Commonwealth of Massachusetts
Executive Office of Energy & Environmental Affairs

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Guidance on Reporting Hydrofluoric Acid as a Higher Hazard Substance under the Toxics Use Reduction Act

As of reporting Year 2016, hydrofluoric acid also known as hydrogen fluoride (HF) – CAS # 7664-39-3 will be designated as a higher hazard substance (HHS) under TURA, lowering the reporting threshold to 1,000 pounds. This is effective for reports covering use in Calendar Year 2016 and due July 1, 2017. This document explains the new reporting requirements and provides general reporting guidance for HF.

REPORTING THRESHOLD LOWERED TO 1,000 POUNDS

Designation as a higher hazard substance lowers the reporting threshold from the current thresholds of 25,000 pounds if the substance is manufactured or processed; and 10,000 pounds if the substance is otherwise used, to 1,000 pounds for each of the three uses. A Form S report is required for each higher hazard substance used at 1,000 or more pounds in a calendar year. Note that these three types of use are NOT additive for the purposes of determining whether the threshold has been exceeded. For example, a facility that manufactured 700 pounds and otherwise used 350 pounds of hydrogen fluoride would not be required to submit a Form S report on the substance, since neither type of use exceeded 1,000 pounds.

USE STATE-ONLY FORM Rs

The TURA e-DEP system will automatically generate State Only Form Rs for all substances for which the TURA reporting threshold is lower than the EPA Toxics Release Inventory threshold, and for all substances which have different "qualifiers" under the TURA and TRI systems. Of course, if federal thresholds are exceeded, submit a separate Form R to the EPA TRI program and generate a State Only Form R as well.

GENERAL REPORTING GUIDANCE

1. How Is Hydrofluoric Acid Commonly Used in Massachusetts?

Hydrofluoric acid is primarily used in Massachusetts for metal cleaning (pickling and desmutting) and etching applications, or is coincidentally manufactured by facilities.

2. Properties of Hydrofluoric Acid

Anhydrous hydrofluoric acid or hydrogen fluoride is a liquid that easily vaporizes at room temperature. Aqueous solutions of hydrofluoric acid are commonly sold in concentrations from 70% to 38% (by weight). Boiling temperatures range from 67 F for anhydrous to 235 F for 35% hydrofluoric acid.

3. How do I determine if I trip the reporting threshold?

Processing HF: Facilities producing specialty blends of fluoride chemicals will primarily report hydrogen fluoride as processed and occasionally as manufactured.

> **Example 1**: The dilution of 1,430 pounds of 70% hydrofluoric acid to 49% hydrofluoric acid for resale would be considered *processing* 1,001 pounds of HF.
> **Example 2**: If 1,430 pounds of 70% hydrofluoric acid is used to manufacture fluoroboric acid, report 1,001 pounds of HF as *processed*.
> **Example 3**: If 2043 pounds of 49% hydrofluoric acid is used in solutions to remove oxides from stainless steel, report 1001 pounds HF as otherwise used.

Processing or Manufacturing HF from Ammonium Bifluoride or Other Fluoride Salts: When dry ammonium bifluoride (ABF) contacts water, it generates hydrofluoric acid. The hydrogen fluoride derived from fluoride salts (such as ABF) is considered *manufactured*. (EPA guidance 745-R-00-005)

Ammonium bifluoride used (*processed*) in dry blends for resale are not likely to have reportable quantities of HF. However, ammonium bifluoride added to water will *manufacture* HF. For example, if ABF is added to water with other proprietary constituents for resale, ABF could *manufacture* reportable quantities of HF depending upon the pH of the solution and other constituents that could affect the dissociation of ammonium bifluoride.

For example, HF for buffered etching solutions may be produced from ammonium bifluoride (CAS 1341-49-7) or ammonium fluoride (CAS 12125-01-8). In crystalline form these two chemicals may sublimate to produce ammonia and HF gases. Some companies, however, prefer to handle and store this solid form rather than a concentrated solution of HF. In solution ammonium bifluoride can typically produce up to **35%** of its weight as hydrogen fluoride. That is, 2,857 pounds of NH_5F_2 can produce 1,000 pounds of HF (and 1,857 pounds of NH_4F). Ammonium fluoride (NH_4F) is considered a neutral salt, but in the presence of a stronger acid is capable of producing up to **54%** of its weight in HF. That is, 1,852 pounds of NH_4F could produce up to 1,000 pounds of HF if driven by the presence of another acid in the solution or an energy source.

Example: In the calendar year 3,000 pounds of ammonium bifluoride is consumed in an etching bath. **35%** of 3,000 pounds *manufactures* 1050 pounds of HF which exceeds the 1,000 pound threshold. This 1,050 pounds of HF is also *otherwise used*. However, under TURA, when a given listed substance is introduced into production anywhere at the facility, it is counted *only once at the facility level*, regardless of how many times that listed substance is used, recycled or reused onsite. Report the first use category that trips the threshold. For example, if 1,050 pounds of HF is manufactured at the facility, it is reported as "manufactured". This amount is not also reported as "otherwise used" because it was already reported as manufactured. However, at *the production unit level*, the reportable substance *is* counted every time it is used (and if non integrally recycled, reused) in the process. In this case, the use range code reported for the production unit would reflect 2,100 pounds -- the sum of the amount manufactured and otherwise used.

Otherwise Use of HF: A substance is *otherwise used* in a production process if it is neither manufactured nor incorporated into the final product. The *de minimis* concentration applies to materials that are otherwise used. Materials below the *de minimis* concentrations (1.0 % for hydrofluoric acid) do not need to be counted toward the 1,000 pound *otherwise used* threshold. However the entire quantity of substances that are present in concentrations above the *de minimis* level must be counted toward the 1,000 pound *otherwise use* threshold.

4. Quantifying Hydrofluoric Acid Use in Combustion

Hydrofluoric acid is often *manufactured* in combustion processes, because. Fluoride compounds in fuels such as oil or municipal waste can be converted to hydrogen fluoride during combustion. The quantity of hydrogen fluoride manufactured at a facility during combustion will depend on a number of factors, including the type of

fuel combusted (e.g., oil or municipal waste), the type of combustor, and combustion conditions (e.g., temperature and air/fuel ratio). Note that the information that follows is provided for general guidance – facilities are required to use the best readily available data applicable to their operations for threshold determinations.

Based on the EPA's AP-42 emission factors, 1,000 or more pounds of hydrofluoric acid are likely to be coincidentally *manufactured* if annual fuel consumption is greater than 26,800,000 gallons (No. 6 oil).

Hydrofluoric acid is also coincidentally generated during municipal waste combustion. EPA has not published emission factors for HF from municipal waste combustion. AP-42 has a general statement about the variability of acid gas emissions including HF. Given the variability in HF amounts, it is incumbent on municipal waste combustors to make their own best engineering judgment on how much HF is coincidentally manufactured in the combustion process. According to one Emission Calculation, prepared by Malcolm Pirnie, for the Palm Beach Renewable Energy Facility permit application, that MWC facility will exceed the 1,000 lb HF threshold when it processes 36,630 ton/year (100 ton/day). [Ref.-13 Appendix B Emission Calculations for Palm Beach Renewable Energy Facility No. 2]

Additional data sources on the coincidental manufacture of Hydrofluoric Acid during combustion can be found in the references cited at the end of this document. De minimis exemptions do not apply to manufactured chemicals.

REFERENCES

It is the responsibility of each facility to determine the best readily available data applicable to their operations. The methods and sources of data for quantifying hydrochloric acid use include, but are not limited to, the following –

1. TURI Summary of Policy Analysis for Hydrogen Fluoride, Aug. 12, 2014
   http://www.mass.gov/eea/docs/eea/ota/tur-prog/hydrogen-fluoride-hhs-comb-8-19-14-admin-council-mtg.pdf

2. Massachusetts Chemical Fact Sheet for Hydrofluoric Acid (1999)
   http://turi.org/content/download/3663/44840/file/Fact%20Sheet%20

3. "Etch Rates for Micromachining Processing" by Kirt R. Williams and Richard S. Muller
   Journal of Microelectromechanical Systems, Vol 5, No 4, December 1996

4. Safety of Hydrofluoric Acid vs. Ammonium Bifluoride
   http://www.finishing.com/94/62.shtml

5. Fuel-specific data for the fuels combusted (e.g., obtained from supplier).

6. Facility-specific monitoring data and/or emission factors.

7. AP-42: Table 1.1-15 Emission Factors for Coal Combustion
   http://www.epa.gov/ttn/chief/ap42/ch01/final/c01s01.pdf

8. AP-42: Refuse Combustion -2.1.3.3 and subsequent tables
   http://www.epa.gov/ttn/chief/ap42/ch02/final/c02s01.pdf

9. Waste Treatment and Disposal / Paul T. Williams, John Wiley & Sons, copyright 2005 –
   chlorine and fluorine in municipal waste

10. For EPRI members – the PISCES database (provides emission factors and models to calculate air emissions), and Toxics Release Inventory for Power Plants (TRIPP) software.

11. EPA's *EPCRA Section 313 Industry Guidance – Electricity Generating Facilities.*

12. EPA emission factors from EPA's *Compilation of Air Pollutant Emission Factors (AP-42), 5th ed. - Chapter 1, External Combustion Sources*. These factors are based on a limited number of samples and may not reflect more accurate information available to the facility for the particular type of fuel combusted and pollution control devices used.

13. Health Effects of Municipal Waste Incineration, Editors Holly A. Hattemer-Frey and Curtis Travis, ISBN 0-8493-4933-8, CRC Press, 1991 copyright, Table 17; MSW Incineration Emission Factors.

14. Appendix B Emission Calculations for Palm Beach Renewable Energy Facility No. 2 http://www.dep.state.fl.us/air/emission/bioenergy/palm_beach/3AppBemissions.pdf