check to ensure the experimental system is functioning as expected. Testing service providers should also be aware of any leaks or instrument malfunctioning that could nullify results of the study.

2.2 Measurement Methodology

This Protocol describes two methodologies for obtaining DRE measurements: Method 1 (Dilution Adjusted Concentration Measurement), which is performed with the plasma off, and Method 2 (Total Volume Measurement), which measures emissions during actual production processing conditions. Two approaches may be followed when using Method 2 to measure the DRE: Sequential Single-Chamber Process Inlet Abatement System Flow Sampling (SSPISF) or Multi-Chamber Process Inlet Abatement System Flow Sampling (MPISF). Proper application of these methods (or approaches) will ensure that the DRE measured has a relative error below ±5 percent. The relative error of the estimated true fraction emitted provides one benchmark for assessing the quality of the sampling methodology, and is the metric used in this Protocol to determine the acceptability of the DRE measurement methodology. If the relative error of the true fraction emitted is less than ±5 percent at one standard deviation the methodology used is in accordance with the best practices defined in this Protocol via Methods 1 and 2.

Whether Method 1 or Method 2 (SSPISF or MPISF) is most applicable depends on several considerations, including the experimental system to be tested, measurement study objectives, and safety (cf., Sec. 2.1.5). All named methods and approaches require similar sampling and analytical methodologies, which are described in detail in this section of the Protocol. Where the methods and approaches differ is Method 1 requires sampling when the process tool is off while Method 2 (SSPISF or MPISF) requires sampling under normal process conditions. The differences in sampling conditions lead to differences in data analysis and DRE calculations for Methods 1 and 2. Using alternate methodologies to the ones described here is acceptable, as long as the relative error in the true fraction emitted measurement is less than ±5 percent. If an alternate methodology is used, the burden falls on the testing service provider to demonstrate that the relative error requirement (±5 percent) is met, to provide detailed descriptions of the methodology used, and to provide the appropriate supporting data analysis.

In instances when concentrations exiting the abatement system are below FTIR detection limits a modification of the performance metric is required. Because the concentrations exiting the abatement system cannot be measured in these instances, a predefined F-GHG concentration is used (which exceeds the lower limit of FTIR detection) to demonstrate proper measurement. To calculate the performance metric, the relative error of that concentration is used, with the result compared to the performance standard of ±5 percent.

Methodologies and approaches described in this Protocol make extensive use of Fourier Transform Infrared (FTIR) Spectroscopy and Quadrupole Mass Spectrometry (QMS) techniques. Testing service providers are directed to the guidance prepared by International SEMATECH Technology Transfer #0612485A-ENG for detailed descriptions for best practice FTIR and QMS Protocols (December, 2006).[7]

2.2.1   Method 1—Dilution Adjusted Concentration Measurement

In Method 1, the process tool plasma (RF) is off while data are collected, so DRE measurement is made with the F-GHG and diluent gases entering the abatement system.   An advantage of Method 1 lies in controlling the flow rates of the F-GHGs measured, resulting in steady-state conditions, which make the subsequent data analysis and DRE calculations simpler than dealing with non-steady state flows. However, when the process tool is off, by-product gas DRE's will not be measured, requiring modification of the process tool setup to imitate by-product gas flows. Method 2 overcomes this difficulty and is, therefore, preferred.

When using Method 1, F-GHG flows entering the abatement system should be 120 percent of the F-GHG flows entering the abatement system during normal production processing to ensure the abatement tool is being tested under conditions that may occur during processing. For example, if the process flow for an F-GHG, f, is x sccms during production processing (which corresponds to y g/sec) and the corresponding default utilization is U_f, then the flow entering the abatement system during testing should be $1.2 * y * (1-U_f)$ g/sec of gas f. In a circumstance when byproducts are formed, the sum of the imitated emissions of the F-GHG and byproduct gas(es) should equal 120 percent of the value obtained using the appropriate IPCC 2006 default emission factors (Volume 3, Table 6.3).

2.2.2   Method 2—Total Volume Measurement

Method 2 involves collecting data during actual process conditions. Method 2 requires no modifications to the process tool for either process or byproduct gas DRE measurements. However, collecting data during actual process conditions may not result in steady-state conditions, making the data analysis and DRE calculations more involved than Method 1 (see section 2.3 for detailed discussion of data analysis). Sampling to measure total F-GHG volume flow leaving the process tool and the abatement system may be accomplished through two approaches, which are applicable to process tools with single or multiple process chambers (reference Fig. 1).

One approach consists of sequentially measuring the F-GHG volume flow entering the abatement system from each chamber while also measuring the corresponding F-GHG volume flow leaving the abatement system. This sampling approach is called the Sequential Single-Chamber Process Inlet Abatement System Flow (SSPISF) method. The second sampling approach consists of simultaneously measuring the volume flow from all operating chambers that

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[7] See Appendix A – Technical Protocols of Air Emissions Characterization of SEMATECH Technology Transfer #0612485A-ENG (December 2006). This Appendix augments EPA Test Method 320, *Measurement of Vapor Phase Organic and Inorganic Emissions by Extractive Fourier Transform Infrared (FTIR) Spectroscopy*, as it might apply to measuring F-GHG emissions in waste streams produced during electronic device manufacture

is entering the abatement system while also measuring the corresponding F-GHG volume flow exiting the abatement system. This second sampling approach is called the Multi-chamber Process Inlet Abatement System Flow (MPISF) method. Both approaches employ sampling during actual process conditions. The SSPISF method uses a slip-stream of the effluent from a single process chamber as its sample and the MPISF method uses multiple slip-streams of the effluent (one for each operating chamber with each representing the appropriate proportion of the total process flow from all operating chambers) that are then mixed to account for actual process conditions. Sampling to measure the total F-GHG volume flow entering the abatement system may be accomplished using the MPISF method provided appropriate safety precautions are taken when mixing the flows of combustible gases.

2.2.3   Equipment Needed

Two FTIRs are optimal for measuring F-GHG concentrations in the effluent streams.[8] One FTIR is used to sample from the process effluent and another to sample from the abatement system effluent. Additionally, a QMS, inert gas supply, and mass flow controller (MFC) are needed to measure the dilution that occurs through the abatement system. When measuring DREs in systems that do not abate CF_4 and/or SF_6, it is possible to measure dilution using an FTIR instead of a QMS/MFC/inert gas supply system. When a tracer other than a noble gas is used, such as CF_4 or SF_6, the metrologist should provide documentation demonstrating that less than 5 percent of the tracer gas is destroyed. For purposes of testing using such tracers, the tracer gas is treated as undestroyed. Two examples of an acceptable demonstration are: (1) the manufacturer of the POU abatement system provides results, based on the methods of this Protocol, that the DRE of the chemical tracer is <5 percent under the operating conditions being tested at the fab using the QMS and the noble gas tracer methodology or (2) in-fab tests showing <5 percent destruction of the chemical tracer on a POU abatement system (based on the QMS and noble gas tracer methodology of this Protocol for one abatement system in the fab) may be used on abatement system in the facility of the same make and model installed and operated in the same manner as the abatement system tested.

Metal bellows sampling pumps should be installed after each FTIR and/or QMS to collect effluent samples. Installing adjustable flow rate valves to control the sample flow rates and capacitance manometers to monitor the sample line pressure are recommended. A sample filter should be used in the abatement system sampling line to prevent particulate emissions from the abatement system from damaging the FTIR or QMS. Lastly, when sampling using the MPISF method, mass flow controllers (MFCs) are needed—one for each operating chamber during sampling—to create a representatively proportional slip stream composition of the total flow. Table 1 provides a summary of the equipment required and Figure 1 shows a sample schematic of the experimental setup.

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[8] One FTIR can be used, but it would be necessary to alternate abatement system inlet and outlet measurements. Steady-state behavior would have to be verified by sampling for a sufficiently long period of time. It must be shown that sufficient precision can be achieved with just one FTIR system. Using one FTIR will require knowing with confidence what the abatement system loading is. If sufficient inlet data is acquired to accomplish this, and then the FTIR is switched to the outlet of the abatement system and the same process is run on the tool then the Protocol will work just as well as using two FTIRs. The emission factors for a particular process run on the same chamber are usually reproducible. Sufficient data can be collected to achieve the desired precision.

Table 1. Measurement Study Equipment Needs[a]

Equipment Type	Quantity Required
FTIR	1-2[b]
QMS	0-1
Inert gas supply/mass flow controller (MFC)	0-1
Metal bellows sampling pumps	2-3
Adjustable flow rate valves	2-3
Capacitance manometers	2-3
Sample filter	1-2
MFC for exhaust streams	No. of chambers tested

.   [a] Not exhaustive
    [b] When using 1 FTIR, it must have variable path length

2.2.4   FTIR and QMS Protocols

FTIR measurements should be taken following the best practice guidelines specified in the guidance prepared by International SEMATECH Technology Transfer #0612485A-ENG (December, 2006).[9] The FTIR should be operated at a resolution of 0.5 cm^{-1} or 1.0 cm^{-1}, provided that calibrations match resolution used during sampling. The sampling frequency for the FTIR should be less than 3 seconds.[10] The FTIR absorbance range should be between 0.1 and 1.0; however, lower and higher absorbencies may be used provided sample data are bracketed by calibration data. Alternate short- and long-path gas cells should be used, to ensure that the measured absorbance for process effluent concentrations and abatement system effluent concentrations falls within the range 0.1 to 1.

QMS measurements should be taken following the best practice guidelines specified in the guidance prepared by International SEMATECH Technology Transfer #0612485A-ENG (December, 2006).[11] To account for fluctuations/drift in QMS sensitivity, the ion signals should be normalized to the signal obtained for the nitrogen fragment N^+, which is formed during ionization of N_2.

2.2.5   Calibration Curves

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[9] See Appendix A.2 – Fourier Transform Infrared (FTIR) Spectroscopy Protocol of SEMATECH Technology Transfer #0612485A-ENG (December 2006).

[10] In the tests EPA performed, 4 FTIR scans were co-added for one data point, which takes 2.2 secs at 0.5 cm^{-1} resolution and provides adequate temporal resolution to follow time-varying process emissions. Thus, each data point requires 2.2 sec, so 40 data points requires approximately 1.5 minutes.

[11] See Appendix A.1 – Mass Spectrometry Protocol of SEMATECH Technology Transfer #0612485A-ENG (December 2006).

The Protocol permits either onsite or offsite calibration for FTIR measurements of F-GHGs, with both governed by the guidance provided in Appendix A.2 of SEMATECH Technology Transfer (December 2006). In either circumstance, the range in absorbance for the calibration curves should bracket the corresponding absorbance range for the onsite measured concentrations, with a preferable range for the absorbance between 0.1 and 1. In situations where the onsite measured absorbance lies outside the 0.1 to 1 range, either (a) a calibration must be available at the high or low absorbance, (b) an alternative absorption band should be used that lies, for that specific molecule, within the 0.1 – 1 absorbance, or (c) an alternate FTIR gas cell should be used.[12] Further, while the measured absorbance of large molecules, like the F-GHGs of concern here, is not expected to be sensitive to reasonable differences in resolution (say, 0.5 vs. 1 cm^{-1}), this concern is mitigated by requiring the use of the same resolution for calibration sampling.
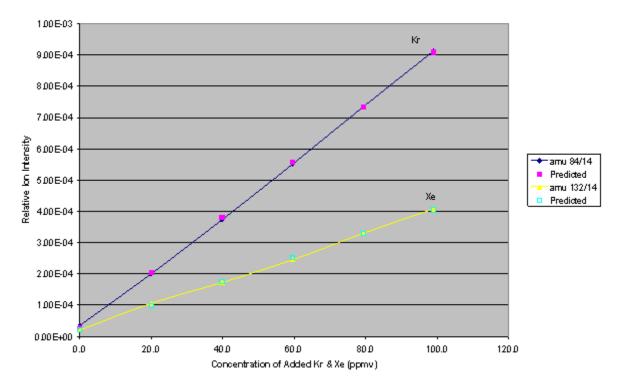
For onsite calibration, the metrologist must report/show the calibration graphs and report the corresponding calibration and measurement conditions for all F-GHGs measured. The measurement conditions to report are gas temperature and pressure, as well as the FTIR resolution used during sampling and calibration. When reported DREs employ offsite calibration, the metrologist must report/show calibration graphs as well as the conditions (temperature, pressure and resolution) used for calibration and during onsite sampling. If calibration and onsite temperatures, pressures or both differ then corrections must be made to account for the change in gas number density. These corrections are often standard features of modern FTIR software packages. The calibration curves for both onsite and offsite testing should be generated using at least three calibration points such that expected measured absorbance range is covered. Quality of calibration may be judged by proximity of R^2 to 1.00. For non-linear calibration curve, it's important that highest observed concentration is within not outside the range of concentrations used to define the calibration curve.

Prior to conducting measurements of the process and abatement system effluents, onsite QMS calibration should be completed for all compounds to be measured. The calibration curves should be generated using at least 1 zero and 5 non-zero data points. The recommended ion intensity range for the QMS should be within one decade. Calibration plots with the signal intensity versus compound concentration data points and the line of best fit should be included in the measurement report. Additionally, the slope, the relative error of the slope (one standard deviation), the y-intercept, and the correlation coefficient (i.e., R^2) of the correlation line should be presented and each parameter clearly labeled (see Figure 2 as an example).

To ensure that the ±5 percent benchmark relative error is achieved, all calibration curves should meet the following criteria:

- Slope must have an error below ±5 percent; and
- Correlation coefficient must exceed 0.98

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[12] Some FTIR quantitative analysis software packages (e.g. AutoQuant Pro used by Midac Corporation) has the ability to shift to different absorbance peaks over several orders of magnitude depending on the concentration of the material being measured. In this case, multiple gas cells may not be required. However, that shifting to another peak may risk influence of interferent that also absorbs at that same wave number. Using multi-path cells is best practice for this FTIR application.

QMS Response to Kr and Xe

Figure 2. Sample Calibration Curve The R^2 and relative error of the slope for both calibration curves shown are >±99 percent and <±1 percent, respectively. Source: EPA, 2008a and 2008b.

2.2.6   Flow and Dilution Measurements

Determining dilution across the abatement system is a two step process. The first step is determining the total volume flow of the process effluent, and the second step is determining the total volume flow of the abatement system effluent. The total volume flow of the process effluent can be estimated by flowing known quantities (flows) of F-GHG through the tool with the RF turned off, while a FTIR system measures the F-GHG concentration of the process effluent. The total volume flow of the abatement system effluent can be estimated by supplying known quantities of inert gas into the process stream effluent, while a QMS system measures the inert gas concentration in the abatement system effluent. Controlled volume flows of inert gas can be supplied to the process effluent using a mass flow controller (MFC).   When measuring DREs in systems that do not abate CF_4 and/or SF_6 it is possible to measure total abatement system flow using an FTIR instead of a QMS. In such systems CF_4 or SF_6 can be used in place of an inert gas since their DREs are zero percent. Table 2 provides a list of acceptable gases for measuring total abatement system flows, along with their use conditions.

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Table 2. Acceptable Gases for Monitoring Total Abatement System Flows

Tracer Gas	Analytical Equipment	Limitations
Kr	QMS	None
Xe	QMS	May be used in some etch processes recipes.
Ar	QMS	Must subtract out air concentration background; cannot use if Argon is used as a process gas.
CF_4	FTIR	DRE must be zero
SF_6	FTIR	DRE must be zero

To ensure that the ±5 percent relative error is met, the following conditions should be met:

- Accuracy of calibration gases in the concentration of the inert gas supplied to the process effluent stream should be ±3 percent or less.
- 3-5 different flow rates should be supplied to the process tool and/or abatement system, and at least 40 distinct measurements made for estimating the average concentration at each flow rate.
- Appropriately sized MFC such that accuracy of lowest flow is ±3 percent or better

2.2.7   F-GHG Measurements

The Protocol suggests that using two FTIRs is optimal.[13] One FTIR is used to measure F-GHG concentration in the process effluent and another to measure F-GHG concentration in the abatement system effluent. The concentration of F-GHGs in both effluent streams should be recorded, as well as the gases/flow rates and/or process recipes that are fed into the process tool. Absorption bands should be chosen to minimize the influence of interfering substances and to hold absorbance within the range 0.1 to 1.

To ensure that the ±5 percent relative error is achieved, the following conditions should be met:

- Method 1: For each process gas tested, 3-5 different flow rates should be supplied to the process tool, and at least 40 process tools and abatement system effluent concentration measurements averaged for each flow rate.
- Method 2 (SSPISF and MPSIF): For each process gas tested, 3-5 data points should be collected for total volume in and total volume out of the abatement system and at least 40 process tools and abatement system effluent concentration measurements averaged for each flow rate.

When the concentration exiting the abatement system approaches or falls below the minimum detectable level the metrologist can demonstrate proper measurement practice by introducing into the sampling stream a flow of that gas such that its concentration entering the abatement is low but exceeds the minimum detection level. This concentration is denoted as C^*. To

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[13] See footnote 8.

demonstrate proper measurement of C^*, the relative error of the C^* measurement is used in place of C_o (the exit concentration) to calculate the performance metric. The precision of C^* is estimated with data from the FTIR used to measure the F-GHG exiting the abatement system.

Table 3 sets forth C^*, in units of ppm-m, for the gases governed by this Protocol. Table 3 identifies the minimum detection (concentration) levels for the gases of interest at standard temperature and pressure (STP), defined as a signal to noise of 3 for a HgCdTe liquid nitrogen cooled detection, 0.5 cm^{-1} resolution. A single value for C^* was chosen for simplicity. It is evident from comparison of the second and third column that, for the selected C^*, the signal to noise ratio (S/N) will be much greater than 3 so the precision should be high. Further, for the typical long-path used in such tests, the C^* concentration being sampled should correspond to DREs in the range 95-99%.

Table 3. Minimum detection levels (C_{MDL}) and threshold F-GHG concentrations (C^*) for measuring relative error of total fraction emitted when sample $C < C^*$, ppm-m

F-GHG	Typical C_{MDL}, ppm-m	C^*, ppm-m	Primary absorbtion band, cm^{-1}
CF_4	0.12	10	1280
CHF_3	0.40	10	1150
C_2F_6	0.21	10	1250
C_3F_8	0.2	10	1150
c-C_4F_8	0.7	10	965
NF_3	1.1	10	910
SF_6	0.1	10	943

Note: C_{MDL} values based on calibration data using path lengths between 10 cm and 5 m, resolution of 0.5 cm^{-1}, gases at STP, HgCdTe liquid cooled detector and a S/N of 3 10^{-3} absorbance units.

Of the several ways for preparing a sample stream with concentration C^*, two that are acceptable are described here. The first is to ask the process tool operator to provide a sufficiently low flow of gas such that after dilution by the pump purge, C^* is achieved at the sampling point ahead of the abatement system. For example, if the target concentration, C^*, is 2 ppm and the pump purge is 50 lpm (determined previously), then 50 ppm is achieved with a process flow of C of 0.1 sccm. For process tools with MFCs that cannot deliver sufficiently low flows, the sampled slip stream can be diluted with nitrogen using either a separate MFC or needle valve. The actual concentration sampled may be within ±20 percent of C^*, i.e., ±0.4 ppm in the example (vide supra).

A second approach for preparing C^* is for the metrologist to have available a gas cylinder with the appropriate concentration to introduce ahead of the abatement system, which, accounting for the pump purge flow, will produce C^* ±20 percent of the value taken from Table 3. The first approach may be preferable because it doesn't require the availability of additional gas cylinders of the appropriate concentrations.

2.3 Data Treatment and Analysis

The procedures for treating flow and concentration measurements as well as calculating total flows, dilution factor and DRE of the abatement system are described in this section. Also described are the methods for consistently estimating the precision associated with measuring gas concentrations, flows, dilution factors and DREs. The data treatment and analysis component consists of two sections. The first section addresses data used to calculate best-estimate values for flows and the abatement system dilution factor as well as their standard deviations. The second section addresses the data used to calculate best-estimate of the abatement system DRE and associated relative errors, using either Method 1 or Method 2. In the following sections absolute error is referred to as σ and relative error is referred to as ε, and all relative and absolute errors are presented at 1 standard deviation.

When an alternative methodology, such as the Physical Flow Measurement method, to the two described in this Protocol is used to estimate DRE, the data treatment and analysis procedure described below may not be applicable. In such cases, the testing service provider should determine and use the appropriate procedures to calculate both the DRE and its corresponding error.

2.3.1 Abatement System Dilution

2.3.1.1 Total Volume Flow

Total volume flow (TVF) is the total volume of gas that flows across a process tool or abatement system, and is generally measured in standard liters per minute (slm). For both Methods 1 and 2, measurements of TVF entering and exiting the abatement system are needed. TVF or F is calculated using Equation 1:

$$F = \frac{S_f}{C_{ef} \times 10^{-6}} \qquad\qquad (1)$$

where,
F = total volume flow based on a single concentration data point [slm]
S_f = spike gas flow into the process tool/abatement system [slm]

C_{ef} = measured concentration of standard gas in the process tool/abatement system effluent [ppmv]

To ensure that the error of TVF is low enough to meet the relative error requirement of ±5 percent, TVF measurements should be collected during at least three different standard gas flow rates. During each gas flow rate, at least 40 concentration measurements (FTIR or QMS scans) should be collected at the effluent side of the process tool/abatement system. For example, when measuring the TVF exiting the process tool, a process gas such as C_2F_6 should be fed into the process tool at multiple flow rates (e.g., 0.2, 0.6, and 1.0 slm), and during each flow rate, a minimum of 40 concentration data points of the process effluent should be collected using a FTIR. Similarly, when measuring the TVF exiting the abatement system, an inert gas such as Kr should be spiked into the abatement system at multiple flow rates (e.g., 0.010, 0.030, and 0.050

slm), and during each flow rate a minimum of 60 concentration data points of the inert gas in the abatement effluent should be measured using a QMS.

The measurements above will result in at least 120 TVF data points, which will need to be averaged appropriately. A simple average, denoted as $\overline{F}$ determines the average TVF and corresponding standard deviation during *each* flow rate applied, denoted by subscript m (see Equation 2 and Equation 3).

$$\overline{F}_m = \sum_{1}^{n} \frac{F_i}{n} \tag{2}$$

where,
$\overline{F}_m$ = simple average of TVF [slm] for the mth flow
n = number of concentration measurements taken while at a constant standard gas flow (e.g., 40 concentration data points collected during a 0.2 slm standard gas flow rate)

$$\sigma_{\overline{F}m} = \sqrt{\frac{1}{n} \sum_{1}^{n} \left(F_i - \overline{F}_m \right)^2} \tag{3}$$

The TVF simple average ($\overline{F}_m$) only applies to values that are collected during the same standard gas flow rate. Therefore, if three different standard gas flow rates are collected, three different simple averages must be derived.

When combining the multiple TVF simple average ($\overline{F}_m$) values for each flow rate into a single average TVF, a variance weighted average must be applied (denoted as $\hat{F}$). The equations for determining the variance weighted average and its corresponding standard deviation, are shown in Equations 4 and 5.

$$\hat{F}_g = \frac{\sum_{1}^{M} \dfrac{\overline{F}_m}{\sigma_{\overline{F}_m}^2}}{\sum_{1}^{M} \dfrac{1}{\sigma_{\overline{F}_m}^2}} \tag{4}$$

where,
$\hat{F}_g$ = variance weighted average TVF [slm] for flow standard gas, g
M = number of flow rates used per standard gas, g

$$\sigma_{\hat{F}_g} = \sqrt{\frac{1}{n}} \times \left(\sum_{1}^{M} \frac{1}{\sigma_{\overline{F}_m}^2} \right)^{-\frac{1}{2}} \tag{5}$$

where,

n = number of concentration measurements

The variance weighted TVF average ($\hat{F}$) can only be calculated using average TVF values ($\bar{F}$) obtained using the same standard gas. For example, if two different standard gases are used, then a variance weighted average is calculated for each standard gas.

Equation 5 assumes that the number of concentration measurements during each flow rate is constant (i.e., n is the same for each simple average). If n varies for each simple average, then Equation 5 must be altered to account for variations in n. Alternatively, when n varies, the lowest n can be used in Equation 5 to generate a conservative estimate of the standard deviation (i.e., the standard deviation will err on the larger side).

In the case when multiple standard gases (e.g., Kr and Xe for abatement system or C_2F_6 and CF_4 for process tool) are used to calculate TVF, then the variance weighted average ($\hat{F}_g$) for each gas, g, can be combined to determine a TVF best estimate (denoted as $\bar{\bar{F}}$) and its corresponding error as shown below (see Equations 6 and 7).

$$\bar{\bar{F}} = \frac{\sum_{1}^{G} \dfrac{\hat{F}_g}{\sigma_{\hat{F}_g}^2}}{\sum_{1}^{G} \dfrac{1}{\sigma_{\hat{F}_g}^2}} \qquad\qquad (6)$$

where,
$\bar{\bar{F}}$ = Best estimate for TVF [slm]
G = number of standard gases used to determine TVF

$$\sigma_{\bar{\bar{F}}} = \left(\sum_{1}^{G} \frac{1}{\sigma_{\hat{F}_g}^2} \right)^{-\frac{1}{2}} \qquad\qquad (7)$$

The absolute errors or standard deviations obtained from equations 3, 5 and 7 measure the precision of each standard gas flow for each gas, for all flows for each gas, and for all gases, respectively, when more than one gas is used (e.g., if Xe and Kr were both used). The overall accuracy is determined by the accuracy of the calibration, calibration standard gas concentrations, and mass flow controller. In order to obtain a DRE relative error of less than ±5 percent, the concentration standard gas should have a relative error of less than 3 percent of the designated concentration, and the accuracy of the MFC should be less than 3 percent for the lowest flow rate used during the measurements.

2.3.1.2 Dilution Factor

The dilution factor describes the total volumetric dilution that occurs across an abatement system. The dilution factor is determined by calculating the best estimate for TVF into ($\overline{\overline{F}}_{in}$) and out of the abatement system ($\overline{\overline{F}}_{out}$). (See Section 2.3.1 for determining the best estimate for TVF). The TVF exiting the abatement system divided by the TVF entering the abatement system defines the dilution factor as shown in Equation 8. The standard deviation or precision of the dilution factor is determined by the standard deviation of each TVF measurement, and is estimated using error propagation techniques (See Equation 9).

$$\overline{\overline{DF}} = \frac{\overline{\overline{F}}_{out}}{\overline{\overline{F}}_{in}} \tag{8}$$

where,

$\overline{\overline{DF}}$ = Best estimate for dilution factor [dimensionless]

$\overline{\overline{F}}_{out}$ = Best estimate for TVF exiting abatement system [slm]

$\overline{\overline{F}}_{in}$ = Best estimate for TVF entering the abatement system [slm]

$$\varepsilon(\overline{\overline{DF}}) = \sqrt{\left(\frac{\sigma_{\overline{\overline{F}}_{out}}}{\overline{\overline{F}}_{out}}\right)^2 + \left(\frac{\sigma_{\overline{\overline{F}}_{in}}}{\overline{\overline{F}}_{in}}\right)^2} \tag{9}$$

where,

$\varepsilon\overline{\overline{DF}}$ = The relative error of $\overline{\overline{DF}}$ (the standard deviation divided by the mean value)

$\sigma_{\overline{F}_{out}}$ = The standard deviation of $\overline{\overline{F}}_{out}$ [slm] (see Equation 7)

$\sigma_{\overline{F}_{in}}$ = The standard deviation of $\overline{\overline{F}}_{in}$ [slm] (see Equation 7)

2.3.2   Abatement System DRE Estimate and Relative Errors

The formulas for calculating DRE depend on the method used. For Method 1, the ratio of the measured effluent concentration to measured influent concentration is multiplied by the measured dilution factor (i.e., dilution adjusted concentration fraction, which equals the mass- or volume-emitted fraction). For Method 2, the ratio of effluent to influent gas volumes is used (i.e., volume fraction); the affect of dilution is accounted for when calculating total flows. For either method it can be shown that, for the formulas given below, the calculated DRE is a best-estimate, i.e., statistically unbiased. The subscripts 1 and 2 differentiate formulas for Method 1 and 2, respectively.

2.3.2.1 Method 1—Dilution Adjusted Concentration Measurements

2.3.2.1.1   Concentration Measurements

During Method 1, the concentration of process gas entering and exiting the abatement system is monitored, while the process tool is off, and while a known flow rate of process gas is fed into the abatement system. For each flow rate, the concentration of process gas in the abatement influent and effluent is in steady state. For each process gas at least three different process gas flow rates should be used to collect a minimum of 60 concentration data points per flow rate, to ensure relative error is achieved. As described in section 2.2, an FTIR should be used to monitor concentration of process gases, and the FTIRs absorbance signal should be converted to a concentration using a calibration curve. The relative error of each concentration data points measured by the FTIR is equal to relative error of the calibration curve slope.[14] Using the concentration data points, the variance weighted average and corresponding error for concentration can be estimated using a procedure analogous to that shown for total volume flow (see Section 2.3.1.1; Equations 1 to 5). The variance weighted average is considered the best estimate for F-GHG concentration entering and exiting the abatement system.

2.3.2.1.2 DRE

$$\overline{\overline{\overline{DRE}}}_1 = \left(1 - \frac{\left(\overline{\overline{C}}_{out} \times \overline{\overline{DF}}\right)}{\overline{\overline{C}}_{in}}\right) \times 100 \, percent \qquad (10)$$

where,

$\overline{\overline{\overline{DRE}}}_1$ = Best estimate for Destruction and Removal Efficiency [percent]

$\overline{\overline{C}}_{out}$ = Best estimate for concentration of F-GHG exiting the abatement system [ppm]

$\overline{\overline{C}}_{in}$ = Best estimate for concentration of F-GHG entering the abatement system [ppm]

$$\varepsilon(\overline{\overline{\overline{DRE}}}_1) = \frac{\lambda_C \overline{\overline{DF}}}{\left(1 - \lambda_C \overline{\overline{DF}}\right)} \sqrt{\left(\frac{\sigma_{\lambda_C}}{\lambda_C}\right)^2 + \left(\frac{\sigma_{\overline{\overline{DF}}}}{\overline{\overline{DF}}}\right)^2} \qquad (11)$$

where,

$$\lambda_C = \frac{\overline{\overline{C}}_{out}}{\overline{\overline{C}}_{in}}$$

$$\varepsilon(\lambda_C) = \sqrt{\left(\frac{\sigma_{\overline{\overline{C}}_{out}}}{\overline{\overline{C}}_{out}}\right)^2 + \left(\frac{\sigma_{\overline{\overline{C}}_{in}}}{\overline{\overline{C}}_{in}}\right)^2}$$

σ_{λ_c} = The standard deviation of λ_c

$\sigma_{\overline{\overline{DF}}}$ = The standard deviation of DF

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[14] The relative error of the calibration curve slope should not exceed ±5 percent (at one standard deviation) to ensure the Protocol benchmark error of ±5 percent is obtained.

$\sigma_{\overline{\overline{C}}_{out}}$ = The standard deviation of $\overline{\overline{C}}_{out}$ [ppm]

$\sigma_{\overline{\overline{C}}_{in}}$ = The standard deviation of $\overline{\overline{C}}_{in}$ [ppm]

2.3.2.2 Method 2—Total Volume Measurements

2.3.2.2.1 Total Volume Measurements

When measuring the DRE using Method 2, the concentration of the gas in the abatement influent and effluent is monitored while the process tool is on, and cannot be assumed to be at steady state. Therefore, the total volume of process gas entering and exiting the abatement system must be estimated by integrating the FTIR signal over time (The absorbance signal should be converted to concentration using the calibration curve, prior to integration). When multiple total volume measurements are collected for a single process, the best estimate and error of the total volume measurement is equal to the simple average and its standard deviation, which are analogous to Equations 2 and 3 in Section 2.3.1.1.

2.3.2.2.2 DRE

$$\overline{\overline{DRE}}_2 = \left(1 - \frac{\overline{\overline{V}}_{out}}{\overline{\overline{V}}_{in}}\right) \times 100 \, percent \tag{12}$$

where,

$\overline{\overline{V}}_{out}$ = Best estimate for total volume of F-GHG exiting the abatement system [sl]

$\overline{\overline{V}}_{in}$ = Best estimate for total volume of F-GHG entering the abatement system [sl].

$$\overline{\overline{V}}_i = \int_0^T Vi(t) = \sum_{j=1}^N F_i C_{i,j} \Delta t_j = F_i \sum_{j=1}^N C_{i,j} \Delta t_j \tag{13}$$

where i denotes either the outlet or inlet F-GHG gas, F denotes the corresponding inlet or outlet flow, Δt_j denotes the integration interval, $C_{i,j}$ is the concentration of F-GHG either entering or exiting the abatement system and the sum is taken over the period, T, of production processing.

$$\varepsilon(\overline{\overline{DRE}}_2) = \frac{\sigma_{\lambda_V}}{(1 - \lambda_V)} \tag{14}$$

where,

$$\lambda_V = \frac{\overline{\overline{V}}_{out}}{\overline{\overline{V}}_{in}}$$

$$\varepsilon(\lambda_V) = \sqrt{\left(\frac{\sigma_{\overline{\overline{V}}_{out}}}{\overline{\overline{V}}_{out}}\right)^2 + \left(\frac{\sigma_{\overline{\overline{V}}_{in}}}{\overline{\overline{V}}_{in}}\right)^2}$$

$\sigma_{\overline{\overline{V}}_{out}}$ = The standard deviation $\overline{\overline{V}}_{out}$ [slm]

$\sigma_{\overline{\overline{V}}_{in}}$ = The standard deviation of $\overline{\overline{V}}_{in}$ [slm].

It can be shown that ε_{λ_V}, the relative error in the true fraction of emitted F-GHG estimated using Method 2 is, to a very good approximation, governed by relative error in the effluent process and abatement system flows, or the relative error in the dilution factor. This simplification occurs because, in calculating the volume flow, integrating the measured concentrations over the period of production processing averages out the uncertainties in FTIR measured concentrations compared to the corresponding measured flow rates.[15] The relative error for Method 2 may be estimated, to a very good approximation, as the relative error in the dilution factor, which is given by Eq. 9.

3. BENCHMARK RELATIVE ERROR

For Protocol to be considered valid, the relative error for true fraction emitted must be less than ±5 percent. Presented below are the formulas for estimating relative error (i.e., $\varepsilon(TFE)$) of the true fraction emitted for both Method 1 (Equation 14) and Method 2 (Equation 15). All the parameters used to estimate the relative error of true fraction emitted have been defined in section 2.3, and therefore, are not redefined here. These formulas may not be applicable when alternative methodologies to those presented in this Protocol are used, and in such cases, testing service providers should determine and use the appropriate formulas to calculate the relative error of the true fraction emitted.

3.1 Method 1—Dilution Adjusted Concentration Measurements

$$\varepsilon(TFE_1) = \sqrt{\left(\frac{\sigma_{\lambda_C}}{\lambda_C}\right)^2 + \left(\frac{\sigma_{\overline{\overline{DF}}}}{\overline{\overline{DF}}}\right)^2} \leq 5\,percent \tag{15}$$

3.2 Method 2—Total Volume Measurements

$$\varepsilon(TFE_2) = \sqrt{\left(\frac{\sigma_{\overline{\overline{V}}_{out}}}{\overline{\overline{V}}_{out}}\right)^2 + \left(\frac{\sigma_{\overline{\overline{V}}_{in}}}{\overline{\overline{V}}_{in}}\right)^2} \leq 5\,percent \tag{16}$$

which may be estimated using Eq. 9.

In those instances where the concentrations exiting the abatement system, C_{out} in the equations is replaced with C^*, so λ_c is calculated using C^*.

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[15] This can be shown using the expression for $\varepsilon(\lambda_V)$ given in Eq. 14 and noting that relative errors, $\varepsilon_{V_O}^2$ and $\varepsilon_{V_I}^2$, are each the sums in quadrature of the relative errors of the outlet/inlet *flows* and outlet/inlet *concentrations*, respectively. Using the method of simulation to estimate the relative error in the outlet or inlet concentrations, it becomes evident that the relative error in measured outlet or inlet concentration is more than an order of magnitude *less* than the relative error in the corresponding measured abatement system outlet or inlet flows. The reduced relative error in the integrated concentration profile occurs because in the course of integrating over the measured FTIR concentration profile the error in each FTIR measurement is reduced through averaging.

4. DOCUMENTATION AND REPORTING

Proper documentation and reporting ensures transparency of the DRE measurement process, allowing users of DREs and third-parties to review and understand the measurements collected as well as the data treatment and analysis conducted. Therefore, it is important that testing service providers adequately document their analyses, and present the results in a clear and concise report. A suggested structure for the report is presented in the text box below.

The Protocol also requires certification by the testing provider. The final report should contain the following language together with the appropriate signature.

The tester/metrologist principally responsible for the measurements and content presented in this report and obtained during the period _____ to _____ at (name of facility) hereby certifies that the methods and calculations set forth in the Protocol were followed and that material departures or deviations therefrom, if any, are fully documented in this report dated, _____. The tester/metrologist also certifies that the calculations and benchmark relative error presented in this report properly and accurately reflect the actual measurements made at the facility during the test period noted in this certification.

Signed _____

Date _____

Final Report Structure

I.   Introduction
    a. General information about testing

II.   Experimental Setup
    a. Actual sampling/testing configuration
    b. Description of how measurements are taken (reference to Protocol encouraged)
    c. Sampling Configuration

III. Data Analysis
    a. Documentation
        i.   Formulas Used
        ii.   Figures showing calibration curves for each F-GHG and tracer gas (the regression equation should be displayed for each. calibration curve along with relative error of the slope and y-intercept).
        iii. Figures showing the FTIR spectra at the abatement inlet and outlet, which each F-GHG peak clearly labeled.
        iv.   Figures showing the temporal concentration profiles of the abatement inlet and outlet concentration for each F-GHG and tracer gas.
        v.   Tables showing the means and standard deviations of the F-GHG and tracer gas inlet and outlet concentrations and/or volumes (see Section 2.3 for description of the means and standard deviations appropriate for each quantity).
        vi.   Tables showing the mean and standard deviation of the dilution factor and DRE for each F-GHG.
    b. Comparison of estimated DRE error with the 5 percent benchmark relative error.

IV.   Discussion

V.   Metrologist certification that reported results conform to Protocol.

Appendix A: Measurement Plan

5. REFERENCES

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Appendix A – History of and Revisions to the Protocol

The Protocol has gone through five stages of development: conceptualization, onsite tests, initial drafting, and two informal peer review processes. During the informal peer review processes EPA received comments from both national and international parties, including semiconductor manufacturers, equipment manufacturers, gas suppliers and analytic service providers. EPA addressed these comments directly with reviewers in verbal and written form.

Modifications were made to the Protocol to address this feedback. In addition to specific technical issues that reviewers raised, an overarching concern emerged that the Protocol provide as much flexibility as possible without compromising the integrity of the Protocol's measurement process. Calls for flexibility stemmed from the diversity of fab environments, as well as from the diversity of established measurement practices and technologies. International reviewers were unanimous in seeking acceptable alternatives to QMS systems (used for measuring abatement system dilution via the gas tracer method of chemical spiking) for onsite testing, although central to the method favorably evaluated by Lee et al. (Lee, 2007) is the use of a magnetic type precision gas mass spectrometer rather than a quadrupole mass spectrometer (QMS). To provide for more flexibility and to address the technical issues that reviewers raised, EPA considered and made substantive changes to the Protocol:

- Removal of suggested temperature limitations at which a POU system would not abate CF_4 or SF_6 in reference to instances where CF_4 or SF_6 may be used as tracers gases to measure flow across the abatement system
- Allowance of off-site Fourier Transform Infrared (FTIR) Spectrometer calibration
- Consideration of alternative DRE measurement methods. The alternative methods considered were:
  - The Multi-chamber Process Inlet Flow Sampling (MPIFS) Method
  - The Physical Flow Measurement Method[16]
  - The Abatement system De-tuning Method[17]
  - The Post-abatement Flow Tracer Method

Of these listed methods, the Protocol expands Method 2 to include the MPIFS method. The MPIFS method was tested in December 2008. The results using the MPIFS method agreed with results obtained using the Sequential Single-Chamber Process Inlet Flow Sampling (SSPIFS).[18]. The Physical Flow Measurement Study, because it is already an EPA method, is allowable under

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[16] Physical Flow Measurement Methods are allowable per the Protocol to measure the Total Volume Flow in order to determine DRE. Acceptable flow measurement methods would be those that have pre-determined specified measurement standards in place, such as EPA Appendix A Method 2 and EPA Appendix E. However, these methods are not preferred because often they require laminar flow regimes, where that is often not the case in in-fab testing. When using a physical method for measuring gas flow rate, the performance benchmark metric and standard given in Section 3 applies.

[17] The Abatement system De-tuning Method involves either turning off the methane or oxygen flow to the burner of the abatement system, lowering the temperature of the abatement system, or a combination of the two. The Protocol does not permit this method because to do so would defeat the purpose of the abatement system and intentionally release F-GHG emissions to the atmosphere during testing.

[18] EPA cautions, however, that the MPIFS method holds potential safety risks when mixing pyrophoric/flammable and oxidizing gases.

this Protocol; and the Abatement system De-Tuning Method in not permitted under this Protocol. The Post-abatement Flow Tracer Method, while theoretically attractive, has not been compared to the pre-abatement tracer method used in the Protocol and is therefore not permitted under this Protocol.[19]

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[19] While the Post-abatement Flow Tracer Method is not permitted in the Protocol, EPA is interested in learning more, through in-fab testing, about the validity of this method.

Appendix B – Sample Calculation
Step 1 Determine the Mean Total Flow

Data		Calculations: Data Treatment					
n =	60						
		Measured effluent flows		**Variance weighted mean of effluent flow**			
		Avg Effluent	Standard deviation in measured effluent	Variance in measured effluent			
Kr Flow (slm)	Avg Kr Conc (ppm)	Flow, F (slm)	flow, σ (slm)	flow, σ^2 (slm^2)	$1/\sigma^2$	F/σ^2	Units
0.01	14.1	709.2	80	6400	0.0001563	0.110816	NA
0.02	25.5	784.3	52	2704	0.0003698	0.290057	NA
0.03	38.8	773.2	34	1156	0.0008651	0.668855	NA
0.04	52.2	766.3	28	784	0.0012755	0.977402	NA
0.05	65.8	759.9	28	784	0.0012755	0.969233	NA

Sum of F/σ^2	=	3.01636	slm^{-1}
Sum of $1/\sigma^2$	=	0.0039421	slm^{-2}
Mean total flow	=	**765**	slm
(Sum of $1/\sigma^2)^{-1/2}$	=	15.927	slm^{-1}
Sqrt (1/n)	=	0.129099	dimensionless
σ of effluent flow		2	slm
95% CI		4	slm
Upper bound of mean flow	=	769	slm
Lower bound of mean flow	=	761	slm
Relative error, %	=	**0.5%**	dimensionless

Step 2 Determine the Dilution Factor

Data			Calculations: Dilution Factor		
	TF (slm)	σ_{TF} (slm)	σ_{TF}/TF	$(\sigma_{TF}/TF)^2$	Units
Out	765	2	0.0026144	0.0000068	NA
In	15.5	0.1	0.0064516	0.0000416	NA
			DF = **49.35483871**		dimensionless
			Sum of $(\sigma_{TF}/TF)^2$ = 0.0000485		dimensionless
			Relative Error = **0.7%**		dimensionless

Step 3 For Method 1: Determine the Relative Error of the TFE
*The TFE error must meet the +/- 5% performance standard

Data			Calculations: λ, DRE, and True Fraction Emitted		
	Value	σ	σ/Best Estimate	$(\sigma$/Best Estimate$)^2$	Units
C_O	200	2	0.0100000	0.0001	NA
C_I	12,134	195	0.0160705	0.000258262	NA
DF	49.4	2	0.0405229	0.001642103	NA
			λ_C =	0.0167450	dimensionless
			σ_λ =	0.0001033	dimensionless
			λ * DF =	0.8264455	dimensionless
			1 - (λ * DF) =	0.1735545	dimensionless
			Sum of $(\sigma_{CO}/C_O)^2$ and $(\sigma_{CI}/C_I)^2$ =	0.0003583	dimensionless
			σ_λ/λ_C =	0.0061710	dimensionless
			$(\sigma_\lambda/\lambda_C)^2$ =	0.0000381	dimensionless
			Sum of $(\sigma_\lambda/\lambda_C)^2$ and $(\sigma_{DF}/DF)^2$ =	0.0016802	dimensionless
			Relative Error λ =	1.9%	dimensionless
			DRE, % =	19%	dimensionless
			Relative Error DRE =	20%	dimensionless
			Relative Error of TFE =	**4%**	dimensionless

Step 3 For Method 2: Determine the Relative Error of the TFE
*The TFE error must meet the +/- 5% performance standard

Data			Calculations: λ, DRE, and True Fraction Emitted			
	Best Est. V (slm)	σ_V (slm)	σ_V/V		$(\sigma_V/V)^2$	Units
Out	0.425	0.005	0.0110448		0.00012198847956824	NA
In	0.443	0.006	0.0127318		0.0001620981711280	NA
			λ_V	=	0.958843303	dimensionless
			σ_λ	=	0.016194732	dimensionless
			$1 - \lambda_V$	=	0.041156697	dimensionless
			Sum of $(\sigma_V/V)^2$	=	0.0002841	dimensionless
			Relative Error λ	=	1.7%	dimensionless
			DRE, %	=	4%	dimensionless
			Relative Error DRE	=	2%	dimensionless
			Relative Error TFE	=	**2%**	dimensionless