Frequently Asked Questions (FAQs) for Method 26A

8/25/16

1. What pollutant(s) does this method seek to measure?

Method 26/26A seeks to measure halides (HCl, HBR, HF), and halogens (Cl_2, Br_2, F_2).

2. How is sampling done?

Both methods collect integrated samples. Method 26 uses midget impingers and a constant nominal sampling rate of 2 liters per minute with a recommended minimum sampling time of one hour. Method 26A is the isokinetic version using full-size impingers with varying sample flow rate averaging about 20 liters per minute. You should sample long enough to assure analysis will be well above the analytical detection limit. Both sampling trains are recovered in three parts. The first part consists of a heated probe and Teflon matte filter whose function is to remove the particulate matter and halogenated salts (e.g NaCl, ammonium chloride, NaF, etc...) while letting the halides and halogens to pass through into the next part. Normally this first part is not recovered or analyzed. The second part consists of a 0.1 normal solution of sulfuric acid whose function is to absorb the halides while letting the halogens pass-through freely. The third part consists of a 0.1 normal basic solution of sodium hydroxide whose function is to absorb the halogens.

3. What filter requirements are there?

The composition of the filter must be at least 75 percent Teflon and matte as opposed to laminate configuration. When the stack gas temperature exceeds 410 degrees Fahrenheit, a quarts fiber filter may be used. The filter temperature must be controlled such that it **never** gets below 250 degrees Fahrenheit during the sampling run. This is important to assure adequate heating to prevent some capture of hydrogen chloride since the probe and filter are not quantitatively recovered.

4. Are there any pre or post test purging requirements?

Method 26 requires a pre-purge of the probe and filter at 2 liters per minute for at least five minutes; Method 26A does not require the pre-purge. The purpose of the pre-purge is to condition probe and filter with stack gas.

Method 26 does not discuss post-test purge while Method 26A has an option post-test moisture removal purge procedure in section 8.1.6. If moisture condensation is present, then this purge step is critical to the recovery of HCl that may be in the moisture. The HCl will evaporate only after the water is all evaporated.

5. Is there an allowed time limit for storing samples before analysis?

Both methods allow the samples to be stored for up to four weeks before analysis for HCl and Cl_2. There's nothing specific about sample storage time for other target compounds.

6. What technique is used for sample analysis?

A known volume of the acidified absorbing solution catch is injected into an ion chromatograph (a form of liquid chromatography) used to separate the anions (Cl^-, Br^-, F^-) which are then measured with a conductivity detector. Because they were not captured on the filter but are captured in the acidified absorbing solution, they are assumed to come from halogens. In a like manner, a known volume of the basic absorbing solution catch is injected, and the anions separated, and measured. Because they were not captured in the filter or the acidified absorbing solution, they are presumed to come from the halogens. Sodium thiosulfate is added to the basic absorbing solution sample after sampling but prior to analysis to ensure that two anions are produced for each molecule of halogen. (Be careful. An earlier version of the methods did not have this step so the analysis only measured 1 chloride ion per molecule of chlorine and the other one was accounted for in the final calculation by multiplying by 2.)

7. Is the method usually completed in the field or back at the laboratory?

We suggest that sampling be done in the field as it is a difficult (or even impossible) to obtain a representative stack sample in the laboratory. We hear rumors from time to time that people do "dry lab". However, in our opinion the risk outweighs the potential benefit :) However, analysis is usually done in the laboratory.

8. Is there an audit sample available for this method?

Yes, there is an audit material available. Please check the EMC web site at Technical Support - Audit Programs for availability.

9. What other QA/QC procedures are required for this method?

A post run leak check is required by both methods. Method 26 allows a leakage rate not in excess of 2 percent of the average sampling rate at a vacuum of at least 10 inches mercury. The 26A leakage rate must be less that 4 percent of the average sampling rate (or 0.00057 cubic meter per minute) whichever is less, at 15 inches mercury vacuum.

Calibration standards must be made in both acid and base to match the sample matrices.

Acid and base absorbing solution blanks are required, blank correction of results not to exceed one ug/ml is allowed.

Duplicate analyses of the sample is required and must be within 5 percent of the mean; otherwise, another set of duplicate injections are required and all four values used to determine the average response.

10. What types of problems have users run into with this method?

When trying to use this method to conduct a RATA of a CEMS, some users have found differences. The usual theories are that absorption of the halides on the filter and particulate result in negative bias. If there is positive bias relative to the CEMS, the common theory is that some halide salts having significant vapor pressure are present, some portion of the salt passes through the filter as a vapor (or as solid because the filter is not 100% efficient), and are captured in the impingers where it disassociates into ions, and hence is counted as halide.

If the PH of the sodium hydroxide absorbing solution becomes acidic then the Cl_2 capture efficiency drops off.

11. What types of variations have been allowed for this method in the past?

More concentrated sodium hydroxide absorbing solution has been allowed.

Method 26A can usually be substituted for Method 26, but Method 26 substitution for Method 26A only works if there is definitely no entrained water droplets.

12. What are the differences between SW 846 Methods 0050 and 0051 and these methods?

For HCl and Cl_2 they are very similar with the largest difference being that 0050 allows a filter temperature of 248 +/- 25 degrees while Method 26A requires a temperature greater than 248 degrees Fahrenheit. (The SW 846 methods do not list the other halides or halogens as target compounds.) There's also a provision in the Method 0051 to conduct the leak check in two parts. First leak check from the probe and filter back to the three-way valve one time prior to the start of the test. The probe/valve assembly would stay in the stack and allow the tester to run several runs exchanging out the impingers without removing the probe/filter/three-way valve from the port. Not only to save some time but more importantly it allows the probe and filter conditioning to stabilize the absorption of HCl in the probe and filter.

Catherine Massimino identified the following 4 additional minor differences: (1) Under Method 26A, Section 2.1.7, conditioning of ambient air coming into the train is optional. In Method 0050, Section 4.1.3.12, ambient air conditioning is required. (2) Under Method 26A, Section 4.1.4, the post leak check procedure references Method 5 Section 4.1.4.3, which allows correction of volume of dry gas metered if it exceeds leakage rate. Under Method 0050 Section 0050, Section 7.4.3, if higher leakage rate is obtained, it requires the tester to void the sampling run. (3) Under Method 26A, Section 4.1.3, the metering system is specified as the one in Method 5. Method 5 requires a system capable of measuring volume to within 2% and indicates, "when the metering system is used in conjunction with a pitot tube, the system shall allow periodic checks of isokinetic rates." In Method 0050, Section 4.1.3.9, a metering system capable of measuring volume to within 1% is required and states "The metering system must be used in conjunction with a pitot tube to enable checks of isokinetic sampling rates." (4) Method 26A, Section 4.1.3, does not include any language concerning that "it is essential that the NaOH filled impingers be maintained strongly basic throughout the sampling run. In highly acid stack environments, this may require measures such as stronger base, more volume of basic solution or change out of impinger liquid during the run. When in doubt the pH of the solution should be monitored frequently or continuously."

Conclusion: Provided the temperature of the filter is maintained at greater than 248 degrees Fahrenheit during the entire sampling run, a method 0050 sample can be called a Method 26A sample with slightly enhanced quality assurance.

13. How do I know how much sodium thiosulfate to add to the sodium hydroxide absorbing solution?

The method calls for you to estimate the concentration of chlorine (ppm) and multiply this by the dry standard volume sampled. If you use standard volume in "cubic meters", add 25 milligrams for each PPM - DSCM, or 7 milligrams for each PPM - DSCF. These values have a safety factor of about 5 so you don't have to be real concerned that you know the PPM precisely. In fact, adding too much sodium thiosulfate may interfere with the analysis so in retrospect, it would probably be better to have a smaller safety factor.

If the PH of the sodium hydroxide absorbing solution becomes acidic then the Cl_2 capture efficiency drops off.

14. When should I add the sodium thiosulfate?

We intended that the sodium thiosulfate be added after sampling is complete.

15. Can I use ASTM Method D6735-01 as an alternative?

Not automatically unless the ASTM method is listed as an acceptable alternative within the regulation. The ASTM method was intended to be used at mineral calcining exhaust sources where there is reactive particulate matter present. To compensate for this, a filter temperature of 350 degrees Fahrenheit and a much longer initial pre-purge are required. Depending on the source, because of the higher temperature, this could result in some salts in a vapor state passing through the filter and being captured in the acidified absorbing solution.

16. How can I use Method 26A to collect a particulate matter sample simultaneously?

The isokinetic version (Method 26A) is sometimes used to concurrently collect a Method 5 (i.e. heated probe filter) particulate sample. The challenge is in first obtaining and using a Teflon matte filter meeting Method 5's 99.95% collection efficiency and second maintaining the filter and probe temperature >248 degrees to satisfy the Method 26A requirement while simultaneously fulfilling the Method 5 temperature requirement. Usually, the Method 5 temperature requirement is to maintain an average temperature 248 +/- 25 degrees Fahrenheit although some regulations specify different temperature ranges.

17. Is there an upper limit to the concentration that this method works for?

Yes, there is a theoretical upper limit since HCl will concentrate only to 37% in water. Breakthrough occurs at some point prior to that concentration being reached in the acidic absorbing solution. Also, for effective capture of chlorine gas, the pH of the basic absorbing solution must be maintained >7. However, in a "normal" combustion exhaust only the latter is a concern because of the acidic nature of the exhaust gas.

18. I have a shelf full of unused glass fiber mat filters bought when I thought everyone would be asking for Method 5 tests a few years ago. Since the New Clean Air Act Amendments were published, I get a lot more requests for testing HAPS, especially HCl. Method 26 doesn't say much about using the glass fiber filters and I wondered if I could put these filters to good use. If so, do I need to treat them chemically somehow?

You must find another use for those glass fiber filters because they're not allowed in the Method 26 train. It has something to do with the HCl in the sample binding on the glass fiber and not showing up in the analysis. My sources tell me that there is not a suitable treatment that will correct this. So, the method specifies Teflon or Quarts filters and that's what it means - no substitutions.