

## METHOD 26 – DETERMINATION OF HYDROGEN HALIDE AND HALOGEN EMISSIONS FROM STATIONARY SOURCES NON-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) that do not emit acid particulate matter. Sources that emit acid particulate matter, such as those controlled by wet scrubbers, cannot use this template and should consider using the template for Method 26A.

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

### Principle

A stack sample is withdrawn from the source through a pre-purged heated probe and filter into dilute solutions, which separately collect the gaseous hydrogen halides and halogens.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

### Interferences

The simultaneous presence of HBr and Cl<sub>2</sub> can cause a positive bias in HCl and a negative bias in Cl<sub>2</sub>, which would affect the HBr/Br<sub>2</sub> split. High concentrations of nitrogen oxides may interfere with the measurements of very low levels of Br<sup>-</sup> 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. The use of a glass wool plug to remove particulate matter could result in a negative bias in the data. Therefore one will not be used.

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 0.0125 ppm (note: this differs from that stated in the method due to errors in the method) for a standard 60 minute (120 liter) 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 26-1 of the method. Specifically, the sampling train will be constructed with components specified under EPA Method 26, Section 6.0, with the following highlights.

#### **Sample Train**

- 1) The **probe liner** will be constructed of glass (Borosilicate or Quartz). To remove particulate matter from the gas stream, a teflon-glass filter in a mat configuration should be used. A glass wool plug is not an acceptable substitution.
- 2) A borosilicate-glass **three-way stopcock** with a heating system will connect to the outlet of the heated filter and the inlet of the first impinger.
- 3) The **impinger train** will consist of five impingers connected in series with leak-free ground glass fittings or other leak-free, non-contaminating fittings. Silicone grease may be used as necessary to prevent leakage. The first and second impingers will be 30 ml midget impingers containing 15 ml of 0.1 N H<sub>2</sub>SO<sub>4</sub>. The third and fourth impingers will also be 30 ml midget impingers containing 15 ml of 0.1 N NaOH. The fifth impinger will contain 6- to 16-mesh silica gel. When sampling at high moisture stacks, a midget impinger with a shortened stem 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).
- 4) A **Heating System** capable of maintaining a temperature of > 248 °F around the probe and filter holder.
- 5) A 25-mm (1 in) Teflon glass mat **filter** will be used. Other filters may be used but they must contain at least 75% Teflon and be of a mat configuration. Note: If the stack gas temperature exceeds 410 °F and the HCl concentration exceeds 20 ppm, a quartz-fiber filter may be used. This does / does not (circle appropriate) apply to this test program.
- 6) A **filter holder** made of Teflon or quartz and a **filter support** made of Teflon.
- 7) A leak-free **sample line**.
- 8) **Rate meter** (rotameter or some equivalent) capable of measuring flow rate to within 2% of the selected flow rate of 2 liters/min (0.07 ft<sup>3</sup>/min).
- 9) **Purge Pump** with the capability to purge the sampling probe at 2 liters/min and a rate meter capable of measuring 0 to 5 liters/min (0.2 ft<sup>3</sup>/min).

## **Sample Recovery**

- 1) Two wash bottles, glass or polyethylene, with capacities of 500-ml or larger.
- 2) Storage bottles, high-density polyethylene bottles, with Teflon screw cap liners.
- 3) Teflon Tape will be used for capping openings and sealing connections, if necessary, on the sampling train.

### **Sampling**

The sample train will be assembled as per Section 8.1.1 and Figure 26-1 of the method. The probe, filter and stopcock will be pre-heated to >248 °F. Once the sample train is assembled a pre-test leak check and purge are required, as stated below.

#### Leak Checks

Pre-test and post-test leak checks will be conducted as follows: temporarily attach a suitable rotameter to the outlet of the dry gas meter and place a vacuum gauge at or near the probe inlet. Plug the probe inlet and pull a vacuum of at least 10 inches of Hg for pre-test leak checks and 1 to 2 in. Hg higher than the highest vacuum during testing for post-test leak checks. A leak rate as indicated by the rotameter shall not exceed 2% of the sampling rate.

#### Pre Test Purge

Prior to testing, the probe is placed inside the stack and purged for 5 minutes (during the purge and test run both the probe temperature and filter temperature should be greater than 248°F).

#### Sample Collection

Once the pre-test purge is completed, the initial meter volume is recorded and sampling begins. Turn on the sampling pump and pull a slight vacuum of approximately 1 in Hg on the impinger train. The sampling rate is adjusted to 2 liters/min (to be maintained to within 10% of this rate during testing). Readings are taken at a minimum of every five minutes for the dry gas meter volume and temperature, vacuum gauge, the probe and filter temperature, stack temperature and exit impinger temperature. 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 detailed above.

### **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 26, including blank corrections. Detailed sample calculations will be included in the final report.

Emissions will be presented in the following units: \_\_\_\_\_.

### **Special Situations**

If sampling for  $\text{Cl}_2$  and/or  $\text{Br}_2$  is not being conducted, analysis of the alkaline impingers may be disregarded.

### **Audit Samples**

If provided, audit samples will be analyzed consistent with Section 11.2 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)