

**Method X: Determination of Metal  
Concentrations in Emissions from Stationary  
Sources  
(Instrumental Analyzer Procedure)**

**DRAFT**

June 7, 2005

Submitted to:

**The Environmental Protection Agency**  
Research Triangle Park, NC

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## **Executive Summary**

Method X is an instrumental analyzer procedure for the determination of multiple metals using x-ray fluorescence as an analytical technique. Method X specifies the criteria for accuracy stability and precision that must be met by an x-ray fluorescence based instrument analyzer. Method X also describes the emission test procedures associated with an x-ray fluorescence based metals measurement system.

## List of Symbols

$B_i$	=	The background concentration of the $i^{\text{th}}$ metal as determined by the instrumental metals measurement system
$CD_i$	=	X-ray fluorescence calibration drift for the $i^{\text{th}}$ metal
$C_i^L$	=	Value of the emission limit for the $i^{\text{th}}$ metal
$CF_i^{RB}$	=	Relative bias correction factor for the $i^{\text{th}}$ metal
$d_i$	=	Difference between paired alternative reference method or reference aerosol and instrumental metals measurement system concentrations for the $i^{\text{th}}$ metal
$\overline{d}_i$	=	Average difference in concentration between the instrumental measurement system and the alternative reference method or aerosol
$L_i^0$	=	Zero reference value for the $i^{\text{th}}$ element at the last calibration
$L_i^{IA}$	=	Concentration reported by the instrumental metals measurement system for the $i^{\text{th}}$ metal
$L_i^{IAC}$	=	Value of the standard reported by the x-ray fluorescence module for the $i^{\text{th}}$ metal
$L_i^{IAU}$	=	Response to the $i^{\text{th}}$ element in the upscale reference
$L_i^{IAZ}$	=	Instrumental metals measurement system response for the $i^{\text{th}}$ metal to the zero reference
$L_i^{std}$	=	Calibrated value of the calibration test standard for the $i^{\text{th}}$ element
$L_i^u$	=	Calibrated value of $i^{\text{th}}$ element on the upscale reference
$n$	=	Number of data points
$PRB_i$	=	<i>Percent</i> relative bias for the $i^{\text{th}}$ metal
$R_i^{RM}$	=	The concentration of the $i^{\text{th}}$ metal in the alternative EPA reference method data set or reference aerosol concentration
$\overline{R_i^{RM}}$	=	Average concentration of the $i^{\text{th}}$ metal in the alternative EPA reference method data set or reference aerosol concentration
$PRSD_i$	=	Percent relative standard deviation of the $i^{\text{th}}$ metal
$SD_i$	=	Standard deviation of differences for the $i^{\text{th}}$ metal
$UD_i$	=	Upscale drift of the $i^{\text{th}}$ metal of an instrumental metals measurement system in percent
$VA$	=	Volume or flow measurement accuracy
$V_c$	=	Volume or flow reported by the instrumental metals measurement system's volume check device
$VD$	=	Volume or flow drift
$V_{IA}$	=	Volume or flow reported by the instrumental measurement system's volume or flow sample measurement device
$V_r$	=	Sample gas volume measured by the independent calibrated reference device

$x_i$  = Value of the  $i^{\text{th}}$  measurement  
 $ZD_i$  = Zero drift of  $i^{\text{th}}$  metal on an instrumental metals measurement system

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## **1.0 Purpose and Applicability**

### *1.1 Purpose*

The purpose of Method X is to define the emission test procedures that must be followed when using an instrumental metals measurement system that reports metal concentrations in emissions from stationary sources using x-ray fluorescence as an analytical technique. These criteria and emission test procedures are in place to assure the accuracy and reliability of the data produced by the system.

### *1.2 Applicability*

This method is applicable to the determination of metal concentrations in emissions from stationary sources using an x-ray fluorescence based instrumental metals measurement system.

## **2.0 Method Summary**

### *2.1 Principle*

A sample of gas is acquired isokinetically from a stack or duct. A portion of that sample source gas is then pulled through a capturing medium where metal analytes are removed from the effluent stream and concentrated. The metal analyte sample is then presented to the x-ray fluorescence module after enough time has elapsed to allow the metal analytes to concentrate sufficiently to be detectable. The masses of metal analytes reported by the x-ray fluorescence module is divided by the volume of stack effluent sampled to obtain the analyte concentration in the source.

## **3.0 Range and Sensitivity**

### *3.1 Analytical range*

The instrumental metals monitoring system must be able to measure metal concentrations in a range from 20% to 400% of the allowed emission limit for each metal as demonstrated by laboratory or field trials.

### *3.2 Sensitivity*

The minimum detectable limit of the instrumental analyzer depends on the analytical range, the signal-to-noise ratio of the measurement system and the presence of interferences. The minimum detectable limit must be less than 10% of the applicable emission standard.

## 4.0 Definitions

**Analytical range:** The range of metal concentrations the instrument can reliably measure.

**Diluent analyzer:** The portion of the instrumental metals measurement system that detects the diluent. The diluent may be detected by the x-ray fluorescence module or by another device or technique.

**Emission limit:** The emission limit for a single metal is equal to the maximum amount allowed under the applicable regulation for its category assuming all of the other metals in its category were not present.

**Element of opportunity:** An element that happens to be present in stack or duct effluent that can be used to determine relative bias.

**EPA reference method:** A method recognized by the United States Environmental Protection Agency as appropriate for the measurement of a pollutant or pollutants in source emissions.

**Instrumental metals analyzer:** The portion of the instrumental metals measurement system containing the components necessary for the measurement of metal concentrations, including the sampling module, the x-ray fluorescence module, and the volume measurement module.

**Instrumental metals measurement system:** All of the equipment required for determining metal concentrations using an x-ray fluorescence based approach. An instrumental metals measurement system may consist of several modules including, but not limited to the following: the sample interface, the x-ray fluorescence module, the diluent analyzer, the sampling module, the volume measurement module, and the data recorder

**Non-quantitative spiking:** The process of introducing an unknown concentration of metal or metals into a gas stream.

**Quantitative spiking:** The process of introducing a known concentration of metal or metals into a gas stream.

**Sample conditioning system:** The portion of the sample interface that conditions the stack or duct gas to prevent concentration loss and or damage to the x-ray fluorescence module. Examples of sample conditioning include heaters and diluent gas to prevent the condensation of water vapor.

**Sample interface:** The portion of the instrumental metals measurement system that is used for extracting a sample from the stack or duct. The sample interface may include some or all of the following systems; a sample probe, sample transport system, and sample conditioning systems.

**Sampling module:** The portion of the instrumental metals measurement system that traps the metals and delivers them to the x-ray fluorescence module.

**Sample probe:** The portion of the sample interface that extracts the gas from the stack or duct.

**Sample transport system:** The portion of the sample interface which transports the sample stack or duct gas from the downstream end of the sample probe to the sampling module.

**Volume drift:** The difference in the reading between the sample volume or flow measurement device and an independently calibrated volume or flow measurement device.

**Volume measurement module:** The portion of an instrumental measurement system that determines sample volume.

**Upscale drift:** The difference in the reading for the upscale reference from the calibrated value after some period of time during which no maintenance or adjustment took place.

**X-ray fluorescence module:** The portion of the instrumental metals measurement system that uses x-ray fluorescence as analytical technique to identify metals and to determine metal concentrations.

**XRF:** x-ray fluorescence.

**Zero drift:** The difference in the reading for zero input from the calibrated value after some period of time during which no maintenance or adjustment took place.

## 5.0 Apparatus and Reagents

### 5.1 Measurement system

#### 5.1.1 Sample interface

The sample interface must collect a sample of source effluent isokinetically and then transport that effluent to the sampling module. The sample interface must at least include the following two elements.

1. **Sample probe** The sample probe may be made of glass, stainless steel, Teflon-coated steel or other material that will prevent loss or contamination of analyte metal or metals. The sample probe may also be heated to prevent the condensation of water vapor.
2. **Sample transport lines** Lines made from any material that will transport the analyte metal with minimal particle loss. The transport lines may be heated or allow for the addition of diluent gas to prevent the condensation of water vapor.

### *5.1.2 Sampling module*

The sampling module must include a method for capturing the metal analytes of interest and presenting them to the x-ray fluorescence module. The sampling module may capture the metals from the entire volume of the sample interface or it may extract a sub-sample of source effluent.

### *5.1.3 X-ray fluorescence module*

The x-ray fluorescence module uses x-ray fluorescence as an analytical technique to identify and determine the mass of metal analytes on the capturing medium.

### *5.1.4 Data recorder*

The data recorder should be able to record metals concentrations and instrument status signals (flags) that indicate whether the metals measurement system is performing appropriately.

### *5.1.5 Volume measurement module*

This module must accurately measure the volume of effluent drawn through the capture media on a dry basis.

## *5.2 Quality assurance and control materials*

### *5.2.1 Zero drift reference*

An instrumental metals monitoring system must include a means to measure zero drift. If feasible this reference should produce an instrumental response indicating the absence of metals. If this is not feasible the zero reference should produce a value between zero and 20% of the emission limit for at least two of the metals measured by the system.

### *5.2.2 Upscale drift reference*

An x-ray based instrumental metals monitoring system must include an upscale drift reference to measure the upscale drift. The upscale drift reference must contain an element measured by each energy condition of the XRF analysis. The mass of each metal in the reference must generate an instrumental response between 80 and 200 percent of the applicable emission limit.

### *5.2.3 Volume or flow drift check device*

An instrumental metals measurement system must include a means of checking the sample volume drift or flow drift against another internal measurement device.

### *5.2.4 Volume or flow calibration check device*

An instrumental metals measurement system must include a means of checking the calibration of the volume or flow measurement device against an externally calibrated measurement device.

#### *5.2.5 X-ray fluorescence calibration check standards*

An instrumental metals measurement system must also include a means of checking the calibration for every metal it measures for compliance purposes. NIST traceable thin film standards are an example of a suitable calibration check standard.

### *5.3 Metals generator*

A method of metals generation is necessary to determine the relative bias of the metals measurement system and is required for the interference check if it is performed. The following are optional sources of metals that may be used for this purpose.

#### *5.3.1 Quantitative aerosol generator*

A quantitative aerosol generator produces known metals concentrations in a gas stream. The known concentrations of the analytes are compared with the values reported by the instrumental metals measurement system.

#### *5.3.2 Non-quantitative aerosol generator*

A non-quantitative aerosol generator produces metals at unknown concentrations in a gas stream. To use this approach the concentrations of metals produced by the non-quantitative aerosol generator must be measured using an independent alternative EPA reference method. The concentration from the alternative reference method can then be compared to the concentration reported by the instrumental measurement system to determine percent relative bias.

#### *5.3.3 Source operation*

The metal used during the relative bias test can also be produced by operating the source. The metal or metals produced in routine operation can then be measured by an appropriate alternative EPA reference method. The concentration, as determined by the alternative reference method is then compared with the concentration from the instrumental metals measurement system. The metal used as the analyte for this test is called an element of opportunity.

### *5.4 Alternative EPA Reference method*

Some of the procedures to determine percent relative bias require the use of an alternative EPA reference method. The alternative reference method must be able to accurately measure the concentration of the metal used during the bias test.

## **6.0 Measurement System Performance Specifications**

### *6.1 Zero drift*

The zero drift, calculated using Equation 3, must be less than 20% of the applicable emission limit for each element and each measurement.

### *6.2 Upscale drift*

The upscale drift, calculated using Equation 4, must be less than 15% of the value determined immediately after calibration for each metal on the upscale reference.

### 6.3 *Volume drift*

The volume or flow drift, calculated using Equation 5, must be less than 10% of the full scale value of the flow or volume measurement device.

### 6.4 *X-ray fluorescence module calibration drift check*

The x-ray fluorescence calibration drift, calculated using Equation 6, must be less than 10% of the known value of the standard for each metal measured by the instrumental analyzer for reporting purposes.

### 6.5 *Volume measurement calibration check*

The volume or flow measurement made by the instrumental system shall be less than 10% (calculated using Equation 7) of the volume or flow measurement made by the externally calibrated volume or flow measurement device.

### 6.6 *Percent relative bias*

If the percent relative bias (calculated using Equation 8) is less than 15% and the relative standard deviation (calculated using Equation 11) is less than 10% no correction is required. If the relative percent bias exceeds 15% and the relative standard deviation is less than 10% then a correction factor must be applied to the data using Equation 12. If the relative percent standard deviation exceeds 10% a correction factor cannot be applied and the instrumental metals measurement system must be adjusted or repaired before it can be used.

### 6.7 *Interference Check*

The average percent relative bias must be less than 15% and the relative standard deviation must be less than 10%.

### 6.8 *Reporting requirements*

An instrumental metals measurement system must report a concentration in the units of the applicable standard or in units that can be converted to the applicable standard.

## **7.0 Measurement System Performance Test Procedures**

The following procedures must be performed prior to emissions testing.

### 7.1 *Measurement system preparation*

Assemble the measurement system following the manufacturer's instructions. Adjust all flow rates and heaters to the settings that will be used during sampling. The following tests are required after the measurement system has been assembled.

### 7.2 *Zero drift check*

A zero drift check must be performed before and after each day of emissions testing. The zero drift check must be performed according to the procedures provided by the instrumental system's manufacturer. If the instrumental metals measurement system fails the zero drift check it must be repaired or recalibrated and all the emission test runs performed since the last successful zero drift check shall be considered invalid. After

appropriate repairs have been made the system must pass a zero drift check before testing can resume. If changes are made to the calibration of the x-ray fluorescence module the measurement system must also pass an x-ray fluorescence calibration drift check.

### *7.3 Upscale drift check*

An upscale drift check must be performed before and after each day of emissions testing according to the procedures provided by the manufacturer. If the instrumental metals measurement system fails the upscale drift check it must be repaired or recalibrated and all emission test results acquired since the last successful upscale drift check shall be considered invalid. After appropriate repairs have been made to the system, it must pass an upscale drift check before emissions testing can resume. If changes are made to the calibration of the x-ray fluorescence module the measurement system must also pass an x-ray fluorescence calibration drift check.

### *7.4 Volume or flow drift check*

A volume drift check must be performed before and after each day of emissions testing according to the procedures provided by the instrumental manufacturer. This is an internal check of the volume or flow measurement against another flow or volume measurement device. If the instrumental metals measurement system fails the volume or flow drift check the volume module must be repaired or adjusted and all emissions test results acquired since the last successful volume or flow drift check shall be considered invalid. The measurement system must successfully pass a volume or flow drift check and a volume or flow calibration drift check before emissions testing can resume.

### *7.5 X-ray fluorescence calibration drift check*

The x-ray fluorescence module calibration drift check must be performed before the start of sample measurement and is only performed once per visit to a site. A calibration drift check should also be performed if the x-ray fluorescence module is recalibrated for any reason during the emissions test.

During a calibration drift check the x-ray fluorescence analyzer is challenged with NIST traceable standards. The calibration of every element that will be measured during the emission test must be checked. Each standard must only be checked once. If the calibration drift exceeds plus or minus 10% of the standard's value the instrument must be recalibrated and retested for that element.

### *7.6 Volume or flow calibration check*

If the instrumental metals measurement system determines volume or flow as part of its metals concentration measurement, a volume or flow calibration check must be performed. This check must be performed at least once per site visit prior to the start of emissions testing. The check must also be executed if adjustments are made during emissions testing to the flow or volume measurement devices.

If the instrumental metals measurement system determines volume, as opposed to flow, the value reported by the system during one sample run must be compared to the value reported by an independently calibrated standard such as a dry gas meter. The sampling

time during the volume measurement must be equivalent to the sampling time that will be used during emissions testing.

If the instrumental metals measurement system measures flow and totalizes that flow to produce a volume, a flow calibration check may be performed in lieu of a volume calibration check. For this calibration check, the flow reported by the instrumental metals measurement system is compared with an independently calibrated flow measurement device such as a NIST traceable Dry Cal<sup>®</sup> at 3 to 5 points throughout a single sampling period. The error of each measurement is calculated and the average error computed.

If the instrumental metals measurement system fails a volume or flow calibration drift check the volume measurement module may need repair. The system must pass another volume or flow calibration drift check before emissions testing can resume.

### *7.7 Relative bias test*

The percent relative bias must be determined using at least one metal which may be an analyte measured for compliance purposes or a surrogate metal (e.g., iron) that can be measured by the instrumental metals measurement system. At least three measurements are required to establish the average relative bias. If the instrumental metals measurement system is being compared to an alternative EPA reference method, at least three simultaneous measurements with the alternative reference method are necessary. The requirements for the relative bias test associated with the three possible metals generation requirements are outlined below.

#### *7.7.1 Option 1: Quantitative spiking*

In this approach to determining bias, an aerosol of known concentration produced according to the specifications laid out in PS-QRAG<sup>1</sup> is spiked into the sample transport line as close as possible to the sample probe. This concentration should be between 80 and 120 percent of the emission limit. (If a surrogate metal is spiked then the concentration should be at 80 to 120 percent of the emission limit for the analyte metal with the highest emission limit). The concentration reported by the instrumental metals measurement system is compared with the known concentration of the spiked aerosol and the percent relative bias and the percent relative standard deviation are calculated.

#### *7.7.2 Option 2: Elements of opportunity*

In this approach the instrumental metals measurement system may be used to determine if an element of opportunity is present in the source. If one is present, the concentration of that metal must be determined using an alternative EPA reference method sampling from the stack or from a point in the transport line as close as possible to the sample probe. The alternative reference method concentration is compared with the concentration reported by the instrumental metals monitoring system. The element of opportunity should be present at concentrations well above method detection limits to be used in the relative bias test.



### *7.7.3 Option 3: Non-quantitative spiking*

An aerosol at a concentration level between 80 and 120 percent of the emission limit is spiked either into the source or into the sample interface as close as possible to the probe. The metal concentration may be determined using a suitable alternative EPA reference method. The alternative reference method concentration is compared with the measurement made by the instrumental metals measurement system. If the metal is spiked into the source the alternative reference method may be located either directly in the source or in the transport line as close as possible to the sample probe. If the metal is spiked into the transport line then the reference method measurements must be made as close as possible to the spiking location.

## *7.8 Interference check*

An interference check tests for interferents in the source emissions that inhibit or prevent the measurement of analyte metals. For this reason, the instrumental analyzer must sample flue gas during the interference check. This check must be performed for each model of x-ray fluorescence instrumental metals analyzer the first time that model is used on a particular source category. The results of this test must then be retained and submitted along with the emissions test results whenever the instrumental metals analyzer is used on that particular source category. If an instrumental metals measurement system fails an interference test it may not be used for emissions test on that particular source category until it does pass an interference check.

The procedures for the interference test are very similar to the sample interface relative bias test. For each test the relative bias and relative percent standard deviation are calculated. As with the relative bias test there are three options for performing (only one of the options must be executed) the interference check based on the type of metals generation performed: 1) Option A. Quantitative spiking, 2) Option B. Element of opportunity, and 3) Option C. Non-quantitative spiking. The inference check, however, is testing for bias resulting from problems with the capture of metal analytes in the sampling module or problems with the x-ray fluorescence, while the relative bias test determines the instrumental metals measurement system bias primarily resulting from the sample interface.

### *7.8.1 Option A: Interference check with quantitative spiking*

For the interference check the quantitative spike injection point should be located as close as possible to the sampling module. Only one metal, either an analyte that will be measured or a surrogate must be spiked. The concentration level of the analyte or surrogate metal in the background should be checked using the instrument analyzer. It is recommended that the spiked metal not be present at detectable concentrations in the stack. If it is present, the bias may be calculated by subtracting the average background concentration using equation 9. At least nine sampling periods of 15 minutes or longer are required. The known concentration of the spiked metal is compared with the concentration reported by the instrumental analyzer to determine percent relative bias.

### *7.8.2 Option B: Interference check with an element of opportunity*

The element of opportunity may be any metal present in the stack gas that can be measured by the instrumental metals analyzer and by an alternative EPA reference method and is present at high enough concentrations to be used. The alternative reference method must be placed as close as possible to the sampling module and the concentration reported by the method is compared with that reported by the instrumental metals analyzer. Nine simultaneous runs of both the alternative reference method and the instrumental analyzer are required.

### *7.8.3 Option C: Interference check using non-quantitative spiking.*

For option C the non-quantitative spike injection point may be anywhere upstream of the sampling module. An alternative EPA reference method is required to use Option C and it must be located as close as possible to the sampling module. Only one metal, either an analyte that will be measured during the emissions test or a surrogate such as iron, must be spiked. As for the element of opportunity nine simultaneous runs of the alternative reference method and the instrumental analyzer are required.

## **8.0 Emissions Test Procedure**

### *8.1 Performance tests prior to emissions testing*

The appropriate measurement system performance tests must be completed according to the procedures in sections 7.1 to 7.8 prior to the start of emissions testing.

### *8.2 Selection of sampling point*

It is recommended that the sampling location be at least two equivalent diameters downstream of any control devices, point of pollution generation, bend or other point at which a change in pollution concentration or flow disturbance may occur and be at least two equivalent diameters upstream of the exhaust. The equivalent diameter is calculated according to 40 CFR Part 60, Appendix A, Method 1, Section 2.1.<sup>2</sup>

### *8.3 Sample collection*

#### *8.3.1 Traverses*

An instrumental metals measurement system must sample at the appropriate traverse points as outlined in Method 1<sup>2</sup> or another EPA approved alternative for the selection of sampling points. A sampling run consists of sampling all required traverse points over a period of 15 minutes to one third the applicable regulation, depending on source conditions and metal concentrations. If feasible all traverse points must be sampled for approximately equal lengths of time.

#### *8.3.2 Isokinetics*

An instrumental metals measurement system must acquire a representative sample of source effluent by either sampling at a flow rate that is plus or minus 10% of isokinetic or by using another means approved by the EPA. Velocity

measurements to determine the percent of isokinetic must be performed according to EPA approved procedures such as those outlined in Method 2.<sup>3</sup>

### 8.3.3 Possible additional measurements

Additional measurements may be required to report the results in units of the applicable standard. Among these are source moisture content and percent oxygen content.

## 9.0 Calculations

### 9.1 Arithmetic mean ( $\bar{x}$ )

$$\bar{x} = \frac{1}{n} \sum x_i \quad \text{Equation 1}$$

Where :

$n$  = Number of data points  
 $x_i$  = Value of the  $i^{\text{th}}$  measurement

9.1.1 *Arithmetic mean of a difference.* To calculate the arithmetic mean of difference use the above equation substitute  $d_i$  for  $x_i$ . The

$$d_i = x_i - y_i \quad \text{Equation 2}$$

Where  $x$  and  $y$  are paired data points from the instrumental metals measurement system and either the reference aerosol or the alternative reference method.

### 9.2 Zero drift ( $ZD_i$ )

$$ZD_i = \frac{|L_i^{IAZ} - L_i^0|}{C_i^L} \times 100 \quad \text{Equation 3}$$

Where:

$ZD_i$  = Zero drift of  $i^{\text{th}}$  metal on the instrumental metals measurement system in percent

$L_i^{IAZ}$  = Instrumental metals measurement system response for the  $i^{\text{th}}$  metal to the zero reference

$L_i^0$  = Zero reference value for the  $i^{\text{th}}$  element at the last calibration

$C_i^L$  = Value of the emission limit for the  $i^{\text{th}}$  metal

### 9.3 Upscale drift ( $UD_i$ )

$$UD_i = \frac{|L_i^{IAU} - L_i^u|}{L_i^u} \times 100 \quad \text{Equation 4}$$

Where:

$UD_i$  = Upscale drift of the  $i^{\text{th}}$  metal of an instrumental metals measurement system in percent.

$L_i^{IAU}$  = Response to the  $i^{\text{th}}$  element in the upscale reference

$L_i^u$  = Calibrated value of  $i^{\text{th}}$  element on the upscale reference

### 9.4 Volume drift ( $VD$ )

$$VD = \frac{|V_{IA} - V_c|}{FS} \times 100 \quad \text{Equation 5}$$

$VD$  = Volume or flow drift

$V_c$  = Volume or flow reported by the instrumental metals measurement system's volume check device

$V_{IA}$  = Volume or flow reported by the instrumental measurement system's volume or flow sample measurement device

$FS$  = The full scale value of the volume or flow measurement device

### 9.5 X-ray Fluorescence calibration drift ( $CD_i$ )

$$CD_i = \frac{|L_i^{IAC} - L_i^{std}|}{L_i^{std}} \times 100 \quad \text{Equation 6}$$

Where:

$CD_i$  = x-ray fluorescence module drift for the  $i^{\text{th}}$  metal

$L_i^{IAC}$  = Value of the standard reported by the x-ray fluorescence module for the  $i^{\text{th}}$  metal

$L_i^{std}$  = Calibrated value of the calibration test standard for the  $i^{\text{th}}$  element

### 9.6 Volume or flow calibration drift (VA)

$$VA = \frac{V_r - V_{IA}}{V_r} \times 100 \quad \text{Equation 7}$$

Where:

VA = Volume (or flow) measurement accuracy

$V_r$  = Sample gas volume (or flow) measured by the independent calibrated reference device

$V_{IA}$  = Sample gas volume (or flow) reported by the instrumental metals measurement system

### 9.7 Relative bias ( $RB_i$ )

$$PRB_i = \frac{|\overline{d}_i|}{R_i^{RM}} \times 100 \quad \text{Equation 8}$$

Where:

$PRB_i$  = Percent Relative Bias for the  $i^{\text{th}}$  metal

$\overline{d}_i$  = Average difference between the instrumental metals measurement system and the alternative reference method or aerosol

9.7.1 For option A: interference check using quantitative spiking

Substitute the following equation for  $d_i$  when using quantitative spiking in the presence of a significant and stable background concentration of the spiked metal

$$d_i = L_i^{IA} - B_i - R_i^{RM} \quad \text{Equation 9}$$

Where:

$L_i^{IA}$  = Concentration reported by the instrumental metals measurement system for the  $i^{\text{th}}$  metal

$B_i$  = The background concentration of the  $i^{\text{th}}$  metal as determined by the instrumental metals measurement system

$R_i^{RM}$  = Concentration of reference aerosol or concentration reported by the alternative EPA reference method for the  $i^{\text{th}}$  metal

9.8 Standard deviation (of differences) ( $SD_i$ )

$$SD_i = \sqrt{\frac{\sum d_i^2 - \frac{1}{n}(\sum d_i)^2}{n-1}} \quad \text{Equation 10}$$

Where:

$SD_i$  = Standard deviation of differences for the  $i^{\text{th}}$  metal

$d_i$  = Difference between paired alternative reference method or reference aerosol and the instrumental metals measurement system concentrations for the  $i^{\text{th}}$  metal

9.9 Percent relative standard deviation ( $RSD_i$ )

$$PRSD_i = \frac{SD_i}{R_i^{RM}} \times 100 \quad \text{Equation 11}$$

Where:

$PRSD_i$  = Percent relative standard deviation of the  $i^{\text{th}}$  element

$\overline{R}_i^{RM}$  = Average concentration of the  $i^{\text{th}}$  metal in the alternative EPA reference method data set or reference aerosol concentration  
 $SD_i$  = Standard deviation of the instrumental measurement system concentrations for the  $i^{\text{th}}$  metal

#### 9.10 Correction factor for relative bias ( $CF_i^{RB}$ )

$$CF_i^{RB} = \frac{1}{1 + \frac{\overline{d}_i}{\overline{R}_i^{RM}}} = \frac{\overline{R}_i^{RM}}{\overline{L}_i^{IA}} \quad \text{Equation 12}$$

Where:

$CF_i^{RB}$  = Relative bias correction factor for the  $i^{\text{th}}$  metal  
 $\overline{R}_i^{RM}$  = Average of the alternative reference method data set or the reference aerosol concentration for the  $i^{\text{th}}$  metal  
 $\overline{d}_i$  = The average difference between the instrumental measurement system and the alternative reference method or reference aerosol for the  $i^{\text{th}}$  metal (where  $d_i$  is calculated according to the following equation)

$$d_i = L_i^{IA} - R_i^{RM} \quad \text{Equation 13}$$

Where:

$L_i^{IA}$  = Concentration reported by the instrumental metals measurement system for the  $i^{\text{th}}$  metal  
 $R_i^{RM}$  = Concentration of reference aerosol or concentration reported by the alternative EPA reference method for the  $i^{\text{th}}$  metal

## 10.0 Safety

People using method X may be exposed to hazardous materials, operational hazards and dangerous site conditions. Method X does not purport to address all of the safety issues associated with its use. Consult the instrumental metals measurement system manufacturer for safety procedures related to its use. Confer with the site safety manager concerning safety procedures particular to the emission test site and review all appropriate material safety data sheets when working with chemical hazards.

## 11.0 Tables, Figures for Method X

**Table 1. Performance Test Procedures and Passing Criteria For Metals IAP**

<b>Test</b>	<b>Procedure</b>	<b>Criteria</b>	<b>Frequency</b>
<b>Zero drift</b>	Run zero standard at least 2 times per sampling day	<20% drift	Before and after each day of sampling
<b>Upscale drift</b>	Run upscale standard at least 2 times per sampling day	<15% drift from original calib.	Before and after each day of sampling
<b>Volume Drift</b>	Run volume drift check at least 2 times per sampling day	<20% drift from independent flow device.	Before and after each day of sampling
<b>X-ray Fluorescence Calibration Drift Check</b>	Run a standard for each metal measured for compliance purposes	<10% for each element	Once each time the instrument is set up in a particular location
<b>Volume Measurement Calibration Check</b>	<ul style="list-style-type: none"> <li>• 1 sampling period</li> <li>• For flow 3 to 5 measurements of flow during a sampling cycle</li> <li>• Calculate difference or for flow average difference</li> </ul>	<10%	Once each time the instrument is set up at a particular location
<b>Sample Interface Relative Bias</b>	<u>Option 1</u> <i>Quantitative spiking at stack</i> <ul style="list-style-type: none"> <li>• 3 measurements of instrumental metals measurement system</li> <li>• Only one metal must be spiked</li> </ul>	<ul style="list-style-type: none"> <li>• RB&lt;15%</li> <li>• %RSD&lt;10%</li> <li>• If RB criteria not met apply a correction</li> </ul>	Once each time instrument is set up at particular location
	<u>Option 2</u> <i>Element of opportunity</i> <ul style="list-style-type: none"> <li>• Determine identity of element of opportunity</li> <li>• Run the instrumental method and the alt. reference method simultaneously</li> <li>• Analyze alt. reference method and compare results</li> </ul>	<ul style="list-style-type: none"> <li>• RB&lt;15%</li> <li>• %RSD&lt;10%</li> <li>• If RB criteria not met apply a correction</li> </ul>	
	<u>Option 3</u> <i>Non-quantitative spike</i> <ul style="list-style-type: none"> <li>• Spike into stack or transport line</li> <li>• Run the instrumental method and the alt. reference method simultaneously</li> <li>• At least three cycles of the instrumental metals measurement system</li> <li>• At least three alt. reference method measurements</li> <li>• Analyze alt. reference method and compare</li> <li>• Only one metal must be spiked</li> </ul>	<ul style="list-style-type: none"> <li>• RB&lt;15%</li> <li>• %RSD&lt;10%</li> <li>• If RB criteria not met apply a correction</li> </ul>	
<b>Interference Check</b>	See table 3 for Interference check options and procedures	<ul style="list-style-type: none"> <li>• Relative Bias&lt;15%</li> <li>• %RSD&lt;10%</li> <li>• No correction factor allowed.</li> </ul>	Once per instrument model on each source category

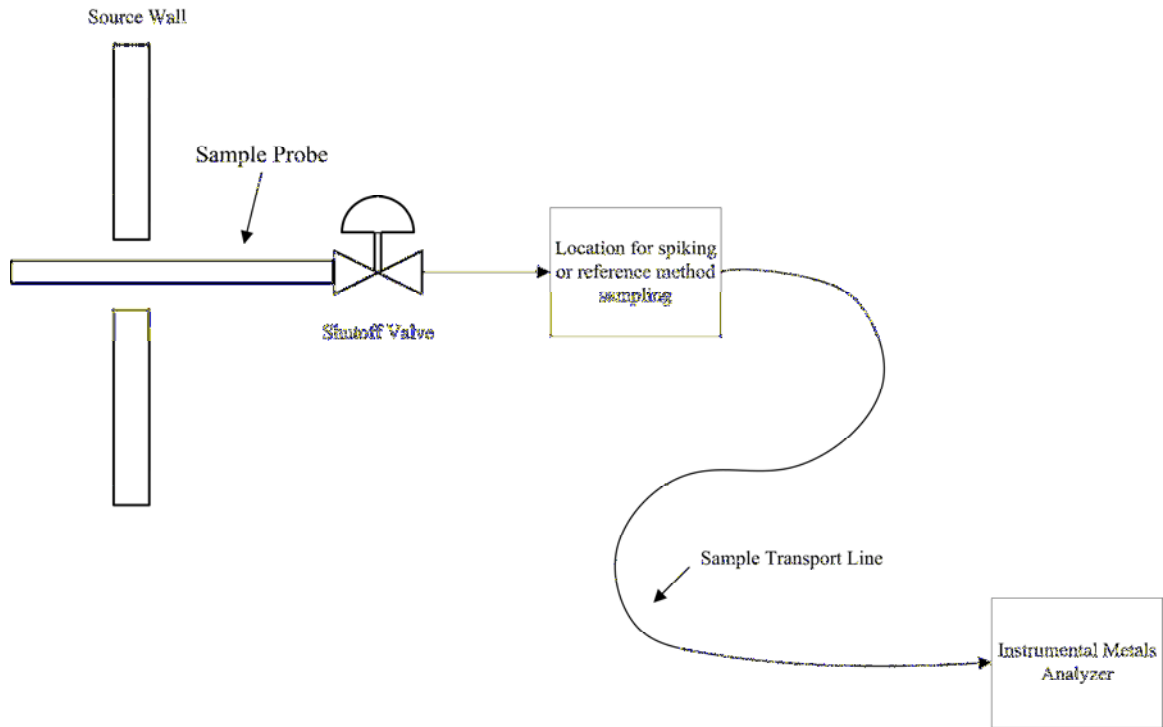


**Table 2. Spiking and Alternative EPA Reference Method Options for Sampling Bias Tests**

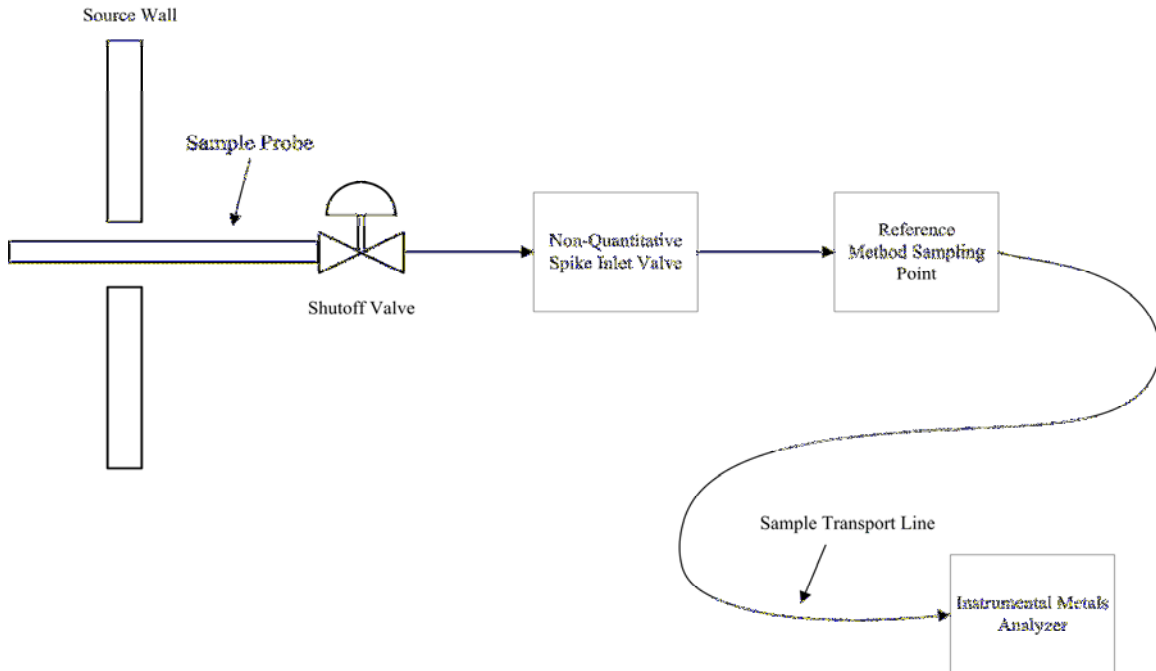
<b>Source of Metals for Bias Test</b>	<b>Location of Spike (if applicable)</b>	<b>Location of Alternative EPA Reference Method (if applicable)</b>
Quantitative Spike	In transport line as close as possible to sample probe.	N/A
Non-Quantitative Spike	<u>Option A</u> In stack	In stack -or- In transport line as close as possible to the sample probe
	<u>Option B</u> In transport line as close as possible to the sample probe	In transport line immediately downstream of spike location
Element of Opportunity	N/A	<u>Option A</u> In stack
		<u>Option B</u> In transport line as close as possible to the sample probe

**Table 3. Spiking and Alternative EPA Reference Method Locations for Interference Checks**

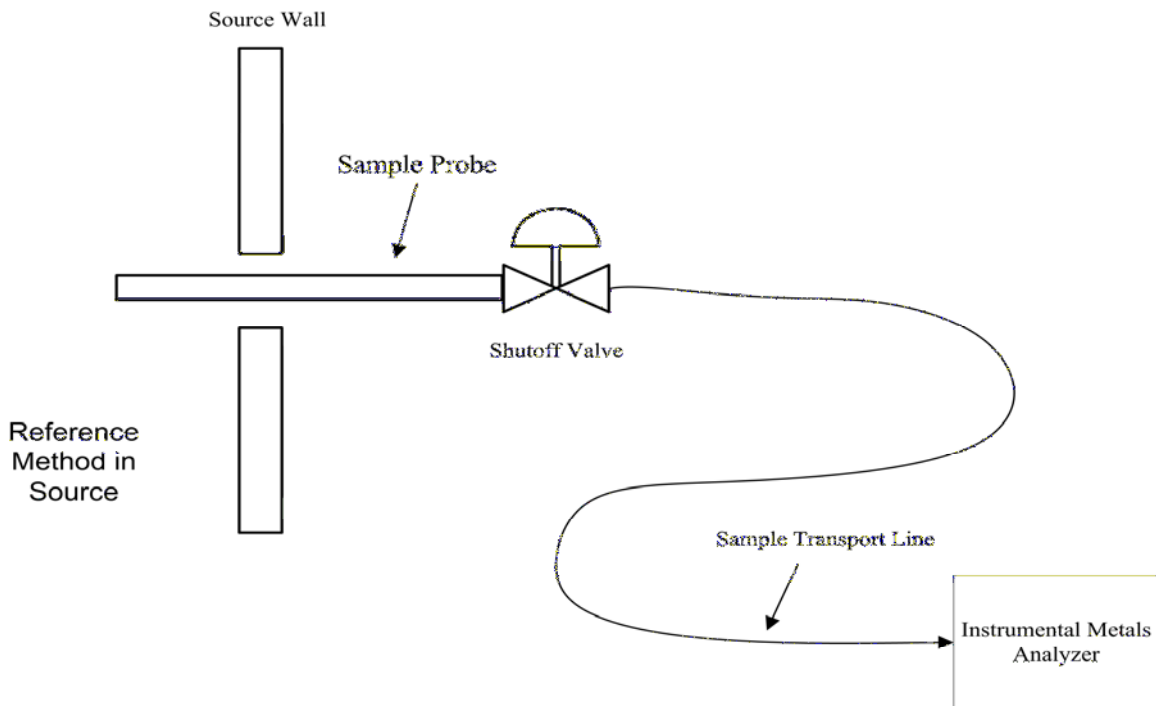
<b>Metals Generation Options</b>	<b>Spiking Location (if applicable)</b>	<b>Location of Alternative EPA Reference Method (if applicable)</b>
<b>Option A:</b> Quantitative spiking	As close as possible to the sampling module	N/A
<b>Option B:</b> Element of opportunity	N/A	As close as possible to the sampling module
<b>Option C:</b> Non-quantitative spiking	Anywhere upstream of the alternative EPA reference method	As close as possible to the sampling module



**Figure 1 Alternative Reference Method or Spiking Location for the Relative Bias Test with (1) Quantitative Spiking , with (2) Non-Quantitative Spiking into the source and using the Alternative Reference Method in the Transport Line, or with (3) an Element of Opportunity using the Alternative Reference Method in the Transport Line.**



**Figure 2. Using Non-Quantitative Spiking into the Transport Line During the Relative Bias Test**



**Figure 3. Using Non-Quantitative Spiking or an Element of Opportunity with the Alternative Reference Method in the Source During the Relative Bias Test.**

## 12.0 References

- 1 Performance Specification XX. Performance Specifications for A Quantitative Reference Aerosol Generator. 2005
- 2 United States. Environmental Protection Agency [EPA]. Technology Transfer Network. Emission Measurement Center. Promulgated Methods. Method 1: Sample and Velocity Traverses for Stationary Sources. Washington, DC: EPA; 2004. Available: <http://www.epa.gov/ttn/emc/promgate/m-01.pdf> via the Internet. Accessed May 8, 2005.
- 3 United States. Environmental Protection Agency [EPA]. Technology Transfer Network. Emissions Measurement Center. Promulgated Methods. Method 2. Determination of Stack Gas Velocity and Volumetric Flow Rate (Type S Pitot Tube). Washington, DC. EPA, 2004. Available: <http://www.epa.gov/ttn/emc/promgate/m-02.pdf> via the internet. Accessed June 6, 2005.