

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

Reporting Detection Limits for Stack Tests

Background

On December 24, 2009, 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.

This technical brief is one in a series that the Electric Power Research Institute (EPRI) has prepared to help power plant owners improve the quality of ICR test results by raising awareness of technical issues related to sampling and analytical methods. Because EPA's plan is to use the ICR results to establish emission limits for the power industry, it is important to collect and report measurements that are accurate and representative of the stationary sources tested.

The objective of the briefs is to provide technical information that will assist power plant owners and stack testing contractors to identify appropriate technical resources, develop test plans, streamline testing, select appropriate sampling and analytical methods, and avoid common errors. The recommendations are not intended as universal guidance; each power plant owner should evaluate their applicability for a specific situation.

About Detection Limit Reporting for the ICR

The ICR requires facilities to report numerical values for all stack test measurements. For measurements that are below the detection limit of a test method, EPA has specified that the detection limit must be reported as the measured value. The detailed instructions for calculating and entering values for measurements below detection limits are laid out in the ICR and Section 114 letters, and are shown below in Appendix A.

In this Technical Brief, EPRI discusses the challenges that facilities will face in attempting to comply with the ICR requirement. The difficulties arise from the fact that laboratories often are unable or unwilling to report detection limits per the EPA requirements. Many laboratories do not report numerical values below laboratory-defined reporting limits, which are higher than detection limits. Their reluctance is due to the fact that a detection limit is, by definition, a concentration at which it is possible to state with good confidence that a chemical is present in a sample. It is not a concentration at which an accurate measurement can be obtained. As an instrument attempts to measure smaller and smaller amounts of a chemical, the precision of the measurement gets poorer and poorer. At the detection limit, the uncertainty of the measurement is very high. To measure a chemical in a sample with an acceptable level of accuracy, the chemical must be at or above a higher concentration – the quantitation level.

Why Do Detection Limits Matter for the ICR?

The data reported to the EPA in Part III of the ICR will be used by EPA to propose Maximum Available Control Technology (MACT) limits. By law, MACT limits must be based on the 12% of units with the lowest emissions. Based on historical data collected by EPRI, many HAPs measurements will be below the detection limit of the test methods. As stack gas concentrations below detection limit will be represented by a detection limit in EPA's calculation of the MACT limits, it is critical that the detection limits reported to EPA are calculated and reported correctly. Incorrect values could result in MACT limits that cannot be complied with (if the values reported are below the actual capability of the method) or could distort the evaluation of control device performance (if reported above the actual detection limit of the method).

The EPA has stated that actual values should be reported for measurements above the "analytical detection limit" and below the "laboratory reporting level or quantitation level." To understand what this means for ICR reporting, a brief explanation of these terms is in order. This discussion applies to methods that involve laboratory analysis. Instrumental methods conducted at the stack are discussed later in this paper. Appendix B lists the ICR stack test methods, along with the approach that is typically used to derive detection limits for each method.

All analytical measurements made with an electronic instrument have uncertainty due to random noise in the electronics, fluctuations in the signal baseline, and other operational parameters unconnected to analyses of samples. Laboratories often identify a value termed the **"instrument detection level (IDL)"**, which is the lowest amount of a chemical that can be distinguished from background noise. The IDL is does not take into account any increases in signal from interfering substances or the sample matrix, or lowered sensitivity due to incomplete recovery of analyte from the sample when it is processed. A positive signal at the IDL is very likely to be due to chance fluctuations. In statistical terms, a large percentage of detections will be false positives (detecting something that is not there) and a large percentage of nondetects will be false negatives (not detecting something that is in fact there). Due to EPA's reporting requirements for the ICR, reporting IDLs as actual values could result in calculation of MACT limits below the measurement capabilities of the test methods. Testers should verify with their laboratories that they are not reporting IDLs and if they are, request them to reissue their reports with appropriate limits.

EPA has not defined an "analytical detection limit" for the purposes of the ICR. Numerous definitions of detection limit have been proposed; however, a common definition is the minimum amount of a substance that can be distinguished from zero with a given level of confidence (usually 99%, or a false positive rate of 1%). The most commonly used detection limit procedure is the **Method Detection Limit (MDL)** defined in 40 CFR Part 136, Appendix B. The MDL is determined by carrying through the entire analytical procedure (including sample preparation) seven replicate samples containing the analyte at a concentration one to five times the estimated detection limit (EDL). The MDL is calculated as three times the standard deviation of the concentration measured in the seven samples.

Alternate Approaches to Deriving Detection Limits

In 2000, the EPA agreed to reevaluate their procedures for deriving detection and quantitation limits. This effort included a comparison of the current MDL procedure with alternative procedures developed by the American Society for Testing and Materials (ASTM), American Council of Independent Laboratories (ACIL) and others. Some of the alternative procedures have greater statistical rigor than the current approach; however, EPA has not yet issued a decision on which method will be adopted. Currently, the MDL remains the standard approach used by U.S. laboratories.

Several methods are allowed for determining an EDL: from an IDL, from the standard deviation of replicate analyses of samples, or from a calibration curve. Because the EDL can be derived in several ways, the standard deviation increases with concentration, and the spiking concentration is not fixed, it is not possible to determine exactly the percentage of false positives or false negatives at the MDL. However, the intent is to control the false positive rate at about 1%, while the false negative rate is not controlled and can be as high as 50%.

It is important to recognize that several of the ICR test methods require analysis of multiple matrices or fractions and that this affects the procedures for reporting detection limits. For example, Method 29 has two different fractions that must be analyzed when it is used to measure non-mercury metals: a filter extract (particulate metals), and a nitric acid/peroxide impinger solution (vapor-phase metals) and acetone rinsate from the probe. The laboratory should ideally have conducted a MDL study for each of these fractions.

The MDL will generally underestimate the actual measurement variability, for several reasons:

- The matrix used in MDL studies is generally clean water (for liquid samples) or clean sand (for solid samples) spiked with the chemicals of interest. Unless a laboratory is contracted to perform a MDL study using the same matrix as the actual samples, the laboratory's MDLs may be lower than the method can achieve in practice. For example, a clean sand sample is likely to be an easier matrix for recovery of organic compounds by solvent extraction than the XAD resin used in EPA Methods 0010/8270D.
- A MDL study is usually run by a single analyst, on a single instrument, on a single day, immediately after calibrating the instrument. Therefore the results ignore many sources of within-laboratory variability that may overestimate the capability of the method.

To account for matrix effects, sensitivity differences among multiple similar instruments, and long-term variability in method performance, laboratories define a "reporting limit (RL)" for each parameter analyzed by a particular method in a particular sample matrix (e.g., water). The RL is a value below which measured concentrations will be reported as non-detected (ND) or <RL. RLs are typically higher than MDLs. They represent the amount of analyte that the laboratory is confident can be detected using any similar instrument and by any analyst on their staff. RLs are generally set at concentrations that ensure that the laboratory can routinely achieve quality control criteria set by the method, to avoid having to reanalyze excessive numbers of samples. There is no standard procedure for determining RL, and the statistical frequency of false positive or false negative errors at the RL will depend on how it is derived. The RL may be a multiplier of the MDL or may be set at the lowest calibration point of the multi-concentration spiking series used to calibrate the instrument. Most laboratories routinely report RLs rather than MDLs. Since there is little consistency among labs in how this is done, it is important to obtain a complete description from the laboratory as to their procedure.

Whether the lab reports a MDL or a RL, the value will be adjusted to account for any dilution to the sample. For example, in analysis of metals by inductively coupled plasma mass spectrometry (ICP-MS), samples high in dissolved solids can quench the plasma, causing a negative bias in the measurement. If a sample is diluted by a factor of ten to reduce this interference, the RL must be multiplied by ten because only a tenth as much analyte is present in the same volume of injected solution. The laboratory report should clearly indicate whether a dilution factor was applied.

To ensure that a measurement is not only correctly identified as present or not present but is also accurate, the value should be greater than the **quantitation limit** of the method. A quantitation limit can be defined as the smallest concentration of analyte greater than the detection limit where the measurement accuracy meets the objectives of the intended purpose. There is little agreement on how a quantitation limit is determined. Some of the definitions in common use include:

- Ten times the standard deviation of a blank (a sample that does not contain the analyte). This quantity is generally termed the Limit of Quantitation (LOQ).
- Ten times the standard deviation of samples at the EDL, or 3.18 times the MDL. The EPA Minimum Level (ML), used in most EPA water methods, employs this definition.
- The lowest concentration of standard solution used to calibrate the instrument (the lowest calibration point).

Some laboratories report a Practical Quantitation Limit (PQL) which they define as the routinely achievable quantitation limit – this can be set as a multiplier of the RL or by using professional judgment. Laboratories may assign a "J" flag to values below the quantitation limit (ML or PQL) and above the detection limit, indicating that the value is an estimate. EPA is requiring all values below the quantitation limit to be entered as "real", unqualified values. However, as the concentrations of values below quantitation limits are of uncertain accuracy, it is important that these flags are retained in the detailed test report submitted to EPA.

The final term that enters into the ICR reporting is the **in-stack detection limit**, which is obtained by converting the analytical detection limit or reporting limit to a stack gas emission rate (in lb/MMBtu) or a stack gas concentration (in ppmvd @7% O₂). Calculation of the in-stack detection limit requires information on the stack gas composition, the heat content and burn rate of the fuel, and the stack gas volume that was sampled. The values reported to EPA in the Electronic Reporting Tool (ERT) are converted to an in-stack detection limit by scripts contained in the application. The EPA's Excel template for methods not supported by the ERT does not perform conversions; the user must calculate in-stack values independently.

Special Considerations and Method-Defined Procedures

Some of the ICR methods require elaboration of the above discussion or have method-defined procedures for determining detection limits.

<u>Semivolatile Organics by EPA Methods 0010/8270D and Volatile Organics by EPA Methods 0031/8260B</u>: These mass spectrometry methods require the mass spectra of the target analytes to match a standard with a specified goodness of fit in order to be considered detected. In addition to detection, each chemical must fulfill the requirements for positive identification. Thus, the MDL for these chemicals may not depend solely on the standard deviation of replicate analyses.

Polychlorinated dibenzodioxins/dibenzofurans (PCDDs/PCDFs) by EPA Methods 23/8290A: Method 8290 uses the principle of isotope dilution, in which radio-labeled versions of some of the dioxin/furan congeners are added to the sample and the sample extract to mimic the behavior of the native compounds. These labeled congeners are used to quantify the native compounds, increasing the accuracy of the method. The method specifies a procedure that calculates an **Estimated Detection Limit (EDL)** from 2.5 times the noise level at baseline in each sample. Thus, EPA Method 23 is the only ICR method that requires a sample-specific instrument detection limit rather than a MDL. Some dioxin laboratories assign a qualifier of EMPC – **Estimated Maximum Potential Concentration** – to detections that exceed the EDL but do not meet all of the chromatographic peak retention time and mass spectra identification criteria set by the method. EPA is requiring that EMPC values be reported as "real" values for the ICR.

<u>Polychlorinated biphenyls (PCBs) by EPA Method 23/1668B</u>: The sensitivity of this method is generally limited not by the instrument detection limit but by the ubiquitous presence of PCBs in the laboratory ambient air. EPA Method 1668B defines **Estimated Method Detection Limits (EMDLs)**, which are the lowest levels which could reliably be distinguished from laboratory contamination over a number of months of operation in a single laboratory. Laboratories generally determine their own MDLs, but these must not exceed 1/3 of the EMDL values listed in the method. <u>Mercury by EPA Method 30B</u>: Procedures for determination of a MDL and an in-stack detection limit are specified in the method, along with quality control measures for ensuring that mercury is recovered adequately from the sorbent trap. It is critical for this method that the MDL study is performed on the exact sorbent material (same sorbent type and vendor) used in the stack test. If a thermal desorption method is used, the same sorbent material employed in the stack test should be used for calibrating the instrument. See the EPRI technical brief on Mercury and Non-Mercury Metallic HAP testing for the ICR for additional information.

<u>Filterable PM by EPA Methods OTM-27, OTM-28 and 5:</u> The in-stack detection limit for gravimetric methods depends on the sampling duration and the amount of residue contributed by the recovery water. All samples will have some detectable residue, but in some cases the mass detected may be approximately the same as that present in the blanks. Although the methods do permit blank corrections for certain fractions, a maximum allowed blank correction is specified in the method that may often be exceeded. For example, OTM-28 allows up to a 2 mg blank correction that is often exceeded by typical recovery reagents. It is important to report the blank results in the detailed test report so that the results can be interpreted correctly.

Detection Limits for Instrumental Methods

Instrumental methods applied at the stack (e.g., Method 25A – Total Hydrocarbons) are not suitable for determination of a MDL, as there is not an easy way to prepare replicate flue gas samples. Generally, there is no defined detection limit for these instruments – a zero or even a negative value can be recorded if the instrument response drifts during testing. The probability of obtaining a nondetect is related to the instrument span selected for testing. An appropriate span for the instrument should be identified in a pre-sampling survey. EPA has stated in their ICR guidance that they require an actual value to be reported for instrumental methods, even if it is a negative number (see Appendix A). The value should also be noted as "above detection limit – ADL".

The ICR reporting requirement will produce calculated emissions even if no analyte is present. To allow proper interpretation of the instrumental method results, is important to provide additional information on the instrument calibration procedure in the test report and Comments field of the ERT. This information should include the calibration concentrations used and the instrument response at each concentration.

<u>EPA Method 320 (Organic Gases by Fourier Transform Infrared (FTIR) Spectroscopy</u>) defines a quantitation limit rather than a detection limit. The quantitation limit is determined from the noise signal in the portion of the spectrum used to measure each target analyte, after correction for spectral interferences. The method does define an instrument detection limit, defined as a multiple of the noise in a zero portion of the spectrum; however, this measure is not appropriate for quantitative measurements as it does not account for interferences on specific compounds by common substances such as carbon dioxide and water.

<u>EPA Method 30A</u> for determination of mercury using a continuous mercury monitor requires calibration of the instrument with calibration standards of elemental and ionic mercury, prepared according to an EPA traceability protocol. The method does not define how a detection limit is determined, based on the assumption that mercury will generally be detectable.

Conversion of Laboratory Detection Limits into In-Stack Detection Limits

Example calculations used to convert laboratory detection limits (or reporting limits) to in-stack detection limits are provided in Appendix C.

In the recently completed Industrial Boiler ICR, the EPA initially made errors in calculating in-stack concentrations based on data reported in the ERT, requiring EPA to issue revisions to their ICR database. To ensure that correct, high quality data is used for the Utility ICR, EPRI recommends that facilities ask their testing contractors to calculate in-stack detection limits and detected concentrations and include these in the detailed test report, along with the measurement units reported to the EPA. The example calculations included in Appendix C will assist facilities to check that these conversions are done correctly.

Reporting Detection Limit Information for the ICR

The ICR requires facilities to note the method used to develop a detection limit in the Comments field of the ERT Lab data tab, and also in the "Other Supporting Information" field in the EPA's "Other Emission Test Methods" template. EPA has also requested that a more detailed explanation of the derivation of detection limits should be appended to the test report. Due to the considerable confusion in terminology that exists surrounding detection and quantitation limits, EPRI recommends that facilities obtain a written explanation from each laboratory as to the derivation of their detection (or reporting) limits for each test method and include this information in the test report.

Facilities should also be aware that stack emissions calculated following the ICR detection limit reporting rules may not be appropriate for use in other contexts, such as the Toxics Release Inventory program. For multi-fraction methods and for dioxins/furans, there will be significant differences in the ICR totals from those calculated using normal reporting conventions. Facilities should consider asking their stack testers to report emissions totals by both approaches.

Appendix A ICR Requirements for Reporting Nondetected Values

Laboratory Methods

Identify the status of measured values relative to detection levels on the spreadsheet or in the ERT using the following descriptions:

- BDL (below detection level) all analytical values used to calculate and report an instack emissions value are less than the laboratory's reported detection level(s);
- DLL (detection level limited) at least one but not all values used to calculate and report an in-stack emissions value are less than the laboratory's reported detection level(s); or
- ADL (above detection level) all analytical values used to calculate and report an instack emissions value are greater than the laboratory's reported detection level(s)

For each reported emissions value, insert the appropriate flag (BDL, DLL, or ADL) in the **Note** line of Excel emission test spreadsheet template or in the **Comments** line of the Electronic Reporting Tool (ERT).

When reporting and calculating individual test run data:

- For analytical data reported from the lab as "nondetect" or "below detection level;"
 - Include a brief description of the procedures used to determine the analytical detection and in-stack detection levels:
 - In the **Note** line of Excel emission test spreadsheet template; or
 - In the **Comments** line of Lab Data tab in the Run Data Details in the **ERT**.
 - Describe these procedures completely in a separate attachment including the measurements made, the standards used, and the statistical procedures applied.
 - Calculate in-stack emissions rate for any analytical measurement below detection level using the relevant detection level as the "real" value.
 - Report the calculated emissions concentration or rate result:
 - As a bracketed "less than" detection level value (e.g., [<0.0105]) in the Excel emission test spreadsheet template and include the appropriate flag in the Note line; or
 - As a "real" value in the ERT with the appropriate flag in the Comments line.
 - Report as "real" values (i.e., no brackets or < symbol) any analytical data measured above the detection level including any data between the analytical detection level and a laboratory-specific reporting or quantification level (i.e., flag as ADL).
 - Apply these reporting and calculation procedures to measurements made with Method 23:
 - Report data in the Excel emission test spreadsheet template for each of the D/F congeners measured with Method 23 below the detection level as [< detection level]
 - Do not report emissions as zero as described in the method
- For pollutant measurements composed of multiple components or fractions (e.g., Hg and other metals sampling trains) when the result for the value for any component is measured below the analytical detection level;
 - Calculate in-stack emissions rate or concentrations as outlined above for each component or fraction;
 - Sum the measured and detection level values as outlined above using the in-stack emissions rate or concentrations for all of the components or fractions; and
 - Report the sum of all components or fractions:
 - As a bracketed "less than" detection level value (e.g., [<0.0105]) in the Excel emission test spreadsheet template and include the appropriate flag in the Note line; or
 - As a "real" value in the **ERT** with the appropriate flag in the Comments line.

- Report also the individual component or fraction values for each run if the Excel emission test spreadsheet template or ERT format allows; if not (i.e., the format allows reporting only a single sum value):
 - For the Excel emission test spreadsheet template, next to the sum reported as above report in the **Notes** line the appropriate flag along with the values for the measured or detection level value for each component or fraction as used in the calculations (e.g., 0.036, [<0.069], 1.239, [<0.945] for a four fraction sample)
 - For the ERT, next to the sum reported as above, report on the **Comments** line the appropriate flag and the measured or detection level value for each component or fraction as used in the calculations (e.g., 0.036, [<0.069], 1.239, [<0.945] for a four fraction sample)

Instrumental Test Methods

- For measurements conducted using instrumental test methods (e.g., Methods 3A, 6C, 7E, 10, 25A)
 - Record gaseous concentration values as measured including negative values and flag as ADL; do not report as BDL
 - Calculate and report in-stack emissions rates using these measured values
 - Include relevant information relative to calibration gas values or other technical qualifiers for measured values in *Comments* line in the ERT
- When reporting and calculating average emissions rate or concentration for a test when some results are reported as BDL
 - Sum all of the test run values including those indicated as BDL or DLL as "real" values
 - Calculate the average emissions rate or concentration (e.g., divide the sum by 3 for a three-run test)
 - Report the average emissions rate or concentration average:
 - As a bracketed "less than" detection level value (e.g., [<20.06]) in the Excel emission test spreadsheet template and include the appropriate flag in the Note line
 - As a "real" value in the ERT and include the appropriate flag in the Comments line.

8

Parameter Acid Gases and HCN Hydrochloric acid/	Docommond and		MDI Or	Mathod-	
Acid Gases and HCN Hydrochloric acid/	Alternate Methods	Sample Type	RL	Defined	Notes
Hydrochloric acid/					
	EPA Method 26A	Impinger liquid	X		
hydrofluoric acid (HCI/HF)	EPA Method 320	Gas stream		×	Uses a quantitation limit in the spectral region of the compound after correction for interferences
Hydrogen cyanide (HCN)	EPA Method CTM-033	Impinger liquid	×		
Metals and Potential Surrogates	Ş				
Total filterable PM	EPA Method 29	Filter extract, impinger liquid	×		Gravimetric methods typically do not report non detects
PM2.5 (filterable), dry stack	OTM 27	Filter extract	×		Gravimetric methods typically do not report non detects
PM2.5 (filterable), wet stack	EPA Method 5	Filter extract	×		Gravimetric methods typically do not report non detects
PM2.5 (condensable)	OTM 28	Filter extract, impinger liquid	×		Gravimetric methods typically do not report non detects
Non-mercury metals	EPA Method 29	Filter extract, impinger liquid	×		
	EPA Method 30B	Sorbent or sorbent extract		Х	MDL procedure is defined in the method
Mercury	EPA Method 30A	Gas stream		×	Method-defined procedure based on calibration with traceable standards
Organics and Potential Surrogates	ates				
Total hydrocarbons (THC)	EPA Method 25A	Gas stream			Not defined – ICR requires reporting zero or negative values
	EPA Method 18	Gas stream		х	Depends on sampling method: direct, bag, or sorbent preconcentration
	EPA Method 320	Gas stream		х	Uses a quantitation limit in the spectral region of the compound after correction for interferences
Formaldehyde	EPA Method 320	Gas stream		×	Uses a quantitation limit in the spectral region of the compound after correction for interferences
	SW-846 Method 0011	Impinger liquid	×		
Volatile organic compounds (VOC)	SW-846 Method 8260B	Sorbent purge/condenser liquid	×		
Semivolatile organic compounds (SVOC)	SW-846 Method 8270D	Sorbent extract	×		
Dioxin/Furans	EPA Method 23	Sorbent extract, solvent rinse		Х	Instrumental detection limit defined in the method
Polychlorinated biphenyls (PCB)	EPA Method 23/1668B	Sorbent extract, solvent rinse		×	MDLs must be lower than method-defined EMDLs

Appendix B Detection Limit Approaches for ICR Stack Test Methods

Appendix C

Conversion Calculations for In-Stack Detection or Reporting Limits

This section illustrates the equations for converting a laboratory or instrument detection (or reporting) limit into an in-stack detection (or reporting) limit. Example reporting limits are shown for each calculation for the purposes of demonstrating the conversion equations. These values are typical of those reported by several laboratories involved in ICR testing, but are not intended as benchmarks and may not meet the ICR requirement of an "analytical detection limit".

Potential Non-Mercury Metallic HAP Surrogates

Methods: EPA Methods 5/OTM-027/OTM-028/ Method 29 Particulate Example Laboratory Reporting Limit: 0.2 mg Example In-Stack Reporting Limit (ISRL): 5.40E-05 lb/MMBtu Equation:

ISRL, *lb/mmBtu* = $\frac{mg}{1000*453.592*V_{mstd}} *F_d * \frac{20.9}{(20.9 - \%O_2)}$

Where:

F _d	=	F-factor, volume of combustion products per unit of heat content, scf/mmBtu
V _{mstd}	=	Stack sample volume corrected to standard conditions (68°F, 1 atm), scf
%O ₂	=	Oxygen content of stack gas, dry basis volume percent
1000	=	Milligrams (mg) to grams (g) conversion
453.592	=	Grams to pounds conversion
mg	=	Laboratory reporting limit for filter plus acetone rinse, mg

Example calculation values:

F _d	=	9,780 scf/mmBtu
V _{mstd}	=	120.070 scf
%O ₂	=	7.0 %

Acid Gases and Hydrogen Cyanide

Methods: EPA Methods M26/26A, CTM-033 **Example Laboratory Reporting Limit:** 0.2 µg/ml (HCl) **Example In-Stack Reporting Limit (ISRL):** 2.81E-05 lb/MMBtu, 0.02 ppmvd @7% O₂ **Equation:**

ISRL, *lb/mmBtu* =
$$\frac{\mu g/ml^* V_{collected}}{1.0E06^* 453.592^* V_{mstd}} * F_d * \frac{20.9}{(20.9 - \%O_2)}$$

Where:

F _d	=	F-factor, volume of combustion products per unit of heat content, scf/mmBtu
V _{mstd}	=	Stack sample volume corrected to standard conditions (68°F, 1 atm), scf
V _{collected}	=	Volume of liquid sample collected*, ml
%O ₂	=	Oxygen content of stack gas, dry basis volume percent
1E06	=	Micrograms to grams conversion
453.592	=	Grams to pounds conversion
µg/ml	=	Laboratory reporting limit expressed as a concentration, equivalent to mg/L

* Liquid sample includes impinger liquid and sampling train rinse.

Example calculation values:

F _d	=	9,780 scf/mmBtu
V _{mstd}	=	88.278 scf
%O ₂	=	10.0 %
V _{collected}	=	300 ml

Equation:

ISRL,
$$ppmvd@7\%O_2 = \frac{\mu g/ml^*V_{collected}}{1.0E06^*453.592^*V_{mstd}} * \frac{385.1^*1E06}{MW} * \frac{(20.9-7)}{(20.9-\%O_2)}$$

Where:

Vmstd	=	Stack sample volume corrected to standard conditions (68°F, 1 atm), scf
$V_{collected}$	=	Volume of liquid sample collected*, ml
%O ₂	=	Oxygen content of stack gas, dry basis volume percent
1E06	=	Micrograms to grams conversion
1E06	=	Volume fraction to ppm conversion
453.592	=	Grams to pounds conversion
385.1	=	Molecular volume, scf/lb-mole (at standard conditions)
MW	=	Molecular weight of target compound, lb/lb-mole
µg/ml	=	Laboratory reporting limit expressed as a concentration, equivalent to mg/L

* Liquid sample includes impinger liquid and sampling train rinse.

Example calculation values:

$V_{collected}$	=	300 ml
V _{mstd}	=	88.278 scf
%O ₂	=	10.0 %
MW	=	36.47 (for HCl)

Method: EPA Method 320 (Acid Gases and HCN) Example Instrument Reporting Limit: 0.015 ppmw (HCl) Example In-Stack Reporting Limit (ISRL): 0.021 ppmvd @7% O₂ (HCl) Equation:

ISRL,
$$ppmvd@7\%O_2 = \frac{ppmvw}{(1 - (\%H_2O/100))} * \frac{(20.9 - 7)}{(20.9 - \%O_2)}$$

Where:

%O ₂	=	Oxygen content of stack gas, dry basis volume percent
$^{\rm H_2O}$	=	Moisture vapor content of the stack gas, volume percent

Example calculation values:

%O ₂	=	10.0 %
$^{8}H_{2}O$	=	8.25 %

Non-Dioxin/Furan Organic HAP

Method: Semivolatile Organic Compounds/POM by EPA Methods 0010/8270C Example Laboratory Reporting Limit: 10 µg Example In-Stack Reporting Limit (ISRL): 6.89E-06 lb/MMBtu, 0.7.50 µg/dscm @ 7% O₂ Equation:

ISRL, *lb/mmBtu* =
$$\frac{\mu g}{1.0E06*453.592*V_{mstd}}*F_d*\frac{20.9}{(20.9-\%O_2)}$$

Where:

F _d	=	F-factor, volume of combustion products per unit of heat content, scf/mmBtu
V _{mstd}	=	Stack sample volume corrected to standard conditions (68°F, 1 atm), scf
%O ₂	=	Oxygen content of stack gas, dry basis volume percent
1E06	=	Micrograms to grams conversion
453.592	=	Grams to pounds conversion
hð	=	Laboratory reporting limit, µg

Example calculation values:

F _d	=	9,780 scf/mmBtu
V _{mstd}	=	60.035 scf
%O ₂	=	10.0 %

Equation:

ISRL,
$$\mu g / dscm@7\%O_2 = \mu g * \frac{35.315}{V_{mstd}} * \frac{(20.9 - 7)}{(20.9 - \%O_2)}$$

Where:

V_{mstd}	=	Stack sample volume corrected to standard conditions (68°F, 1 atm), scf
%O ₂	=	Oxygen content of stack gas, dry basis volume percent
35.315	=	Cubic feet to cubic meters conversion
hð	=	Laboratory reporting limit, µg

Example calculation values:

V _{mstd}	=	60.035 scf
% O ₂	=	10.0 %

Note: These same equations, with the appropriate conversion factors, can be used for any of the organics methods with a detection limit in mass (µg) units. A typical RL for VOCs (Methods 0030 or 0031) is 10 ng, resulting in an ISRL of 6.89E-09 lb/MMBtu or 7.50E-03 µg/dscm @ 7% O_2

Non-Dioxin/Furan Organic HAP Surrogates

Method: EPA Methods 25A (Total Hydrocarbons), Method 320 (CH₄ and formaldehyde), **Example In-Stack Reporting Limits (ISRL):** 0.1 ppmvw (THC), 0.5 ppmvw (CH₄), 0.05 ppmvw (formaldehyde), 7.97E-05 lb/mmBtu (formaldehyde) **Equation:**

ISRL, $lb/mmBtu = \frac{ppmvw}{(1 - (\%H_2O/100))} * \frac{MW}{385.1*1E06} * \frac{20.9}{(20.9 - \%O_2)}$

12

Where:

F _d	=	F-factor, volume of combustion products per unit heat content, scf/mmBtu
%O ₂	=	Oxygen content of stack gas, dry basis volume percent
$^{\rm H_2O}$	=	Moisture vapor content of the stack gas, volume percent
385.1	=	Molecular volume, scf/lb-mole (at standard conditions)
1E06	=	Volume fraction to ppm conversion
MW	=	Molecular weight of target compound, lb/lb-mole
ppmvw	=	Concentration in the gas, wet basis volume
ppmvw	=	Concentration in the gas, wet basis volume

Example calculation values:

F _d	=	9,780 scf/mmBtu
%O ₂	=	10.0 %
%H2O	=	8.25
MŴ	=	30.03 (formaldehyde)

Method: EPA Method 18 (Methane - CH₄) Example In-Stack Reporting Limit (ISRL): 0.1 ppmvw, 7.81E-05 lb/mmBtu Equation:

ISRL, *lb/mmBtu* = ppmvd *
$$\frac{MW}{385.1*1E06}$$
 * F_d * $\frac{20.9}{(20.9 - \%O_2)}$

Where:

F _d	=	F-factor, volume of combustion products per unit heat content, scf/mmBtu
%O ₂	=	Oxygen content of stack gas, dry basis volume percent
385.1	=	Molecular volume, scf/lb-mole (at standard conditions)
1E06	=	Volume fraction to ppm conversion
MW	=	Molecular weight of target compound, lb/lb-mole
ppmvd	=	Concentration in the gas, dry basis volume

Example calculation values:

F _d	=	9,780 scf/mmBtu
%O ₂	=	10.0 %
MW	=	16.04 for Methane

Method: EPA Method 0011 (Formaldehyde)

Example Laboratory Reporting Limit: 0.001 µg/ml

Example In-Stack Reporting Limit (ISRL): 1.38E-07 lb/mmBtu, 1.20E-04 ppmvd @ 7% O₂ Equation:

ISRL, *Ib/mmBtu* =
$$\frac{\mu g/m! * V_{collected}}{1.0E06 * 453.592 * V_{mstd}} * F_d * \frac{20.9}{(20.9 - \%O_2)}$$

F _d	=	F-factor, volume of combustion products per unit heat content, scf/mmBtu
V _{mstd}	=	Stack sample volume corrected to standard conditions (68°F, 1 atm), scf
$V_{collected}$	=	Volume of liquid sample collected*, ml
%O ₂	=	Oxygen content of stack gas, dry basis volume percent
1E06	=	Micrograms to grams conversion
453.592	=	Grams to pounds conversion
µg/ml	=	Laboratory reporting limit expressed as a concentration, equivalent to mg/L

* Liquid sample includes impinger liquid and sampling train rinse.

Example calculation values:

F _d	=	9,780 scf/mmBtu
V _{collected}	=	200 ml
V _{mstd}	=	60.035 scf
%O ₂	=	10.0 %

Equation:

		* 385.1*1 <i>E</i> 06	(20.9 – 7)
ISRL, $ppmvd@7\%O_2 =$	1.0E06*453.592*V _{mstd}	MW	(20.9 – % <i>O</i> ₂)

Where:

V _{mstd}	=	Stack sample volume corrected to standard conditions (68°F, 1 atm), scf
$V_{collected}$	=	Volume of liquid sample collected*, ml
%O ₂	=	Oxygen content of stack gas, dry basis volume percent
1E06	=	Micrograms to grams conversion
453.592	=	Grams to pounds conversion
385.1	=	Molecular volume, scf/lb-mole (at standard conditions)
1E06	=	Volume fraction to ppm conversion
MW	=	Molecular weight of target compound, lb/lb-mole
µg∕ml	=	Laboratory reporting limit expressed as a concentration, equivalent to mg/L

* Liquid sample includes impinger liquid and sampling train rinse.

Example calculation values:

$V_{collected}$	=	200 ml
V _{mstd}	=	60.035 scf
%O ₂	=	10.0 %
MŴ	=	30.03 (formaldehyde)

Dioxin/Furan Organic HAP

Method: EPA Method 23 (PCDD/PCDF) Example Laboratory Reporting Limit: 2.3 pg Example In-Stack Reporting Limit: 3.2E-13 lb/mmBtu, 3.51E-04 ng/dscm @7%O₂ Equation:

ISRL, *lb/mmBtu* =
$$\frac{\text{pg}}{1E12*453.592*V_{mstd}}*F_d*\frac{20.9}{(20.9-\%O_2)}$$

Where:

F _d	=	F-factor, volume of combustion products per unit heat content, scf/mmBtu
V _{mstd}	=	Stack sample volume corrected to standard conditions (68°F, 1 atm), scf
%O ₂	=	Oxygen content of stack gas, dry basis volume percent
453.592	=	Grams to pounds conversion
1E12	=	Picograms (pg) to grams (g) conversion
pg	=	Laboratory detection limit for homolog group, pg

Example calculation values:

F _d	=	9,780 scf/mmBtu
V _{mstd}	=	300.175 scf
%O ₂	=	10.0 %

Equation:

ISRL, ng /
$$dscm@7\%O_2 = \frac{pg}{1000} * \frac{35.315}{V_{mstd}} * \frac{(20.9 - 7)}{(20.9 - \%O_2)}$$

Where:

V _{mstd}	=	Stack sample volume corrected to standard conditions (68°F, 1 atm), scf
%O ₂	=	Oxygen content of stack gas, dry basis volume percent
35.315	=	Cubic feet to cubic meters conversion
1000	=	Picograms (pg) to nanograms (ng) conversion
pg	=	Laboratory detection limit for homolog group, pg

Example calculation values:

V _{mstd}	=	300.175 scf
%O ₂	=	10.0 %

Mercury and Non-Mercury Metallic HAP

Method: EPA Method 29 (Non-Mercury metals) Example Laboratory Reporting Limit: 0.6 µg (antimony) Example In-Stack Reporting Limit (ISRL): 4.96E-07 lb/mmBtu (antimony) Equation:

ISRL, *lb/mmBtu* =
$$\frac{\mu g_{TOTAL}}{1.0E06*453.592*V_{mstd}}*F_d*\frac{20.9}{(20.9-\%O_2)}$$

Where:

F _d	=	F-factor, volume of combustion products per unit heat content, scf/mmBtu
V _{mstd}	=	Stack sample volume corrected to standard conditions (68°F, 1 atm), scf
%O ₂	=	Oxygen content of stack gas, dry basis volume percent
1E06	=	micrograms to grams conversion
453.592	=	Grams to pounds conversion
HG ^{TOTAL}	=	Laboratory reporting limit, total mass of laboratory fractions 1A and 2A, ng

Example calculation values:

F _d	=	9,780 scf/mmBtu
µg _{total}	=	0.6 µg (0.3 µg for Fraction 1A and 0.3 µg for Fraction 2A)
V _{mstd}	=	120.070 scf
%O ₂	=	10.0 %
-		

Method: EPA Method 30B (Mercury)

Example Laboratory Reporting Limit: 2 ng

Example In-Stack Reporting Limit (ISRL): 4.88E-08 lb/mmBtu Equation:

ISRL, Ib/mmBtu =
$$\frac{ng}{1.0E90} * \frac{0.02832}{V_{mstd} * 453.592} * F_d * \frac{20.9}{(20.9 - \%O_2)}$$

Where:

F _d	=	F-factor, volume of combustion products per unit heat content, scf/mmBtu
V _{mstd}	=	Stack sample volume corrected to standard conditions (68°F, 1 atm), scf
%O ₂	=	Oxygen content of stack gas, dry basis volume percent
1E09	=	Nanograms to grams conversion
453.592	=	Grams to pounds conversion
0.02832	=	Cubic meters to cubic feet conversion
ng	=	Laboratory reporting limit, ng

Example calculation values:

F _d	=	9,780 scf/mmBtu
V _{mstd}	=	0.048 dscm
%O ₂	=	10.0 %

Contacts

This document was prepared by EPRI, with assistance from TRC Environmental Corporation

For further information, contact Naomi Goodman, <u>ngoodman@epri.com</u>, Electric Power Research Institute (EPRI) 3420 Hillview Avenue Palo Alto, CA 94304 650.855.2193.

1021357

May 2010

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

© 2010 Electric Power Research Institute (EPRI), Inc. All rights reserved. Electric Power Research Institute, EPRI, and TOGETHER... SHAPING THE FUTURE OF ELECTRICITY are registered service marks of the Electric Power Research Institute, Inc.