
**EMISSION MEASUREMENT CENTER
GUIDELINE DOCUMENT**

EMTIC WORKSHOP BACKGROUND PAPER FOR METHOD 26 AND 26A

DESCRIPTION OF METHOD

Method 26 is a proportional sampling procedure that uses midget (Method 6 type) impingers whereas Method 26A uses large (Method 5 type) impingers and the sample is collected isokinetically. Note that it is necessary to use Method 26A when water droplets are present, such as after a scrubber, and one wants to account for the halides in the water.

Both sampling trains use a heated teflon matte filter to remove the particulate salts prior to the impingers. Both procedures have provisions for using alternative filter types in some cases. In the halogen and halide analysis scheme everything up to and including the filter is discarded and not part of the sample although it may be recovered as a Method 5 particulate sample in some cases for Method 26A.

The first set of impingers in both trains contain a dilute 0.1 N H₂SO₄ solution and the back set of impingers contain a dilute 0.1 N NaOH solution. In Method 26A there are options to add a cyclone when heavy particulate matter loadings are expected or to keep the moisture droplets off the filter, and an additional impinger if a lot of moisture condensation is anticipated.

A pre-purge of the probe and filter with stack gas is required in Method 26 to avoid a significant bias, because of the smaller volumes sampled, resulting from sampling clean gas initially. For Method 26A, if the optional cyclone is used, or if moisture condensation is observed, then it is necessary to conduct a post-test purge to evaporate the halogens, halides, and the condensed moisture before the filter so it can be captured and recovered in the impinger solutions. Failure to do this drying completely results in significant negative bias.

The separation of the halides from the halogens is accomplished physically in the impingers. Halogens (Cl₂ and Br₂) have a low solubility in an acidified solution and hence tend to not be captured to a large extent in the first set of impingers containing 0.1 N sulfuric acid, whereas they are captured effectively in the 0.1 N NaOH solution. Meanwhile, the halides (HCl, HF, and HBr) are effectively captured in the 0.1N H₂SO₄ and hence removed before they can get to the NaOH solution. Analysis is accomplished in both sets of solutions by ion chromatography looking for the halide ions (Cl⁻, F⁻, or Br⁻) using standards prepared in the appropriate solution matrix.

DISCUSSION OF IMPLEMENTATION PROBLEMS OR ISSUES**HCl**

It is important, but difficult to confirm, that any condensed moisture present during sampling be removed completely during a post purge of the Method 26A train to avoid a significant negative bias. As little as one drop moisture is sufficient to cause a significant negative bias because of the solubility of halides in water.

From an analysis of data available today, it is also likely important that the probe and filter temperature be maintained at greater than 250 °F to assure transmission of at least HCl (and likely HF) through the probe and filter in the gas streams with moisture as little as 2% by volume to avoid a negative bias. Additional data are being collected to confirm this observation. However, if volatile halide salts such as ammonium chloride are present, there is an increased risk of a significant fraction of ammonium chloride being in the vapor state, passing through the filter, and being captured in the 0.1 N H₂SO₄ solution. When this happens, the ammonium chloride disassociates in the solution, the Cl⁻ is measured, and reported as HCl.

Ammonium chloride (NH₄Cl) in the vapor state also disassociates into HCl and NH₃ at higher temperatures. The exact temperature dependency is not clear at this point. Hence one theory exists that choice of sampling location can become critical if the measurement location stack temperature is much hotter than the stack temperature just prior to exiting the stack. The theory is that some of the HCl would form NH₄Cl before it leaves the stack and hence sampling in the "wrong" location results in overestimating emissions of HCl from the process.

If the filter and probe temperature is much greater than the stack temperature, this same logic indicates that a positive bias can be introduced in this case too.

Conversely, if the probe and filter temperature results in cooling of the gas stream, it is possible to introduce a negative bias too.

Use of glass fiber filters is not allowed especially at low concentrations of HCl because of the potential for reaction with the filter. In those cases where higher stack temperatures preclude the use of teflon filters because the teflon would be unstable, quartz filters are recommended although the exact effect of using these filters is not clear at present.

HF

Hydrogen fluoride (HF) likely reacts with the glass probe liner to form silicon tetrafluoride (SiF₄) but because of SiF₄ vapor pressure at 250 °F we think it will pass through the filter and be captured in the 0.1N H₂SO₄

solution and correctly be reported as HF. If, however SiF₄ is present in the sample matrix, it will likely be a positive interference by passing through the filter and being captured in the impinger solution. The data we have at present is too limited to confirm that this is quantitative; however, we are presently collecting data that may confirm that if there is a HF reaction with the probe, SiF₄ will still be captured and reported. We are not collecting data at present to confirm that the reaction actually takes place.

Both methods allow use of teflon probe liner, filter holder, and impingers. It is possible that a positive HF bias can be introduced from the heating of the probe and filter. Some degassing of HF was observed from the heated teflon sample line in another study currently underway to evaluate HF monitors. Likely this can be minimized by preconditioning the teflon at the temperature the train is anticipated to see during the test, but we have limited data to define how effective this preconditioning may be.

Simultaneous Presence of HBr and Cl₂

If HBr and Cl₂ are present at the same time, it appears that the HBr and Cl₂ values will be under-reported and the corresponding HCl and Br₂ values will be over-reported.

Analysis

There was a recent change made to both methods requiring that sodium thio-sulfate be added to the 0.1N NaOH solution after sample recovery. The purpose of this requirement is to assure that the hypohalous acid ion is reacted to form a second Cl₋ (or Br₋) for each Cl₂ (or Br₂) molecule. In earlier versions of the methods, the assumption was made that one Cl⁻ (or Br⁻) and one HClO⁻ (or HBrO⁻) was formed for each Cl₂ (or Br₂) present in the sample matrix. This assumption was not always precisely correct. The equations were therefore changed in the latest version of the methods to avoid duplicating this correction.