

# Responding to the EPA Information Collection Request for Electric Utility Steam Generating Units

Non-Dioxin/Furan Organic HAP

# Background

On December 24, 2009, the U.S. Environmental Protection Agency (EPA) issued an Information Collection Request (ICR) requiring owners of coal- and oil-fired power plants to test stack emissions from selected electricity generating units (EGUs) for a range of hazardous air pollutants (HAPs) and potential surrogate species. The ICR also requires facilities to sample and analyze the fuels burned during the test period. The Electric Power Research Institute (EPRI) has prepared a series of technical papers to help power plant owners improve the quality of the test results by raising awareness of technical issues related to the sampling and analytical methods. As EPA's plan is to use the ICR results to establish emission standards for the power industry, it is important to collect and report measurements that are accurate, unbiased, and representative of the stationary sources tested.

The objective of these papers is to provide technical information that will assist power plant owners and stack testing contractors in identifying appropriate technical resources, developing test plans, streamlining testing, selecting appropriate sampling and analytical methods, and avoiding common errors. The information provided includes "lessons learned" and recommendations from several stack testing firms that provided testing services on recent EPA ICRs. These recommendations are not intended as universal guidance; each power plant owner should evaluate their applicability for a specific situation.

Changes and clarifications to the ICR requirements are posted on the Electric Utilities MACT ICR web page: <u>http://utilitymacticr.rti.org/FAQ.aspx</u>. Power plant owners should consult that resource for any guidance that may impact the recommendations in this paper.

# **About This HAP Group**

The ICR requires selected facilities to test for a group of HAPs that include speciated volatile organic compounds (VOCs) and speciated semivolatile organic compounds (SVOCs) including selected polycyclic organic matter (POM) constituents. These units must also test for potential organic surrogates and combustion gases, including carbon monoxide (CO), total hydrocarbons (THC), NO<sub>x</sub>, formaldehyde, methane, O<sub>2</sub>, and CO<sub>2</sub>. Methods for analysis of formaldehyde, methane, and THC are addressed in a separate paper in this series: *Potential Organic HAP Surrogates*. Measurement of NOx, CO, O<sub>2</sub>, and CO<sub>2</sub> is routine and is not addressed in these papers.

The specific chemicals included in these two categories are defined by the analytical methods. The VOC analyte list is defined by EPA Method 8260B. The SVOC analyte list is defined by EPA Method 8270D. The lists for these two methods were developed for the Resource Conservation and Recovery Act (RCRA) program; most of the analytes are not found in combustion flue gases. The lists include industrial solvents such as acetone and trichloroethylene, pesticides, phthalates, and many other bulk industrial chemicals. Many of the analytes that are included in these methods are not on the Section 112(b) HAPs list. Until EPA specifies which of the VOCs and SVOCs are of interest; it should be assumed that all analytes listed in either of the two methods should be measured and reported. Laboratory information management systems are set up to report the entire analyte list for each method; if EPA requires only HAPs to be reported it will be necessary to reduce the data to the required HAP compounds before transferring the data to the Electronic Reporting Tool (ERT).

The Method 8270D analyte list includes POM compounds. EPA has informed EPRI that they are planning to post the list of analytes in the POM category that must be reported on the ICR web site.

With a few exceptions, only a few VOC and SVOC HAPs are detected in power plant flue gas, and the detections tend to be sporadic and close to detection limits. For this reason, the primary challenge in conducting these methods is to ensure that background contamination does not lead to false positive detections. Stringent measures are required to maintain the cleanliness of sampling equipment and ultra-pure water or solvents must be used in sample recovery. Reducing laboratory cross-contamination is also a challenge. It is critical for data quality evaluation to collect and analyze field blanks and to report the results along with the sample results.

# **Method Options**

The ICR lists the following methods to measure the VOC and SVOC HAP:

Parameter	Primary Method	Alternative Method
VOC	EPA Method 0031 with SW-846 Method 8260B	None
SVOC/POM	EPA Method 0010 with SW-846 Method 8270D	None

# EPA Method 0031 (VOST)/EPA Method 8260B

# Method Title and Source

The ICR lists EPA Method 0031 (VOST) as the recommended sampling method for Speciated VOC HAP. The full title of this method is:

TEST METHOD 0031 - SAMPLING METHOD FOR VOLATILE ORGANIC COMPOUNDS

Method 0031 (VOST) and is contained in the EPA publication SW-846 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods. The method is available from:

http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/0031.pdf

Method 8260B is contained in the same publication. The full title and source of this method are:

VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/8260b.pdf

#### Safety Tips

- Wear thin, nitrile rubber gloves for the Tenax trap recovery.
- Wear safety glasses during sampling and recovery of the traps.

## **Method Overview**

The method uses a non-isokinetic, single-point sampling train operation. The VOST train is designed for sampling for VOCs with boiling points below 121 °C. The sampling train uses a condenser, followed by three sorbent traps (two Tenax<sup>®</sup>-GC and one Anasorb<sup>®</sup>-747). The sorbent traps and condensate liquid are sent to the laboratory for analysis by purge and trap preconcentration and a gas chromatography/mass spectroscopy analytical finish. The primary difficulty in the operation of the VOST is the initial assembly and set-up. Method 0031 provides illustrations and diagrams of the train set-up that aid greatly in the assembly. The sampling operation is fairly straight-forward, using a constant sampling rate.

In the performance of the analyses, surrogate compounds should be spiked and analyzed for recovery, a field blank (one per run) should be analyzed, and a trip blank should also be included and analyzed.

#### **Method Limitations**

With the exception of particulate matter, which is removed by a glass wool plug inserted at the probe tip per Method 0031, there are no significant interferences that would affect the sampling and analysis. High moisture content in the stack gas is not an issue for this method.

#### **Method Details**

#### Material Requirements

- Contract with a laboratory to supply the sample traps. Use lab-supplied glass containers to hold the sample traps.
- Use only glass, quartz, Teflon<sup>®</sup>, or Teflon<sup>®</sup>-lined sampling train components.
- Use only glassware cleaned according to the method specifications to prevent contamination.
- Use organic-free high performance liquid chromatography (HPLC) water for recovery. If possible, contract the analytical lab to supply the HPLC water.
- HPLC water wash bottles should be Teflon<sup>®</sup>.

#### Sampling

- Keep glassware, VOST sampling train, and collected samples away from ALL solvents (VERY IMPORTANT!) to prevent contamination. Many solvents used in the laboratory are included on the Method 8260B analyte list.
- No smoking should be allowed anywhere near the sampling or sample recovery area. Cigarette smoke contains contaminants include on the Method 8260B analyte list.
- Use the sample traps within 2 weeks of preparation.
- The ICR specifies that testers must collect a minimum of four sets of sorbent traps for each 2-hour run (20 minutes per set) at a sampling rate of one liter per minute. In past ICRs, EPA has accepted having the laboratory analyze three of the four sets of traps (including three of the four condensate samples) and use the fourth set as a backup in case of any problems with the first 3 sets.
- Collect the water condensate from the first water knockout once per test run by filling a 40 ml VOA vial to zero headspace with the condensate. If the condensate is less than 40 mls, complete the filling of the vial to zero headspace with high performance liquid chromatography (HPLC) water.

- Use a small submersible pump to recycle iced water for the condenser coils. Monitor and record the condenser temperature on the data sheet. The temperature should be kept below 68 °F.
- Don't disassemble the VOST after each run, just the traps.
- Collect one field blank per test run, one trip blank per entire test, and an HPLC water blank, and have them analyzed.
- Leak-check the entire train prior to each 2-hour run using a set of traps designated as a "Field Blank". Replace with the first set of run-traps and leak check these traps separately before starting the run.
- Remove the sample traps from the sampling train on the stack platform, away from organic solvent fumes or engine exhaust.
- When shipping samples to the labs, keep the samples at < 4 °C using double-bagged (baggies) and place ice around them.

#### Analysis

- There are very few laboratories in the U.S. that are capable of performing Method 8260B. There is no comprehensive list of laboratories accredited for this method, but several state agencies have accreditation programs.
- Verify that the laboratory can complete the analyses within the method holding times of 7 days until extraction, 40 days until analysis.
- Each Tenax<sup>®</sup> trap should be analyzed separate to assess breakthrough, which is defined as the back trap (Anasorb trap) containing more than 30% of the quantity collected on the two front traps (Tenax<sup>®</sup>) for each analyte. This acceptance criterion does not apply when the analyte amount on the third trap is less than 75 ng.
- The analytical laboratory should spike the required Method 8260B suite of surrogates prior to analysis.
- The analytical lab should NEVER analyze low-level traps after analysis of high-level samples. To avoid this occurrence with samples of unknown concentration, the lab should conduct a blank run on the analytical instrument immediately after analyzing any high-level samples, to prevent cross-contamination.
- For the EPA ICR, reporting of tentatively identified compounds (TICs) will not be required and should not be requested of the lab.

# EPA SW-846 Method 0010/EPA Method 8270D

#### Method Title and Source

The ICR lists EPA SW-846 Method 0010 (SVOC) as the recommended method to sample for Speciated SVOC HAP. The method may also be used to analyze for the target POM compounds. The full title of this method is:

TEST METHOD 0010 - MODIFIED METHOD 5 SAMPLING TRAIN

EPA SW-846 Method 0010 (SVOC) is contained in EPA publication SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods. The method is available from:

http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/0010.pdf

EPA Method 8270D is contained in the same publication. The full title and source of this method are:

SEMIVOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/8270d.pdf

## Safety Tips

This method requires recovery of the sampling train with two solvents: methanol and methylene chloride (MeCl<sub>2</sub>). MeCl<sub>2</sub> is a regulated toxic compound and a suspected human carcinogen. The OSHA Short-Term Exposure Limit (STEL) for MeCl<sub>2</sub> is 125 ppm and the action level is 12.5 ppm. Unfortunately, the odor threshold is around 250 ppm. This means that, if you can smell it, you have already been overexposed at a level double the STEL. For adequate protection, methylene chloride must be handled under a laboratory hood. Filtering facepiece respirators (half- or full-face) may not be used as a regular solution to control methylene chloride exposures. You will not be able to smell it to know your filter is used up. Testers should also have nitrile rubber gloves, safety goggles and a lab coat or long sleeve shirt when handling MeCl<sub>2</sub>. If it contacts the skin, wash it off immediately. Wear safety glasses during sampling and recovery of the traps.

## **Method Overview**

This method uses isokinetic sampling based on the EPA Method 5 sampling train. Similar to EPA Method 23, the Method 0010 sampling train uses a quartz fiber filter media followed by a condenser packed with an adsorbent media (XAD resin) assembly to collect the target analytes. The operation of the sampling train generally follows EPA Method 5 protocol except with the addition of the condenser/XAD resin trap assembly. The primary difficulty in the operation of the Method 0010 sampling train is the initial assembly and set-up. Method 0010 provides illustrations and diagrams of the train set-up that aid greatly in the assembly.

After sampling, the sorbent module is removed from the sampling train and shipped to a laboratory (along with the filter and a solvent rinse of the sampling train components) for solvent extraction and analysis of the extract by high resolution gas chromatography/ mass spectrometry (GC/MS). Normally, Method 8270D is performed using low-resolution mass spectrometry; the EPA has indicated that either low-resolution or high-resolution MS can be used. The XAD sorbent is spiked with a suite of surrogate compounds prior to extraction to evaluate recovery. Internal standards (deuterium-labeled versions of various target species) are injected into the extracts before analysis for quantification of the analytes.

EPA has specified that the analysis should be performed in accordance with Method 8270D. Many analytical labs have not fully implemented the Method 8270D updates and are currently using Method 8270C for the SVOC analyses. The differences in the "D" update are subtle, with the primary difference in analytical lab QA/QC. The analyte list between the two remains the same. EPA has stated that labs can use 8270C but must demonstrate that the results satisfy 8270D performance criteria.

The SVOCs are sampled using the same sorbent used for collection of dioxin/furan/PCB organic HAP samples; therefore, it is possible for facilities that must conduct both tests to use the same sorbent sample for both, thus reducing the number of testing days. However, this combination has drawbacks, including longer sampling duration for the SVOCs, greater laboratory cost if the samples must be analyzed by high resolution MS, and the fact that most high-resolution GC/MS laboratories are not set up to do this method.

## **Method Limitations**

Power plant owners should consider the following limitations of Methods 0010/8270D relative to ICR testing:

- High moisture content in the stack gas is not an issue for this method.
- High levels of nitrogen oxides (>5,000 ppmv) have been reported to possibly destroy the spiked base/ neutral surrogates and may have the same effect on the base/neutral compounds on the 8270D list. To date, this issue has not been resolved.

# **Method Details**

## Material Requirements

- Use only glass, quartz, Teflon<sup>®</sup>, or Teflon<sup>®</sup>-lined sampling train components (although the method allows the use of a stainless steel nozzle).
- Use a Teflon<sup>®</sup> frit filter support rather than the glass frit filter support allowed by the method.
- If at all possible, use new glassware cleaned according to Method 0010 specifications. If using existing glassware, ensure that it is diligently cleaned according to the method specifications, including all components of the sampling train (filter holders, nozzles, etc.).
- Use high quality, pesticide-grade solvents.
- The use of **quartz** filters instead of glass fiber is recommended (although the method allows glass fiber).
- Wash bottles should be pre-cleaned and made of Teflon® or glass.
- If possible, contract with the analytical lab to supply pesticide-grade solvents that have been pre-analyzed for the target analytes .
- Contract with a laboratory to supply the XAD resin traps and filters. It is recommended that the laboratory be asked to pre-analyze the lot of XAD resin and provide the analytical results prior to testing. It is recommended that lab pre-spike the XAD traps with a surrogate compound (such as terphenyl D<sub>10</sub>). This spike is not required by the method, but is a good check for loss of SVOC during the whole sampling/analysis process.
- Use Teflon<sup>®</sup> tape (or aluminum foil rinsed with methylene chloride) to seal impinger openings before/after sampling.

# Sampling

- Use the XAD traps within 4 weeks of preparation. Keep the traps cool at all times prior and after use (<68 °F) and protected from direct sunlight using aluminum foil wrapped around the traps to prevent degradation of UV light-sensitive analytes and to aid in the cooling process.
- The ICR requires a minimum sample volume of 1.7 cubic meters and a minimum sampling duration of 2 hours. The method was originally designed and capable of sampling for at least 4 hours. Sample at a rate of < 0.75 dscf per minute.
- Use a small submersible pump to recycle iced water for the XAD jacket and the condenser. Monitor and record the XAD trap temperature on the data sheet. During sampling, orient the XAD vertically to prevent possible channeling .
- Use 1" wide Teflon<sup>®</sup>. tape or aluminum foil to seal impinger openings
- Use amber glass sample bottles with Teflon lids for collection of samples.
- There is no good reason to measure the weight gain in the XAD traps before or after sampling for stack gas moisture content measurements, due to the insignificant increase in weight (<0.5 grams) and potential contamination from exposing the trap ends with the removal of the caps or Teflon<sup>®</sup> tape.

- Be sure to collect the first impinger condensate catch and submit it to the lab for analysis, as required by Method 0010.
- Collect blanks of all chemical reagents and have them analyzed.
- Collect a train blank that can be archived (and analyzed in case of questionable test results).
- EPRI recommends that at least one field blank be analyzed for the sampling series. This blank should include all fractions required by the method, including recovery of a complete sampling train and XAD module, treated identically to a sample. Archiving a field blank is not sufficient, because the short timeframe of the ICR will prevent learning the results before the data must be reported to the EPA.
- Don't allow any solvents other than the recovery chemicals in the sampling or recovery area, and no smoking should be allowed anywhere near the sampling or sample recovery area. The site area used for sampling train assembly and sample recovery must be clean, dust-free (including coal dust), and far from any combustion gas sources such as engine exhaust. If these requirements cannot be met by a facility, it is recommended to ship the XAD resin module back to the laboratory for recovery. If off-site recovery is used, the glass components must be packaged carefully to avoid breakage.
- It is recommended that new chemical solvents and reagents be used in the performance of this method.
  Each solvent/reagent lot should be accompanied by a certificate of analysis to support the absence of background contamination.
- When shipping samples to the labs, keep the samples at < 4 °C using ice packs (ice cubes in doublebagged plastic bags has been found more effective than commercial ice packs) and enclose the filters in double baggies to prevent any in-leakage to the petri dishes by melted ice or moisture.

#### Analysis

- Use an experienced lab that has performed stack gas SVOC analyses routinely by Method 8270D.
- Either low-resolution or high-resolution MS may be used for SVOC analysis. Most laboratories that perform EPA Method 8270D will use low-resolution MS. EPA has indicated that the mass spectrometer must be operated in specific (or single) ion monitoring (SIM) mode. SIM mode is more sensitive than full scan mode, because the instrument spends more dwell time on the mass/charge ratios of the ions that are characteristic of each of the target analytes.
- EPA has specified that results must be reported separately for the following fractions: 1) the combined filter and cartridge, 2) the solvent rinses (including the XAD rinse), 3) the XAD condensate, and 4) the impinger solutions. Report the results separately for each of the four fractions. Do not combine the front half (filter, cyclone, and cartridge) with the back half (condensate, solvent, and impingers).
- Include instructions in the laboratory contract to ensure that both the front half (probe/nozzle rinse and filter) and backhalf (impinger condensate) fractions are spiked with the Method 8270D specified suite of internal standards.
- Verify that the lab will extract the samples within 30 days of sample collection and analyze the samples within 45 days of sample collection. Request standard turn-around time (TAT) of 2-3 weeks. If high-resolution MS is used, a longer TAT (4 weeks or more) should be expected.

#### Reporting

EPA has not provided guidance as of the publication date of this paper on how VOCs and SVOCs should be reported. These methods were not included in the Boiler MACT ICR. The following procedures are recommended.

• Have the lab report each analyte in total weight per sample (i.e., micrograms).

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- The EPA ICR does not require the reporting of TICs, thus, they should not be requested of the lab for reporting.
- Method and field blank results should be included in the detailed test report sent to EPA.

# **Unlisted Methods**

There are no alternative methods available for analysis of this group of chemicals.

# **Contacts**

This document was prepared by TRC Environmental For further information, contact Naomi Goodman, <u>ngoodman@epri.com</u>, 650.855.2193.

**Electric Power Research Institute** 

3420 Hillview Avenue, Palo Alto, California 94304-1338 • PO Box 10412, Palo Alto, California 94303-0813 USA 800.313.3774 • 650.855.2121 • askepri@epri.com • www.epri.com

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