TECHNICAL SUPPORT DOCUMENT FOR EMISSIONS FROM PRODUCTION OF FLUORINATED GASES:

FINAL RULE FOR MANDATORY REPORTING OF GREENHOUSE GASES

Office of Air and Radiation
U.S. Environmental Protection Agency

November 5, 2010

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1. Source Description

A. Facilities Subject to the Rule

This source category, fluorinated gas production, covers emissions of fluorinated greenhouse gases (GHGs) that occur during the production of fluorinated gases. It also covers emissions of fluorinated GHGs that occur during transformation of fluorinated gases, destruction of fluorinated GHGs, and venting of residual fluorinated GHGs from returned containers when those processes are co-located with fluorinated gas production processes. Fluorinated GHGs include hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), sulfur hexafluoride (SF_6), nitrogen trifluoride (NF_3), and other fluorinated GHGs such as fluorinated ethers. Fluorinated gases include fluorinated GHGs, chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs). However, the source category excludes generation and emissions of HFC-23 during the production of HCFC-22, which is covered by subpart O of part 98 of the Mandatory Reporting Rule.

Producing a fluorinated gas includes the manufacture of a fluorinated GHG, CFC, or HCFC from any raw material or feedstock chemical. This includes the manufacture of fluorinated gases for use in a process that will result in their transformation either at or outside of the production facility, including manufacture of a CFC or HCFC as an isolated intermediate for use in a process that will result in the transformation of the CFC or HCFC either at or outside of the production facility. Producing a fluorinated gas does not include the reuse or recycling of a fluorinated gas, the creation of HFC-23 during the production of HCFC-22, the creation of intermediates that are created and transformed in a single process with no storage of the intermediates, or the creation of fluorinated GHGs that are released or destroyed at the production facility.

B. How Fluorinated GHGs are Generated and Released at Fluorinated Gas Production Facilities

Fluorinated GHGs can be generated and emitted from production, transformation, destruction, and other processes at production facilities in a number of ways. Emissions from fluorinated gas production include fluorinated GHG products that are emitted upstream of the production measurement and fluorinated GHG by-products that are generated and emitted either without or despite recapture or destruction. Emissions from fluorinated gas transformation include emissions of fluorinated GHG feedstocks and possibly by-products of the transformation process. Emissions from fluorinated GHG destruction include fluorinated GHGs that survive the destruction process (or that are created as products-of-incomplete-combustion (PICs) from destruction). Other emissions sources are discussed further below.

Many reactions producing fluorinated GHGs, CFCs, and HCFCs also generate significant quantities of chemically related by-products, e.g., through over-fluorination or side reactions. Table 1 provides an overview of some commonly produced fluorinated GHGs, CFCs, and HCFCs and their known fluorinated GHG by-products. Note that production of CFCs and HCFCs can generate and emit fluorinated GHGs such as various HFCs and some PFCs. These fluorinated GHG by-products occur due to the chemical similarities between HFCs, PFCs, HCFCs, and CFCs and the common use of halogen replacement chemistry to produce them. Also note that Table 1 is not exhaustive. It omits the most commonly known product and byproduct, HCFC-22 and HFC-23, which are covered by subpart O of the Mandatory Reporting

Rule. In addition, it does not include all of the by-products and products that have been identified by fluorinated gas producers.

Table 1. Some Fluorinated Products and their By-products

Product	By-product(s)	Source of information
HFC-134a	HFC-143a	Italy National Inventory Report, 2009
SF_6	CF_4	Italy National Inventory Report, 2009
Electrochemical fluorination plant that produces a broad range of fluorochemical products, mainly for electronics industry	SF_6, CF_4, C_2F_6, C_3F_8, C_4F_{10}, C_5F_{12}, C_6F_{14}, CF_3SF_5, C_7F_{16}, C_8F_{18} and $C_8F_{16}O$	Belgium National Inventory Report, 2009 http://unfccc.int/files/national_reports/annex_i_ghg_inventories/national_inventories_submissions/application/zip/bel_2009_nir_15apr.zip
CFC-11, CFC-12	CF_4	2006 IPCC Guidelines
CFC-115	C_2F_6	Italy National Inventory Report, 2009 http://unfccc.int/files/national_reports/annex_i_ghg_inventories/national_inventories_submissions/application/zip/ita_2009_nir_15apr.zip
Trifluoroacetic acid (TFA)	CF_4, HFC-125	French National Inventory Report, 2009 http://unfccc.int/files/national_reports/annex_i_ghg_inventories/national_inventories_submissions/application/zip/fra_2009_nir_7apr.zip

The quantities of by-products generated, as a share of the product, depend on the product and the process. Based on conversations with fluorinated gas producers, by-product generation rates generally range between one and five percent but can sometimes be higher or lower.

Emissions of products, by-products, and feedstocks may occur from process vents, from equipment leaks from flanges, connectors, and other equipment pieces in the production line, from storage tanks storing either raw materials or products, from wastewater streams, from control devices (e.g., thermal oxidizers), and during the filling of tanker trucks, railcars, cylinders, or other containers that are distributed by the producer. Undesired by-products may be deliberately vented, and some product (or reactant) may be vented at the same time due to imperfect separation of by-products, products, and reactants. Emissions can also occur during scheduled maintenance and occasional service work on production equipment, during the blending and recycling of fluorinated GHGs, and during the evacuation of residual fluorinated GHGs from containers used to distribute products. EPA estimates that total emissions from this source category were approximately 10.6 million metric tons CO_2e (mt CO_2e) in 2006.[1,2]

C. Background on Uses of Fluorinated Gases

Fluorinated gases are man-made gases used in several sectors. As noted above, they include fluorinated GHGs (HFCs, PFCs, SF_6, NF_3, and a number of fluorinated ethers), CFCs, and HCFCs, all of which are manufactured through various chemical processes.

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[1] Fluorinated GHG production data were from 2006; CFC and HCFC production data were from 2008.

[2] Memorandum from Schaffner, K. and Hancy, C., RTI International, to Ottinger, D., EPA/OAR/CCD. Threshold Analysis for Emissions, Promulgation of 40 CFR Part 98, subpart L, Fluorinated Greenhouse Gas Production. November 4, 2010.

Hydrofluorocarbons (HFCs) are the most commonly used fluorinated GHGs, used primarily to replace ozone-depleting substances in a number of applications, including air-conditioning and refrigeration, foams, solvents, and aerosols. PFCs are used in fire fighting and to manufacture semiconductors and other electronics. SF_6 is used in a diverse array of applications, including electrical transmission and distribution equipment (as an electrical insulator and arc quencher) and in magnesium casting operations (as a cover gas to prevent oxidation of molten metal). Nitrogen trifluoride (NF_3) is increasingly used in the semiconductor industry, to reduce overall semiconductor GHG emissions through processes such as NF_3 remote cleaning and NF_3 substitution during in-situ cleaning. Fluorinated ethers (HFEs and HCFEs) are used as anesthetics (e.g., isofluorane, desflurane, and sevoflurane) and as heat transfer fluids (e.g., the H-Galdens). The manufacture of CFCs and HCFCs for emissive uses is being phased out under the Montreal Protocol, but production of these materials for use as feedstocks is permitted to continue indefinitely. As discussed further below, the volume of CFCs and HCFCs used as feedstocks in the U.S. is significant; even excepting HCFC-22, this volume is actually larger than the volume of fluorinated GHGs produced in the U.S. Fluorinated GHGs are powerful greenhouse gases whose ability to trap heat in the atmosphere is often thousands to tens of thousands of times greater than that of CO_2, on a pound-for-pound basis. Some fluorinated GHGs are also very long lived; SF_6 and the PFCs have lifetimes ranging from 3,200 to 50,000 years.[3]

D. Potential Overlap Emission Points for Production and Suppliers.

The facilities that are covered under the fluorinated gas production source category are many of the same facilities that are covered under the industrial gas supply source category. In general, the industrial gas supply source category is intended to cover or capture the quantities of fluorinated GHGs that are entering and leaving the U.S. supply of industrial gases, (i.e., amount of product), while the fluorinated gas production source category is intended to cover or capture the quantities of fluorinated GHGs emitted at fluorinated gas production facilities. Specifically, the industrial gas suppliers source category is meant to track the quantities of fluorinated GHGs that are (1) produced, (2) transformed, (3) destroyed, (4) imported, and (5) exported. The industrial gas suppliers source category would essentially track the amount of final product made (produced) at a production facility but not the emissions of fluorinated GHG from the production steps from raw material to final product.

There are several areas of potential overlap between the emissions that are reported under the industrial gas suppliers source category and those that could be reported under the fluorinated gas production source category. The areas of overlap concern “downstream” emissions, meaning they occur at the fluorinated GHG production facility after the fluorinated GHG product measurement. Downstream emissions include those from container filling (if this occurs after the production measurement), fluorinated GHG transformation processes, destruction of fluorinated GHGs that are removed from the U.S. supply, recycling or reclamation of fluorinated GHGs, and evacuation of fluorinated GHG heels from returned cylinders or containers. (“Upstream” emissions occur at the fluorinated GHG production facility prior to the fluorinated GHG product measurement.)

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[3] IPCC, 2006.

Fluorinated gas production facilities sometimes make a fluorinated GHG product that is later used as a raw material in making another product. For example, fluorinated GHG product is used as a raw material in transformation processes to produce fluoropolymers (the fluoropolymer product would not be considered a fluorinated GHG). Emissions of fluorinated GHGs that occur from transformation processes are an area of potential overlap, since the quantities produced for transformation may be reported under the industrial gas suppliers source category. Transformation processes may occur at the same site where fluorinated GHG products are produced, or they may occur at another fluorinated GHG production facility to which the fluorinated GHG feedstock is shipped.

The emissions of fluorinated GHG from destruction processes used to remove fluorinated GHG from the U.S. supply is another area of overlap. The fluorinated GHG is returned to the facility and subtracted from the U.S. supply, however some emissions may occur from the destruction process, either as fugitives from the handling of the fluorinated GHG or as undestroyed emissions at the outlet of the destruction device.

Filling cylinders or other containers (loading emissions) with fluorinated GHG product and blending of fluorinated GHG with other gases will most likely occur after the production measurement, classifying emissions for cylinder filling (loading) and blending as downstream processes.

Recycling of used gas may be performed by the producers of new gas or by offsite recycling firms. Emissions may occur during handling and purification of old gas and during packaging of recycled gas.[4] Since the used gas has already been counted as produced (used gas is removed from, and then added back into, the gas supply), recycling emissions are considered to be downstream of the production measurement.

Evacuation of fluorinated GHG from returned cylinders or containers results in emissions that vary depending on process type and the composition and amount of the heel (residual gas) present.

In theory, it might be possible to track emissions from transformation and destruction simply using quantities reported under 40 CFR part 98 subpart OO. However, this would require that (1) fluorinated GHGs that are produced only to be transformed or destroyed be tracked separately, (2) production, transformation, and destruction be measured to very good precision and accuracy (e.g., 0.2 percent), and (3) that no by-products be formed or emitted during these processes. If all of these conditions were met, emissions could be equated to the differences between production and transformation and production and destruction. In practice, however, it would be difficult to meet all of these conditions.

E. Total U.S. Production and Associated Emissions

The production of fluorinated gases includes production of fluorinated GHG (HFCs, PFCs, SF_6, and NF_3, HFEs), CFCs and HCFCs (except for HCFC-22 production processes). In 2006 (some data are from 2003 and 2007), 12 U.S. facilities collectively produced over 350 million $mtCO_2e$ (170,000 tons) of HFCs, PFCs, SF_6, and NF_3. EPA estimates that an additional

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[4] 2006 IPCC, Chapter 3.10.

six facilities collectively produced 1 million $mtCO_2e$ of fluorinated anesthetics (HFEs) in 2005. The total U.S. production of CFCs and HCFCs (except HCFC-22) in 2008 was estimated to be approximately 266,000 tons. The majority of the CFC and HCFC production processes are co-located at facilities that also produce fluorinated GHGs. Another 2 facilities that produce CFC and HCFC products were identified that were not already included in the 12 facilities identified above for HFC, PFC, SF_6, and NF_3 production. Fluorinated gas production processes are sometimes co-located with fluorinated gas transformation processes or fluorinated GHG destruction processes. The total amounts of fluorinated gases transformed into other products or destroyed are not known.

Fluorinated GHG emissions (actual emissions, following application of control techniques where applicable) from U.S. facilities producing fluorinated GHGs are estimated to range from 0.8 percent to 2 percent of the amount produced, depending on the facility. An emission rate of 1.5 percent is assumed for fluorinated GHG production processes. At an emission rate of 1.5 percent, the 12 fluorinated GHG facilities together are estimated to have emitted approximately 5.3 million $mtCO_2e$ of HFCs, PFCs, SF_6, and NF_3. The six additional HFE production facilities are estimated to have emitted approximately 17,000 $mtCO_2e$ of fluorinated anesthetics, using an emission rate of 1.5 percent.

The quantity of emissions of fluorinated GHGs from production of CFCs and HCFCs is uncertain. However, the magnitude of by-product generation during F-GHG production (e.g., quantities equivalent to one to five percent of the mass of the product) suggests that significant quantities of by-product F-GHGs may be generated during production of chemically similar substances. Given the substantial amounts of CFCs and HCFCs that are produced in the U.S., emission rates could be relatively low and still result in significant emissions. In 2008, the combined tonnage of U.S. HCFC and CFC production was higher than that of all fluorinated GHG production in 2006 (the latest year for which data were available), with CFCs produced as feedstocks comprising the majority. (Although production of HCFCs and CFCs is limited under the regulations implementing Title VI of the CAA, production of these substances for use as feedstocks is permitted to continue indefinitely.) Assuming that this production resulted in emissions of fluorinated GHG by-products equal to one percent of the mass of CFCs and HCFCs produced,[5] and that these byproducts had an average global warming potential (GWP) of 2000, emissions from CFC and HCFC production are estimated to have totaled 5.3 million $mtCO_2e$ in 2008, the same as estimated emissions from fluorinated GHG production in 2006. (No estimate of fluorinated GHG emissions from transformation processes, or fluoropolymer production processes, is available.) These emissions, combined with those from fluorinated GHG production, lead to a total for the source category of 10.6 million $mtCO_2e$.

2. Options for Reporting Threshold

EPA evaluated a range of threshold options for fluorinated gas production facilities. These included 1,000 mt CO_2e, 10,000 $mtCO_2e$, 25,000 $mtCO_2e$, and 100,000 $mtCO_2e$. Emission levels on both an uncontrolled and a controlled basis were evaluated. Because EPA

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[5] The emission rate from CFC and HCFC production is assumed to be lower than that from fluorinated GHG production because only by-products are included in the former, while both products and by-products are included in the latter.

has little information on combustion-related emissions at fluorinated gas production facilities, these emissions were not included in the threshold analysis.

A. Uncontrolled Emissions Threshold

Facility-specific uncontrolled emissions (i.e., pre-control) were estimated for fluorinated GHG production processes (including fluorinated anesthetics production processes) by multiplying a factor of 3.0 percent by the estimated production at each facility. For CFC and HCFC production processes (except for HCFC-22 production processes), uncontrolled emissions were estimated by multiplying a factor of 2 percent by the estimated production at each facility. Uncontrolled emissions are strongly influenced by by-product generation rates, which are known to vary between zero and several percent for fluorinated gas production processes; thus, these estimates are uncertain. The results of the analysis for uncontrolled emissions from the production of HFCs, PFCs, SF_6, NF_3, CFCs, and HCFCs are shown in Table 2. (No emissions of fluorinated GHG from transformation processes, such as fluoropolymer production processes, are included in the analysis.)

All or most production facilities would be covered by uncontrolled emission thresholds, i.e., 14 of 14 or 13 of 14 facilities would be covered depending on the cutoff level. Use of the uncontrolled emissions threshold would not allow for applying reductions from destruction devices, which may or may not be achieving the demonstrated destruction efficiency on a continuous operating basis. Under the uncontrolled emissions threshold option, emissions reductions would not be overstated and emissions to the atmosphere would not be understated. (It is uncertain where the emission levels of the individual anesthetic facilities would fall, and the anesthetic facilities and emissions are not included in Table 2. There are 6 anesthetic facilities that are estimated to generate a total of approximately 30,000 mt CO_2e of emissions, by multiplying a factor of 3.0 percent by the estimated production.) Emissions from combustion sources at facilities are not included in the emissions estimate shown in Table 2.

Table 2. Threshold Analysis for Fluorinated GHG Emissions from Production of HFCs, PFCs, SF6, NF3, CFCs, and HCFCs (Uncontrolled Emissions)

Threshold Level (mt CO_2e/r)	Total National Emissions (mt CO_2e)	Number of Facilities	Emissions Covered		Facilities Covered	
			mt CO_2e	Percent	Number	Percent
1,000	10,600,000	14	10,600,000	100%	14	100%
10,000	10,600,000	14	10,600,000	100%	14	100%
25,000	10,600,000	14	10,600,000	100%	14	100%
100,000	10,600,000	14	10,600,000	100%	13	93%

B. Controlled Emissions Threshold

Facility-specific controlled emissions (i.e., those following the control device, if in place) were estimated for fluorinated GHG production processes (including anesthetics production processes) by multiplying a factor of 1.5 percent by the estimated production at each facility. For CFC and HCFC production processes (except for HCFC-22 production processes), controlled emissions were estimated by multiplying by a factor of 1.0 percent by the estimated production at each facility. Controlled emissions were assumed to be half of uncontrolled emissions at each facility. The results of the analysis for controlled emissions from the production of HFCs, PFCs, SF_6, NF_3, CFCs, and HCFCs are shown in Table 3. No emissions of fluorinated GHG from transformation processes (other than those that produce fluorinated GHGs) are included in the analysis.

All or most of the production facilities would be covered by controlled emission thresholds, depending on the cutoff, although fewer facilities would be covered under the controlled emission threshold option (10 facilities) than under the uncontrolled emission threshold option (13 facilities) at the highest cutoff (i.e., 100,000 mtCO_2e). Use of the controlled emissions threshold option would allow facilities to account for emission reductions achieved by destruction devices that had a demonstrated destruction efficiency. It is possible that emission levels may be understated using the controlled emissions option. (It is uncertain where the emission levels of the individual anesthetic facilities would fall, and the anesthetic facilities and emissions are not included in Table 3. There are 6 anesthetic facilities that are estimated to emit a total of approximately 15,000 mt CO_2e of emissions, by multiplying a factor of 1.5 percent by the estimated production.) Emissions from combustion sources at facilities are not included in the emissions estimate shown in Table 3.

Table 3. Threshold Analysis for Fluorinated GHG Emissions from Production of HFCs, PFCs, SF6, NF3, CFCs, and HCFCs (Controlled Emissions)

Threshold Level (mt CO_2e/r)	Total National Emissions (mt CO_2e)	Number of Facilities	Emissions Covered		Facilities Covered	
			mt CO_2e	Percent	Number	Percent
1,000	10,600,000	14	10,600,000	100%	14	100%
10,000	10,600,000	14	10,600,000	100%	14	100%
25,000	10,600,000	14	10,600,000	100%	14	100%
100,000	10,600,000	14	10,300,000	97%	10	71%

C. No Emissions Threshold (i.e., All-in)

Under an "all-in" approach, no emissions threshold level would be included in the rule and all facilities in the fluorinated gas source category, including facilities producing anesthetics, would be subject to the rule regardless of emission levels. The all-in approach would ensure that all facilities identified and quantified their fluorinated GHG emissions, even if they initially believed those emissions to be small. Some facilities that initially believed their emissions to be small could find that those emissions actually exceeded 25,000 mt CO_2e (e.g., because a previously unidentified fluorinated GHG with a high GWP was being generated and emitted as a by-product). Facilities whose emissions remained below 25,000 mt CO_2e or 15,000 mt CO_2e could cease reporting after five or three years respectively. In addition, an all-in approach would provide an essentially level playing field because all facilities in the source category would be subject to the rule and be subject to the same economic impact from the reporting rule. However, an all-in approach would also increase the burden on facilities with uncontrolled emissions below 25,000 mt CO_2e. This could result in higher reporting costs per metric ton CO_2e for these facilities than for higher emitting facilities.

3. Monitoring Methods, Data Collection and Current Plant Practices

A. Scoping Speciation and Options for Characterizing Emitted Streams

i. Reliance on previous bench- and pilot-scale testing

During research and development of a fluorinated gas product, companies develop laboratory, bench-scale, and pilot-scale processes to manufacture new products. During laboratory and bench-scale development of the process, companies generate small quantities of the product. The companies monitor and measure all aspects of the process, including rates and extent of reaction, reactant and full product and byproduct identity and compositions, and physical characteristics of the compounds. This testing and analysis of compounds in the various process streams generally identifies the product and all byproducts generated in the process. During these laboratory or bench-scale processes, process optimization is addressed by defining operating conditions that generate the best product yields and least byproducts, considering the most efficient use of resources. Following the laboratory and bench-scale level of process development, a process may be scaled to a larger basis, i.e., pilot-scale basis, to continue research and development of the process and to continue to refine process optimization. The pilot-scale process, meant to simulate a full-scale production process, generates a larger quantity of product than the laboratory scale process but less than a full-scale production process. The equipment used in pilot-scale processes is similar in design to what the full-scale process might be, and is used to continue research on the process, as the data available from earlier laboratory and bench-scale systems are applied. However, some data may not be directly applicable to the pilot-scale system. As part of the continued research, the company continues to test and analyze the products and byproducts from the pilot-scale process to confirm what compounds are generated in the process as operating conditions are refined (i.e., changed).

The findings regarding the identities of the compounds generated during these stages of process research and development may be used to help understand the identities of the compounds present in emission and waste streams for the full-scale production process. The analyses are typically rigorous as the company is eager to know and learn as much as possible and limit side reactions and increase yields. A potential drawback to use of the laboratory and pilot scale compound and composition analyses is that there may be some differences in the products and byproducts as the process is scaled from laboratory/bench-scale to pilot-scale to full-scale production units. The earlier data may not be fully applicable to the larger scale processes. Differences are likely to occur between the laboratory and pilot-scales, and streams may need to be tested and analyzed again to detect changes between the pilot- and full-scale production processes.

ii. Initial Scoping Speciation

To ensure that all fluorinated GHGs that occur in emitted streams are accurately identified, an initial scoping speciation or test on vents and streams from fluorinated gas processes may be conducted. The initial scoping speciation would be conducted using methods that allow detection and identification of all compounds in the vent or stream. The identity of the specific compounds that are generated during the fluorinated gas production process is important to the emissions estimate. Some facilities have indicated that even with extensive laboratory and bench-scale compositional and quantitative analysis from research, development, and design stages of the process, unexpected F GHGs can be found in emissions streams.[6] In some cases,

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[6] Based on conversations with Fluorinated GHG producers, as referenced in section 7.

this may have occurred because the analytical methods used at the pilot- or laboratory-scale were not sensitive enough to detect fluorinated GHGs that occurred at low (but still higher than trace) concentrations; in other cases, it may have occurred because subtle differences between the laboratory- and full-scale processes led to the generation of new or different by-products.

The results of the scoping speciation can be used to inform both the mass-balance and emission-factor approaches (described further below). In the mass balance approach, a total fluorine balance is conducted to account for all fluorine into the process (i.e., in the form of fluorine-containing reactants) and all fluorine out of the process (i.e., in the form of the fluorine-containing product, and destroyed or recaptured fluorine-containing by-products, unconsumed reactants, or products). The difference, in terms of fluorine, is assumed to be emitted. The facility would determine what fraction of the total fluorine is emitted as the fluorine-containing reactant, by-products, or product by conducting emission characterizations for process vents by measurement to speciate the total fluorine. Because byproducts are created, knowledge of these informs the emissions estimate so that the byproduct compounds are appropriately represented in the emissions. For example, for facilities using the mass-balance approach, the scoping speciation can be used to determine whether some emissions are correctly assumed to occur in the form of the reactant, product, or by-products. For those facilities using an emissions factor approach, the results from the scoping speciation will ensure that emissions factors are appropriately developed for all byproduct compounds. The scoping speciation will identify byproducts that should be measured in subsequent emissions testing to develop emission factors. Note that some facilities may find it most convenient to conduct the initial scoping speciation, the emission measurements for mass balance emission characterization, and/or the emission testing for emission factor development at the same time).

Accurately identifying the compounds emitted provides for a better fluorinated GHG emissions estimate and also a better CO_2e emissions estimate because the appropriate GWPs are applied to the emitted compounds. If there is a difference between the GWPs of a product and a byproduct and if the emissions are assumed to consist exclusively of the product, the CO_2e emissions could be overestimated or underestimated. Underestimation is a particular concern where the process unexpectedly generates a fluorinated GHG that is difficult to destroy (e.g., CF_4). In this case, applying the destruction efficiency (DE) of the destruction device to the emissions may overestimate destruction and underestimate emissions.

Facilities would conduct an initial scoping speciation on each fluorinated gas process at the facility that has at least one process vent over a threshold level.EPA evaluated emissions cutoffs on a process vent basis to be consistent with other approaches where emission cutoffs are also on a process vent basis. Only those processes with at least one process vent with fluorinated GHG emissions above a cutoff level would conduct the initial scoping speciation. We considered a limit based on CO_2e on an uncontrolled basis for each process vent, and note that a cutoff based on fluorinated GHG, rather than CO_2e, emissions may be appropriate because the identity and the GWP of some fluorinated GHG compounds may not be known. The fluorinated GHG emissions cutoff for process vents would be 1 metric ton fluorinated GHG. The estimate of emissions from each process vent could be determined using standard engineering calculations, previous measurements, and engineering assessments (i.e., similar to preliminary emission estimates discussed under process-vent-specific emissions calculation factors below). Because the specific fluorinated GHG byproducts may not be known, it may be appropriate to apply the 1-metric-ton-fluorinated-GHG-emission cutoff to uncontrolled emissions. As noted above, the application of the destruction device's DE may underestimate emissions (and therefore fail to trigger testing) if difficult-to-destroy fluorinated GHGs occur unexpectedly in the stream.

A facility would not have to measure every stream or process vent to complete the initial scoping speciation. For each process with fluorinated GHG emissions above the cutoff level for process vents, facilities could select which process vents or streams to measure, focusing on those streams that are most likely to contain all of the fluorinated GHG (e.g., byproducts) anticipated to be generated or emitted. It is preferable that these fluorinated GHGs be at their maximum concentrations, although streams with smaller concentrations of byproducts may be tested if the scope and sensitivity of the analytical method allow detection of the compounds at lower concentration levels .

Sampling and analytical methods capable of detecting and speciating fluorinated GHG compounds and capable of identifying multiple compounds simultaneously would be the best choices for the initial scoping speciation. For example, methods that use gas chromatography with mass spectrometry (GC/MS) are capable of detecting and identifying multiple fluorinated GHG compounds. Another example of an appropriate sampling and analytical method includes Fourier transform infrared (FTIR) analysis. There are several EPA reference methods and other consensus vetted methods that may be used to sample and analyze fluorinated GHG; these methods include EPA Method 18 - Measurement of Gaseous Organic Compound Emissions by Gas Chromatography (GC/ECD, GC/MS), EPA Test Method 320 Measurement of Vapor Phase Organic and Inorganic Emissions by Extractive Fourier Transform Infrared (FTIR) Spectroscopy, and ASTM D6348-03 (FTIR) Standard Test Method for Determination of Gaseous Compounds by Extractive Direct Interface Fourier Transform Infrared (FTIR) Spectroscopy. Each of these is briefly described below in the section on Process-Vent-Specific Emission Factor Approach. If speciation measurements are conducted at the stack, the facility would also conduct an EPA Method 1 series (Sample and Velocity Traverses for Stationary Sources), Method 2 series (Determination of Stack Gas Velocity and Volumetric Flow Rate), Method 3 series (Gas Analysis for Carbon Dioxide, Oxygen, Excess Air, and Dry Molecular Weight), and Method 4 (Determination of Moisture Content in Stack Gases). If a facility is not able to conduct EPA Method 2, alternative flow rate methods could be used, such as OTM 24 (Tracer Gas Protocol For the Determination of Volumetric Flow Rate Through the Ring Pipe of the Xact Multi-Metals Monitoring System), or ALT-012 (Emission Measurement Center Approved Alternative Method). Other validated methods that are capable of detecting the analyte of interest at the concentration of interest could also be used.

B. Options for Developing Emissions Estimates

i. Default Emission Factor

One option that was considered for characterizing fluorinated GHG is the use of default emission factors. These factors would provide a rough estimate of the quantity of fluorinated GHGs emitted. Although the default emission factor approach is simple and easily-implemented, it is also highly imprecise; emissions of fluorinated GHG products in U.S. plants are estimated to vary from 0.8 percent to 2 percent of production, more than a factor of two (RTI, 2008).[7] Thus, applying a default factor (1.5 percent, for example) is likely to significantly overestimate emissions at some plants while significantly underestimating them at others.

Under a somewhat more rigorous default emission factor approach, emission factors would be developed for similar types of emission points at multiple facilities within a source category. The emission factors for each type of emission point would be averaged to develop an industry-wide emission factor for that type of emission point. Because these EFs would represent average values over multiple facilities, some facilities would be above the EF and some would be below. As a result, such factors may not provide an accurate emissions determination for a single facility. Default EFs would not account for inter-facility variability that can occur due to the age of facility and equipment, equipment sizes, equipment design, differences in raw materials and suppliers, different typical operating parameters, and variations in the process operation that may not be readily apparent or known. In addition, default EFs would not provide information that EPA may need to compare the best and worst performers, or provide insights into which facilities have the most or fewest opportunities to obtain additional reductions.

ii. Mass Balance

In the total fluorine mass-balance approach, emissions are determined in terms of total fluorine[8] rather than the fluorinated GHG product. Facilities determine the total fluorine emitted from the process by determining the total fluorine fed to the process, subtracting the total fluorine in the product resulting from the process, and subtracting the total fluorine that is destroyed or recaptured. Facilities would weigh or meter the reactants fed into the process, the product resulting from the process, and any streams that are destroyed and recaptured that contain reactants, byproducts, and product. Destroyed streams include those sent to the thermal oxidizer or other equipment, and recaptured streams may be sold, sent to another facility for destruction, or held for another purpose.[9] Facilities calculate the total fluorine emitted as the difference in the total fluorine mass fed into the process, the total fluorine mass of the main product, and the total fluorine mass that is destroyed or recaptured.[10] As discussed further below, it is EPA's understanding that some facilities perform similar types of measurements and calculations to monitor their processes and yields.

The difference is then assigned to loss of reactants, loss of product, and/or loss of byproducts. Facilities could assume that all the fluorine is emitted in the form of the fluorinated GHG that has the most significant GWP, or facilities could determine from measurements the

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[7] The emission rates cited were estimated for HCFC-22, which is an ozone-depleting substance and therefore excluded from the proposed rule. However, the production processes for many fluorinated GHGs are similar to those for HCFC-22 (2006 IPCC Guidelines, Volume 3, section 3.10.2.1), and therefore their emission rates are likely to be similar as well.

[8] Facilities could use another element as long as it occurred in all of the fluorinated GHGs fed into or generated by the process.

[9] Note that if these recaptured materials are fed back into the process, they must be counted at that time as fluorine additions to the process.

[10] The fluorine itself, of course, is not destroyed, but any fluorinated GHGs containing the fluorine are (to the destruction efficiency of the device). In the equations below, non-GHG fluorine-containing compounds that are removed from the process are treated as completely destroyed, since none of the fluorine in them is emitted as a fluorinated GHG. Fluorinated GHGs are assumed to be destroyed to the DE of the device for each fluorinated GHG.

fractions of the total fluorine emissions that consist of reactants, product, and byproducts. There may be only one reactant that contains fluorine, or if there are several reactants, the fluorine would be summed for the reactants. There may be processes with one by-product, or cases with several by-products, where the fluorine would be summed for all the by-products. There is likely one product.

Because the mass-balance approach relies on the calculation of relatively small differences between relatively large numbers, measurements must have good precision to avoid large uncertainties in the emissions estimates. EPA evaluated methods to estimate and limit the error associated with the mass balance approach.

1. Error Limits

Precision and Accuracy Requirements for Individual Measurements

One approach to limiting the error associated with emissions estimates developed using the mass-balance approach is to establish specific precision and accuracy requirements for each measurement used in the mass-balance equation. These measurements include mass measurements for reactants, products, and fluorinated GHG by-products, including feed streams, final product streams, emitted streams, and destroyed or recaptured streams. In addition, they include concentration measurements where products or by-products occur in streams with other substances. To limit the uncertainty of the emission estimate to ± 30 percent of the estimate, devices used to measure masses (e.g., flowmeters and scales) would need to be able to achieve precisions and accuracies near ± 0.2 percent or better, at least for streams with a large impact on the mass-balance calculation. Concentration measurements would need to be conducted with precisions and accuracies of ± 10 percent or better. This approach limits error and is straightforward to implement and enforce. However, it may require substantial expenditures to obtain accurate and precise measurements of quantities whose errors have little impact on the overall error of the emissions estimate. For example, under this approach, facilities might be required to upgrade flowmeters in streams that affect the emission estimate (and its uncertainty) only slightly. The approach also limits flexibility. Even a facility with a relatively large error in one stream may be able to bring the total error of its emissions estimate to a tolerable level by improving the accuracy and precision of other measurements that are used in the mass-balance equation, such as the mass flows of reactants and products. Thus, while this approach may be appropriate as an additional option for ensuring that emissions estimates are accurate and precise, it is probably not appropriate as the sole option. (See section 6 below for more discussion of this alternative approach.)

Error Limit for the Emission Estimate as a Whole.

Another approach to limiting the error of the mass-balance approach is to establish a limit on the error of the overall emission estimate. To estimate the statistical error associated with use of the mass-balance approach, facilities would be required to use error propagation, considering the accuracy and precision of their measurements and the calculation methods of the mass-balance approach. Under this approach, EPA would not specify precision and accuracy requirements for individual mass or concentration measurements. Instead, EPA would require that the error associated with the overall estimate of fluorinated GHG emissions fall under a specific limit. This limit could be expressed in terms of a fraction of the emissions estimate (relative error) or as a specific quantity (absolute error). Facilities could achieve this level of precision and accuracy however they chose.

A maximum relative error of ± 30 percent would be comparable to that cited by a facility that has used an emission factor approach to estimate its fluorinated GHG emissions. It is also comparable to the error that EPA calculates for a facility with an emission rate of two percent and with good precisions and accuracies for its mass flow measurements (± 0.2 percent) and for its concentration measurement (± 10 percent) of a waste stream constituting five percent of the process's fluorinated GHG output flow. For facilities whose emissions constitute a very small share of their inputs and outputs (e.g., one percent or less), a relative error of ± 30 percent would be very difficult to achieve using a mass-balance approach. At the same time, the absolute error of such a facility's estimate may be smaller than the absolute error of a facility that meets the relative error test but that has a higher emission rate. It may therefore be appropriate to establish a maximum permissible absolute error of 3,000 $mtCO_2e$ for facilities whose estimates have relative errors greater than 30 percent. This absolute error is equivalent to 30 percent of the 10,000 $mtCO_2e$ threshold that is used elsewhere in the subpart to establish requirements for different sources (e.g., process vents). Under this approach, processes whose emissions were lower than 10,000 $mtCO_2e$ could have relative errors higher than 30 percent so long as they met the limit on absolute error. This approach would avoid penalizing processes and facilities with low emissions.

The absolute and relative errors associated with using the mass balance approach on a process may be estimated using Equations L-1, L-2, L-3, and L-4 in conjunction with either Equations L-7 through L-10 or Equation L-17. Alternatively, facilities may estimated these errors based on the variability of previous process measurements (e.g., the variability of measurements of stream concentrations), provided these measurements are representative of the current process and current measurement devices and techniques. Once errors have been calculated for the quantities in these equations, those errors would be used to calculate the errors in Equation L-6 and L-5. Where the measured quantity is a mass, the error in the mass would be equated to the accuracy or precision (whichever is larger) of the flowmeter, scale, or combination of volumetric and density measurements at the flowrate or mass measured. Where the measured quantity is a concentration, the error of the concentration would be equated to the accuracy or precision (whichever is larger) with which the concentration measurements estimate the mean concentration of that stream component, accounting for the variability of the process, the frequency of the measurements, and the accuracy or precision (whichever is larger) of the analytical technique used to measure the concentration at the concentration measured. If the variability of process measurements is used to estimate the error, this variability would be assumed to account both for the variability of the process and the precision of the analytical technique. Facilities may use standard statistical techniques such as the student's t distribution to estimate the error of the concentration measurements as a function of process variability and frequency of measurement.

Equation L-1 provides the general formula for calculating the absolute errors of sums and differences where the sum, S, is the summation of variables measured, a, b, c, etc. (e.g., $S = a + b + c$):

$$e_{SA} = \left[(a * e_a)^2 + (b * e_b)^2 + (c * e_c)^2 \right]^{1/2} \qquad \text{(Eq. L-1)}$$

Where:

e_{SA} = absolute error of the sum, expressed as one half of a 95 percent confidence interval.
e_a = relative error of a, expressed as one half of a 95 percent confidence interval.
e_b = relative error of b, expressed as one half of a 95 percent confidence interval.
e_c = relative error of c, expressed as one half of a 95 percent confidence interval.

Equation L-2 provides the general formula for calculating the relative errors of sums and differences:

$$e_{SR} = \frac{e_{SA}}{(a + b + c)} \qquad \text{(Eq. L-2)}$$

Where:

e_{SR} = relative error of the sum, expressed as one half of a 95 percent confidence interval.
e_{SA} = absolute error of the sum, expressed as one half of a 95 percent confidence interval.
a+b+c = sum of the variables measured.

Equation L-3 provides the general formula for calculating the absolute errors of products (e.g., flow rates of GHGs calculated as the product of the flow rate of the stream and the concentration of the GHG in the stream), where the product, P, is the result of multiplying the variables measured, a, b, c, etc. (e.g., P = a*b*c):

$$e_{PA} = (a * b * c)\left(e_a^2 + e_b^2 + e_c^2\right)^{1/2} \qquad \text{(Eq. L-3)}$$

Where:

e_{PA} = absolute error of the product, expressed as one half of a 95 percent confidence interval.
e_a = relative error of a, expressed as one half of a 95 percent confidence interval.
e_b = relative error of b, expressed as one half of a 95 percent confidence interval.
e_c = relative error of c, expressed as one half of a 95 percent confidence interval.

Equation L-4 provides the general formula for calculating the relative errors of products:

$$e_{PR} = \frac{e_{PA}}{(a * b * c)} \qquad \text{(Eq. L-4)}$$

Where:

e_{PR} = relative error of the product, expressed as one half of a 95 percent confidence interval.
e_{PA} = absolute error of the product, expressed as one half of a 95 percent confidence interval.

a*b*c = product of the variables measured

To estimate the annual CO2e emissions of the process for use in the error estimate, facilities would apply the mass-balance equations below to representative process measurements. If these process measurements represented less than one year of typical process activity, facilities would adjust the estimated emissions to account for one year of typical process activity. To estimate the terms FERd, FEP, and FEBk for use in the error estimate for Equations L-11, L-12, and L-13 of this section, facilities could use emission testing, monitoring of emitted streams, and/or engineering calculations or assessments, or in the alternative assume that all fluorine is emitted in the form of the fluorinated GHG that has the highest GWP among the fluorinated GHGs that occur in more than trace concentrations in the process. To convert the fluorinated GHG emissions to CO2e, facilities could use Equation A-1 of §98.2. For fluorinated GHGs whose GWPs are not listed in Table A-1 to subpart A of this part, facilities could use a default GWP of 2,000.

2. Mass Balance Approach Equations.

Estimating Fluorine Emissions

The following set of equations summarizes the mass-balancing method for estimating fluorinated GHG emissions based on a total fluorine balance (another element could also be used in place of fluorine).

The total mass of each fluorinated GHG emitted annually from each fluorinated gas production process and each fluorinated GHG transformation process would be estimated by using Equation L-5:

$$E_{FGHGf} = \sum_{p=1}^{n}\left(E_{Rp-FGHGf} + E_{Pp-FGHGf} + E_{Bp-FGHGf}\right) \qquad \text{(Eq. L-5)}$$

Where:

E_{FGHGf} = Total mass of each fluorinated GHG f emitted annually from production or transformation process i(metric tons).

$E_{Rp\text{-}FGHGf}$ = Total mass of fluorinated GHG reactant f emitted from production process i over the period p (metric tons, calculated in Equation L-11).

$E_{Pp\text{-}FGHGf}$ = Total mass of the fluorinated GHG product f emitted from production process i over the period p (metric tons, calculated in Equation L-12).

$E_{Bp\text{-}FGHGf}$ = Total mass of fluorinated GHG by-product f emitted from production process i over the period p (metric tons, calculated in Equation L-13).

n = Number of concentration and flow measurement periods for the year.

The total mass of fluorine emitted from process i over the period p would be estimated at least monthly by calculating the difference between the total mass of fluorine in the reactant(s) (or inputs, for processes that do not involve a chemical reaction) and the total mass of fluorine in the product (or outputs, for processes that do not involve a chemical reaction), accounting for the total mass of fluorine in any destroyed or recaptured streams that contain reactants, products, or by-products (or inputs or outputs). An element other than fluorine may be used in the mass-balance equation, provided the element occurs in all of the fluorinated GHGs fed into or generated by the process. In this case, the mass fractions of the element in the reactants, products, and by-products must be calculated as appropriate for that element. This calculation must be performed using Equation L-6:

$$E_F = \sum_{1}^{v} (R_d * MFF_{Rd}) - P * MFF_P - F_D \qquad \text{(Eq. L-6)}$$

Where:

E_F = Total mass of fluorine emitted from process i over the period p (metric tons).

R_d = Total mass of the fluorine-containing reactant d that is fed into process i over the period p (metric tons).

P = Total mass of the fluorine-containing product produced by process i over the period p (metric tons).

MFF_{Rd} = Mass fraction of fluorine in reactant d, calculated in Equation L-14.

MFF_P = Mass fraction of fluorine in the product, calculated in Equation L-15.

F_D = Total mass of fluorine in destroyed or recaptured streams from process i containing fluorine-containing reactants, products, and by-products, calculated in Equation L-7.

v = Number of fluorine-containing reactants fed into process i.

The mass of total fluorine in destroyed or recaptured streams containing fluorine-containing reactants, products, and by-products would be estimated at least monthly using Equation L-7. In Equation L-7, the concentration of individual fluorinated GHGs present in each destroyed or recaptured stream (i.e., speciated approach) is measured and determined, and the amount of fluorine present is then calculated. (An alternative approach to determining the total fluorine in destroyed or recaptured streams, as shown using Equations L-17 and L-18, is discussed below in section 3.B.ii.3.)

$$F_D = \sum_{j-1}^{q} P_j * MFF_P + \sum_{k-1}^{u}\left[\left(\sum_{j-1}^{q} B_{kj} + \sum_{l-1}^{x} B_{kl}\right) * MFF_{Bk}\right] + \sum_{d-1}^{v}\left(\sum_{j-1}^{q} R_{dj} * MFF_{Rd}\right) \qquad \text{(Eq. L-7)}$$

Where:

F_D = Total mass of fluorine in destroyed or recaptured streams from process i containing fluorine-containing reactants, products, and by-products over the period p.

P_j = Mass of the fluorine-containing product removed from process i in stream j and destroyed over the period p (calculated in Equation L-8 or L-9).

B_{kj} = Mass of fluorine-containing by-product k removed from process i in stream j and destroyed over the period p (calculated in Equation L-8 or L-9).

B_{kl} = Mass of fluorine-containing by-product k removed from process i in stream l and recaptured over the period p.

R_{dj} = Mass of fluorine-containing reactant d removed from process i in stream j and destroyed over the period p (calculated in Equation L-8 or L-9).

MFF_{Rd} = Mass fraction of fluorine in reactant d, calculated in Equation L-14.

MFF_{P} = Mass fraction of fluorine in the product, calculated in Equation L-15.

MFF_{Bk} = Mass fraction of fluorine in by-product k, calculated in Equation L-16.

q = Number of streams destroyed in process i.

x = Number of streams recaptured in process i.

u = Number of fluorine-containing by-products generated in process i.

v = Number of fluorine-containing reactants fed into process i.

The mass of each fluorinated GHG removed from process i in stream j and destroyed over the period p (i.e., P_j, B_{kj}, or R_{dj}, as applicable) would be estimated by applying the destruction efficiency of the device that has been demonstrated for the fluorinated GHG f to fluorinated GHG f using Equation L-8:

$$M_{FGHGfj} = DE_{FGHGf} * c_{FGHGfj} * S_j \qquad \text{(Eq. L-8)}$$

Where:

M_{FGHGfj} = Mass of fluorinated GHG f removed from process i in stream j and destroyed over the period p. (This may be P_j, B_{kj}, or R_{dj}, as applicable.)

DE_{FGHGf} = Destruction efficiency of the device that has been demonstrated for fluorinated GHG f in stream j (fraction).

c_{FGHGfj} = Concentration (mass fraction) of fluorinated GHG f in stream j removed from process i and fed into the destruction device over the period p. If this concentration is only a trace concentration, $c_{F\text{-}GHGfj}$ is equal to zero.

S_j = Mass removed in stream j from process i and fed into the destruction device over the period p (metric tons).

The mass of each fluorine-containing compound that is not a fluorinated GHG and that is removed from process i in stream j and destroyed over the period p (i.e., P_j, B_{kj}, or R_{dj}, as applicable) would be estimated using Equation L-9:

$$M_{FCgj} = c_{FCgj} * S_j \qquad \text{(Eq. L-9)}$$

Where:

M_{FCgj} = Mass of non-fluorinated GHG fluorine-containing compound g removed from process i in stream j and destroyed over the period p. (This may be P_j, B_{kj}, or R_{dj}, as applicable).

c_{FCgj} = Concentration (mass fraction) of non-fluorinated GHG fluorine-containing compound g in stream j removed from process i and fed into the destruction device over the period p. If this concentration is only a trace concentration, c_{FCgj} is equal to zero.

S_j = Mass removed in stream j from process i and fed into the destruction device over the period p (metric tons).

The mass of fluorine-containing by-product k removed from process i in stream l and recaptured over the period p would be estimated using Equation L-10:

$$B_{kl} = c_{Bkl} * S_l \qquad \text{(Eq. L-10)}$$

Where:

B_{kl} = Mass of fluorine-containing by-product k removed from process i in stream l and recaptured over the period p (metric tons).

c_{Bkl} = Concentration (mass fraction) of fluorine-containing by-product k in stream l removed from process i and recaptured over the period p. If this concentration is only a trace concentration, c_{Bkl} is equal to zero.

S_l = Mass removed in stream l from process i and recaptured over the period p (metric tons).

Attributing Fluorine Emissions to Reactants, Products, and By-Products (Characterizing Emissions)

To estimate the terms FER_d, FEP, and FEB_k for Equations L-11, L-12, and L-13, facilities could assume that the total mass of fluorine emitted, E_F, estimated in Equation L-6, occurs in the form of the fluorinated GHG that has the highest GWP among the fluorinated GHGs that occur in more than trace concentrations in the process unless facilities possess emission characterization measurements showing otherwise. The sum of the terms FER_d, FEP, and FEB_k would equal 1. Facilities would document the data and calculations that are used to speciate individual compounds and to estimate FER_d, FEP, and $FEB_{k.}$ Facilities should exclude from calculations the fluorine included in F_D, because this quantity has already been subtracted from emissions in Equation L-6. For example, they should exclude fluorine-containing compounds that are not fluorinated GHGs and that result from the destruction of fluorinated GHGs by any destruction devices (e.g., the mass of HF created by combustion of an HFC). However, they should include emissions of fluorinated GHGs that survive the destruction process.

It may be appropriate scale emission characterization requirements to the size of the emissions from the process and process vent. For processes and process vents that have total emissions greater than a certain threshold, facilities would conduct measurements to determine what fraction of the emissions are each individual fluorinated GHG (FER_d, FEP, and FEB_k). For processes and process vents with emissions below the threshold, facilities could conduct measurements or rely on previous measurements.

Facilities could estimate the total process emissions by relying on the estimate of total process emissions developed for the error estimate. To estimate emissions from process vents, facilities could conduct emission calculations or engineering assessments. For example, if the facility calculated that a process emitted 25,000 metric tons CO_2e or more, the facility would then estimate the emissions from each process vent, considering controls, using engineering calculations or engineering assessments. The facility would characterize by measurement any process vent that emits 25,000 metric tons CO_2e or more and determine the fraction of each fluorinated GHG.

For other vents, including vents from processes that emitted less than 25,000 metric tons CO_2e, facilities would characterize emissions either by taking measurements or by using previous measurements on the process, bench-scale, or pilot-scale process to determine the fraction of each fluorinated GHG.

If the emissions in either of the above cases were controlled and if the facility speciated the destroyed streams to estimate $F_{D,}$ the facility could use these monthly (or more frequent) measurements, along with the appropriate DEs of the destruction device, to characterize emissions after the destruction device. For vents that were uncontrolled or for which the facility quantified total fluorine, the facility would use previous or new measurements, as appropriate.

If there was only one process vent associated with the process, the measurement would require only the fraction of each fluorinated GHG. When there is more than one process vent, the facility would have to include a flow rate for each process vent and develop a weighted average across the process for the fraction of each fluorinated GHG. The flow rates could be measured or estimated. For fluorine emissions that are not accounted for by vent estimates (i.e., fugitive emissions), facilities would apply the weighted average of the emission characterization from process vents to the emissions.

The total mass of fluorine-containing reactant d emitted would be estimated at least monthly based on the total fluorine emitted and the fraction that consists of fluorine-containing reactants using Equation L-11. If the fluorine-containing reactant d is a non-GHG, facilities assume that FER_d is zero.

$$E_{R-ip} = \frac{FER_d * E_F}{\left(\sum_{d=1}^{v} FER_d * MFF_{Rd} + FEP * MFF_P + \sum_{k=1}^{u} FEB_k * MFF_{Bk} \right)} \qquad \text{(Eq. L-11)}$$

Where:

E_{R-ip} = Total mass of fluorine-containing reactant d that is emitted from process i over the period p (metric tons).

FER_d = The fraction of the mass emitted that consists of the fluorine-containing reactant d.

E_F = Total mass of fluorine emissions from process i over the period p (metric tons), calculated in Equation L-6.

FEP = The fraction of the mass emitted that consists of the fluorine-containing product.

FEB_k = The fraction of the mass emitted that consists of fluorine-containing by-product k.

MFF_{Rd} = Mass fraction of fluorine in reactant d, calculated in Equation L-14.

MFF_P = Mass fraction of fluorine in the product, calculated in Equation L-15.

MFF_{Bk} = Mass fraction of fluorine in by-product k, calculation in Equation L-16.

u = Number of fluorine-containing by-products generated in process i.
v = Number of fluorine-containing reactants fed into process i.

The total mass of fluorine-containing product emitted would be estimated at least monthly based on the total fluorine emitted and the fraction that consists of fluorine-containing products using Equation L-12. If the fluorine-containing product is a non-GHG, facilities may assume that FEP is zero.

$$E_{P-ip} = \frac{FEP * E_F}{\left(\sum_{d=1}^{v} FER_d * MFF_{Rd} + FEP * MFF_P + \sum_{k=1}^{u} FEB_k * MFF_{Bk} \right)} \qquad \text{(Eq. L-12)}$$

Where:
E_{P-ip} = Total mass of fluorine-containing product emitted from process i over the period p (metric tons).
FEP = The fraction of the mass emitted that consists of the fluorine-containing product.
E_F = Total mass of fluorine emissions from process i over the period p (metric tons), calculated in Equation L-6.
FER_d = The fraction of the mass emitted that consists of fluorine-containing reactant d.
FEB_k = The fraction of the mass emitted that consists of fluorine-containing by-product k.
MFF_{Rd} = Mass fraction of fluorine in reactant d, calculated in Equation L-14.
MFF_P = Mass fraction of fluorine in the product, calculated in Equation L-15.
MFF_{Bk} = Mass fraction of fluorine in by-product k, calculation in Equation L-16.
u = Number of fluorine-containing by-products generated in process i.
v = Number of fluorine-containing reactants fed into process i.

The total mass of fluorine-containing by-product k emitted would be estimated at least monthly based on the total fluorine emitted and the fraction that consists of fluorine-containing by-products using Equation L-13. If fluorine-containing by-product k is a non-GHG, facilities may assume that FEB_k is zero.

$$E_{Bk-ip} = \frac{FEB_k * E_F}{\left(\sum_{1}^{v} FER_d * MFF_{Rd} + FEP * MFF_P + \sum_{k=1}^{u} FEB_k * MFF_{Bk} \right)} \qquad \text{(Eq. L-13)}$$

Where:
E_{Bk-ip} = Total mass of fluorine-containing by-product k emitted from process i over the period p (metric tons).
FEB_k = The fraction of the mass emitted that consists of fluorine-containing by-product k.
FER_d = The fraction of the mass emitted that consists of fluorine-containing reactant d.
FEP = The fraction of the mass emitted that consists of the fluorine-containing product.
E_F = Total mass of fluorine emissions from process i over the period p (metric tons), calculated in Equation L-6.

MFF_{Rd} = Mass fraction of fluorine in reactant d, calculated in Equation L-14.
MFF_P = Mass fraction of fluorine in the product, calculated in Equation L-15.
MFF_{Bk} = Mass fraction of fluorine in by-product k, calculation in Equation L-16.
u = Number of fluorine-containing by-products generated in process i.
v = Number of fluorine-containing reactants fed into process i.

The mass fraction of fluorine in reactant d would be estimated using Equation L-14:

$$MFF_{Rd} = MF_{Rd} * \frac{AW_F}{MW_{Rd}} \qquad \text{(Eq. L-14)}$$

Where:
MFF_{Rd} = Mass fraction of fluorine in reactant d (fraction).
MF_{Rd} = Moles fluorine per mole of reactant d.
AW_F = Atomic weight of fluorine.
MW_{Rd} = Molecular weight of reactant d.

The mass fraction of fluorine in the product would be estimated using Equation L-15:

$$MFF_P = MF_P * \frac{AW_F}{MW_P} \qquad \text{(Eq. L-15)}$$

Where:
MFF_P = Mass fraction of fluorine in the product (fraction).
MF_P = Moles fluorine per mole of product.
AW_F = Atomic weight of fluorine.
MW_P = Molecular weight of the product produced.

The mass fraction of fluorine in by-product k would be estimated using Equation L-16:

$$MFF_{Bk} = MF_{Bk} * \frac{AW_F}{MW_{Bk}} \qquad \text{(Eq. L-16)}$$

Where:
MFF_{Bk} = Mass fraction of fluorine in the product (fraction).
MF_{Bk} = Moles fluorine per mole of by-product k.
AW_F = Atomic weight of fluorine.
MW_{Bk} = Molecular weight of by-product k.

3. Mass Balance Equations – Alternative Approach for Determining Total Fluorine in Destroyed and Recaptured Streams.

As an alternative to the approach in Equation L-7 for determining the mass of total fluorine destroyed or recaptured, facilities could use the approach in Equation L-17. In Equation L-17, rather than determine the individual fluorinated GHGs present in each destroyed or recaptured stream (i.e., speciated approach) and then determine the amount of fluorine present using Equation L-7, facilities may use a measurement technique on destroyed or recaptured streams that provides the total mass of fluorine (i.e., no speciation of individual fluorinated GHGs). This approach may be particularly useful for process with multiple byproducts.

The total mass of fluorine in destroyed or recaptured streams containing fluorine-containing compounds (including all fluorine-containing reactants, products, and by-products) would be estimated at least monthly using Equation L-17.

$$F_D = \sum_{j=1}^{q} DE_{avgj} * c_{TFj} * S_j + \sum_{l=1}^{x} c_{TFl} * S_l \qquad \text{(Eq. L-17)}$$

Where:

F_D = Total mass of fluorine in destroyed or recaptured streams from process i containing fluorine-containing reactants, products, and by-products.

DE_{avgj} = Weighted average destruction efficiency of the destruction device for the fluorine-containing compounds identified in destroyed stream j under §98.124(b)(4)(ii) and (5)(ii) (calculated in Equation L-18)(fraction).

c_{TFj} = Concentration (mass fraction) of total fluorine in stream j removed from process i and fed into the destruction device over the period p. If this concentration is only a trace concentration, c_{TFj} is equal to zero.

S_j = Mass removed in stream j from process i and fed into the destruction device over the period p (metric tons).

c_{TFl} = Concentration (mass fraction) of total fluorine in stream l removed from process i and recaptured over the period p. If this concentration is only a trace concentration, c_{Bkl} is equal to zero.

S_l = Mass removed in stream l from process i and recaptured over the period p.

q = Number of streams destroyed in process i.

x = Number of streams recaptured in process i.

The weighted average destruction efficiency that is applicable to a destroyed stream and that is used in Equation L-17 would be calculated using Equation L-18. Equation L-18 treats non-GHG fluorine-containing compounds as being completely destroyed, since none of the fluorine in them is emitted as a fluorinated GHG. Fluorinated GHGs are assumed to be destroyed to the DE of the device for each fluorinated GHG.

$$DE_{avgj} = \frac{\sum_{f=1}^{w} DE_{FGHGf} * c_{FGHGf} * S_j * MFF_{FGHGf} + \sum_{g=1}^{y} c_{FCg} * S_j * MFF_g}{\sum_{f=1}^{w} c_{FGHGf} * S_j * MFF_{FGHGf} + \sum_{g=1}^{y} c_{FCg} * S_j * MFF_g} \qquad \text{(Eq. L-18)}$$

Where:

DE_{avgj} = Weighted average destruction efficiency of the destruction device for the fluorine-containing compounds identified in destroyed stream j under §98.124(b)(4)(ii) or (b)(5)(ii), as appropriate.

DE_{FGHGf} = Destruction efficiency of the device that has been demonstrated for fluorinated GHG f in stream j (fraction).

c_{FGHGfj} = Concentration (mass fraction) of fluorinated GHG f in stream j removed from process i and fed into the destruction device over the period p. If this concentration is only a trace concentration, $c_{F\text{-}GHGfj}$ is equal to zero.

c_{FCgj} = Concentration (mass fraction) of non-fluorinated GHG fluorine-containing compound g in stream j removed from process i and fed into the destruction device over the period p. If this concentration is only a trace concentration, c_{FCgj} is equal to zero.

S_j = Mass removed in stream j from process i and fed into the destruction device over the period p (metric tons).

MFF_{FGHGf} = Mass fraction of fluorine in fluorinated GHG f, calculated in Equation L-14, L-15, or L-16, as appropriate.

MFF_{FCg} = Mass fraction of fluorine in non-fluorinated-GHG fluorinated compound g, calculated in Equation L-14, L-15, or L-16, as appropriate.

w = Number of fluorinated GHGs in destroyed stream j.

y = Number of non-fluorinated-GHG fluorine-containing compounds in destroyed stream j.

4. Frequency of Measurement and Calculation.

EPA considered several measurement and calculation frequencies for the mass balance approach. The total mass of each fluorinated GHG emitted from production processes could be estimated on a daily, weekly, or monthly basis by calculating the total fluorine in the reactants, subtracting the measured total fluorine in the product, and subtracting the measured total fluorine that is destroyed or recaptured. The daily measurement requires additional man hours to conduct more frequent measurements; however, in situations where input or output flows are estimated by multiplying concentrations by total mass flow rates of streams, and where one or both of these vary, frequent measurements will lead to more accurate and precise estimates than less frequent.

A number of fluorocarbon producers have noted that daily measurements are burdensome and lead to large errors in the estimates of daily emissions. Many streams may contain acidic and reactive constituents such as HF, and sampling from these streams can create safety hazards. Daily product measurements can also vary significantly (sometimes exceeding 100 percent) for three reasons. First, when continuous processes are initially started, there is a lag time between the time the reactants are fed into the process and the time products emerge. Second, even after the process has been running for a while, the quantity of material in the process can vary based on changes in production rates and other conditions. Third, the relatively large errors in measurements of in-process product holding tanks (e.g., based on sight-glass readings) have a significant impact on daily mass balances. Over time, all of these effects smooth out, making longer term mass balances more reliable than daily mass balances.[11] In view of these considerations, a requirement to perform measurements daily may not be justified, particularly for processes where concentrations show little variability.

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[11] Note, however, that the sum of the daily mass-balances would also smooth out.

Because different processes operate with different ranges of process variability, it would be reasonable to require more frequent measurements for more variable processes. The appropriate frequency of measurement could be determined using the error calculation described above along with standard statistical techniques such as the Student's t test.

As discussed below in the context of emission testing, the more variable a parameter is, the more samples must be taken to precisely characterize the mean of that parameter. The number of samples required to estimate the mean of the parameter with a given level of confidence can be calculated based on the relative standard deviation (RSD) of the samples and on some assumptions about the distribution of the parameter. Where the set of samples is relatively small and only the sample standard deviation "s" is known (rather than the true standard deviation of the parameter), the appropriate statistic is often the Student's t test.

Monthly sampling will generate twelve concentration measurements per stream per year. If the variability among the concentration measurements is high enough that these 12 measurements per year (i.e., monthly measurements) result in relative and absolute errors above the 30-percent and 3,000-mtCO2e limits, based on the Student's t test, then the facility would need to increase the frequency of its measurements to meet the error limits. For example, facilities may find that weekly measurements are necessary to meet the error criteria for certain processes. By including process variability in the error calculation, facilities could make more frequent measurements if this were necessary to address process variability, but they would not need to incur the costs and risks of sampling for processes where less frequent measurements yielded precise results.

Facilities that use the alternative to the error calculation (discussed further below) could make weekly measurements and calculations. EPA calculates that at a weekly frequency, these measurements will lead to reasonably accurate emission estimates (with an error near 30 percent) even if the concentrations in the process are highly variable (e.g., even if the RSD of the concentration measurements is 50 percent, which would be unusually high.)

There are two other measurement practices that could address process variability. First, facilities could ensure that they made concentrations measurements that reflect the full range of conditions within the process, e.g., catalyst age. Facilities could also account for emissions that occur during process startups, shutdowns, and malfunctions, either recording fluorinated GHG emissions during these events or documenting that these events do not result in significant emissions. Together, these practices would limit the impact of sampling bias on emissions estimates.

5. Alternative Precision and Accuracy Requirements

An alternative to requiring facilities to perform the error calculation would be to specify conditions under which the error of the estimate would be expected to fall under the 3,000 $mtCO_2e$ error limit. (The 3,000 mtCO2e absolute error was identified as the limit because it is consistent with the absolute error limit in the error calculation approach.) These conditions would include specific accuracy, precision, and frequency requirements for measurements and a process throughput limit.

To determine the appropriate requirements, one must consider the five factors that affect the absolute accuracy and precision of mass-balance estimates: (1) the relative accuracy and precision of the mass measurements, (2) the relative accuracy and precision of the methods used to measure concentrations (irrespective of process variability), (3) process variability, (4) the frequency of the measurements, and (5) the quantity of the fluorinated GHG throughput of the process, that is, the total masses of the fluorinated GHG reactants, products, and by-products fed into and generated by the process. A number of different combinations of measurement precisions, accuracies and frequencies would result in an emissions estimate with an acceptable absolute error; but some combinations are likely to be more easily achieved than others. Based on the research performed for this rule, one robust combination of requirements that is likely to be achievable for a number of processes is (1) to measure the masses identified in the rule with an accuracy and precision of ±0.2 percent of full scale or better, (2) to measure the concentrations identified in the rule using analytical methods with an accuracy and precision of ±10 percent or better, (3) to conduct these measurements at least weekly, and (4) to limit the fluorinated GHG throughput of the process (including fluorinated GHG reactants, products, and by-products) to 500,000 mtCO2e or less. At an emission rate of two percent, the 500,000-mtCO_2e throughput limit would result in emissions of 10,000 mtCO_2e. In combination with the precision, accuracy, and frequency requirements for measurements, this throughput would be expected to result in a maximum absolute error of 3,000 mtCO_2e.

Although some of the requirements could be relaxed and still result in an error near or below 3,000 mtCO2e, this would require a tightening of the other requirements. For example, if the requirements for the precision and accuracy of the mass measurements were relaxed to ±0.4 percent, the requirements for the precision and accuracy of the concentration measurements would have to be tightened, e.g., to ±5 percent, and the frequency of these measurements would have to be increased. Comments received on the April 10, 2009 and April 12, 2010 proposed rules indicate that achieving precisions and accuracies of ±5 percent for concentration measurements, and conducting these measurements more often than weekly, could be quite challenging. The precision and accuracy requirements for concentrations and for the frequency of measurement are less stringent than those initially proposed in the April 10, 2009 rule; those for masses are the same as those initially proposed.

Facilities that could not or chose not to meet these requirements would remain free to use the error calculation to demonstrate compliance with the mass-balance error limits. Under the error calculation, facilities have the flexibility to focus on improving the accuracy and precision of those measurements that have a significant impact on the overall error of the estimate rather than expending resources to improve the accuracy and precision of measurements that are not as important to the accuracy and precision of the emissions estimate.

6. Comparison Between Proposed and Final Mass-Balance Approaches

The version of the mass-balance approach adopted in the final rule is based on the same basic principle as the version that was proposed, but it also differs from the proposed version in some key respects. Both the proposed and final mass-balance approaches use the difference between the fluorine (or other element) fed into the process and the fluorine removed from the process to estimate the mass emitted. However, they differ in how they characterize the mass emitted. The proposed version of the mass-balance approach required calculation of the quantity of by-product generated, which in turn required monitoring of any stream where by-products occurred in more than trace concentrations. Emissions of the by-product were assumed to equal the difference between the quantity of by-product generated and the quantity of by-product destroyed. Any remaining emissions were assumed to consist of the product. The final version of the mass-balance approach requires emission characterization measurements, which focus on the actual emissions from the process.

The mass-balance approach in the final rule is fundamentally more flexible than that in the proposed rule. First, it allows for the possibility that emissions can consist of reactants as well as products and byproducts. Thus, the finalized version of the mass-balance approach is capable of quantifying emissions from transformation processes in which fluorinated GHGs are reactants as well as production processes in which fluorinated GHGs are products. Fluorinated GHG producers indicated in their comments that they would prefer a version of the mass-balance approach that was capable of quantifying emissions from transformation processes.

Second, because emissions are characterized at the vent, the finalized mass-balance approach does not require facilities to speciate the flows in their streams. Instead, they are required to track the total fluorine in destroyed or recaptured streams. (While they may speciate these streams to do so, they may also use an analytical method that tracks total fluorine, such as ASTM D7359-08.)

The facility must conduct emission characterization measurements, or use previous measurements, to develop the break out among the fluorinated GHG emitted. This emission measurement would focus on partitioning emissions among the various fluorinated GHGs (i.e., speciating the compounds).

7. Current Plant Practices for Mass Balance

A few facilities indicated that they conduct a form of the mass balance approach for determining fluorinated GHG emissions. Facilities noted overall that the difficulty of the mass balance approach depends on how sophisticated or complex the process is, i.e., how many input and output streams there are, and whether there are by-products generated and how many. Facilities that use a form of the mass balance approach indicated that it is often used in conjunction with an emissions factor based approach, to track yields and subtle or incremental changes in the process. These facilities conduct a “material balance” on the process, tracking the product yield, using the emission factor for some emission points, and the composition and concentration of the streams to determine if something in the process has changed. Generally, facilities have a good understanding of the chemistry for all processes and understand what raw materials are fed to the process, what side reactions occur, and what products and by-products are created. Facilities have laboratory-scale, pilot-plant, and full-scale stream analysis results. Facilities stated that with the original plant design, the mass balance equation is predicted. Facilities noted in particular that at the bench-scale phase of product and process development, they analyze every/all streams to identify all species and compounds. However, one facility indicated that while they do regularly measure byproduct concentrations in the product as a quality check, they do not regularly measure byproduct concentration across all process vents and streams.

Some facilities indicated that they conduct the mass balance on the fluorinated organic component only.

Facilities noted, in particular, that they reconcile and calculate the production levels on a monthly basis rather than on shorter time frames such as daily or weekly.

iii. Monitoring of Process Vents

The emissions from process vents may be determined by a number of methods. These include emissions testing, engineering assessments, or calculations based on chemical engineering principles. All three methods may also be used to develop a site-specific emissions factor based on the emissions estimate and the process activity observed during the test or assumed for the calculations. These methods or approaches to determining emissions from fluorinated gas production processes provide emissions estimates of varying accuracy and precision.

1. Process-Vent-Specific Emission Factor Approach.

One method for estimating fluorinated GHG emissions is based on monitoring or estimating the composition and flow rate of the process vent streams along with the production activity parameter to develop a site-specific, process-vent-specific emission factor. Fluorinated gas producers have indicated that they develop and apply emission factors to estimate emissions from a range of processes. Typically a facility conducts an initial emissions test or engineering calculation to develop an emission factor or emissions calculation factor and updates the emissions factor as needed with process changes. Site-specific, process-vent-specific emission factors can be developed based on either measurement of process vent emissions or calculation of process vent emissions. The measurement of process vent emissions to develop an emissions factor is addressed in this section, and the calculation of process vent emissions is discussed below in Process-Vent-Specific Emission Calculation Factor approach.

Under this approach, facilities would develop a process-vent-specific emission factor for each fluorinated GHG from each process vent by emissions testing. Facilities would use EPA, ASTM, industry-developed, and other testing methods, including consensus standards and industry-validated methods for determining the process emissions for emission factor development. The methods used would be quality-assured methods, capable of detecting the analyte of interest at the concentration of interest, and validated with the compound of interest at the concentration of interest. There are several EPA test methods available to sample and measure fluorinated GHG from processes in the fluorinated gas production source category, including EPA Method 320 (ASTM D6348-03) and EPA Method 18. Method 1 or 1A, Method 2, 2A, 2B, 2C, or 2D, 2F, or 2G, Method 3, 3A, or 3B, and Method 4 must be conducted along with EPA Method 18.

Method 320 and ASTM D6348-03. For Method 320, a gas sample is extracted through a heated gas transport and handling system and analyzed using FTIR spectroscopy to identify and quantify the gas stream components. It is applicable only for vapor phase analysis of organic or inorganic compounds. The sensitivity of this method can be adjusted based on the reference standards used to configure the FTIR, but also depends on the gas composition, moisture content, and sampling losses. The ASTM D6348-03 FTIR method utilizes the same principles as Method 320 but has some improved calibration requirements.

Method 18. Method 18 utilizes gas chromatography (GC) and flame ionization, photoionization, electron capture, mass spectroscopy, or another applicable detection method to identify and quantify gaseous organic compounds. For the fluorinated GHG industry, electron capture and mass spectroscopy and possibly photoionization are the most appropriate detectors for identifying fluorinated GHG compounds. The identity and concentration levels are determined by comparison to known standards, which are used to calibrate the GC. Stack gas samples may be collected through direct interface sampling, dilution interface sampling, adsorption tube sampling, or bag sampling. One needs to consider whether significant temporal changes in flow rate and/or concentration occur in the process (e.g., batch processes) when selecting and applying the sampling approach for this method. The direct interface, dilution interface, and adsorption tube sampling are not designed for sources that vary in concentration. Instead, an integrated bag sample with proportional sampling (sample rate adjusted proportionally with changes in stack gas flow rate) would be appropriate for an emission source with a varying flow rate and concentration. If the direct interface method is used, the timeframe of temporal changes of concentration in relation to the analytical timeframe needs to be considered. For example, if significant changes in concentration are expected to occur rapidly (e.g., 10-minute time frame), but the GC analytical cycle is 30 minutes, a representative sample analysis may not be obtained; on the other hand, for this situation, if the analytical cycle is 5 minutes, a representative sample would be obtained. Variations in vent gas flow rate also need to be considered; for example, if vent flow rates and concentration are varying with time and the direct interface method is being used, the vent flowrate should be continuously monitored so that the flowrate and concentration can be correlated to determine mass emissions. For any of the sampling methods, all samples must be analyzed within a few hours of collection.

Method 320, ASTM D63248-03 and Method 18 also require that the flow rate be relatively constant during sampling. If the flow rate varies significantly over the course of the sampling, then this fluctuation must be accounted for when measuring concentration and calculating mass emissions.

OTM 24, the Tracer Gas Protocol For the Determination of Volumetric Flow Rate Through the Ring Pipe of the Xact Multi-Metals Monitoring System (OTM 24) uses a GC equipped with an FID to measure the concentration at a specific point. A tracer gas is introduced into the process to perform a volumetric flow rate determination, which depends on the tracer flow rate, concentration at the measurement point and calibration and analysis data.

The Emission Measurement Center Approved Alternative Method (ALT-012) is designed for measuring particulate emissions in situations where gas velocities are low and difficult to measure and subject to variations over time. ALT-012 can also be used to measure ducts and stacks that are not subject to stratification. First, locations are identified upstream, for injecting the tracer gas, and downstream, for the tracer gas measurement. For a complete measurement, three ten-minute long sampling intervals must be completed at the downstream location.

Nuclear magnetic resonance (NMR) spectroscopy is a commonly used analytical technique in organic chemistry. Organic compounds are placed in a magnetic field and exposed to electro-magnetic energy, usually in the form of radio frequency (RF), and the nuclei of certain atoms absorb the radiation, which causes the nuclear spin to realign in the higher energy direction. The wavelength the atom absorbs is dependent on the neighboring atoms in the compound, and the resulting spectrum is called the NMR spectrum. This is a complex laboratory analytical method used to determine the structure of molecules. Much like using infrared spectroscopy (IR) to identify functional groups, analysis of a NMR spectrum provides information on the number and type of chemical entities in a substance. Also, the dependence of the transition energy on the position of a particular atom in a molecule makes NMR spectroscopy extremely useful for determining the structure of molecules.

Using the applicable method(s), process activity (e.g., production or feed) would be monitored at the same time as emissions; the emission factor would be developed by dividing the emissions by the activity. Both continuous and batch processes are used in the fluorinated gas production source category. Typically, for continuous processes, facilities would measure and determine the fluorinated GHG emission rate based on test runs of at least 1 hour duration. For continuous processes, facilities would use Equation L-19.

$$E_{ContPV} = \frac{C_{PV}}{10^6} * MW * Q_{PV} * \frac{1}{SV} * \frac{1}{10^3} * \frac{60}{1} \qquad \text{(Eq. L-19)}$$

Where:

E_{ContPV} = Mass of fluorinated GHG f emitted from process vent v from process i during the emission test during test run r (kg/hr).

C_{PV} = Concentration of fluorinated GHG f during test run r of the emission test (ppmv).

MW = Molecular weight of fluorinated GHG f (g/g-mole).

Q_{PV} = Flow rate of the process vent stream during test run r of the emission test (m^3/min).

SV = Standard molar volume of gas (0.0240 m^3/g-mole at 68°F and 1 atm).

$1/10^3$ = Conversion factor (1 kilogram/1,000 grams).

60/1 = Conversion factor (60 minutes/1 hour).

To develop the site-specific, process-vent-specific emission factor, facilities would track the process activity during the emissions testing and combine it with the emissions. For continuous processes, a facility would divide the fluorinated GHG emissions during the test by the process activity during testing. Equation L-20 would be used to estimate the average emission factor.

$$EF_{PV} = \frac{\sum_{1}^{r}\left(\frac{E_{PV}}{Activity_{EmissionTest}}\right)}{r} \qquad \text{(Eq. L-20)}$$

Where:

EF_{PV} = Average emission factor for fluorinated GHG f emitted from process vent v during process i (e.g., kg emitted/kg activity).

EPV = Mass of fluorinated GHG f emitted from process vent v from process i during the emission test during test run r (kg emitted/hr for continuous).

$Activity_{EmissionTest}$ = Process feed, process production, or other process activity rate during the emission test during test run r (e.g., kg product/hr).

r = Number of test runs performed during the emission test.

Development of the emissions testing program requires testing during representative process operation. To develop a representative emission factor for the process vent, the facility should give some consideration to what process variability might be present in the process. For each operating scenario of the process, the emissions test data must be representative of the typical process operation while also including process variability.[12] The full range of process operating conditions should be included. The typical process operation conditions would include yield, temperature, pressure, and flow rates. The operating conditions and the process activity should be measured during the emissions test. See section 3.B.iii.3 below for more information on representativeness.

Emission factors may be developed on an uncontrolled or a controlled basis depending on the emission level of the process vent. Using the process-vent-specific emissions factor method, a facility would estimate emissions using the emission factor and would track process activity on an on-going basis. To estimate annual fluorinated GHG emissions from each vent, facilities would multiply each uncontrolled emission factor by the appropriate activity data and account for the use (and uptime) of destruction devices. Where controlled emission factors are developed, a facility would multiply each controlled emission factor by the appropriate activity data for periods when the process vent is vented to the destruction device. For periods when the process vent is not venting the destruction device (i.e., bypassing), the facility would develop an emission factor for these periods as well (i.e., an uncontrolled emission factor) or would develop an emission calculation factor.

For facilities that conduct emissions testing on a controlled vent, the emissions of each fluorinated GHG for each process vent would be calculated using Equation L-21.

$$E_{PV} = EF_{PV-C} * Activity_C + ECF_{PV-U} * Activity_U \qquad \text{(Eq. L-21)}$$

Where:

E_{PV} = Mass of fluorinated GHG f emitted from process vent v from process i, for the year (kg).

EF_{PV-C} = Average emission factor for fluorinated GHG f emitted from process vent v during process i based on testing after the destruction device (kg emitted/activity)(e.g., kg emitted/kg product).

$Activity_C$ = Total process feed, process production, or other process activity during the year for which emissions are vented to the properly functioning destruction device (i.e., controlled).

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[12] Operating scenarios and other issues associated with developing representative emission factors are discussed further below under "Obtaining and Maintaining Representative Emission Factors."

ECF_{PV-U} = Emission calculation factor for fluorinated GHG f emitted from process vent v during process i during periods when the process vent is not vented to the properly functioning destruction device (kg emitted/activity)(e.g., kg emitted/kg product).

$Activity_U$ = Total process feed, process production, or other process activity during the year for which the process vent is not vented to the properly functioning destruction device (e.g., kg product)

For facilities that conduct emissions testing on an uncontrolled vent, the emissions would be calculated by applying the destruction efficiencies of the device that have been demonstrated for the fluorinated GHGs in the vent stream to the fluorinated GHG emissions for the process vent, using Equation L-22 of this section. Facilities would apply the destruction efficiency only to the portion of the process activity during which emissions are vented to the properly functioning destruction device (i.e., controlled).

$$E_{PV} = EF_{PV-U} * \left(Activity_U + Activity_C * (1 - DE)\right) \qquad \text{(Eq. L- 22)}$$

Where:

E_{PV} = Mass of fluorinated GHG f emitted from process vent v from process i, for the year, considering destruction efficiency (kg).

EF_{PV-U} = Emission factor (uncontrolled) for fluorinated GHG f emitted from process vent v during process i (kg emitted/kg product).

$Activity_U$ = Total process feed, process production, or other process activity during the year for which the process vent is not vented to the properly functioning destruction device (e.g., kg product).

$Activity_C$ = Total process feed, process production, or other process activity during the year for which the process vent is vented to the properly functioning destruction device (e.g., kg product).

DE = Demonstrated destruction efficiency of the destruction device (weight fraction).

When there is more than one operating scenario associated with a process, the emissions factor developed for the first operating scenario of the process may be adjusted for other operating scenarios depending of the magnitude of emissions. Facilities would use Equation L-23 to develop an adjusted process-vent-specific emission factor.

$$EF_{PVadj} = \frac{ECF_{UT}}{ECF_T} * EF_{PV} \qquad \text{(Eq. L-23)}$$

Where:

EF_{PVadj} = Adjusted process-vent-specific emission factor for an untested operating scenario.

ECF_{UT} = Emission calculation factor for the untested operating scenario developed under paragraph (c)(4) of this section.

ECF_{T} = Emission calculation for the tested operating scenario developed under paragraph (c)(4) of this section.

EF_{PV} = Process-vent-specific emission factor for the tested operating scenario.

Facilities may sum the emissions of each fluorinated GHG from all of the process vents in a process for the year to estimate the total process vent emissions of each fluorinated GHG. Facilities would use Equation L-24.

$$E_{Pfi} = \sum_{1}^{v} E_{PV} \qquad \text{(Eq. L-24)}$$

Where:

E_{Pfi} = Mass of fluorinated GHG f emitted from process vents for process i, for the year (kg).

E_{PV} = Mass of fluorinated GHG f emitted from process vent v from process i, for the year, considering destruction efficiency (kg).

v = Number of process vents in process i.

2. Process-Vent-Specific Emission Calculation Factor Approach.

As mentioned above, another method for estimating fluorinated GHG emissions is based on use of engineering calculations to determine the composition and flow rate of the process vent streams. These emissions estimates are divided by the production activity parameter to develop a site-specific, process-vent-specific emission calculation factor. A variation of this method includes use of engineering assessments to develop process-vent-specific emission calculation factor. Facilities have indicated that they regularly use engineering calculations and engineering assessments to estimate fluorinated GHG emissions.

Engineering calculations use chemical engineering principles and component property data to calculate emissions. Acceptable calculation methods for uncontrolled and controlled process vent emissions are included in a number of rule texts and EPA guidance documents. Other promulgated rule texts that contain appropriate calculation equations include the Miscellaneous Organic NESHAP (MON) NESHAP in §63.2460(b)(1) through (4) (the MON rule text also refers to equations in the Pharmaceutical NESHAP in §63.1257(d)(2)(i) for uncontrolled and §63.1257(d)(3)(i) for controlled emissions with some noted caveats to the calculations). These rule texts include process calculation methods and equations for vapor displacement, purging, heating, depressurization, vacuum systems, gas evolution, air drying, and empty vessel purging. An even more recent guidance document that provides appropriate calculations for chemical manufacturing operations is the *Methods for Estimating Air Emissions from Chemical Manufacturing Emissions, Volume II: Chapter 16, of the Emission Inventory Improvement Program*.

Engineering assessments may be conducted using previous emissions test data or other information available on the process. Facilities typically have component and composition data available from the original research and development activities on the process and from the process' lifetime of operation. If the facility performed a scoping speciation as described in section 3.A.ii above, the results of that test should also be considered. For process vent emissions determinations, facilities could conduct an engineering assessment to calculate uncontrolled emissions for each process vent and for each emission episode. Various rules for other regulatory programs include use of engineering assessments to estimate emissions from processes and process vents. Other promulgated rules that allow use of engineering assessments include NESHAP rules in 40 CFR part 63, such as subpart GGG for Pharmaceutical Manufacturing in §63.1257(d)(2)(ii) and subpart FFFF for MON in §63.2460(b). Engineering assessments include use of previous emissions test data where the emissions are representative of current operating practices; bench-scale or pilot-scale streams analysis results for identifying stream components and composition for products, byproducts, and wastes; design analysis based on chemical engineering principles, measurable process parameters, or physical or chemical laws or properties. These previous emissions data, analysis, and calculations may be used to identify fluorinated GHG compounds and their concentrations in various streams.

To develop the site-specific, process-vent-specific emissions calculation factor, facilities would first calculate the fluorinated GHG emissions and divide them by the appropriate process activity associated with the emissions calculation. Equation L-25 would be used to estimate the emission calculation factor.

$$ECF_{PV} = \frac{E_{PV}}{Activity_{\mathrm{Re}\ presentative}} \qquad \text{(Eq. L-25)}$$

Where:

ECF_{PV} = Emission calculation factor for fluorinated GHG f emitted from process vent v during process i (e.g., kg emitted/kg product).

E_{PV} = Average mass of fluorinated GHG f emitted, based on calculations, from process vent v from process i during the period or batch for which emissions were calculated, for either continuous or batch (kg emitted/hr for continuous, kg emitted/batch for batch).

$Activity_{Representative}$ = Process feed, process production, or other process activity rate corresponding to average mass of emissions based on calculations (e.g., kg product/hr for continuous, kg product/batch for batch).

As with the process-vent-specific emissions factor, a facility would estimate emissions using the emissions calculation factor and would track process activity on an on-going basis. To estimate annual fluorinated GHG emissions from each vent, facilities would multiply each emission calculation factor by the appropriate activity data and account for the use (uptime, bypass, and/or downtime) of destruction devices. Equation L-26 would be used to estimate emissions for each individual process vent if the process vent is not vented to a destruction device, and Equation L-27 would be used if the process vent is vented to a destruction device.

$$E_{PV} = ECF_{PV} * Activity \qquad \text{(Eq. L-26)}$$

Where:

E_{PV} = Mass of fluorinated GHG f emitted from process vent v from process i, for the year (kg).

ECF_{PV} = Emission calculation factor for fluorinated GHG f emitted from process vent v during process i (kg emitted/activity) (e.g., kg emitted/kg product).

Activity = Process feed, process production, or other process activity during the year.

$$E_{PV} = ECF_{PV} * \left(Activity_U + Activity_C * (1 - DE)\right) \qquad \text{(Eq. L-27)}$$

Where:

E_{PV} = Mass of fluorinated GHG f emitted from process vent v from process i, for the year considering destruction efficiency (kg).

ECF_{PV} = Emission calculation factor for fluorinated GHG f emitted from process vent v during process i (e.g., kg emitted/kg product).

$Activity_U$ = Total process feed, process production, or other process activity during the year for which the process vent is not vented to the properly functioning destruction device (e.g., kg product).

$Activity_C$ = Total process feed, process production, or other process activity during the year for which the process vent is vented to the properly functioning destruction device (e.g., kg product).

DE = Demonstrated destruction efficiency of the destruction device (weight fraction).

The emissions of each fluorinated GHG from all process vents in the process would be summed to obtain the total emissions from process vents for the facility as a whole. Equation L-28 would be used to sum fluorinated GHG emissions over all process vents for the process, and Equation L-29 would sum the emissions from all processes. Other emission points at the facility such as equipment leaks, storage tanks, or wastewater would have to be accounted for separately and added in to the facility total.

$$E_{Pfi} = \sum_{1}^{v} E_{PV} \qquad \text{(Eq. L-28)}$$

Where:

E_{Pfi} = Mass of fluorinated GHG f emitted from process vents for process i, for the year (kg).
E_{PV} = Mass of fluorinated GHG f emitted from process vent v from process i, for the year, considering destruction efficiency (kg).
v = Number of process vents in process i.

3. Obtaining and Maintaining Representative Emission Factors

Process conditions

Emission rates from a process depend on the operating conditions of that process. Thus, to ensure that emission factors are representative, facilities should define the operating scenario that encompasses the typical range of operating conditions for the process. If the process has multiple operating scenarios, the facility should develop a representative emissions factor for each operating scenario. To define the process operating scenario, a facility could include information on the process description, the specific process equipment used, and the range of operating conditions; the process vents, emission episodes and durations, and the quantity of uncontrolled fluorinated GHG emissions; the control device or destruction device used to control emissions; and the manifolding of process vents within the process and from other processes. Other operating scenarios should also be defined for differences in operating conditions that affect emissions. Examples of situations where process differences may warrant separate operating scenarios include the following: making small volumes of a product in one set of batch process equipment part of the year and making larger volumes in larger batch process equipment part of the year; use of two different types of catalyst in the same process; deliberate alterations in process conditions such as temperature or pressure to shift the reaction to a particular product; and making small volumes of a product in a batch process part of the year and making large volumes in a continuous process part of the year. A facility would need to develop a representative emissions factor for each process operating scenario because each operating scenario for a process will result in different emissions levels.

Prior to developing an emissions factor, facilities should observe the operating conditions of the process over a period of time and note how changes to the operating conditions affect emissions rates. The time periods may vary from facility to facility and perhaps from process to process, but typically may include an examination period of one year or one month and could include examination of startup and shutdown periods. An examination of the previous year of process operating conditions might take note of whether there is month-to-month or seasonal variability in the process. For example, seasonal variability might be caused by production rate changes or might be caused by changes in the ambient temperature from summer to winter. An examination of one month of process operating conditions might reveal some short-term process variability. A review of startup and shutdown process operating conditions may include an assessment of how frequently startups and shutdowns occur, what effect startups and shutdowns have on emission rates, and whether or not the impact on emissions can be quantified.

In general, emissions testing during process startups and shutdowns would not be expected to lead to representative emission factors, because emission rates tend to fluctuate during such events. Exceptions to this could include long-term monitoring that would not over-represent startup or shutdown conditions in the resulting emission factor, and monitoring specifically to obtain emission factors for startups and shutdowns conditions. Several companies indicated that they have analyzed the emissions profile during startup events and during shutdown events. They found that the emission rates during these events departed from those at steady state conditions, but that emissions profiles were consistent between one startup event and another.

Number of samples

Emission samples should be taken over the full range of process conditions within a given operating scenario. To assess the variability of emission rates within the operating scenario, a minimum of three emission test runs is appropriate. If the emission factors based on the three test runs show relatively little variability, i.e., if their relative standard deviation (RSD) is low, then the three sample emission factors can probably be averaged to obtain a robust, representative emission factor for the process. However, if the emission factors based on the three test runs show high variability, that is, a high RSD, then the average of the three emission factors may be a poor estimator of the actual mean emission rate from the process. In this case, additional samples should be taken to develop a robust emission factor.[13] The equation to estimate the RSD is shown in Equation RSD-1.

$$RSD = \frac{s}{\overline{EF}} \qquad \text{(Eq. RSD-1)}$$

Where:

RSD = Relative standard deviation, fraction

s = sample standard deviation, calculated in Eq. RSD-2

EFbar = average emission factor for all test runs combined

Equation RSD-2 is used to estimate the sample standard deviation, s.

$$s = \sqrt{\frac{\left(EF_1 - \overline{EF}\right)^2 + \left(EF_2 - \overline{EF}\right)^2 + \left(EF_3 - \overline{EF}\right)^2 + \ldots}{n-1}} \qquad \text{(Eq. RSD-2)}$$

Where:

s = sample standard deviation

EF_i = the individual emission factor value from test run 1, 2, 3, etc.

EFbar = average emissions factor across all test runs (sample mean emission factor), calculated in Equation RSD-3

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[13] The fact that emission rates from a process show high variability does not mean that a representative emission factor cannot be developed; it simply means that more samples must be taken to do so. Note, however, that if the variability of the process can be attributed to the variability of a controllable and measurable process parameter, it is probably appropriate to develop one or more additional operating scenarios, each with its own emission factor, to capture this variability.

n = number of test runs

Eq. RSD-3 (which corresponds to equation L-20 in the regulatory text) is used to estimate the mean emissions factor, EFbar.

$$\overline{EF} = \frac{EF_1 + EF_2 + EF_3 + ...}{n} \qquad \text{(Eq. RSD-3)}$$

Where:

EFbar = average emissions factor for all test runs combined (sample mean emission factor)

EF_i = the individual emission factor value from test run 1, 2, 3, etc.

n = number of test runs

In general, more samples are required to characterize the mean of a population or parameter that has high variability than are required for a population or parameter that has low variability. The number of samples required to estimate the mean of the parameter with a given level of confidence can be calculated based on the RSD of the samples and on some assumptions about the distribution of the parameter. Where the set of samples is relatively small and only the sample standard deviation “s” is known (rather than the true standard deviation of the parameter), the appropriate statistic is often the Student’s t test. The Student’s t test presumes an approximately normal, bell-shaped distribution of the underlying parameter, which implies that the distribution of the average is the Student’s t distribution.

For this situation, the Student’s t test can be written:

$$-t_{statistic-95\%CI} < \left(\frac{\left(\overline{EF} - EF_T\right)}{\frac{s}{\sqrt{n}}} \right) < +t_{statistic-95\%CI} \qquad \text{(Eq. RSD-4)}$$

Where:

EFbar = Average emission factor across all test runs (sample mean emission factor)

EF_T = True mean emission factor of the process

s = Sample standard deviation

n = Number of samples

$t_{statistic-95\%CI}$ = Value of student’s t statistic chosen to represent a 95-percent confidence interval with n-1 degrees of freedom. For a sample size of 3, this value is 4.30.

Dividing through by the sample mean emission factor, EFbar, we obtain:

$$-t_{statistic-95\%CI} < \left(\frac{\left(\overline{EF} - EF_T\right) / \overline{EF}}{\frac{RSD}{\sqrt{n}}} \right) < +t_{statistic-95\%CI} \qquad \text{(Eq. RSD-5)}$$

To choose a RSD above which we will require more than three samples, we first decide how much error we are willing to tolerate in our emission factor. Suppose we want the emission factor to have a 95 percent chance of being within 30 percent of the true mean emission rate of the process. The requirement for the emission factor to be within 30 percent of the true mean emission rate can be expressed as follows:

$$\left((\overline{EF} - EF_T) / \overline{EF}\right) < 0.3 \qquad \text{(Eq. RSD-6)}$$

Equation RSD-5 can also be rearranged as follows:

$$\left((\overline{EF} - EF_T) / \overline{EF}\right) < \frac{RSD}{\sqrt{n}} * t_{statistic-95\%CI} \qquad \text{(Eq. RSD-7)}$$

Subtracting Equation RSD-7 from Equation RSD-6, we obtain:

$$0 < 0.3 - \frac{RSD}{\sqrt{n}} * t_{statistic-95\%CI}$$

Plugging in the values for t and n and solving for RSD, we obtain

$$\frac{0.3 * \sqrt{3}}{4.3} > RSD$$

$$0.12 > RSD$$

We conclude that if the RSD exceeds 0.12 (or 12 percent), we should test more than three samples. Unfortunately, it may be difficult to obtain an RSD of less than 0.12 even when the real emission rate is nearly constant. This is because the error of the concentration measurements used in the testing can be near 10 percent. Thus, we might want to consider whether we can tolerate a somewhat higher error in our emission factor.[14] If we require that the emission factor be within 40 percent of the true mean emission rate and solve the above equation, we arrive at the conclusion that we should test more if the RSD exceeds 0.16 (16 percent). If we require that the emission factor be within 50 percent of the true mean emission rate (with 95-percent confidence) and solve the above equation, we arrive at the conclusion that we should test more if the RSD exceeds 0.20 (20 percent).

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[14] Another approach to minimizing the error is to require more samples initially, e.g., 4 instead of 3. With 4 initial samples, the emission factor has a 95 percent chance of being within 30 percent of the true mean emission rate if the RSD is less than 19 percent.

With an additional three samples (n=6), the uncertainty of the emission factor declines significantly. For n = 6, Equation RSD-5 becomes:

$$-2.57 < \left(\frac{\left(\overline{EF} - EF_T\right) / \overline{EF}}{\frac{RSD}{\sqrt{6}}} \right) < +2.57$$

Plugging an RSD of 0.20 (20 percent) into this equation, we find that after six samples, there is a 95 percent chance that the sample mean (emission factor) is within 21 percent of the true mean (average emission rate of the process).

4. Updates to emission factors and emission calculation factors.

The emission rate from a process is likely to change as the process evolves or is altered. Process changes that can affect the fluorinated GHG emission rate include changes in raw materials, equipment, production levels, or operating conditions. These changes can occur all at once or gradually, over time. Facilities that have measured and re-measured their emission factors over a period of several years have found that gradual, incremental changes to the process (e.g., to improve yields) have significantly changed emission factors[15]. To ensure that emission factors and emission calculation factors continue to accurately represent emission rates, they should be updated when significant process changes occur. In addition, it may be appropriate to update emission and emission calculation factors at regular intervals (e.g., five to ten years) to capture the cumulative impact of small changes to the process.

5. Potential Process Vent Emission Threshold.

In discussions with EPA, representatives of fluorinated gas producers stated that more effort and resources should be expended to accurately estimate the size of large emission streams than to estimate the size of small ones. Consistent with this principle, EPA evaluated process vent emissions cutoffs above which facilities would be required to conduct emissions testing to develop a site-specific emissions factor and below which facilities could conduct emissions calculations to develop a site-specific emissions factor.

There are various rules for other regulatory programs that have established emission cutoffs above and below which there are different control, monitoring, and reporting requirements. For example, there are process or process vent cutoffs in various NESHAP rules in 40 CFR part 63, such as subpart GGG for Pharmaceutical Manufacturing, subpart FFFF for Miscellaneous Organic NESHAP (MON), and subpart VVVVVV for Chemical Manufacturing Area Source rule. Because some producers mentioned the rule requirement cutoffs in subpart FFFF, Miscellaneous Organic NESHAP (MON), the initial step in the cutoff development was reviewing the 10,000 lb/yr (i.e., 5 ton/yr) of uncontrolled organic HAP emissions cutoff for processes in that rule. (While these data and facility practices for the MON source category may not be completely analogous to the data and practices at fluorinated gas production facilities, this information was used to inform the reporting rule-making process.) Similar to the fluorinated gas production industry, the MON source category includes both continuous and batch processes.

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[15] Based on conversations with Fluorinated GHG producers, as referenced in Section 7.

At the MON facilities, we looked at the emissions levels of MON process vents to identify the number of vents covered and the emissions covered by various cutoffs. For continuous processes, approximately 26 percent of process vents have emissions greater >10,000 lb/yr and more than 99 percent of the total organic HAP emissions from continuous process vents occur from these vents. For batch processes, 13 percent of batch process vents have emissions >10,000 lb/yr and the organic HAP emissions from these vents are 96 percent of the total organic HAP emissions from batch process vents. The 10,000 lb/yr organic HAP cutoff for requiring control of the process vent in the MON rule provides a good balance for minimizing the number of process vents required to implement control and maximizing the emissions covered or captured by the rule.

In evaluating cutoffs for the process vents in the fluorinated gas production source category, we began by analyzing a 10,000 lb/yr fluorinated GHG uncontrolled emissions cutoff. Because the quantities of these emissions in terms of CO_2e would vary significantly depending on the specific fluorinated GHG compound emitted and its GWP, we decided to evaluate the cutoff in terms of CO_2e. We assumed an average GWP of approximately 2,000 for the fluorinated GHG, and given the cutoff value of 10,000 lb/yr fluorinated GHG, we developed a cutoff of 10,000 mt CO_2e. Process vents above the 10,000 lb/yr limit would be required to conduct an emissions test to develop a site-specific emissions factor for the vent, and process vents below the 10,000 mt CO_2e could develop a site-specific emissions calculation factor based on engineering calculations or engineering assessments.

Depending on the specific fluorinated GHG emitted, the emissions of the fluorinated GHG in terms of the actual gas could vary significantly. In Table 4, the emissions in terms of the fluorinated compounds that are translated from the CO_2e cutoff are shown. The fluorinated compounds are shown in order of increasing GWP. For example, for fluorinated GHG compounds as diverse as HFC-134a to SF_6, the cutoff of 10,000 mt CO_2e would translate into fluorinated GHG emissions ranging from 16,962 lb/yr to 923 lb/yr, respectively. However, the detection limits of fluorinated GHG, depending on process vent flow rates, are likely sufficiently low to allow detection and quantification of these compounds at these emission levels.

The emission threshold for process vents could also be based on controlled emissions, for example, emission levels considering destruction efficiency are less than 10,000 mtCO2e on an annual basis.

Another potential approach for selecting a process vent cutoff might include a combined approach, i.e., meeting both a CO_2e emissions cutoff and also a cutoff in terms of pounds of fluorinated GHG. For example, if a process vent had emissions less than 25,000 mt CO_2e and also less than 10,000 lb of fluorinated GHG emissions, i.e., the process vent meets both criteria, then it would be considered below the cutoff.

An issue related to setting a process vent cutoff based on CO_2e is related to fluorinated GHGs that do not have published GWP. In this instance, a lower level cutoff could be established for those fluorinated GHG whose GWP does not appear in Table A-1 of 40 CFR part 98 subpart A, for example, less than 1 metric ton for emissions that include a compound without GWP. In addition, an average GWP, e.g., average GWP of 2,000, could be applied for all fluorinated GHG whose GWP does not appear in Table A-1 of 40 CFR part 98 subpart A.

Table 4. Analysis of Uncontrolled Process Vent Cutoffs: Translate Emissions from CO_2e to Pounds of Fluorinated GHG, and vice versa.[1]

Vent limit in mtCO2e	**In pounds of fluorinated GHG:**						
	HFC-134a	**HFC-125**	**HFC-143a**	**CF4**	**C2F6**	**NF3**	**SF6**
Convert CO2e vent cutoff to lb of fluorinated GHG							
25,000	42,404 *	19,688 *	14,507 *	8,481	5,992	3,205	2,306
20,000	33,923 *	15,750 *	11,605 *	6,785	4,793	2,564	1,845
10,000	**16,962 ***	**7,875**	**5,803**	**3,392**	**2,397**	**1,282**	**923**
5,000	8,481	3,938	2,901	1,696	1,198	641	461
Vent limit in pounds of fluorinated GHG	**In mtCO$_2$e:**						
	HFC-134a	**HFC-125**	**HFC-143a**	**CF4**	**C2F6**	**NF3**	**SF6**
Convert lb of fluorinated GHG to mt CO2e							
10,000	5,896	12,698	17,234	29,478 *	41,723 *	78,005 *	108,390 *
5,000	2,948	6,349	8,617	14,739	20,862	39,002	54,195

[1] The GWP for fluorinated GHG are HFC-134a is 1,300; HFC-125 is 2,800; HFC-143a is 3,800; CF4 is 6,500 C2F6 is 9,200; NF3 is 17,200; and SF6 is 23,900.

* denotes that the level exceeds a 10,000-lb cutoff (in top table) or a 10,000-mtCO_2e cutoff (in bottom table).

6. Process Vent Preliminary Emission Estimates.

To determine whether a process vent is above or below the 10,000 mt CO_2e threshold, facilities could use any of several emission estimation methods discussed above. In this preliminary step, it seems reasonable to allow use of engineering calculations or engineering assessments similar to those identified in Section 3.B.iii.2 to determine the emissions of fluorinated GHG from the process. Acceptable calculation methods for uncontrolled and controlled process vent emissions may include those from various rule text or guidance documents, such as the MON, Pharmaceutical, and other examples provided in Section 3.B.iii.2 above.

Engineering assessments are another reasonable approach to determining preliminary emissions from process vents. Engineering assessments include the types of information discussed in Section 3.B.iii.2 above (previous test data, bench-scale or pilot-scale test data, design analysis, etc.) Facilities typically have component and composition data available from the original research and development activities on the process and from the process' lifetime of operation. For process vent emissions determinations, facilities could conduct an engineering assessment to calculate uncontrolled emissions for each process vent and for each emission episode, and apply destruction efficiencies for periods of control, as applicable.

7. Current Plant Practices for Process Vent Monitoring

Several facilities with fluorinated gas production processes have indicated that they conduct monitoring and analysis on individual process vents and that they characterize streams from processes. They typically develop facility-specific or process-specific EFs and track production activity data to estimate fluorinated GHG emissions.

Facilities indicated that a variety of approaches are used to estimate fluorinated GHG emissions and develop process-specific emissions factors, including sampling and measurement (i.e., direct testing) and chemical engineering calculations and estimates. At most facilities, a combination of these approaches is used to estimate fluorinated GHG emissions from the various process vents at the site. Some facilities indicated, for example, that facility staff measure the concentrations and flows for reactor vessel process vents and conduct engineering calculations to estimate concentration and flows from process dryers. Engineering calculations are based on common chemical engineering principles and empirically based data and process knowledge. The engineering calculations may also be based on emission estimation equations contained in rules, for example in the Pharmaceutical NESHAP, or may be conducted using purchased process modeling software packages, such as ASPEN and EmissionsCalculator.

Facilities indicated that each of these approaches, emission testing and engineering calculations, are valid and produce reasonable fluorinated GHG emission estimates and that flexibility in which approach is applied to any particular process vent is appropriate. Facilities particularly noted that they match the level of effort and “rigorousness” in the emissions determination approach with the emissions source size. That is, they devote more effort to characterizing emissions from relatively large fluorinated GHG emissions points, pursuing emissions testing for these sources, and less effort to characterizing emissions from relatively small fluorinated GHG emissions points, applying engineering calculations to these sources. Some facilities noted that certain process vents are not measured directly because the emission stream contains a compound that is hazardous for plant and personnel safety, e.g., if HF is present in a stream. The facilities noted that emission points that are not safe to measure are typically estimated from chemical engineering calculations and from process design data. In using FTIR instruments, some vendors have noted that specialty glass sample cells are available that are more resistant to HF. Some facilities noted that measuring fluorinated organics can be done easily if the HF can be removed from the sampling stream. One option may be to flow the sample stream through containers of water to remove HF prior to measuring the fluorinated organic. While this approach may be successful at measuring the fluorinated organic, the flow rate of the stream cannot be determined with any accuracy. This approach also does not alleviate the personnel safety concerns.

Facilities further expanded on the use of previous stream analysis results as appropriate data to be used. Generally, facilities have a good understanding of the chemistry for all processes and understand what raw materials are fed to the process, what side reactions occur, and what products and by-products are created. Facilities have laboratory scale, pilot plant, and full scale streams analysis results. Facilities noted that in particular, at the bench-scale phase of a product and process development, they analyze all streams to identify all species and compounds such as product, byproducts, and waste. The process design from when the process was originally developed and built is detailed, and more recently installed processes will have excellent design and chemistry documentation available. Older processes may tend to have less detail.

Facilities indicated that they typically conduct an initial analysis to develop the process-specific emission factor or emission calculation factor and do not continuously measure and calculate emissions from process vents and streams. When there is a process change, i.e., a change in the operating conditions or a change in the process equipment used, they will conduct a reanalysis of the process. Facilities pointed out that prior to making process change, they analyze the theoretical chemistry and predict the likely changes in the set of fluorinated GHG compounds generated and in the fluorinated GHG emissions levels. They typically begin with engineering calculations to determine the impacts of the change on species generated or emission levels, and follow that with retesting and recalculations when appropriate. Some facilities noted that after a process change, they will sample and analyze to identify every species or compound generated, in either process vents or process streams.

8. Potential use of continuous emissions monitors to measure emissions from vents.

Another potential monitoring option EPA considered was requiring that facilities measure emissions from fluorinated gas production facilities using continuous emissions monitors (CEMS). If properly selected and maintained, CEMS would be expected to provide estimates of emissions more accurate than either the mass-balance or the process-vent approach. Under this approach, facilities would install and operate CEMS capable of measuring fluorinated GHGs to measure process emissions. The requirements for the CEMs would be similar to those in subpart C, adjusted, as appropriate, to accommodate CEMS for fluorinated gases. One possible option is to use Fourier Transform Infrared Spectrometers (FTIRs) CEMS in scrubber stacks to measure emissions. FTIR spectroscopy is presently used to conduct short-term fluorinated GHG emission measurements from processes. In recent discussions with FTIR CEMS vendors, they noted that the units can operate continuously. Some units require liquid nitrogen cooling and the liquid nitrogen vessel (dewar) has a limited capacity. These nitrogen cooled units can operate for up to 12 hours on a single charge (nitrogen), and continuous operation of the unit could be achieved through the use of an extended dewar with an automated fill cycle. With the extended dewar, the unit can operate for approximately 3 days. (The detector is nitrogen cooled, and a dewar, which is an insulated container with a vacuum between its inner and outer layers, is used to hold the liquid nitrogen.) FTIR CEMS vendors noted that the sample cell can be adjusted to accommodate concentration levels, where a shorter cell length can be used for higher concentrations and longer cell lengths can be used for lower concentrations. Another option for high concentrations might include use of dilution and a standard cell. The vendor typically sets up a software package based on the compounds expected in the measured vent, and the software is revised for other compounds as needed.

However, potential drawbacks to requiring CEMS are that they would be relatively expensive to install and they may not tolerate the acidic and reactive environments (e.g., high HF concentration) found in vents at many fluorinated gas production facilities. Some FTIR CEMS vendors utilize specially configured gas cells that run hot and utilize mirror coatings to protect the cell from high HF concentrations and use special types of unit seals (o-rings) that are inert to corrosive compounds. In any case, vendors noted that HF in the vent streams is a common problem, and that HF concentrations in the percent range are a difficult issue to deal with. The latter concern might be mitigated by installing CEMS after a scrubber, if this is practicable. Given these potential concerns, it may be appropriate to require CEMS for particularly large emission streams, e.g., those resulting in emissions of more than 50,000 $mtCO_2e$ annually.

9. Equipment Leak Emissions Estimates.

Process vents are only one of several sources of fluorinated GHG emissions at fluorinated gas production facilities. Another potentially significant source is equipment leaks, whose emissions do not occur through process vents. Emissions from equipment leaks may be estimated using EPA Method 21, EPA Protocol for Equipment Leak Emission Estimates (EPA-

453/R-95-017) (EPA Protocol for Equipment Leaks), and other validated methods and procedures capable of detecting the analyte of interest at the concentration of interest. Leak monitoring could be performed periodically, which typically would be quarterly, semi-annually, or annually. Due to the nature and scope of the reporting rule, which is focused on monitoring and emission estimation rather than on leak repair (control), equipment leak monitoring on an annual basis should be sufficient. The EPA Protocol for Equipment Leaks includes four methods for estimating equipment leaks. These are, from least to most accurate, the Average Emission Factor Approach, the Screening Ranges Approach, EPA Correlation Approach, and the Unit-Specific Correlation Approach. The Average Emission Factor Approach relies on emission factors and equipment counts, the service of each component, the composition of the stream, and the length of time the equipment was in service to estimate emissions, and does not require any real-world data be collected from the processes. The remaining three methods, The Screening Ranges Approach, EPA Correlation Approach and the Unit-Specific Correlation Approach all depend on the collection and use of facility-specific and process-specific screening data to estimate emissions.

To use these three screening data methods, the facility would need to have (or develop) Response Factors relating concentrations of the target fluorinated GHG (or surrogate gas co-occurring in the stream) to concentrations of the gas with which the leak detector is calibrated. Our understanding is that flame ionization detectors (FIDs) are generally insensitive to fluorinated GHGs, and that they are therefore not likely to be effective for detecting and quantifying fluorinated GHG leaks. An exception to this would be a situation in which the fluorinated GHG occurred in a stream along with a substance (e.g., a hydrocarbon) to which the FID was sensitive; in this case, the other substance could be used as a surrogate to quantify leaks from the stream. We understand that at least two fluorocarbon producers currently use methods in the EPA Protocol for Equipment Leaks to quantify their emissions of fluorinated GHGs with different levels of accuracy and precision. Other analytical techniques that are sensitive to fluorinated compounds may be available to monitor concentrations of equipment leaks, including photoionization, ultraviolet, infrared, and others.

A preliminary review revealed a handful of detectors capable of detecting fluorinated GHGs. While some fluorinated GHGs can be detected using instruments that meet EPA Method 21 specifications, others cannot. These detectors use various operating principles, including, infrared, photoionization and ultraviolet detection. Although instruments for detecting leaks of HFCs and SF_6 from air-conditioning, refrigeration, and electrical equipment have existed for some time, most of these instruments do not quantify emissions and/or detect only one or two gases. In many cases, therefore, these instruments are not capable of quantifying emissions of the broad range of fluorinated GHGs that can leak from process equipment in fluorinated gas production facilities. One issue that arose with these detectors was their high sensitivity. For some of the equipment, maximum readings were well below the 10,000 ppm leak/no-leak threshold of the Screening Ranges Approach, meaning that the Screening Ranges Approach could not be used with these detectors. Those capable of reading the 10,000 ppm concentration had sampling rates that exceeded the rates established by Method 21. However, the EPA Correlation Approach and the Unit-Specific Correlation Approach could be used with these detectors, assuming that the detectors do not hit their maximum readings (peg) in the facility.

Under the preliminary review of detectors, EPA did not identify equipment capable of detecting and quantifying all fluorinated GHG emissions that can also meet all of the Method 21 specifications, or found that the equipment reaches its maximum ("pegs") at relatively low concentrations. In general, in identifying the need for alternatives to EPA methods, EPA discovered that the equipment and methods for detecting and quantifying emissions of fluorinated GHGs from equipment leaks have not advanced as far as those for monitoring emissions of VOC from equipment leaks. Additional alternatives for monitoring of equipment leaks beyond Method 21 and the EPA Protocol for Equipment Leaks are likely warranted. For example, facilities could monitor leaks using other approaches such as soap bubble testing combined with the Average Emission Factors or the Screening Ranges Approach; use of alternatives allowed under other regulatory programs, such as alternative leak detection methods in 40 CFR 63, 63.1036, alternative means of emission limitations: batch processes; or use of alternative work practices using optical imaging combined with Average Emission Factors. One facility noted that they conducted room air exhaust monitoring to identify emissions from equipment leaks and simultaneously conducted direct monitoring of pieces of equipment in service within the room; the analytical results from the room air exhaust showed that concentrations were at non-detect levels for all but one or two F GHG compounds, and the monitoring of pieces of equipment showed non-detect levels for all but one or two F GHG. In a monitoring approach for room air exhausts, facilities would need to explain how the approach accounts for variations in concentrations in the room air and possibility that some emissions may not be accounted for in the measurements (i.e., concentrations below non-detect levels due to large room air volume or room air exhaust gas flow).

Another approach for monitoring leaks from pieces of equipment may include use of the Alternative Work Practice (AWP) for EPA Method 21 (similar to monitoring requirements under 40 CFR part 60, subpart A, §40 CFR part 60.18; 40 CFR part 63, subpart A, §40 CFR part 63.11; or 40 CFR part 65, subpart A, §40 CFR part 65.7). This approach would include monitoring leaking equipment with an optical gas imaging instrument. Emissions from those pieces of equipment found to be leaking could be estimated based on emission factors. Under this approach, facilities could image each piece of equipment in fluorinated GHG service, and all emissions imaged by the optical gas imaging instrument would be considered leaks and would be subject to emissions estimation.

Several fluorinated gas producers have indicated that equipment leaks account for a small share of facility-wide fluorinated GHG emissions. Although this generalization is largely based on experience with VOC and HAP, two fluorinated gas producers have surveyed at least some of their process equipment with detectors sensitive to fluorinated GHGs and have found a similar low level of emissions.

10. Container Heel Venting

In addition to the emission sources mentioned above, the venting of container or cylinder heels is an additional source of fluorinated GHG emissions. Emissions from returned containers and from recycling depend heavily on the practices of individual facilities. If the facility recovers container heels or simply refills containers on top of heels, then emissions from returned containers will be small. However, if the facility vents heels, then emissions can be significant, even dominating overall facility emission rates.

According to the 2006 IPCC Guidelines [16], SF_6 production operations in Germany whose customers did not require highly purified gas had emission rates in the range of 0.2 percent of the total quantity of SF_6 produced. On the other hand, SF_6 production operations in Japan whose customers required highly purified gas had emission rates of 8 percent due to the venting of heels whose purity was in doubt.

An analysis of the possible emissions from venting of residual fluorinated GHGs in containers showed that these emissions could be significant. Cylinder heel venting was assumed to occur only for fluorinated GHG that are used in etch and chemical vapor deposition chamber clean processes in electronics. Because the electronics industry requires extremely high purity for these etch and chamber clean gases, fluorinated gas producers may be reluctant to recycle them, because recycling could inadvertently introduce impurities. Chemicals made in U.S. that are used in etch and chamber clean processes include CF_4, C_2F_6, C_3F_8, c-C_4F_8O, CHF_3 (HFC-23), NF_3, SF_6.[17] A total of 6 companies produce these etch and chamber clean gases at 7 facilities in the U.S. To estimate the annual emissions from cylinder heel venting, it was assumed that 100 percent of the production of each of these chemicals, except SF_6, was used in electronics. For SF_6, it was assumed that approximately 10 percent of SF_6 production was used in electronics, based on historical SF_6 usage patterns. For 2006, the total production of etch and chamber clean fluorinated GHG listed above, including 10 percent of the SF_6 production, was over 60 million mtCO_2e. Assuming that half of the producing facilities are venting cylinders and emit a 10 percent heel, the emissions from cylinder heel venting are estimated to be approximately 3 million mtCO_2e.

The situation is similar for recycling. Emissions during recycling include emissions during transfer of gas from containers to process equipment, but they also include emissions associated with ridding the gas of contaminants, such as noncondensables (air, nitrogen, etc.) and oil. (Since lubricants are chosen to be miscible with refrigerants, a significant quantity of refrigerant can remain mixed into the oil when the oil is removed from the system or container.) If facilities carefully recover and purify gas that is returned for recycling, emissions are likely to be in the neighborhood of one percent or less of the quantities returned.[18] However, if facilities use crude methods to purge noncondensables from containers, e.g., venting from the headspace of the cylinder, or if they don't attempt to minimize fluorinated GHG emissions from lubricants, then emissions can be closer to five or ten percent of the quantities returned. (Early standards for recycling equipment allowed emissions from purging as high as five percent;[19] these limits have been lowered considerably since.) In the worst case, facilities could simply vent returned fluorinated GHGs, e.g., in cases where they are irretrievably contaminated.

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[16] From IPCC 2006, 2006 IPCC Guidelines for National Greenhouse Gas Inventories, Prepared by the National Greenhouse Gas Inventories Programme, Eggleston H.S., Buendia L., Miwa K., Ngara T. and Tanabe K. (eds). Published: IGES, Japan., page 3,104 of Volume 3, Industrial Processes and Product Use.

[17] CH_2F_2 (HFC-32) is also made in the U.S. and is used in etch and clean, but the fraction of the gas used for this purpose was not known and therefore it was not included in the total (although it is expected to comprise a small share of the total).

[18] From IPCC Volume 3, Chapter 8. http://www.ipcc-nggip.iges.or.jp/public/2006gl/pdf/3_Volume3/V3_8_Ch8_Other_Product.pdf

[19] SAE J1990, 1989 Extraction and Recycle Equipment for Mobile Automotive Air-Conditioning Systems; ARI Standard 740-1993, For Performance of Refrigerant Recovery and/or Recycling Equipment.

To estimate fluorinated GHG emissions from container venting, facilities could either measure the emissions vented from each container or develop site-specific emission factors, i.e., a heel factor, for each combination of fluorinated GHG, container size, and container type that are vented. To measure the fluorinated GHG emissions, a facility would make a measurement for each container, either by weighing the container or by measuring the pressure of the container and calculating the mass using an equation of state.

The total emissions for venting of residual fluorinated GHG from containers may be summed at the facility based on the number of containers received and vented. Equation L-32 could be used to calculate the annual emissions of each fluorinated GHG…

$$E_{Cf} = \sum_{1}^{n} H_{Bfj} - \sum_{1}^{n} H_{Efj} \qquad \text{(Eq. L-32)}$$

Where:

E_{Cf} = Total mass of each fluorinated GHG f emitted from the facility through venting of residual fluorinated GHG from containers, annual basis (kg/year).
H_{Bfj} = Mass of residual fluorinated GHG f in container j when received by facility.
H_{Efj} = Mass of residual fluorinated GHG f in container j after evacuation by facility. (Facility may equate to zero.)
n = Number of vented containers for each fluorinated GHG f.

A facility could develop heel factors based on representative samples of the containers received by the facility from fluorinated GHG users. A facility would select a representative sample of containers for each combination of fluorinated GHG, container size, and container type that a facility vents. A representative sample would reflect the full range of quantities of residual gas returned in that container size and type. To determine the residual weight or pressure, facilities could monitor the mass or the pressure of your cylinders/containers. If the facility monitors the pressure, the ideal gas law in equation L-33 would be used to convert the pressure to mass.

$$pV=ZnRT \qquad \text{(Eq. L-33)}$$

Where:

p = Absolute pressure of the gas (Pa)

V = Volume of the gas (m^3)

Z = Compressibility factor

n = Amount of substance of the gas (moles)

R = Gas constant (8.314 Joule/Kelvin mole)

T = Absolute temperature (K)

Facilities would use the container residual mass for each specific fluorinated GHG to determine what mass fraction of the initial mass in the container is vented.

Facilities would then calculate the annual fluorinated GHG emissions based on the gas-specific heel factor and the number of containers that are returned to the facility, using Equation L-34.

$$E_{Cf} = \sum_{j=1}^{n} h_{fj} * N_{fj} * F_{fj} \qquad \text{(Eq. L-34)}$$

Where:

E_{Cf} = Total mass of each fluorinated GHG f emitted from the facility through venting of residual fluorinated GHG from containers, annual basis (kg/year).

h_{fj} = Facility-wide gas-specific heel factor for input gas f (fraction) and container size and type j, as determined in §98.124(j) of this subpart.

N_{fj} = Number of containers of size and type j returned to the fluorinated gas production facility.

F_{fj} = Full capacity of containers of size and type j containing fluorinated GHG f (kg).

n = Number of combinations of container sizes and types for fluorinated GHG f.

11. Destruction Efficiency Testing

It may be appropriate to require that fluorinated gas producers that destroy F-GHGs conduct emissions testing periodically, for example every five or ten years, to determine the destruction efficiency (DE) of the destruction device. The testing for determining the DE would be similar to the emissions testing that could be conducted to develop site-specific process-vent-specific emission factors. Facilities would need to conduct testing that shows the destruction device can successfully destroy emissions at worse-case operating conditions, for example when operating at high loads reasonably expected to occur and when destroying the most-difficult-to-destroy fluorinated GHG fed into the device (or when destroying a surrogate that was more difficult to destroy than that fluorinated GHG). The last point is particularly important because some fluorinated GHGs (e.g., CF_4, SF_6[20] and other PFCs) are extremely difficult to destroy; DEs determined for other fluorinated GHGs (or for typical Class 1 POHCs) would overestimate the destruction of these fluorinated GHGs.

For destruction of fluorinated GHG compounds to occur, temperatures must be quite high, fuel must be provided, flow rates of fuels and air (or oxygen) must be kept above certain limits, flow rates of fluorinated GHG must be kept below others, and for some particularly

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[20] For example, SF_6 ranks 4th in the Class 1 incinerability rankings of the Office of Research and Development and Office of Solid Waste and Emergency Response of U.S. Environmental Protection Agency's *Guidance on Setting Permit Conditions and Reporting Trial Burn Results Handbook, Volume II.* EPA Publication No. EPA/625/6-89/019. January 1989.

difficult-to-destroy chemicals, pure oxygen must sometimes be fed into the process. If one or more of these process requirements is not met, destruction efficiencies can drop sharply (in some cases, by an order of magnitude or more), and fluorinated GHGs will simply be exhausted from the device. For more discussion of this issue, see the Technical Support Document for Industrial Gas Supply: Production, Transformation, and Destruction of Fluorinated GHGs and N_2O, Docket number EPA-HQ-OAR-2008-0508-041.

In the destruction and removal efficiency testing that is performed at hazardous waste combustors pursuant to part 63, subpart EEE, facilities that demonstrate 99.99 percent DRE for a POHC within a thermal stability class are typically allowed to assume that 99.99 percent DRE would also be achieved for the other compounds in that class and for compounds in other thermal stability classes with lower thermal stability rankings. This approach is based on the general conclusion that, for POHCs that are in the same class and that occur in significant volumes, differences in DREs tend to be small, and that compounds in other thermal stability classes with lower stability rankings are easier to destroy.

However, it would be a misapplication of the thermal stability index to conclude that a combustor that has demonstrated 99.99 percent DRE for any Class 1 compound[21] would also achieve 99.99 percent DRE for SF_6, a Class 1 compound, and for perfluoromethane (CF_4). While achieving 99.99 percent DRE for SF_6 ensures 99.99 percent DRE for other Class 1 compounds, the converse may not be true. SF_6 is substantially more thermally stable than other Class 1 compounds (and CF_4 is substantially more thermally stable than SF_6).

The theoretical considerations that support the conclusion that fluorinated GHGs are extremely thermally stable relate to the high energies of the C-F and S-F bonds. These energies make it difficult to break the bonds through reaction with oxygen, hydrogen, or the hydroxyl radical, the typical means of destroying other class 1 compounds. Essentially, the only path available to destroy these fully fluorinated compounds in hazardous waste combustors or thermal oxidizers is through thermal decomposition at very high temperatures.[22] These temperatures are significantly higher than those required for the thermal decomposition of most other class 1 compounds. For SF_6, the thermal stability index indicates that the temperature to achieve 99 percent destruction with a two-second residence time is 1,090°C; for CF_4, we project that the temperature would be on the order of 1,380°C.[23] Researchers have suggested that CF_4 may break down only in the flame zone.[24]

Experimental evidence supports the idea that SF_6 and CF_4 are difficult to destroy. Due in part to the theoretical considerations outlined above, several studies have evaluated the use of SF_6 as a possible surrogate for POHCs in evaluating DREs. Most studies have verified that the DRE measured for SF_6 is likely to be lower than that for POHCs, i.e., that it is likely to yield a

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[21] Class 1 is the group of POHCs and surrogates with the highest thermal stability, meaning they are the most difficult compounds to destroy.

[22] W. Tsang et al make this case for perfluoromethane in Tsang, W., Burgess Jr., D. R., and Babushok, V. (1998) “On the Incinerability of Highly Fluorinated Organic Compounds,” Combustion Science and Technology, 139:1, 385-402. An analogous argument can be made for sulfur hexafluoride.

[23] SF_6 temperature is from Appendix VIII ranking of POHCs; CF_4 temperature is estimated based on the rate constant provided in Tsang, p. 393.

[24] Tsang, p. 387.

conservative estimate of the DREs for POHCs under most conditions. In one experiment at a full-scale hazardous waste incinerator, the investigators found that even at high-temperature conditions, SF_6 had a DRE that led to emissions approximately an order of magnitude higher than those of other POHCs, including both class 1 and class 2 compounds. At lower-temperature conditions, SF_6 had a DRE that was over 100 times lower than those of other POHCs.[25] As noted above, CF_4 is even more difficult to destroy than SF_6. This has been confirmed in testing of point-of-use thermal abatement devices used in electronics manufacturing, which destroyed CF_4 with an efficiency that was significantly lower (sometimes orders of magnitude lower) than the efficiency with which they destroyed SF_6.[26]

Other fluorinated compounds are not likely to be as stable as CF_4 and SF_6 because they can be dissociated at C-H and C-C bonds (which are weaker than C-F and S-F bonds). Nevertheless, higher molecular weight perfluorocarbons such as C_2F_6 are still expected to be relatively difficult to incinerate.[27] As is true for CF_4, the mechanism of destruction is expected to be thermal decomposition rather than attack by radicals, although the decomposition temperature will be lower than for CF_4 due to the fact that the C-C bond is weaker than the C-F bond.

It may be appropriate to allow facilities to rely on data from destruction device testing that has been conducted within the five or ten years prior to the effective date of the rule. Facilities that have conducted an emissions test on their destruction device within the five or ten years prior to the effective date of the rule may be allowed to use the DE determined during that test if the test was conducted in accordance with the proposed test requirements. Facilities could also potentially use the DREs determined during principal organic hazardous constituent testing and hazardous waste combustor testing, provided those tests determined the DRE based on the most-difficult-to-destroy fluorinated GHG fed into the device (or based on a surrogate that was more difficult to destroy than the most-difficult-to-destroy fluorinated GHG).

C. Other Potentially Significant Emission Points

In addition to the fluorinated GHG emissions captured via the Mass Balance method or either of the Process Vent methods, other potentially significant emission points exist both upstream and downstream of the production measurement. These other emission points under this source category may include fluorinated GHG emissions from equipment leaks, storage tanks, wastewater, container filling (loading), refrigerant blending, and reclamation and recycling processes, , particularly where these emissions occur before the production measurement at

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[25] A. Trenholm, C. Lee, and H. Jermyn, "Full-Scale POHC Incinerability Ranking and Surrogate Testing," 17th Annual RREL Hazardous Waste Research Symposium, EPA Office of Research and Development, EPA/600/9-91/002 April, 1991, pp. 79-88.

[26] USEPA, "Developing a Reliable Fluorinated Greenhouse Gas (F-GHG) Destruction or Removal Efficiency (DRE) Measurement Method for Electronics Manufacturing: A Cooperative Evaluation with Qimonda," March 2008, EPA 430-R-08-017; USEPA, "Developing a Reliable Fluorinated Greenhouse Gas (F-GHG) Destruction or Removal Efficiency (DRE) Measurement Method for Electronics Manufacturing: A Cooperative Evaluation with IBM," June 2009, EPA 430-R-10-004; and USEPA, "Developing a Reliable Fluorinated Greenhouse Gas (F-GHG) Destruction or Removal Efficiency (DRE) Measurement Method for Electronics Manufacturing: A Cooperative Evaluation with NEC Electronics, Inc.," December 2008, EPA 430-R-10-005.

[27] Tsang, p. 401.

fluorinated GHG production facilities. (Equipment leak emissions and container heel evacuation are discussed above in separate sections.)

Fluorinated GHG emissions from wastewater will depend directly on the concentration and volume of the contaminants that are present in the wastewater. Based on an evaluation using EPA's Estimation Program Interface (EPI) Suite, approximately 90 percent or more of all fluorinated GHG compounds present in wastewater will be emitted to the atmosphere. The operating permits for some facilities referred to wastewater treatment activities for fluorinated compounds, although it is unclear what level of emissions might occur from wastewater and whether there would be wastewater emissions at all facilities.

The fluorinated GHG emissions from storage tanks are anticipated to be small to insignificant due to the use of pressurized tanks for storage. Emissions from blending activities are also likely to be relatively small. In both cases, however, emissions can be more significant if leaks or catastrophic failures occur.

Currently, it is EPA's understanding that most fluorinated GHG production facilities measure their production before container filling (loading), e.g., by using flowmeters just upstream of the container connection to measure the mass flowing into the containers. If this is the case, emissions that occur during or after filling (e.g., from hoses and connections) would have been included in the production (supply) measurement. However, if production is measured by weighing containers before and after filling, then emissions during container filling would not have been included in the production measurement. In these cases, facilities using the emission factor approach would need to quantify container filling emissions for completeness.

The IPCC Guidelines (Volume 3, Chapter 7) estimate that emissions related to container management (including refrigerant transfers between containers and handling of returned containers) range between 2 and 10 percent of the refrigerant market.

In the event that the other potentially significant emission points were included under the rule, possible methods for tracking these emissions include engineering estimates (e.g., for container filling), equipment leak testing (e.g., for storage tanks and blending activities), default or site-specific emission factors (all sources), and mass balances (e.g., weighing returned container heels).

4. Procedures for Estimating Missing Data

In the event that a scale or flowmeter normally used to measure reactants, products, by-products, or wastes fails to meet a test to verify its accuracy or precision, malfunctions, or is rendered inoperable, facilities may estimate these quantities using other measurements where these data are available. For example, facilities that ordinarily measure production by metering the flow into the day tank could use the weight of product charged into shipping containers for sale and distribution as a substitute. It is our understanding that the types of flowmeters and scales used to measure fluorocarbon production (e.g., Coriolis meters) are generally quite reliable, and therefore that it should rarely be necessary to rely solely on secondary production measurements. In general, production facilities rely on accurate monitoring and reporting of the inputs and outputs of the production process. In the event that a secondary mass measurement for the stream is not available, producers can use a related parameter and the historical relationship between the related parameter and the missing parameter to estimate the flow.

If concentration measurements are unavailable for some period, we are proposing that the facility use the average of the concentration measurements from just before and just after the period of missing data.

5. QA/QC Requirements

Typical QA/QC requirements for measuring devices include initial and periodic verification and calibration. (For example, see the requirements of EPA's Acid Rain regulations at 40 CFR Part 75.) In this case, it may be appropriate to require an initial verification of flowmeters and weigh scales and periodic calibration in accordance with the applicable industry standards or manufacturer directions. If the flowmeter manufacturer performed this verification at the flowmeter factory and did not recommend a second verification upon installation, the factory verification should suffice. Calibration of flowmeters and scales could be performed prior to the reporting year; after the initial calibration, recalibration could be performed as frequently as specified by the manufacturer. Under this approach, producers could perform the verification and calibration of their weigh scales during routine product line maintenance.

For the gas chromatography analytical method described under the monitoring section of this document, monthly calibration, using known certified standards should be used. The calibration involves validating accurate measurement of these fluorocarbon standards across a range of possible concentrations, depending on which process streams are being measured.

For development of process-vent-specific emission factors, facilities would need to conduct and meet the QA/QC procedures specified in the test methods used.

6. Reporting and Recordkeeping Procedures

To verify and document their emissions estimates, owners and operators of facilities producing fluorinated gases would report the following information, depending on their activities and on the estimation approach that they used. All facilities would report both their fluorinated GHG emissions and the quantities used to estimate them on a process-specific basis. They would also report the results of each initial scoping speciation, specifically, the chemical identities of the contents of potentially emitted streams. Facilities using the mass-balance approach would report the masses of the reactants, products, by-products, and wastes, and, if applicable, the quantities of any product in the by-products and/or wastes (if that product is emitted at the facility). They would also report the chemical identities of reactants, products, and by-products, along with the chemical equations used to estimate emissions. Facilities using the emission factor approach would report the activity data used to calculate emissions (e.g., the quantity produced, transformed, or destroyed) and the emission factors used to estimate them. Owners and operators would report annual totals of these quantities by process and facility.

Where fluorinated GHG production facilities have estimated missing data, the facility would report the reason the data were missing, the length of time the data were missing, the method used to estimate the missing data, and the estimates of those data.

Maintaining records of the information used to determine the reported GHG emissions would enable us to verify that the GHG emissions monitoring and calculations were performed correctly. Owners and operators of facilities producing fluorinated GHGs would retain records documenting the data reported, including records of monthly emission estimation calculations, all data that went in to the calculations, calibration records for flowmeters, scales, and gas chromatographs, and documentation of emission factor development activities.

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Appendix A.

Mass Balance Approach: Equations from Re-Proposal TSD (March 22, 2010).

Appendix A

Mass Balance Approach: Equations from Re-Proposal TSD (March 22, 2010).

In the mass-balance approach, facilities weigh or meter the reactants fed into the process, the product resulting from the process, and any byproducts and wastes that are removed from the process (i.e., sent to the thermal oxidizer or other equipment, not immediately recycled back into the process). Facilities then calculate the difference between the mass of reactants fed into the process and the sum of the masses of the main product and those of any byproducts and/or wastes. This difference is then assigned to loss of reactants, loss of product, and/or conversion to byproducts.

The following set of equations was included in the re-proposal TSD for the mass-balancing method for estimating fluorinated GHG emission.

The total mass of each fluorinated GHG product emitted annually from all fluorinated gas production processes would be estimated by using Equation L-5:

$$E_P = \sum_{p=1}^{n} \sum_{i=1}^{m} E_{Pip} \qquad \text{(Eq. L-5)}$$

Where:

E_P = Total mass of each fluorinated GHG product emitted annually from all production processes (metric tons).

E_{Pip} = Total mass of the fluorinated GHG product emitted from production process i over the period p (metric tons, defined in Equation L-7).

n = Number of concentration and flow measurement periods for the year.

m = Number of production processes.

The total mass of fluorinated GHG by-product k emitted annually from all fluorinated gas production processes shall be estimated by using Equation L-6:

$$E_{Bk} = \sum_{p=1}^{n} \sum_{i=1}^{m} E_{Bkip} \qquad \text{(Eq. L-6)}$$

Where:

E_{Bk} = Total mass of fluorinated GHG by-product k emitted annually from all production processes (metric tons).

E_{Bkip} = Total mass of fluorinated GHG by-product k emitted from production process i over the period p (metric tons, defined in Equation L-8 on this section).

n = Number of concentration and flow measurement periods for the year.

m = Number of production processes.

The total mass of each fluorinated GHG product emitted from production process i over the period p would be estimated by calculating the difference between the expected production of the fluorinated GHG based on the consumption of one of the reactants (e.g., HF or a chlorofluorocarbon reactant) and the measured production of the fluorinated GHG, accounting for yield losses related to by-products and wastes. This calculation shall be performed using Equation L-7.

$$E_{Pip} = \frac{R * MW_P * SC_P}{MW_R * SC_R} - P - \sum_{j=1}^{q}\left(C_P * W_{Dj}\right) - \sum_{k=1}^{u} L_{Bkip} \qquad \text{(Eq.L-7)}$$

Where:

E_{Pip} = Total mass of each fluorinated GHG product emitted from production process i over the period p (metric tons).

P = Total mass of the fluorinated GHG produced by production process i over the period p (metric tons).

R = Total mass of the reactant that is consumed by production process i over the period p (metric tons, defined in Equation L-8).

MW_R = Molecular weight of the reactant.

MW_P = Molecular weight of the fluorinated GHG produced.

SC_R = Stoichiometric coefficient of the reactant.

SC_P = Stoichiometric coefficient of the fluorinated GHG produced.

c_P = Concentration (mass fraction) of the fluorinated GHG product in stream j of destroyed wastes. If this concentration is only a trace concentration, c_P is equal to zero.

W_{Dj} = Mass of wastes removed from production process i in stream j and destroyed over the period p (metric tons, defined in Equation L-9).

L_{Bkip} = Yield loss related to by-product k for production process i over the period p (metric tons, defined in Equation L-10).

q = Number of waste streams destroyed in production process i.

u = Number of by-products generated in production process i.

The total mass of the reactant that is consumed by production process i over the period p shall be estimated by using Equation L-8:

$$R = R_F - R_R \qquad \text{(Eq. L-8)}$$

Where:

R = Total mass of the reactant that is consumed by production process i over the period p (metric tons).

R_F = Total mass of the reactant that is fed into production process i over the period p (metric tons).

R_R = Total mass of the reactant that is permanently removed from production process i over the period p (metric tons).

The mass of wastes removed from production process i in stream j and destroyed over the period p would be estimated using Equation L-9:

$$W_{Dj} = W_{Fj} * DE \qquad \text{(Eq. L-9)}$$

Where:

W_{Dj} = The mass of wastes removed from production process i in stream j and destroyed over the period p (metric tons).

W_{Fj} = The total mass of wastes removed from production process i in stream j and fed into the destruction device over the period p (metric tons).

DE = Destruction Efficiency of the destruction device (fraction).

Yield loss related to by-product k for production process i over period p would be estimated using Equation L-10:

$$L_{Bkip} = \frac{\left(B_{kip} * MW_P * ME_{Bk}\right)}{\left(MW_{Bk} * ME_P\right)} \qquad \text{(Eq. L-10)}$$

Where:

L_{Bkip} = Yield loss related to by-product k for production process i over the period p (metric tons).

B_{kip} = Mass of by-product k generated by production process i over the period p (metric tons, defined in Equation L-11).

MW_P = Molecular weight of the fluorinated GHG produced.

MW_{Bk} = Molecular weight of by-product k.

ME_{Bk} = Moles of the element shared by the reactant, product, and by-product k per mole of by-product k.

ME_P = Moles of the element shared by the reactant, product, and by-product k per mole of the product.

If by-product k is responsible for yield loss in production process i and occurs in any process stream in more than trace concentrations, the mass of by-product k generated by production process i over the period p would be estimated using Equation L-11:

$$B_{kip} = \sum_{j}^{q} c_{Bjk} * S_j \qquad \text{(Eq. L-11)}$$

Where:

B_{kip} = Mass of by-product k generated by production process i over the period p (metric tons).

c_{Bkj} = Concentration (mass fraction) of the by-product k in stream j of production process i over the period p. If this concentration is only a trace concentration, c_{Bkj} is equal to zero.

S_j = Mass flow of process stream j of production process i over the period p.

q = Number of streams in production process i.

If by-product k is responsible for yield loss, is a fluorinated GHG, occurs in any process stream in more than trace concentrations, and is not completely recaptured or completely destroyed; the total mass of by-product k emitted from production process i over the period p would be estimated using Equation L-12:

$$E_{Bkip} = B_{kip} - \sum_{j=1}^{q} c_{Bkj} * W_{Dj} - \sum_{l=1}^{x} c_{Bkl} * S_{Rl} \qquad \text{(Eq. L-12)}$$

Where:

E_{Bkip} = Mass of by-product k emitted from production process i over the period p (metric tons).

B_{kip} = Mass of by-product k generated by production process i over the period p (metric tons).

c_{Bkj} = Concentration (mass fraction) of the by-product k in stream j of destroyed wastes over the period p. If this concentration is only a trace concentration, c_{Bj} is equal to zero.

W_{Dj} = The mass of wastes that are removed from production process i in stream j and that are destroyed over the period p (metric tons, defined in Equation L-9).

c_{Bkl} = The concentration (mass fraction) of the by-product k in stream l of recaptured material over the period p. If this concentration is only a trace concentration, c_{Bkl} is equal to zero.

S_{Rl} = The mass of materials that are removed from production process i in stream l and that are recaptured over the period p.

q = Number of waste streams destroyed in production process i.

x = Number of streams recaptured in production process i.

Choice of Reactant Whose Yield Is Measured.

EPA has considered use of one reactant to estimate emissions under the mass-balance approach (rather than both as originally proposed). Some fluorinated GHG producers have noted that, for various reasons, it is sometimes considerably more difficult to track the yields of some reactants than others (e.g., HF vs. an organic feedstock). EPA notes that facilities estimating their emissions based on the yield of one reactant would still need to be able to demonstrate that their estimate met the statistical error test that might be required.

If an alternate reactant was measured, it would be necessary for facilities to be extremely thorough in the monitoring approach and calculations in order to account for all potential emissions. The reactant whose yield is measured and its relationship to fluorinated GHG emissions for a particular process must be fully analyzed to ensure that it provided an accurate representation of the emissions.