ENTHALPY analytical, inc.

EPA Methods 25D, 305, & 624/625

Though seemingly addressing wastewater issues, analytical Methods 305 and 25D are really air emissions testing methods, because their intent is to measure the movement of organics into the atmosphere. Air emissions specialists Enthalpy Analytical, Inc. have applied their extensive experience in analyses for air pollution test methods to these most recent procedures since the inception of the methods.

Method Overview

Methods 305 and 25D were designed to measure the amount of volatile organics contained in a liquid stream, and are intended to determine whether a liquid stream is subject to provisions of the Hazardous Organic NESHAPS, (the "HON" Rule).

When developing the HON, EPA believed that regulated facilities were sending significant amounts of organics to open surface treatment plants where the organics were lost to the atmosphere via evaporation rather than degraded through biological activity.

The proposed wastewater sections of the HON Rule regulate wastewater streams that contain significant concentrations of volatile organics. No stream containing Hazardous Air Pollutants (HAPs) above certain threshold levels may be released to open surface impoundments or open drain systems. Defined in Tables 8 and 9 of CFR40 Part 63 Subpart F; the threshold levels are set at 10 ppmw for highly toxic HAPs and at 1000 ppmw for less toxic compounds.

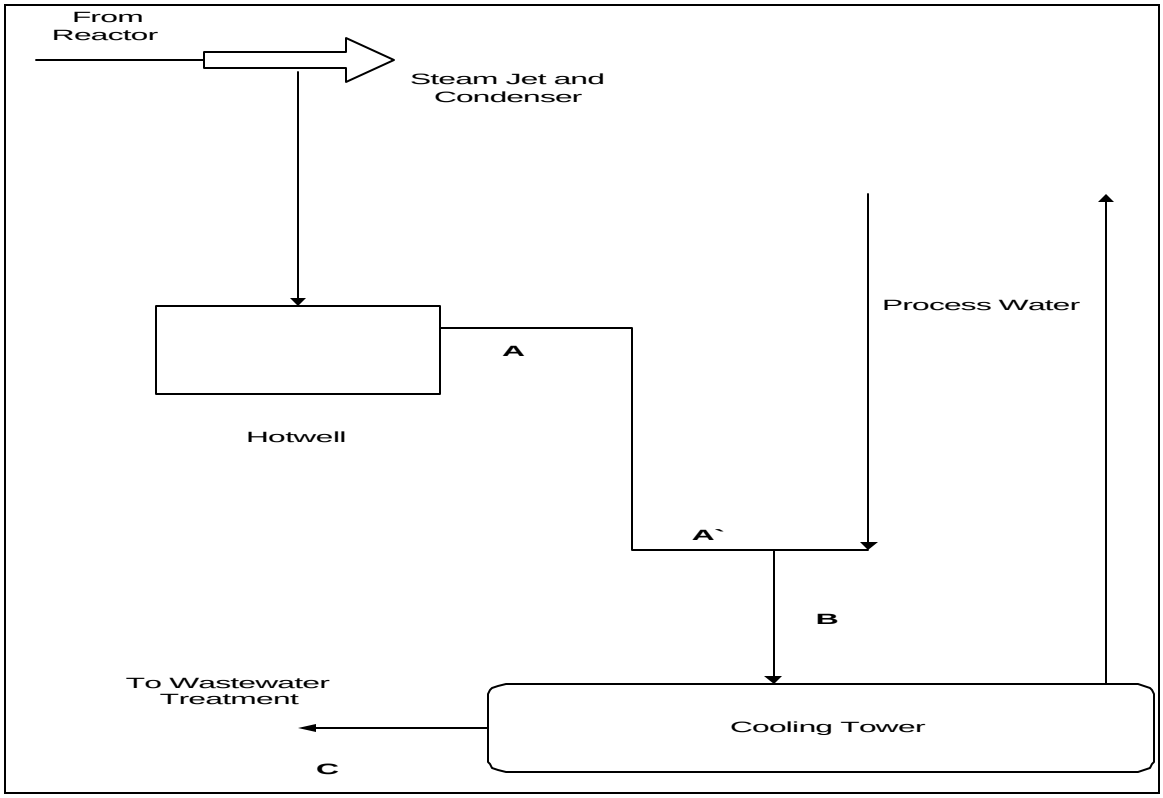
The rule categorizes wastewater streams into two groupings, with Group 1 sources containing HAPs above the threshold and Group 2 sources HAPs below the threshold. Group 1 sources must be contained in closed-pipe systems until steam stripped or destroyed in a RCRA or BIF incinerator.

The EPA considers a wastewater stream to be a "source" when it leaves the chemical manufacturing process unit (cmpu). A cmpu is defined as a process unit that makes a product included in Table 1of the HON Rule and uses one of the compounds that are included in Table 2 of the HON as a reactant or major intermediate. A typical cmpu would include storage tanks, mixing tanks, connective piping, strippers, reactors, separators (gravity, evaporative, distillation, adsorption, absorption, etc.), and recovery devices associated with making the product. Control devices are not considered part of the cmpu.

In a typical loop in a cmpu, (Diagram 1), a steam jet keeps a reactor under vacuum. The reactor is the first step in making a product listed in Table 1 of the Rule. The feeds to the reactor include a chemical listed in Table 2 of the Rule. The condensed effluent of the steam jet collects in a hotwell. The hotwell water (A) is returned to a cooling tower, and a slipstream (C) is diverted to the wastewater treatment plant with fresh water added to account for the loss. Assuming that the hotwell effluent is a Group 1 source (containing HAPs above the threshold), then the new rules do not allow its discharge to open wastewater containment.

The EPA defines two terms relative to the hotwell effluent. The first is "point of generation." In this case, the point of generation is "A" on the diagram or the line leading from the hotwell to the cooling tower prior to including the process line.

The second, "point of determination", is where the source exits the cmpu. In this example, the points of generation and of determination are the same. Samples must be collected at point A or at point B to determine whether the hotwell effluent should be controlled. If the samples are collected at point B, the flow rate of the hotwell effluent as well as the process water stream would need to be measured so that the concentration at point B could be corrected for the dilution from the process water that occurred between A and B.

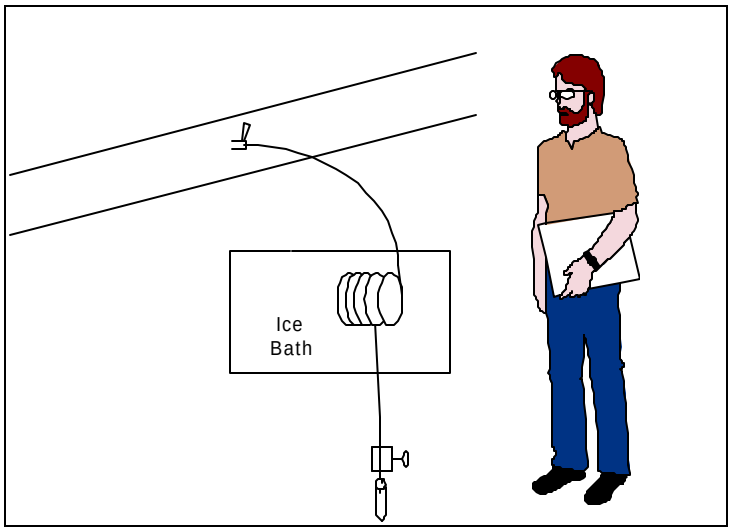


If a gravity separator were placed between points A and A`, and the recovered material returned to the process for reuse, then the point of determination would

become A`. The sample could then be taken at A` or B. Again, process water flow rates would be measured to determine dilution effects.

Sampling and Analysis

Each sample is collected in triplicate for each source. Enthalpy provides four 40mL VOA vials (3 samples, 1 blank) containing approximately 30mL of polyethylene glycol (PEG), that stabilizes the sample until analysis. Before shipping, Enthalpy purges the PEG to assure a low background level, then tares the PEG containing VOA vials.



The sample must be collected in a manner that minimizes loss of volatile compounds. Precautions include adding wastewater until each vial is full with no headspace. EPA Method 25D recommends using chilled coil to vent the sample from the closed-pipe system, and purging small amount of sample prior to collection vials to ensure no carryover from a previous sample. The purged sample is returned to the process. The tared vials are returned to Enthalpy on ice and reweighed to determine the weight of sample added.

A trip blank with no sample added is also returned. Samples should be representative of the 12 month average process conditions. If no typical condition can be defined, then samples may be drawn periodically (typically monthly) to determine the average HAP concentration for a wastewater stream.

Alternatives

Sampling can be avoided in two ways. The first is to simply designate the stream as a Group 1 source, and keep it covered and controlled. Some streams will obviously exceed the threshold values, and no sampling is needed if the facility is designates the source as requiring controls. The second is to demonstrate through engineering or past analytical data that the wastewater stream contains no HAPs or very low concentrations of HAPs, and designate the stream as a Group 2 source. Otherwise, the source must determine the HAP content of the stream. The three primary choices of analytical method include:

EPA Method 25D - All volatile organic compounds are removed from the sample and quantified with a detector specific to hydrocarbons and a second detector specific to

halogens. One disadvantage to this approach is that results may be biased high by any non-HAP compounds in the samples.

EPA Method 305 - Volatile organics are removed by sparging with nitrogen at 75ºC, then collected and concentrated on a solid adsorbent media. The media is analyzed for the specific HAPs expected.

EPA Method 624/625 - This drinking water method is suitable if the HAPs are on the 624/625 target list. For HAPs are not on the list, Method 624/625 may be used if method validation procedures are performed to assure that the compound can effectively be analyzed by Method 624/625.

Enthalpy Qualifications

Enthalpy can provide each of these analytical options. Enthalpy analysts were involved with the method validation for EPA M25D before it was proposed, and have since used the method extensively. We perform Method 305 on a monthly basis for a number of HON sources. Also, Enthalpy routinely consults with clients in selecting the media and test conditions to collect HAPs and a wide range of other organics on solid sorbents, as well as providing analyses by GC/MS, GC/FID, HPLC, and other detectors. This experience, combined with 10 years of collecting samples from hot, wet gas streams provides extensive if not unique qualifications to perform these methods.

We also provide Method 624 as an analytical choice. While hundreds of labs offer Method 624, consider that the typical lab receives drinking water samples containing organics in the ppb range, and may not be equipped to handle process wastewater samples at up to 10,000 times routine concentrations. And, because of our size, your samples will receive the close attention of a senior analyst. Ms. Denise Adcock manages all GC/MS analyses, and brings 10 years GC/MS experience with these types of air test samples to her supervision of your project.

Note: Volatile Organics and Heat Exchangers

Another application of water sampling for volatile organics specified in the HON Rule is for heat exchanger equipment. When water is a heat exchange fluid, and the pressure on the process side of the exchanger is equal to or greater than the pressure on the water side, then the water stream must be monitored for the HAPs present in the process fluid being cooled. Three samples are taken of the water upstream, and three samples downstream of the heat exchanger. An average concentration of HAPs in the downstream samples higher than the 95% confidence interval of the upstream average provides a 95% chance that the process fluid is leaking into the cooling water. The samples are taken monthly for the first 6 months and quarterly thereafter. The options for sample analysis are the same as those for determining the Group 1 or Group 2 status.

EPA Methods 25D, 305, & 624/625

****

Pricing for each analytical option is dependent upon the target HAPs. In general, a typical target list is about $ 750 for a set of three samples and a trip blank. Please contact us for quotations that address your unique requirements.