Procedure Z: Quality Assurance Requirements for X-Ray-Fluorescence Based Multi-Metals Continuous Emission Monitoring Systems at Stationary Sources

DRAFT

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The Environmental Protection Agency
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Prepared by:

Cooper Environmental Services, LLC
10180 SW Nimbus Blvd Suite J6
Portland, Oregon 97223

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J.A. Cooper, K. Petterson, B.E. Johnsen,
C. A. Yanca, M. Nakanishi, D. Barth

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Cooper Environmental Services, LLC
10180 SW Nimbus Blvd Suite J6
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Prepared by:_____ Date:_____
Krag A. Petterson, Environmental Scientist

Reviewed by: _____ Date:_____
Cay A. Yanca, Environmental Scientist

Reviewed by: _____ Date:_____
Bruce E. Johnson, QA Manager

Approved by: _____ Date:_____
John A. Cooper, Director

Executive Summary

Procedure Z outlines the continuing quality control and quality assurance requirements for an x-ray fluorescence based multi-metal CEMS. Procedure Z requires daily checks of the upscale, zero and volume measurement drift. It also specifies quarterly checks of the x-ray fluorescence calibration and of the volume measurement calibration. Finally procedure Z requires that the entire XRF multi metal CEMS accuracy be verified on an annual basis.

List of Symbols

b_o	=	The y intercept of the best fit line
b_1	=	The slope of the best fit line
CA_i	=	X-ray fluorescence calibration accuracy
C_i^C	=	Corrected CEMS concentration for the ith element
C_i^{CEMS}	=	The concentration of the ith element as reported by the CEMS
$\overline{C_i^{CEM}}$	=	The average reported concentration of the CEMS for the ith element
CF_i^{PT}	=	Correction factor for percent transport for the ith element
CF_i^{RB}	=	The relative bias correction factor for the ith element
C_i^L	=	The emission limit of the ith element
C_i^S	=	Concentration of the ith element at the stack
C_i^{sm}	=	Concentration of the ith element at the sampling module or as reported by the XRF multi-metals CEMS.
d_i	=	Difference between two paired measurements
$\overline{d}$	=	Arithmetic mean of differences
FS	=	Full scale value of your CEMS volume (or flow) measurement device
L_i^0	=	The calibrated value of the ith element on the zero standard
L_i^{cem}	=	The value of the standard reported by your CEMS
L_i^{cemo}	=	The measured CEMS response to the zero standard for the ith element
L_i^{cemu}	=	The measured CEMS response to the ith element in the upscale standard
L_i^{std}	=	The known value of the XRF calibration check standard
L_i^u	=	The value of the ith element of the upscale standard
n	=	Number of data points
PT_i	=	The percent transport of the ith element

$\overline{PT}_i$	=	Average percent transport for the ith element
PRB_i	=	Percent relative Bias of the ith element
$\overline{R_i^{RM}}$	=	The average of the reference method measurements for the ith metal
$PRSD_i$	=	The relative percent standard deviation for the ith metal
r	=	The correlation coefficient
SD_i	=	The standard deviation of differences for the ith element
V_{cemr}	=	Sample gas volume (or flow) as measured by the CEMS volume check device
VD	=	Volume drift
V_m	=	Volume (or flow) reported by your multi-metals CEMS
UD_i	=	The upscale drift of the ith element on your CEMS in percent.
$\bar{x}$	=	Arithmetic mean
x_i	=	Value of each data point
y_i	=	CEMS reported concentration for the ith element
ZD_i	=	The zero drift of the ith element on your CEMS in percent

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1.0 Using Procedure Z

1.1 What is the purpose and applicability of Procedure Z?

The purpose of Procedure Z is to establish the minimum requirements for quality control (QC) and quality assurance (QA) procedures for x-ray fluorescence (XRF) based multi-metals CEMS. These quality control and quality assurance procedures are in place to ensure the accuracy and validity of the data reported by your multi-metal CEMS for emission compliance purposes. You must meet these minimum requirements if you plan to use your multi-metal CEMS for reporting purposes, however, we encourage you to develop a more extensive QA program or to continue with such programs where they already exist. Any XRF multi-metals CEMS used to report to us, the state, or a local enforcement agency must comply with procedure Z immediately after the completion of the initial performance specification test outlined in Performance Specification YY[1].

*1.2 What are the basic requirements of Procedure Z**?***

Procedure Z requires you to perform several drift checks and audits which ensure the accuracy of the data reported by your XRF multi-metals CEMS. You are required to, on a daily basis, record and calculate zero drift, upscale drift, and, a sample volume drift. On a quarterly basis you are required to perform an XRF calibration audit (XFCA) and a sample volume audit (SVA). On an annual basis you are required to execute either a linearity audit (LA) or a relative bias audit (RBA) and, if applicable, a transport efficiency audit (TEA). The criteria for passing these audits and drift checks are outlined in procedure Z. Procedure Z also summarizes the requirements for when and if your CEMS fails an audit or drift test. Finally, Procedure Z also covers the requirements for and timelines associated with periods when your XRF multi-metals CEMS is out of control.

1.3 What special definitions apply to procedure Z?

Linearity Audit: (LA) An assessment of the validity of the original linear correlation of your CEMS.

Reference material: A material of known value used to check the calibration drift of your XRF multi-metal CEMS.

Relative Bias: The difference between a reference method or aerosol concentration and the concentration recorded by your CEMS divided by the concentration of the reference measurement.

Relative Bias Audit: (RBA) An assessment of the bias in your CEMS.

Sample Interface: The portion of the CEMS used for one or more of the following: sample acquisition from the stack or duct effluent, sample transport, sample conditioning, or protection of the monitor from the effects of stack gas.

Sample Module: The portion of the XRF multi-metal CEMS that traps the metals and delivers them to the x-ray fluorescence module.

Standard Volume Audit: (SVA) This is an evaluation of your XRF multi-metals CEMS sample volume measurement system. This is required if your CEMS uses a volume measurement to report metal concentrations and is accomplished by comparing the volume measured by your CEMS with the volume measured by an independently calibrated device.

Transport Efficiency Audit: (TEA) An assessment of the transport efficiency of the sample interface of your multi-metals CEMS. This audit applies to your XRF multi-metals CEMS if either the RBA or LA challenged only the sampling and XRF modules.

Transport System: The portion of the CEMS that transports a representative sample of source effluent from the sample probe to the sample module.

X-Ray Fluorescence Calibration Audit: (XFCA) This is an evaluation of how well the x-ray fluorescence portion of your multi-metals CEMS has maintained its original calibration. This is accomplished by challenging the XRF module with a standard of known concentration for each metal measured by your CEMS for compliance. The analyzer response is compared with the known concentration of the standard.

X-Ray Fluorescence Module: The portion of an XRF based multi-metal CEMS which identifies and measures metal masses or concentrations using x-ray fluorescence.

XRF Multi-Metals Continuous Emission Monitor (CEMS): All of the equipment required for determining metal concentrations using x-ray fluorescence as an analytical technique. The system may consist of several major subsystems including the sample interface, the x-ray fluorescence module, the volume measurement module, diluent analyzer, data recorder, and sampling module.

2.0 Interferences, Safety, and Equipment Requirements

2.1 What interferences are associated with procedure Z?

There may be interferences arising from the x-ray fluorescence, the trapping media, or from condensation in the effluent gas. Check with your multi-metal CEMS manufacturer to find out more about potential interferences.

2.2 What do I need to know to ensure the safety of persons using Procedure Z?

Persons using procedure Z may be exposed to hazardous materials, equipment, and operations. Procedure Z does not purport to address all of the safety issues associated with its use. It is your responsibility to establish appropriate safety and health practices before using this procedure. You may consult with your CEMS manual and/or manufacturer for precautions specific to your multi-metal CEMS. If standard reference methods are used then you may also consult the appropriate reference methods to address safety concerns.

2.3 What equipment and supplies do I need?

[reserved]

2.4 What reagents and standards do I need?

Reference materials for the zero and upscale drifts along with a reference measurement device for the sample volume check.

2.4.1 Zero drift reference

Every XRF multi-metals CEMS must be equipped with a zero reference that can be checked on a daily basis. This reference should produce a CEMS response indicating the absence of metals. If this is not feasible this standard should produce a value between zero and 20% of the emission limit for at least two elements measured by your XRF multi-metals CEMS when the instrument is operating appropriately.

2.4.2 Upscale drift reference

The reference for the upscale drift check should generate a response for at least one metal from each condition used in the XRF analysis. This response must be at least 80 percent of the emission limit.

2.4.3 Sample volume or flow check

If your XRF multi-metals CEMS makes volume or flow measurements it must be equipped to perform a daily sample volume check.

2.4.4 Sample volume audit standard

If your XRF multi-metals CEMS makes volume or flow measurements, periodic standard volume or flow audits must be performed. An independently calibrated volume or flow measurement device or standard such as a Dry Cal® is required for these audits. The standard must be able to acquire a volume or flow measurement at sampling rates typical of your XRF multi-metals CEMS.

2.4.5 X-ray Fluorescence Calibration Check Standards

Your XRF multi-metals CEMS must include a means of checking the x-ray fluorescence calibration against an external standard. NIST traceable thin film standards are an example of a suitable x-ray fluorescence calibration check standard.

2.4.6 Reagents and standards for the Linearity Audits and Relative Bias Audits

You will need other reagents and standards for the linearity audit or relative bias audit. The regents and standards required will differ depending on how these audits are performed.

2.4.7 Regents and standards for the Transport Efficiency Audit

The regents and standards for the transport efficiency audit also depend upon how the audit is performed.

2.5 What sample collection, preservation, storage, and transport procedures are relevant to Procedure Z?

[reserved]

3.0 Quality Control, Calibration, and Standardization

3.1 What quality control measures are required by this procedure for my multi-metal CEMS?

You must develop and implement a quality control program that, at a minimum includes detailed written procedures for all of the following activities.

1. Procedures for performing drift checks on a daily basis, including but not limited to, zero drift, upscale drift, and sample volume measurement drift.
2. Procedures and methods of adjusting your multi-metal CEMS in response to the results of the drift checks.
3. Preventative maintenance of your XRF multi-metals CEMS.
4. Data recording, calculations, and reporting.
5. Procedures for required audits, including transport efficiency audits (if necessary), linearity audits, and relative bias audits.
6. Procedures for adjusting your CEMS based on audit results.
7. A program of corrective action and stack operation procedures in case of a CEMS malfunction and an out of control period.

You are required to keep written documentation of your QA/QC procedures on record and available for inspection for the life of the CEMS or until you are no longer subject to the requirements of this procedure. If you fail two consecutive audits you must revise your QA/QC procedures.

3.2 What calibration checks and audit procedures must I perform for my multi-metal CEMS?

3.2.1 Daily drift check procedures

Your XRF multi-metals CEMS must have the capacity to perform each of the following checks on at least a daily basis.

- **Zero drift:** You must check the zero drift to ensure the stability of your CEMS response to the zero drift reference. The zero drift must be less than plus or minus 20% of the emission limit each day. Follow your CEMS manufacturer's instructions for proper zero drift check procedures.
- **Upscale drift:** You must check the upscale drift to ensure the stability of your XRF multi-metal CEMS response to the upscale standard. The daily upscale drift must be less than 15% of the upscale reference value determined immediately after the x-ray fluorescence module has been calibrated. Follow your CEMS manufacturer's instructions for proper upscale drift check procedures.
- **Daily volume or flow check:** You must check the sample volume or flow measurement to verify the accuracy of the volume measurement on your CEMS. This volume check must be done at the normal sampling rate for the CEMS. Your CEMS is out of control if the one day value exceeds 20% of the full scale of the volume or flow measurement device. Follow your CEMS manufacturer's instructions for proper volume or flow check procedures.

3.2.2 Audit procedures

Audit procedures and criteria are listed below. These requirements are also summarized in Table 1 in section 5.3.

1. **X-Ray Fluorescence Calibration Audit (XFCA):** You must perform an XFCA once each quarter. To perform an XFCA you must challenge the x-ray fluorescence module of your multi-metal CEMS with a standard of known concentration for each metal measured by your CEMS for compliance purposes and compare the value reported by the CEMS with the known value of the standard. If you wish you may make only one measurement of a standard for each element. If your multi-metal CEMS fails on the initial measurement you may make two more measurements of each standard and average all three measurements. If the average CEMS response over the three measurements deviates by less than 10% from the known standard the CEMS has passed the XFCA. If the average exceeds 10% your CEMS has failed the XFCA and is out-of-control. You must follow the procedures outlined in Section 5.2. An XFCA is required once per quarter. The minimum allowed time between each audit is two months and the maximum allowed time is four months.
2. **Sample volume (or flow) audit (SVA):** You must perform a sample volume audit of your XRF multi-metals CEMS at least once per quarter and prior to any linearity or relative accuracy audit. To perform an SVA you must independently measure the volume of sample gas extracted from the stack or duct over the sampling period. You may make this measurement either at the inlet or outlet of your CEMS. You must make volume measurements during three different sampling cycles and the measurements must be able to make corrections for moisture content if necessary.

If your CEMS measures flow and totalizes that flow to determine volume you may perform a flow audit instead. You must make flow measurements during three different sampling cycles and for each sampling cycle you must make at least 3 to 5 simultaneous measurements of flow on your CEMS and on the independent flow measurement device. You must calculate the error from each set of measurements according to equation 6 and then calculate the average error in the flow during each sampling period. Finally you must calculate the average error from all three sampling periods and this average must be less than 10% of the independent flow or volume measurement device.

A sample volume audit is required on a quarterly basis. The minimum required time between each SVA is at least two months while the maximum allowed time between audits is four months.

Accuracy Audits: As outlined in Performance Specification YY it is acceptable during the initial performance specification test to assess the accuracy and precision of the XRF and sampling modules of your XRF multi-metal CEMS separately from the sample interface. You may also do this during the Linearity or Relative Bias Audits that are required for Procedure Z. If you choose to challenge the sampling module and XRF systems separately from the sampling interface you must also perform a Transport Efficiency Audit (TEA). If you challenge the entire XRF multi-metals CEMS during the Linearity and Relative Bias Audits you are not required to perform an independent check of the CEMS transport efficiency. For the purposes of Procedure Z you are required to perform either a linearity audit or a relative bias audit, but not both. You are also not required to perform the same kind of tests for the audit as were performed during the initial performance specification test. For example, if a linearity test was performed during the initial accuracy tests, either a relative bias audit or a linearity audit is acceptable.

There are four different options available for the accuracy audits depending on whether or not a linearity or relative bias audit is performed and depending on whether or not the entire CEMS is challenged by the audit. The audit requirements are listed below.

Linearity Audits

Option A

In this option a linearity audit is performed on the entire CEMS. The types of metals generation and their associated requirements are identical to those for Option A in performance specification YY section 3.1.4.[1] If you do not meet the linearity criteria you must apply a correction according to the procedures outlined in performance specification YY.[1]

Option B

In this option a linearity audit is performed on the sampling and XRF modules of the CEMS separately from the sample interface. The types of metals generation and their associated requirements are identical to those for Option B

in performance specification YY section 3.1.4.[1] A transport efficiency audit must also be completed.

Relative Bias Audit

Option C

In this option a relative bias audit is performed on the entire CEMS. The types of metals generation and their associated requirements are identical to those for Option C in performance specification YY section 3.1.4.[1] If your CEMS fails to meet the criteria you must apply a correction factor according to the procedures in performance specification YY.[1]

Option D

In this option a relative bias audit is performed on the sampling and XRF modules of the CEMS separately from the sample interface. The types of metals generation and their associated requirements are identical to those for Option D in performance specification YY section 3.1.4.[1] A transport efficiency audit must also be completed.

An accuracy audit is required on an annual basis. The minimum time between successive accuracy audits is 9 months while the maximum allowed time is 15 months.

3. **Transport Efficiency Audit (TEA):** You are required to perform a TEA only if you choose to challenge the sampling and XRF modules of your XRF multi-metals CEMS separately from the sampling interface. The procedures for performing a TEA are the same as those for determining the transport efficiency during the initial performance specification test and are outlined in Performance Specification YY[1]. If the transport efficiency of your CEMS is between 90 and 110 percent no correction is necessary. If your transport efficiency is less than 90 percent or greater than 110 percent then you must establish a correction factor according to the procedures outlined in section 3.1.7 of Performance Specification YY[1]. The minimum time between successive transport efficiency tests is 9 months while the maximum allowed time is 15 months.

4.0 Calculations

4.1 What calculations and data analysis must I perform?

4.1.1 Arithmetic Mean

Calculate the arithmetic mean of a data set as follows

$$\bar{x} = \frac{1}{n}\sum x_i \qquad \textbf{Equation 1}$$

Where :

$\bar{x}$ = Arithmetic mean

n = Number of data points

x_i = Value of each data point

4.1.2 Arithmetic Mean of Difference

To calculate the arithmetic mean of difference use the above equation substitute d for *x*. Then

$$d_i = x_i - y_i$$ **Equation 2**

Where x and y are paired data points from the CEMS and either the reference aerosol or the reference method.

4.1.3 Daily Zero Drift

$$ZD_i = \frac{\left|L_i^{cemo} - L_i^0\right|}{C_i^L} \times 100$$ **Equation 3**

Where:

ZD_i = The zero drift of the i[th] element on your CEMS in percent

L_i^{cemo} = The measured CEMS response to the zero standard for the i[th] element

L_i^0 = The calibrated value of the i[th] element on the zero standard

C_i^L = The emission limit of the i[th] element

4.1.4 Daily Upscale Drift

$$UD_i = \frac{\left|L_i^{cemu} - L_i^u\right|}{L_i^u} \times 100$$ **Equation 4**

Where:

UD_i = The upscale drift of the i[th] element on your CEMS in percent.

L_i^{cemu} = The measured CEMS response to the i[th] element in the upscale standard

L_i^u = The calibrated value of the i[th] element of the upscale standard

4.1.5 Daily Sample Volume Check

$$VD = \frac{\left|V_{cemr} - V_m\right|}{FS} \times 100$$ **Equation 5**

Where:

VD = Volume drift

V_{cemr} = Sample gas volume or flow measured by the CEMS volume or flow check measurement device

V_m = Sample gas volume or flow reported by your multi-metal CEMS

FS = Full scale value of the CEMS volume measurement device

4.1.6 Sample Volume Audit Accuracy

$$VA = \frac{|V_r - V_m|}{V_r} \times 100$$ **Equation 6**

Where:

VA = Volume or flow measurement accuracy

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

V_m = Sample gas volume or flow reported by your multi-metal CEMS

4.1.7 X-Ray Fluorescence Calibration Audit Calibration

$$CA_i = \frac{\left|L_i^{cem} - L_i^{std}\right|}{L_i^{std}} \times 100$$ **Equation 7**

Where:

CA_i = X-ray fluorescence calibration accuracy

L_i^{cem} = The value of the standard reported by your CEMS

L_i^{std} = The known value of the standard

4.1.8 Relative Bias

$$PRB_i = \frac{\left|\overline{d_i}\right|}{R_i^{RM}} \times 100$$ **Equation 8**

Where $\overline{d}_i$ is the mean difference, $\overline{R_i^{RM}}$ is the average of the reference method set or reference aerosol concentration for the ith element, and PRB_i is the relative bias for the ith element

4.1.9 Transport Efficiency

$$PT_i = \frac{C_i^{sm}}{C_i^S} \times 100$$ **Equation 9**

Where:

C_i^S = Concentration of the i[th] element at the stack

C_i^{sm} = Concentration of the i[th] element at the sampling module or as reported by the XRF multi-metals CEMS.

PT_i = The percent transport of the i[th] element

Report the average percent transport ($\overline{PT}$) of all measurements for each element that was tested (only one element is required though more can be tested).

4.1.10 Linearity Audit – Least Squares Linear Regression

Calculate the linear correlation equation given below.

$$\hat{y} = b_o + b_1 x$$ **Equation 10**

Where:

b_o = The y intercept

b_1 = The slope

The intercept is calculated according to the following equation.

$$b_o = \bar{y} - b_1 \bar{x}$$ **Equation 11**

Where:

$$\bar{x} = \frac{1}{n} \sum_{i=1}^{n} x_i$$

$$\bar{y} = \frac{1}{n} \sum_{i=1}^{n} y_i$$

The slope of the line is calculated according to equation below.

$$b_1 = \frac{\sum_{i=1}^{n} (x_i - \bar{x})(y_i - \bar{y})}{\sum_{i=1}^{n} (x_i - \bar{x})^2}$$ **Equation 12**

The linear correlation coefficient is calculated according to the following equation.

$$r = \frac{\sum_{i=1}^{n}(x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^{n}(x_i - \bar{x})^2 \sum_{i=1}^{n}(y_i - \bar{y})^2}}$$ **Equation 13**

4.1.11 Standard Deviation (of differences)

$$SD_i = \sqrt{\frac{\sum d_i^2 - \frac{1}{n}\left(\sum d_i\right)^2}{n-1}}$$ **Equation 14**

Where:

SD_i = The standard deviation of differences for the i[th] element

n = The number of data points

d_i = The difference between the concentration measured by the reference method or the concentration of the reference aerosol and the CEMS reported concentration.

4.1.12 Percent standard deviation

$$PRSD_i = \frac{SD_i}{\overline{R_i^{RM}}} \times 100$$ **Equation 15**

Where:

$\overline{R_i^{RM}}$ = The average of the reference method data set for the i[th] element

$PRSD_i$ = The relative percent standard deviation for the i[th] metal

4.1.13 Linearity Test Correction Factors (Applicable only when the linearity test challenges the entire CEMS)

1. Correction equation if CEMS does not meet either the slope or the intercept criteria.

$$C_i^C = \frac{y_i - b_0}{b_1}$$ **Equation 16**

Where:

C_i^C = Corrected CEMS concentration for the i[th] element

y_i = CEMS reported concentration for the i[th] element

b_0 = The intercept of the least squares linear regression line

b_1 = The slope of the least squares linear regression line

2. Correction factor if CEMS meets intercept criteria, but does not meet the slope criteria.

$$C_i^C = y_i - b_0$$ **Equation 17**

3. Correction factor if CEMS meets slope criteria but does not meet intercept criteria.

$$C_i^C = \frac{y_i}{b_1}$$ **Equation 18**

4.1.14 Relative Bias Correction Factors

$$CF_i^{RB} = \frac{1}{1 + \frac{\overline{d_i}}{\overline{R_i^{RM}}}} = \frac{\overline{R_i^{RM}}}{\overline{C_i^{CEM}}}$$ **Equation 19**

Where:

CF_i^{RB} = The relative bias correction factor for the i[th] element

$\overline{C_i^{CEM}}$ = The average reported concentration of the CEMS for the i[th] element

$\overline{R_i^{RM}}$ = The average of the reference method measurements for the i[th] metal

4.1.15 Percent transport correction factor

$$CF_i^{PT} = \frac{1}{\overline{PT_i}}$$ **Equation 20**

Where

CF_i^{PT} = Correction factor for percent transport for the i[th] element

$\overline{PT}_i$ = Average percent transport for the i[th] element

4.2 What waste management procedures are required for procedure Z?

All chemicals used to produce a reference aerosol or in performing standard methods need to be disposed of properly. Please consult the appropriate reference methods.

5.0 Other Requirements and Information

5.1 What pollution prevention measures must I take when using procedure Z?

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5.2 What criteria are necessary for my XRF multi-metal CEMS to be in control and what do I do if it is out of control?

5.2.1 Required Corrective Action for Drift Checks and Audits

- **Daily Zero Drift:** If the one day drift exceeds 20% you are required to rerun your zero drift reference. If the XRF multi-metal CEMS meets the criteria during the second test you may continue to operate. If the CEMS fails to meet the zero drift criteria again then it is out of control. It is recommended that you examine the zero drift standard for defects. After repairs to the CEMS are completed you are required to perform at least five successful zero drift checks within a 24 hour period. After the five checks have been successfully completed then you CEMS is in control. If the repairs were made to the XRF module of the multi-metals CEMS you are also required to complete an x-ray fluorescence calibration audit (XFCA) to verify the accuracy of your x-ray fluorescence calibration.
- **Daily Upscale Drift:** If the one day drift exceeds 15% you are required to retest the upscale drift reference. If the XRF multi-metals CEMS meets the criteria during the second test you may continue to operate, however, if the CEMS fails the second upscale drift check it is out of control. It is recommended that you examine the upscale drift standard for defects. After repairs to the CEMS are completed you are required to perform at least five successful upscale drift checks within a 24 hour period. After the five drift checks are successfully completed the CEMS is back in control. Again, if repairs were made to the XRF module of the multi-metal CEMS you are also required to successfully complete an x-ray fluorescence calibration audit (XFCA) to verify the accuracy of the calibration.
- **Daily Sample Volume Check:** If your sample volume or flow drift exceeds 20% it has failed the daily volume check and you must perform another daily volume check. If the CEMS passes the second check you may continue to operate. If your CEMS fails the second test it is out of control and your CEMS must be repaired. After repairs have been made the CEMS must successfully complete five sample volume checks within a 24 hour period. Upon successful completion of the five checks your CEMS is back in control. If the repairs

were made to a volume or flow measurement device you are also required to successfully complete a sample volume audit (SVA).

- **Quarterly Sample Volume Audit (SVA):** Your XRF multi metals CEMS is out of control if volume (or flow) measured by your CEMS differs from that measured by the independent standard by more than 10% percent. A failure of this audit may indicate that repairs need to be made to the volume measurement system. Upon completion of these repairs you must perform and pass another SVA.
- **Quarterly X-Ray Fluorescence Calibration Audit (XFCA):** The response of your XRF multi-metals CEMS must be within 10% of the standard's value for each metal measured for compliance purposes by your CEMS. If your CEMS fails the XFCA initially, rerun each standard two more times and take the average of the three measurements. If the average CEMS response meets the XFCA criteria you may continue to operate, however, if the CEMS fails to meet the criteria then it is out of control. After the CEMS has been repaired you must complete another XFCA. Upon successful completion of the XFCA the CEMS is back in control.
- **Annual CEMS Accuracy Tests**

  Linearity Audit

  Option A (Linearity audit of the entire CEMS).

  If you challenge the entire CEMS system (including sampling interface and the sampling and XRF modules) with a linearity audit you do not need to apply a correction factor to your CEMS data if it meets the following criteria:

  1. a slope between 0.85 and 1.15
  2. the correlation coefficient equal to 0.90 or more
  3. an intercept of less than 20 percent of the emission limit

  If your CEMS does not meet the slope or intercept criteria you must apply a correction factor according to the procedures described in Performance Specification YY Section 4.2.12.[1] Your CEMS, however, must still meet the correlation criteria.

  If your CEMS fails the linearity test it is out of control. After the necessary repairs are made it must pass a linearity or relative bias test to be considered back in control.

  Option B (Linearity audit of the sampling module and XRF module only followed by a TEA)

  If you challenge the sampling and XRF modules separately from the sample interface, your XRF multi-metal CEMS is out of control if the linear least squares regression analysis of your audit data does not meet the following criteria for each of the metals measured by your CEMS for compliance purposes:

1. a slope between 0.85 and 1.15
2. the correlation coefficient equal to 0.90 or more
3. an intercept of less than 20 percent of the emission limit

If your XRF multi-metals CEMS fails a linearity audit you must make the necessary repairs to your CEMS and successfully complete either a relative bias audit or a linearity audit before it is considered to be back in control.

You must also complete a transport efficiency audit (TEA) along with your linearity audit.

Relative Bias Audit

Option C (Relative bias test of the entire CEMS)

If your CEMS meets the following criteria it has passed the relative bias audit and you do not need to apply a correction factor to your CEMS.

1. the percent relative bias (*PRB*) exceeds 15%
2. the percent relative standard deviation(*PRSD)* exceeds 10%
3. the correlation coefficient (r) for linearity portion of the relative bias audit is less than 0.90

If your XRF multi-metals CEMS fails to meet the relative bias criteria you may apply a correction factor according the procedures described in performance specification YY Section 4.2.13[1]. However, if your CEMS fails to meet either the percent relative standard deviation criteria or the correlation coefficient criteria it is out of control. If your XRF multi-metal CEMS fails a relative bias audit it must successfully compete another linearity or relative bias audit to be considered in control.

Option D (Perform a relative bias test on the sampling and XRF modules)

Your XRF multi-metals CEMS is out of control if:

1. the percent relative bias (*PRB*) exceeds 15%
2. the percent relative standard deviation(*PRSD)* exceeds 10%
3. the correlation coefficient (r) for linearity portion of the relative bias audit is less than 0.90

You must successfully complete another RBA or a linearity audit before your CEMS is considered to be in control. You must also successfully complete a transport efficiency audit along with the relative bias audit.

Transport Efficiency Audit (TEA): A TEA is only required if you challenge your sampling XRF modules separately from your sample interface (Options B and D). If the percent transport is between 90 and 110 percent no correction factor is necessary, however, if the percent transport is less than 90 percent or greater than 110 percent then you must apply a correction factor to the results reported by your multi metal CEMS. The procedures for applying a correction factor using the equation in Section 4.1.15.

5.2.2 General out of control guidelines

- **Out of control period:** The out of control period begins immediately after the failed drift test or audit and is over immediately following the successful completion of required procedures associated with the failure of the audit test. During the out of control period you may not use the data generated by your XRF multi-metal CEMS for compliance purposes.
- **Reporting guidelines:** You must include in your report to us, the state, or local enforcement agency the results of the failed audit or drift check, the corrective action that was taken, and the results of the successful audit or drift check.
- **Rules governing auditing time periods:** The X-Ray Fluorescence Calibration Audit (XFCA) and the Sample Volume Audit (SVA) are required once a quarter. Two months must pass between successive quarterly audits and no more than four months may pass.. The Linearity Audit (LA) and the Relative Bias Audit (RBA) are required on an annual basis. Successive LAs and RBAs must be separated by at least nine months and no more than 15 months.

5.3 What tables, diagrams and flow charts are relevant to Procedure Z?

Table 1: Continuing QA Procedures for XRF Multi-Metals CEMS

Test Frequency	Test	Test Procedures	Passing Criteria
Daily	Zero Drift	Check zero standard and calculate drift	< 20% drift each day
	Upscale Drift	Check upscale standard and calculate drift	< 15% drift each day
	Volume or Flow Drift	Check flow drift and calculate drift	< 20% drift each day
Quarterly	X-Ray Fluorescence Calibration Audit	Test a standard for each element measured for compliance by your CEMS (1 time per standard)	• < 10% difference for every element measured for compliance by your CEMS • If criteria not initially met you may take the average of 3 measurements
	Sample Volume (or Flow) Audit	Volume • Compare CEMS volume against a standard during 3 sampling cycles • Average all three Flow • 3 to 5 flow measurements with standard and CEMS per sample cycle • Measure in 3 CEMS sample cycles • Calculate average difference between CEMS and standards over all measurements	<10% difference from the standard
Annually	Option A Perform a linearity test on entire CEMS	• At least one metal from each category • Need at least 3 concentration levels which include a 2 fold conc. change and the emission limit • If spiking, spike into source, or spike into transport line as close as possible to the probe	• Slope = 0.85 to 1.15 • r ≥ 0.90 • intercept < 20% of emission limit • if above criteria is met then no correction • if not met apply a correction
	Option B • Perform a linearity test on sampling and XRF modules only • Determine transport efficiency separately	• At least one metal from each category • Need at least 3 concentration levels which include a 2 fold conc. change and the emission limit • Spike or measure concentrations with reference method as close as possible to the sampling module	Linearity Criteria • Slope = 0.85 to 1.15 • r ≥ 0.90 • intercept < 20% of emission limit • the linearity criteria must be met Percent Transport Criteria • 90≤PT≤110 • If percent transport criteria are not met apply a correction factor
	Option C Perform a relative bias test on entire CEMS	• At least one metal from each category at 80 to 120 percent of emission limit • One other metal at 3 conc. levels which include a 2 fold conc. change and the emission limit • If spiking, spike into source or spike into transport line as close as possible to the probe	• Percent relative Bias • RB≤ 15% • %RSD ≤ 10% • r ≥ 0.90 for metal with three fold conc. change • If Criteria not met apply a correction factor (correlation coefficient criteria must be met
	Option D • Perform a relative bias test on sampling and XRF modules only • Determine transport efficiency separately	• At least one metal from each category at 80 to 120 percent of emission limit • One other metal at 3 conc. levels which include a 2 fold conc. change and the emission limit • Spike or measure concentrations with reference method as close as possible to the sampling module	Percent Relative Bias Criteria • RB≤ 15% • %RSD ≤ 10% • r ≥ 0.90 for metal with three fold conc. change Percent Transport Criteria • 90≤PT≤110 • If percent transport criteria are not met apply a correction

5.4 What references are relevant to Procedure Z?

1. Performance Specification YY: Specifications and Test Procedures for Batch Multi-Metals Continuous Emission Monitoring Systems at Stationary Sources. 2005.