

METHOD 26A – DETERMINATION OF HYDROGEN HALIDE AND HALOGEN EMISSIONS FROM STATIONARY SOURCES ISOKINETIC METHOD

Applicability

This method is applicable for the determination of hydrogen halides and halogens emissions from stationary sources (see list below; parameters to be measured have been checked), including sources that emit acid particulate matter.

| <u>Hydrogen Halides</u> | | <u>Halogens</u> | |
|-------------------------|--|-----------------------------|--|
| Hydrogen Chloride (HCl) | | Chlorine (Cl ₂) | |
| Hydrogen Bromide (HBr) | | Bromine (Br ₂) | |
| Hydrogen Fluoride (HF) | | | |

Principle

A stack sample is withdrawn from the source isokinetically through a heated probe and filter into dilute solutions, which collect the gaseous hydrogen halides and halogens. The samples are then separately measured by ion chromatography (IC).

Interferences

The simultaneous presence of HBr and Cl₂ can cause a positive bias in HCl and a negative bias in Cl₂, which would affect the HBr/Br₂ split. High concentrations of nitrogen oxides may interfere with the measurements of very low levels of Br⁻ due to the production of nitrates. In cases where HF is of concern, any new Teflon components will be preconditioned by means of heating since there is evidence that the HF may be out-gassed by the Teflon components.

Based on the above we (appropriate box checked):

Do not expect any interference.

Do expect interference. The description and discussion of the anticipated interference follows.

In-Stack Detection Limits & Sample Times

The minimum detection limit of the method has been determined to be approximately 0.02 ppm (note: this differs from that stated in the method due to errors in the method) for a standard 60 minute (1 dscm) sample. Actual in-stack method detection limits (ISDL) are based on actual source sampling parameters and analytical results. Actual detection limits can be improved through increased stack gas sampled (sample time).

For this source, the in-stack concentration is:

Allowable = _____ lbs/hr

Stack flow = _____ dscfm

MW = molecular weight.

ppm = (lb / hr) x 387E6 / (dscfm x MW x 60) = _____ ppm.

Therefore, the sample time will be _____ minutes.

Sample Train & Recovery Components & Supplies

A schematic of the sampling train is shown in Figure 26A-1 of the method. Specifically, the sampling train will be constructed with components specified under EPA Method 26A, Section 6.0 (similar to a Method 5 train), with the following exceptions and/or highlights.

Sample Train

- 1) The probe **nozzle** will be constructed of glass (borosilicate or quartz) and calibrated according to Method 5, Sections 6.1.1.1 and 10.1, and joined to the **probe liner** using a Teflon union. The probe liner will be constructed of glass (borosilicate or quartz). A Teflon probe liner can be used for stack temperatures between 250°F and 410°F. If the stack temperature exceeds 410°F, a one-piece glass nozzle/probe liner assembly must be used.
- 2) To remove particulate matter from the gas stream, a Teflon **filter** in a mat configuration will be used. Note: If the stack gas temperature exceeds 410°F, a quartz fiber filter may be used. This does / does not (circle appropriate) apply to this test program.
- 3) A **filter holder** made of borosilicate or quartz glass, or Teflon, with a Teflon **filter support** and a Teflon **sealing gasket**.
- 4) An optional **cyclone** (glass or Teflon) can be used only when the sample gas stream is saturated with moisture. The cyclone is recommended to protect the filter from any liquid droplets that may be present in the gas stream. The cyclone (check one) will ___ will not be needed.
- 5) The **impinger train** will consist of five impingers connected in series with leak-free ground glass fittings or other leak-free, non-contaminating fittings. The first and second impingers will be of the Standard Greenburg-Smith design and will contain 100 ml of 0.1 N H₂SO₄. The third and fourth impingers will be of the modified Greenburg-Smith design and will contain 100 ml of 0.1 N NaOH. The fifth impinger, also a modified Greenburg-Smith impinger, will contain with 6- to 16-mesh silica gel. When sampling at high moisture stacks, a knockout impinger with a shortened stem containing 50 ml of 0.1 N H₂SO₄ will be used in front of the first impinger (the stem should be sufficiently short to keep the gas stream from bubbling through the condensate). Teflon impingers are an acceptable alternative.

- 6) A **heating system** capable of maintaining a temperature of $> 248^{\circ}\text{F}$ around the probe and filter holder.
- 7) An **optional ambient air conditioning tube** tightly packed with approximately 150 g of fresh 8 to 20 mesh sodium hydroxide-coated silica, or equivalent, is used to dry and remove acid gases from the ambient air used to remove moisture from the filter and cyclone, when the cyclone is used.
- 8) A leak-free **sample line**.
- 9) A **pitot tube, differential pressure gauge and metering system** as described in Method 5.

Sample Recovery

- 1) The wash bottles, graduated cylinder and/or balance and rubber policeman will be the same as in Method 5. Funnels will be glass or high-density polyethylene.
- 2) The storage bottles should be high-density polyethylene bottles with Teflon screw cap liners.
- 3) Polypropylene Tweezers and/or Plastic Gloves will be used for recovery of the filter from the sampling train filter holder.
- 4) Teflon Tape will be used for capping openings and sealing connections, if necessary, on the sampling train.

Sampling

The sample train is assembled as per Section 8.1.3 and Figure 26A-1 of the method. Once the sample train is assembled a pre-test leak check is required, as stated below.

Leak Checks

Pre-test and post-test leak checks will be conducted following the procedures of Method 5. The pre-test leak check will be conducted at 15" Hg vacuum (or a lower rate not to be exceeded during sampling) and the post-test leak check will be conducted at or above the highest vacuum reached during sampling. A leakage rate in excess of 0.02 cfm is unacceptable and will void the test run.

Sample Collection

Prior to testing, both the probe and filter temperature should be greater than 248°F . Once the pre-test leak check is completed, the initial meter volume is recorded and sampling begins. Follow the general procedure given in Method 5, Section 8.5. For each run, the required data should be recorded on a data sheet such as the one shown in Method 5, Figure 5-3. If the optional knockout impinger becomes too full, it may be emptied (and saved for moisture determination and sample analysis) and charged with a new 50-ml solution of 0.1 N H_2SO_4 . Before this impinger is removed a post leak check must be conducted in order to ensure that the sample train was collecting the proper sample during the elapsed time period. This procedure may be conducted as many times as

necessary. At the conclusion of the test run, the probe is removed from the stack and allowed to cool. A post-test leak check is performed, as mentioned above. If applicable, the post-test moisture removal procedures listed in Section 8.1.6 of the method will be performed.

Sample Recovery

After the post-test leak check, the glassware is disconnected and the contents of the acid impingers (and knockout impinger if used) are poured into a leak-free storage bottle. The impingers and connecting glassware are rinsed with water and these rinses are added to the storage bottle. This procedure is repeated for the alkaline impingers and connecting glassware, using a separate storage bottle. For the alkaline impingers, add 25 mg of sodium thiosulfate per the product of ppm of halogen anticipated to be in the stack gas times the volume (dscm) of stack gas sampled (0.7 mg/ppm-dscf).

Portions of the absorbing reagents, equivalent to the amount used in the sample train, will be saved and water added to dilute to the approximate volume of the collected samples. Also, the same amount of sodium thiosulfate added to the alkaline solution samples will be added to the alkaline solution blank. Finally, a portion of the water used to rinse the sample train will also be saved.

All sample collection bottles are sealed, labeled and the fluid levels marked.

Sample Preparation and Analysis

The liquid levels on the storage containers will be noted at the laboratory and if leakage occurred, the run will either be void or methods will be used, only with the approval of BTS, to correct the final results. Sample solutions will be quantitatively transferred to 100-ml volumetric flasks, and diluted to 100 ml with water. Analysis will be by ion chromatography, per the method. All analysis will include duplicate injections, which must agree within $\pm 5\%$. Analysis will be performed no later than 4 weeks after sample collection.

Calculations

All calculations will be performed as per Method 26A, including blank corrections. Detailed sample calculations will be included in the final report.

Emissions will be presented in the following units: _____.

Special Situations

- 1) If sampling for Cl_2 and/or Br_2 is not being conducted, analysis of the alkaline impingers may be disregarded.

- 2) Due to different filter temperature requirements, Method 26A cannot be combined with the NJ Air Test Method 1 (the standard particulate test method used in NJ). However, particulate testing can be combined with Method 26A testing if the Permit states that the allowable(s) for particulate are to be based on EPA Method 5 testing. If this is to be done, an attachment to this Template will be included in the protocol submittal, detailing the procedures.

Audit Samples

If provided, audit samples will be analyzed consistent with Section 11.4 of the method and the results will be provided in the final stack test report. It is understood that failure to meet acceptance criteria for the audit could result in the requirement to repeat the stack test program.

Proposed Deviations from this BTS Template or the Method

(Insert any proposed deviations here)