Performance Specification YY: Specifications and Test Procedures for X-Ray Fluorescence Based Multi-Metals Continuous Emission Monitoring Systems at Stationary Sources

DRAFT

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Submitted to:

The Environmental Protection Agency
Research Triangle Park, NC

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Executive Summary

Performance Specification YY details the performance requirements for a multi-metals continuous emissions monitor that utilizes x-ray fluorescence (XRF) as an analytical technique. Each XRF based multi-metals CEMS must meet the criteria for accuracy, stability, and instrumental response laid out in this document. In addition, every XRF multi-metals CEMS must meet the installation requirements in PS-YY and the on-going quality control and quality assurance procedures set forth in procedure Z if it is used for emissions compliance purposes.

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

$\bar{d}$ = Arithmetic mean of differences

FS = Full scale value of your CEMS volume (or flow) measurement device

L_i^0 = The value of the ith element on the zero standard determined immediately after calibration

L_i^{cem} = The value of the calibration check 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 calibration check standard

L_i^u = The calibrated 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 = 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.

$\overline{x}$ = 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 PS-YY

1.1 What is the purpose and applicability of Performance Specification YY?

1.1.1 Purpose

The purpose of Performance Specification YY is to establish the performance requirements that must be met by a multi-metals continuous emission monitoring system (CEMS) that utilizes x-ray fluorescence (XRF) to determine metal concentrations in stationary sources. Assurance of the continuing quality of the CEMS data may be achieved by following the procedures defined in *Procedure Z – XRF Based Multi-Metal CEMS Quality Assurance Procedures.*

1.1.2 Application

PS-YY applies to you if you intend to use an XRF multi-metals CEMS for purposes of establishing compliance with federal regulations for metal emissions from stationary sources.

1.1.3 Measurement Capabilities

A multi-metals CEMS must be capable of measuring total concentrations of at least two metals in the units of the applicable standard or in units that can be converted to units of the applicable standard.

1.1.4 Other Monitoring

If your XRF based multi-metals CEMS is capable of reporting a metal concentration in the units of the existing regulation no additional monitoring is necessary. If your CEMS does not report concentrations in the units of the existing standard then other monitoring (e.g., oxygen, temperature, and pressure) are necessary to convert the units reported by your CEMS to the units of the standard.

1.2 What will be discussed in PS-YY?

PS-YY covers two basic topics: (1) the instrument requirements for a XRF based multi-metals CEMS and (2) the requirements that each XRF multi-metals CEMS must meet during the initial performance specification test.

1.2.1 Instrument Requirements

A multi-metals CEMS must be able to accurately report the concentrations of at least two metals. It may do so by extracting a representative sample (path or point sampling may be used if the sample is representative) of stack effluent and capturing the metal analytes of interest on a medium. The CEMS must have a cycle time that is less than one third the period of the applicable standard. The range of the instrument must be from 10 percent to at least 400% of the applicable regulation as determined by field or laboratory tests. Finally, the instrument or operator must be able to perform daily upscale, blank, and flow quality assurance checks to ensure the accuracy, precision, and stability of the instrument and its data.

1.2.2 Initial Performance Specification Tests

The purpose of the initial performance specification test is to establish the stability, accuracy, and precision of your XRF multi-metals CEMS. The performance specification test can be divided into two phases: (1) the stability test, and (2) the accuracy test.

The stability test consists of a seven day check of the zero and upscale calibration drift and is done prior to the accuracy testing. For the accuracy tests, three methods of metals generation (quantitative spiking, non-quantitative spiking, and stack operation) and two methods of data analysis (percent relative bias, and linearity) are available. The sampling and XRF modules of your CEMS may also be tested separately from your stack sampling interface. Some options may be better than others depending on your multi-metals CEMS, or the conditions existing at your stack.

1.3 What are the installation and pre-performance specification test requirements?

1.3.1 Installation Requirements

The sampling location of an XRF multi-metals CEMS should be downstream of all pollution control equipment at a position where the metals concentrations are directly representative or can be corrected so as to be representative of total emissions from the stationary source. It is recommended that the sampling location be at least two equivalent diameters downstream of the nearest control devices, point of pollution generation, bend, or other point at which a change in pollutant concentration or flow disturbance may occur. The sampling location is also recommended to be at least two equivalent diameters upstream from the exhaust. The equivalent diameter is calculated according 40 CFR Part 60, Appendix A, Method 1, Section 2.1[1].

Either point or path sampling may be used. For point sampling the measurement point should be no less than 1.0 meter from the stack or duct wall or located over the centroidal area of the stack or duct cross section. For a path sampling CEMS the effective measurement path should be (1) totally within the inner area bounded by a line 1.0 meter from the stack or duct wall, or (2) have at least 70 percent of the path within the inner 50 percent of the stack diameter or duct cross section. The sample collection and instrumental analyzer portions of your XRF multi-metals CEMS may be located any distance from the sampling point provided the transmission efficiency from the sampling point to the sample collection point can be determined and meets the criteria outlined later in this performance specification. It is also recommended that the sampling probe for your multi-metal CEMS be located at point without stratification. You may test for stratification at the proposed CEMS sampling point by using either PM (as outlined in PS-11), velocity tests as described in Method 2[2], or metals concentrations using Method 29 or an acceptable alternative.

1.3.2 Sampling Requirements

Your multi-metal CEMS should sample from the source at a flow rate which is within 10 percent of true isokinetic. If your multi-metal CEMS does not maintain an isokinetic sampling rate you must use actual site-specific data or data from a similar installation to prove to us, the State, and/or local enforcement agency that isokinetic sampling is not necessary.

1.3.3 Pre-Test Preparation Requirements and Suggestions

Prior to the initial performance specification test you need to ensure that your multi-metal CEMS data logger accurately records emissions levels as well as signals (flags) that indicate both normal and abnormal operation. Prior to start of the seven day stability test the daily drift measurements (upscale and zero values) should be monitored to ensure that the instrument is operating in an appropriate and stable manner. We recommend that you use your XRF multi-metal CEMS for a sufficient length of time to become comfortable with its operation prior to the start of the initial performance specification test.

1.4 What special definitions apply to PS-YY?

Calibration Drift: The difference in the CEMS output readings from the established reference value after a stated period of operation during which no unscheduled maintenance or adjustment took place.

Cycle Time: The time between when the stack gas first comes in contact with the concentrating media and when the concentration value for that sample is reported.

Data Recorder: The portion of the CEMS that provides a record of analyzer output including metal concentrations, flags which indicate normal operation, and flags indicating abnormal operation. The data recorder may record other pertinent data such as effluent flow rates, and various instrument temperatures.

Diluent module: The part of the CEMS in which any diluent is added and measured.

Drift Calibration Standard: A standard containing a constant amount of metal used to establish the drift in the x-ray fluorescence module response.

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 is present in the stack effluent and can be used to establish transport efficiency.

Instrument Measurement Range: The range of metal concentrations the instrument can reliably measure from the lowest concentration to the highest. The instrument measurement range may be different for different metals. If the upper end of the measurement range is more than four times the emission limit, the upper limit does not need to be definitively established.

Path Sampling CEMS: A CEMS that samples the source effluent along a path greater than 10 percent of the equivalent diameter of the stack or duct cross section.

Point Sampling CEMS: A CEMS that samples the source effluent at a single point.

Non-Quantitative Spiking: The process of introducing an unknown amount of metal or metals into the effluent or sample stream.

Quantitative Spiking: The process of introducing a known amount metal or metals into the effluent or sample stream.

Percent Relative Bias: The difference between a reference value and the CEMS measured value divided by the reference value.

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

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

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

Spiking: The process of introducing metals into the effluent stream or the sampling stream.

Transport Efficiency: The percent of metal that is transported from the sample probe to a point as close as possible to the sampling module.

Upscale Drift: The upscale drift is the difference in the reported value for the upscale reference from its value at the last calibration, divided by the value at the last calibration. It is used to monitor the stability of the x-ray fluorescence analysis.

X-Ray Fluorescence (XRF) 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 Monitoring System (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 but not limited to the following the sample interface, the x-ray fluorescence module, diluent module, data recorder, sampling module and volume measurement module.

Zero Drift: The zero drift is the difference in the CEMS readings for the zero reference from their values after the most recent calibration, divided by the emission limit for each element.

2.0 Interferences, Safety, and Equipment Requirements

2.1 Are there any potential interferences for my XRF multi-metal CEMS?

There may be interferences arising from the x-ray fluorescence analysis, 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 PS-YY?

People using PS-YY may be exposed to hazardous material, operational hazards, and hazardous site conditions. PS-YY does not address all the safety issues associated with its use. It is your responsibility to ensure the safety of persons using PS-YY. Some helpful references may include the CEMS manual, the CEMS manufacturer, other reference methods, and on-site safety regulations.

2.3 What equipment and supplies do I need?

2.3.1 Equipment for the CEMS

1. **Sample interface:** This portion of the CEMS must present a sample of source effluent to the sampling module that is directly representative or can be corrected so as to be representative of source. To accomplish this, the sample interface may contain, among other things, heaters or heating systems, and dilution air.
2. **Sampling module:** The sampling module must collect and trap all the analytes of interest from a representative sample of stack effluent without significant loss. The trapped analytes then must be presented to the XRF module.
3. **XRF module:** The XRF module uses x-ray fluorescence to determine the mass or concentration of metal captured by the sampling module.
4. **Volume measurement module:** This portion of the CEMS measures the volume of source effluent from which the metal analytes were captured in the sampling module. This volume along with the data from the XRF to determine concentration of source effluent.
5. **Diluent Module:** If your multi-metals CEMS uses a diluent such as air or nitrogen it is added to the effluent sample and measured using the diluent module.
6. **Quality assurance and quality control materials:** Your multi-metal CEMS must possess the necessary equipment to perform daily upscale and zero checks. Your multi-metal CEMS must also possess the equipment to perform a daily check of the sample volume at normal sample flow rates.
7. **Data recorder**: Your XRF multi-metal CEMS must be able to record metal concentrations and instrument status signals (flags).

2.3.2 *Other Equipment Needed for the Performance Specification Test*

PS-YY does not specify all the equipment and supplies necessary for the performance specification tests. Some of this information is included in the applicable reference methods (e.g., Method 29 or an acceptable alternative).

2.4 *What regents and standards do I need?*

2.4.1 *Zero Drift Reference*

Your multi-metals CEMS must include a standard for the measurement of the daily zero drift. 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 *Volume Drift measurement device*

During the initial performance specification test the volume measurement must be compared on a daily basis against an internal volume or flow measurement device. This volume or flow measurement device must be calibrated independently of the sample volume or flow measurement device and must be as accurate or more accurate than the sample volume or flow measurement device.

2.4.4 *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.

3.0 Performance Evaluation Procedures and Reporting

3.1 *What is the purpose of the initial performance specification tests and what is required to perform the tests?*

The purpose of the initial performance specification tests is to determine the bias, precision, stability, and cycle time of your multi-metal CEMS.

3.1.1 Pretest Preparation

Prior to the start of your initial performance specification tests you must be sure that your CEMS is installed according to the specifications laid out in this document. After installing your XRF multi-metals CEMS we recommend that you use the CEMS for a period of time to familiarize yourself with its operation. We also recommend that you conduct daily checks of the zero and upscale drift to verify that the instrument is functioning properly. When you are confident that the instrument is performing satisfactorily it is time to prepare for the initial performance specification tests.

3.1.2 X-ray Fluorescence Calibration Check

If your CEMS measures more metals for compliance purposes than will be evaluated during the CEMS accuracy testing described later in this document you must perform a calibration check of the x-ray fluorescence module for these additional metals. During the calibration check you must challenge the x-ray fluorescence module with a standard or standards for each metal measured by your XRF multi-metal CEMS. Each metal must be measured at least three times and the error is calculated according to Equation 13 for each measurement. The average error of the three measurements must be less than 10% of the calibration standard's value for each metal, if not your CEMS may not be properly calibrated. The x-ray fluorescence calibration check may occur at anytime during the initial performance specification test. .

3.1.3 Stability – The 7-day Calibration Drift Tests

Prior to the start of the accuracy test you must perform a calibration drift test for a period of at least seven days. The purpose of this test is to verify that the instrument operation is stable. During the calibration drift test period you must determine the magnitude of the zero calibration drift (as calculated in Section 4.2.9), the upscale calibration drift (as calculated in Section 4.2.8), and the volume (or flow) drift (calculated using Equation 14) at least once each day. During the stability tests no adjustments or calibrations may be made to the CEMS. The results of the stability test must be reported along with the results of the accuracy tests.

3.1.4 CEMS Accuracy

The accuracy of your XRF multi-metal CEMS may be determined using one of the following four options.

1. Option A: Linearity test of the entire CEMS
2. Option B: Linearity test of the XRF and sampling modules separately from the sample interface.
3. Option C: Relative bias test of the entire CEMS.
4. Option D: Relative bias test of the XRF and sampling modules separately from the sample interface.

There are also several options for generating the metals that will be analyzed by your multi-metal CEMS including, metals that are generated as a by-product of normal stack operation, quantitative spiking, and non-quantitative spiking. Regardless of the generation option you choose you must be able to produce concentrations for some of the analytes of interest at 80 to 120 percent of the emission limit. All of the CEMS and reference method measurements must be conducted while sampling flue gas.

You do not need to test every metal that your CEMS measures, however, you must generate at least one metal from each category of metals measured by your CEMS for the accuracy tests. For instance, if your XRF multi-metals CEMS measures semi-volatile, low volatile, and high volatile metals you must test at least one metal from each of those categories. (Low volatile metals may also be used to verify the capture efficiency and detection of non-enumerated metals). You must also prove that the XRF module is properly calibrated to measure the elements that are not being measured during the accuracy test by following the procedures described in Section 3.1.2. The test requirements for each option are explained below and summarized in Table 1.

- **Linearity Test Requirements (Options A and B):** The bias and precision of your XRF multi-metals CEMS may be determined by checking the linearity of the instrument response over a series of concentrations. If quantitative spiking is used, then the concentration of the aerosol is paired with a reported CEMS concentration acquired at the same time. Each data point is then plotted with the spiked concentration on the X axis and the reported CEMS concentration on the Y axis. If either non-quantitative spiking or stack by product is used, then the reported CEMS concentration is plotted on the Y axis versus the concentration reported by method 29 or a suitable alternative.

  Linear least squares regression analysis is then used to fit the data points to a line. If you challenge only the XRF module and the sampling module the slope of this line, which is an indication of the accuracy of your XRF multi-metal CEMS, is required to be between 0.85 and 1.15 for each metal. The coefficient of correlation must be greater than 0.90 and is an indication of the precision of your multi-metal CEMS. Finally, the intercept of this best fit line must be less than 20% of the applicable emission limit. If you challenge the entire CEMS system and do not meet the slope or intercept criteria you must apply a correction factor according to the procedures in Section 4.2.12. You are, however, still required to have a correlation coefficient of 0.90 or greater.

  To perform the linearity test you must be able to generate at least three concentration levels for one metal from each class of metals (high volatile, low volatile and semi-volatile) measured by your CEMS. The three levels must incorporate at least a two fold concentration change and one level must be between 80 and 120 percent of the emission limit. You may acquire a blank sample if you wish, either by sampling ambient air, or by operating the source in such a way that metals are not produced (e.g., burning only natural gas). At least three measurements are required at each concentration level and a total of 15 measurements are required overall. You may make additional measurements, however, you must report all the results. If you are not using quantitative spiking you must make 15 corresponding measurements using method 29 or a suitable alternative. We recommend using duel trains for the reference method measurement to identify and screen the reference method data for imprecision and bias.

Additional requirements for each of the two linearity test options are outlined below. You may also want to refer to figures 1 through 8 for guidance on which option to choose.

Option A: Total CEMS Linearity

In option A the entire CEMS system is challenged during the linearity tests. Any one of the three methods of metals generation may be used during the test. Some of the testing requirements associated with metals generation are outlined below

1. Metals generated as a result of stack operation

   If metals for the test are generated as a result of stack operation you must measure the concentration of the metals in the stack using method 29 or a suitable alternative and compare the values with those reported by your CEMS. We recommend using dual reference method trains to screen the reference method for precision and bias.

2. Non-quantitative spiking

   You may either spike non-quantitatively into the stack or duct itself or into the transport system as close as possible to the sample probe. If you spike into the source you must measure the concentration in the source using method 29 or a suitable alternative. This measurement is then compared to the result of your CEMS. If you choose to spike into the transport line you must measure the concentration immediately downstream of the spike point with a method 29 or a suitable alternative and compare that measurement with the concentration reported by your CEMS.

3. Quantitative Spiking

   You may spike a quantitative aerosol directly into the source or into the transport line as close as possible to sample probe. Either way the known spiked concentration is compared with that measured by the CEMS.

Option B: Linearity for Sampling and XRF Modules Only

In option B only the sampling and XRF modules of your multi metals CEMS are challenged with a linearity test. You must also complete a transport efficiency test along with the linearity test. The procedures for performing a transport efficiency test are described in section 3.1.5. The procedures for option B associated with each metals generation option are listed below.

1. Metals generated as a result of stack operation

If metals concentrations for the accuracy test are generated as a result of stack operation you must measure the concentration of the metals as close as possible to the sampling module using method 29 or a suitable alternative and compare the values with those reported by your CEMS. We recommend using dual reference method trains to screen the reference method for precision and bias.

2. Non-quantitative spiking

   You may either spike non-quantitatively into the stack or duct itself or into the transport system. Either way you must measure the concentrations of the analytes as close as possible to the sampling module and compare that concentration with that reported by your multi metal CEMS.

3. Quantitative Spiking

   You must spike at a location as close as possible to the sampling module and compare the known spiked concentration with that reported by your CEMS.

- **Relative Bias Test Requirements (Options C and D):** There are two relative bias options available: one that challenges the entire CEMS and one that challenges the sampling and XRF modules separately from the sample interface. Either option requires at least 12 CEMS measurements be made at a concentration level 80 to 120 percent of the emission limit for a metal from each category of metals analyzed by your XRF multi metal CEMS. If you are not using quantitative spiking you must also have at least 12 corresponding runs of method 29 or a suitable alternative at this concentration level. We recommend using dual trains for the reference method to screen the data for imprecision and bias.

  Additionally, for at least one metal measured at the emission limit or for a surrogate metal that can be measured by your CEMS (such as iron) you must test the CEMS at three different concentration levels. These three levels must incorporate at least a two-fold change in concentration and one of the levels must be between 80 and 120 percent of the emission limit (the concentration of the emission limit for the surrogate metal is equal to that for the metal measured by your CEMS with the highest emission limit). You are required to obtain at least three measurements at each concentration level and are required to have a total of at least 12 measurements. You must report the results of all measurements. The relative bias is an indicator of accuracy and should be calculated using equation 5 for each element. Also, the percent relative standard deviation, which is an indicator of precision, should be calculated for each metal

  If you challenge the entire CEMS system and you do not meet the test criteria you may apply a correction factor to your CEMS data. Calculate a correction factor for each metal in the relative bias test according to the equation found in section 4.2.13. If you challenge the sampling and XRF modules separately from the sample interface you may not apply a correction factor to the data from the relative bias test, you may, however, apply a correction factor to the results of the transport efficiency test. For the metal that was spiked over several concentrations you must perform linear least squares regression analysis on the data. The correlation coefficient for this fit must be better than 0.90. This is to demonstrate that the instrument response is valid over its applicable range. If the criteria for this test is met then the correction factors are assumed to be valid over the range of the instrument.

Option C

In accuracy test option C the entire CEMS is subjected to a relative bias test. The options for metals generation and the associated spiking and reference method requirements are the same as those for Option A under the linearity tests.

Option D

In accuracy test option D only the XRF and sampling modules are subjected to a relative bias test. The options for metals generation and their associated spiking and reference method requirements are the same as those for Option B. You are also required to perform a transport efficiency test.

3.1.5 Transport Efficiency Test

You must perform a transport efficiency test if you have only challenged the sampling and XRF modules during the accuracy tests (options B and D). Any one of the four methods described below are valid ways of determining percent transport for your multi-metals CEMS.

- **Particulate Matter (PM):** In this approach particulate matter is measured concurrently in two locations, (1) in the stack effluent stream as close as possible to your multi-metals CEMS sample interface, and (2) at a point in the transport system as close as possible to the sampling module. You may use any standard reference method to measure PM including Method 5, Method 5i, or Method 17 (40 CFR 60, Appendix A)[3,4,5]. Particulate matter must be generated by operating the source. You must acquire at least 12 paired concentration measurements (each pair consists of the measurement made as close as possible to the sample interface and the measurement made as close as possible to the sampling module. The percent transmission is calculated for each pair using equation 6 and the overall percent transmission is determined by calculating the average of all twelve runs.
- **Element of opportunity:** Alternatively, transport efficiency can be determined using a surrogate metal such as iron or zinc that is commonly present in stack effluent. Method 29 (40 CFR 60, Appendix A)[6] or a suitable alternative can be used to measure the metal concentration in the stack effluent stream as close as possible to the sample probe and at a point in the transport system as close as possible to the sampling module. Also, if your XRF multi-metals CEMS is

capable of measuring the element of interest, you may compare the measured concentration on the CEMS with that measured in the stationary source using the reference method. Transport efficiency is calculated using equation 6. You are required to make at least twelve paired concentration measurements to determine the mean transport efficiency.

- **Non-quantitative spiking:** An aerosol containing a surrogate metal or a metal analyte can be spiked non-quantitatively into the stack or duct gas stream or into the transport system as close as possible to the sampling probe. The concentration of the spiked metal is measured by method 29 (40 CFR 60, Appendix A)[5] or a suitable alternative as close as possible to the CEMS' sample probe and by another Method 29 or a suitable alternative as close as possible to the sampling module. If you spike directly into the transport line you must make your upstream concentration measurement as close as possible to the spike location and your downstream measurement as close as possible to the sampling module. If your XRF multi-metals CEMS is capable of measuring the spiked metal, you may compare its reported concentration with the in source metals measurement or with the upstream in transport line measurement to calculate transport efficiency according to equation 6. You are required to make at least twelve paired concentration measurements to determine the mean transport efficiency.

- **Quantitative Spiking**: An aerosol containing a surrogate metal or a metal analyte can be spiked quantitatively into the stack or duct gas stream or into the transport system as close as possible to the sampling probe. The concentration may be measured on the CEMS or by using method 29 or a suitable alternative as close as possible to the sampling module. This measurement is then compared with the known concentration of the spiked aerosol to determine the percent transport.

3.1.6 Dual Train Requirements

If you use a reference method (eg., method 29 or 5i) during the linearity, relative bias, or transport efficiency tests it is recommended that you use dual trains to screen the reference method for bias and imprecision.

3.1.7 Cycle Time Requirements

The cycle time for your XRF multi-metals CEMS should be no greater than one-third of the averaging period for the applicable standard. During all phases of the performance specification test including the CEMS must use the same cycle time as will be used during day to day operation.

3.2 How do I report the results of the initial performance specification test?

Summarize the results of the calibration drift and accuracy tests in tabular form. Include all data sheets, calculations, and records of CEMS measurements necessary to substantiate the performance of the CEMS and any other devices or methods (e.g., method 29). The CEMS measurements shall be reported to the agency in units of µg/m³ on a dry basis, corrected to 20°C.

4.0 Performance Criteria and Calculations

4.1 What are the performance criteria for my XRF multi-metals CEMS?

You must demonstrate that your XRF multi-metal CEMS has adequate stability, precision, accuracy, cycle time and data reporting capabilities to determine if your facility is in compliance with metal emission standards or operating permit limits as specified in applicable regulations or permits. You will demonstrate this capacity by showing that your XRF multi-metal CEMS meets the following performance criteria.

4.1.1 7-day Drift Check Criteria – Stability

Upscale Drift: The upscale drift as calculated in section 4.2.8 must be less than 15% of the original calibration value of the upscale reference each day for seven consecutive days.

Zero Drift: The zero drift as calculated in Section 4.2.9 must be less than 20% of the emission limit each day for seven consecutive days.

Volume or Flow Drift: The volume or flow drift as calculated in Section 4.2.11 must be less then 20% of the full scale value of the flow or volume measurement device each day for seven consecutive days.

4.1.2 X-Ray Fluorescence Calibration Drift Criteria

For each metal measured by your multi-metal CEMS for compliance purposes the x-ray fluorescence calibration drift must be less than 10% of the value of the standard. (Note: you are not required to calculate the XRF calibration drift for those metals used during the bias and precision testing).

4.1.3 Relative Bias Criteria – Accuracy and Precision

The relative bias of the instrument must be less than 15% and the relative percent standard deviation (RSD) must be 10% or less if you challenge the XRF and sampling modules of your CEMS separately from your transport system. If you challenge your entire CEMS and it does not meet the above relative bias criteria you must apply a correction factor to the results reported by your CEMS. The correction factor is calculated using the equation in section 14.2.13. Also, the correlation coefficient for a least squares linear regression fit of the metal that was spiked at three different concentration levels must be greater than 0.90. This is to help assure that the correction factor is applicable over the range of the instrument.

4.1.4 Linearity Test Criteria – Accuracy and Precision

If you choose to do linearity tests to determine the accuracy and precision of your XRF multi-metals CEMS the slope of the least squares linear fit should be between 0.85 and 1.15. The correlation coefficient must be 0.90 or better and the intercept should be less than 20% of the applicable emission limit. If you challenge only the XRF module and the sampling module of your CEMS you must meet the above criteria. If you challenge your entire CEMS and you do not meet the slope or intercept criteria you must adjust the results reported by your CEMS, you must however, still meet the correlation coefficient criteria. The correction factor is calculated according to the procedures in section 4.2.12.

4.1.5 Transport efficiency – Accuracy

If the average transport efficiency is between 90 and 110 percent, then no correction for transport efficiency needs to be applied to concentrations reported by your XRF multi-metals CEMS. If, however, your average transport efficiency is less than 90 percent or more than 110 percent then you must use a correction factor. You may use your transmission efficiency test data to establish a correction factor that would change the reported CEMS concentrations for each metal to a value that would reflect 100% transmission efficiency.

4.1.6 Cycle time – Appropriate Reporting

The cycle time for your XRF multi-metals CEMS must be no greater than one-third of the averaging period for the applicable standard.

4.2 What calculations, equations, and data analyses are needed?

4.2.1 Arithmetic Mean

Calculate the arithmetic mean of a data set as follows.

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

Equation 1

Where :

$\bar{x}$ = Arithmetic mean

n = Number of data points

x_i = Value of each data point

4.2.2 *Arithmetic Mean of Difference*

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

$$d_i = C_i^{CEMS} - R_i^{RM}$$ **Equation 2**

Where:

C_i^{CEMS} = The concentration of the ith element as reported by the CEMS

R_i^{RM} = The concentration of the ith element as reported by the reference method or aresol

4.2.3 *Standard Deviation (of differences)*

$$SD_i = \sqrt{\frac{\sum d_i{}^2 - \frac{1}{n}\left(\sum d_i\right)^2}{n-1}}$$ **Equation 3**

Where:

SD_i = The standard deviation of differences for the ith 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 concentration reported by the CEMS.

4.2.4 *Percent relative standard deviation*

$$PRSD_i = \frac{SD_i}{\overline{R_i^{RM}}} \times 100$$ **Equation 4**

Where:

$\overline{R_i^{RM}}$ = The average of the reference method data set or the reference aerosol concentration for the ith element

$PRSD_i$ = The relative percent standard deviation for the ith metal

4.2.5 *Relative Bias*

$$PRB_i = \frac{\left|\overline{d_i}\right|}{\overline{R_i^{RM}}} \times 100$$ **Equation 5**

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

4.2.6 *Percent Transmission*

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

Equation 6

Where:

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.

PT_i = The percent transport of the ith 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).

4.2.7 *Best Fit Line for Linearity Test*

Calculate the linear correlation equation given below.

$$\hat{y} = b_o + b_1 x$$

Equation 7

Where:

b_o = The y intercept

b_1 = The slope

The intercept is calculated according to the following equation.

$$b_o = \overline{y} - b_1 \overline{x}$$

Equation 8

Where:

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

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

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 9**

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 10**

4.2.8 Upscale Drift

$$UD_i = \frac{\left|L_i^{cemu} - L_i^{u}\right|}{L_i^{u}} \times 100$$ **Equation 11**

Where:

UD_i = The upscale drift of the ith element on your CEMS in percent.

L_i^{cemu} = The measured CEMS response to the ith element in the upscale standard

L_i^{u} = The calibrated value of the ith element of the upscale standard

4.2.9 Zero Drift

$$ZD_i = \frac{\left|L_i^{cemo} - L_i^{0}\right|}{C_i^{L}} \times 100$$ **Equation 12**

ZD_i = The zero drift of the ith element on your CEMS in percent

L_i^{cemo} = The measured CEMS response to the zero standard for the ith element

L_i^{0} = The calibrated value of the ith element on the zero standard

C_i^{L} = The emission limit of the ith element

4.2.10 X-Ray Fluorescence Calibration Accuracy

$$CA_i = \frac{\left|L_i^{cem} - L_i^{std}\right|}{L_i^{std}} \times 100$$ **Equation 13**

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

4.2.11 *Daily Sample Volume Check*

$$VD = \frac{\left|V_{cemr} - V_m\right|}{FS} \times 100$$ **Equation 14**

Where:

VD = Volume drift

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

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

FS = Full scale value of the CEMS volume (or flow) measurement device

4.2.12 *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 15**

Where:

C_i^C = corrected CEMS concentration for the ith element

y_i = CEMS reported concentration for the ith 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 16**

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

$$C_i^C = \frac{y_i}{b_1}$$ **Equation 17**

4.2.13 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 18**

Where:

CF_i^{RB} = The relative bias correction factor for the ith element

$\overline{C_i^{CEM}}$ = The average reported concentration of the CEMS for the ith element

$\overline{R_i^{RM}}$ = The average of the reference method measurements for the ith metal

4.2.14 Percent transport correction factor

$$CF_i^{PT} = \frac{1}{\overline{PT_i}}$$ **Equation 19**

Where

CF_i^{PT} = Correction factor for percent transport for the ith element

$\overline{PT}_i$ = Average percent transport for the ith element

5.0 Other Requirements and Information

5.1 What quality control measures are required?

Quality control measures for an XRF multi-metal CEMS are addressed in procedure Z "Quality Assurance Requirements for X-Ray Fluorescence Based Multi-Metals Continuous Emission Monitors."

5.2 What calibration and standardization procedures must I perform?

Refer to your CEMS owner's manual and manufacturer to determine what calibration and standardization procedures are required for your multi-metal CEMS.

5.3 What pollution prevention procedures must I follow? [reserved]

5.4 What waste management procedures must I use?

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

5.5 What reference tables and figures are relevant to PS-YY?

Table 1. Initial Performance Specification Tests and Criteria

Test Category	Test	Test Requirements	Test Criteria
Seven Day Stability	Zero Drift	Monitor zero standard for 7 consecutive days under normal operating conditions	< 20% drift every day for seven consecutive days
	Upscale Drift	Monitor upscale standard for 7 consecutive days under normal operating conditions	< 15% drift every day for seven consecutive days
	Flow Drift	Monitor flow drift for 7 consecutive days under normal operating conditions	< 20% drift every day for seven consecutive days
Calibration	X-Ray Fluorescence Calibration Drift Check	Test a standard for each element measured for compliance by your CEMS 3 times	< 10% drift for every element measured for compliance by your CEMS
Accuracy	<u>Option A</u> 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 the above criteria are met then no correction • if not met apply a correction (correlation criteria must be met)
	<u>Option B</u> • Perform a linearity test on sampling module and XRF module 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	<u>Linearity Criteria</u> • Slope = 0.85 to 1.15 • r ≥ 0.90 • intercept < 20% of emission limit • the linearity criteria must be met <u>Percent Transport Criteria</u> • 90≤PT≤110 • If percent transport criteria are not met apply a correction factor
	<u>Option C</u> 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)
	<u>Option D</u> • Perform a relative bias test on sampling module and XRF module 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	<u>Percent Relative Bias Criteria</u> RB≤ 15% %RSD ≤ 10% r ≥ 0.90 for metal with three fold conc. change <u>Percent Transport Criteria</u> • 90≤PT≤110 • If percent transport criteria are not met apply a correction factor

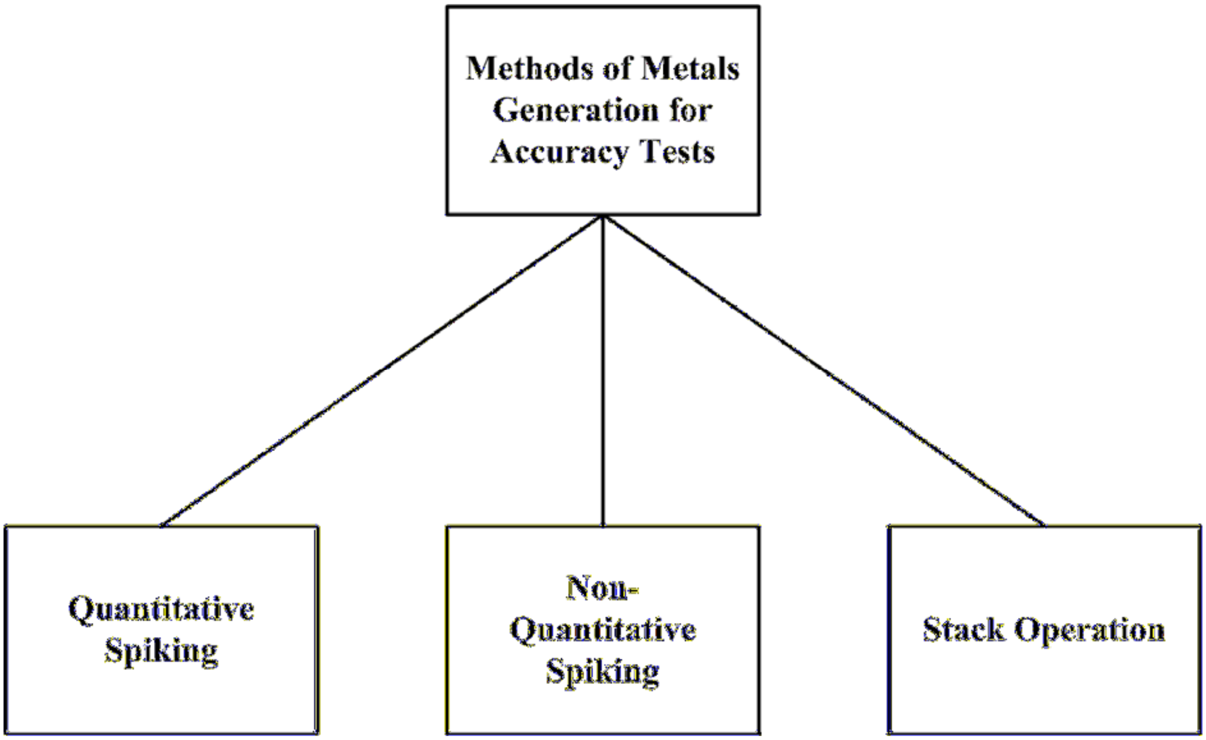

Figure 1: Types of metals generation available for accuracy tests.

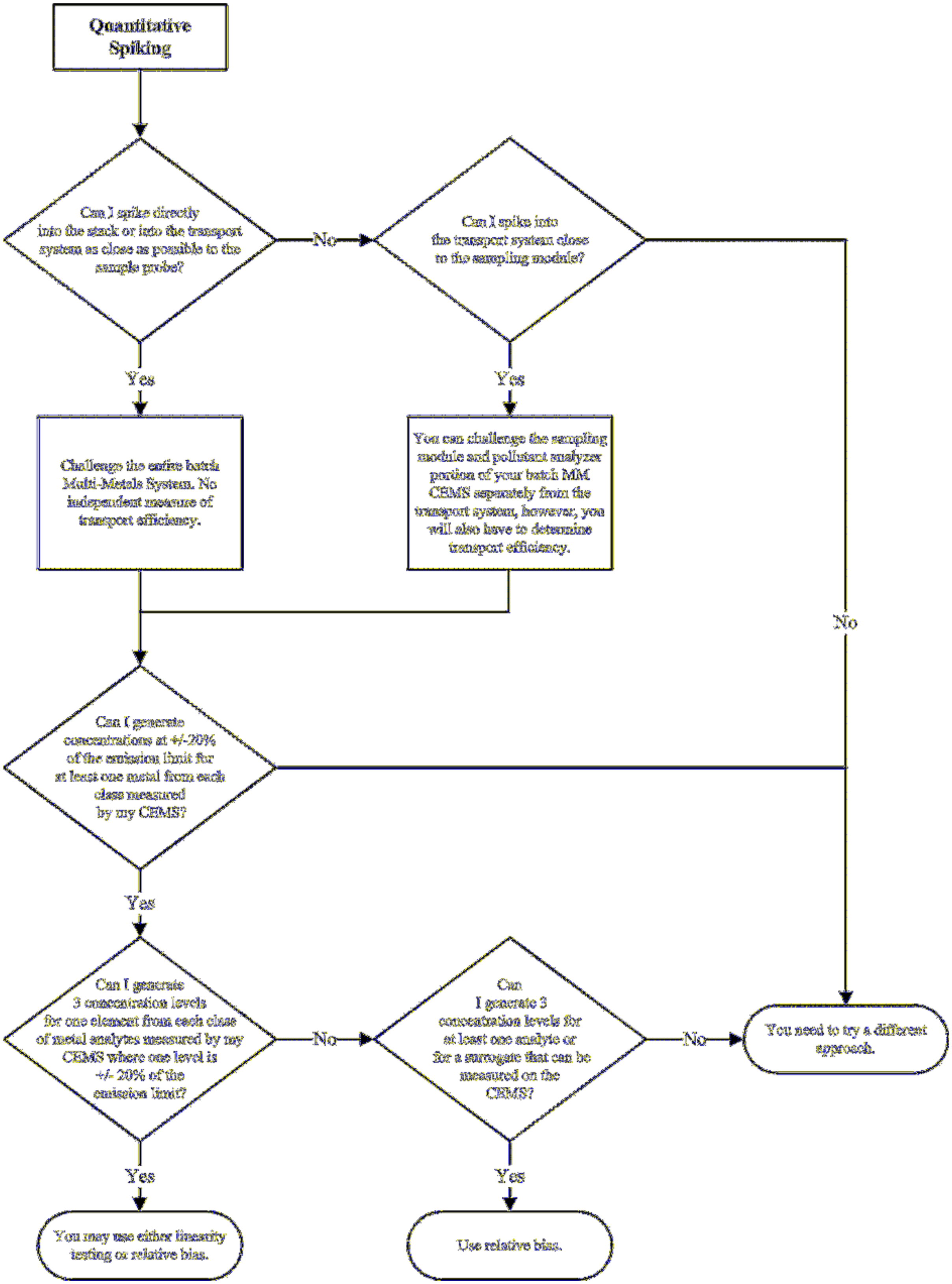

Figure 2: Flow chart for using quantitative spiking during the accuracy tests.

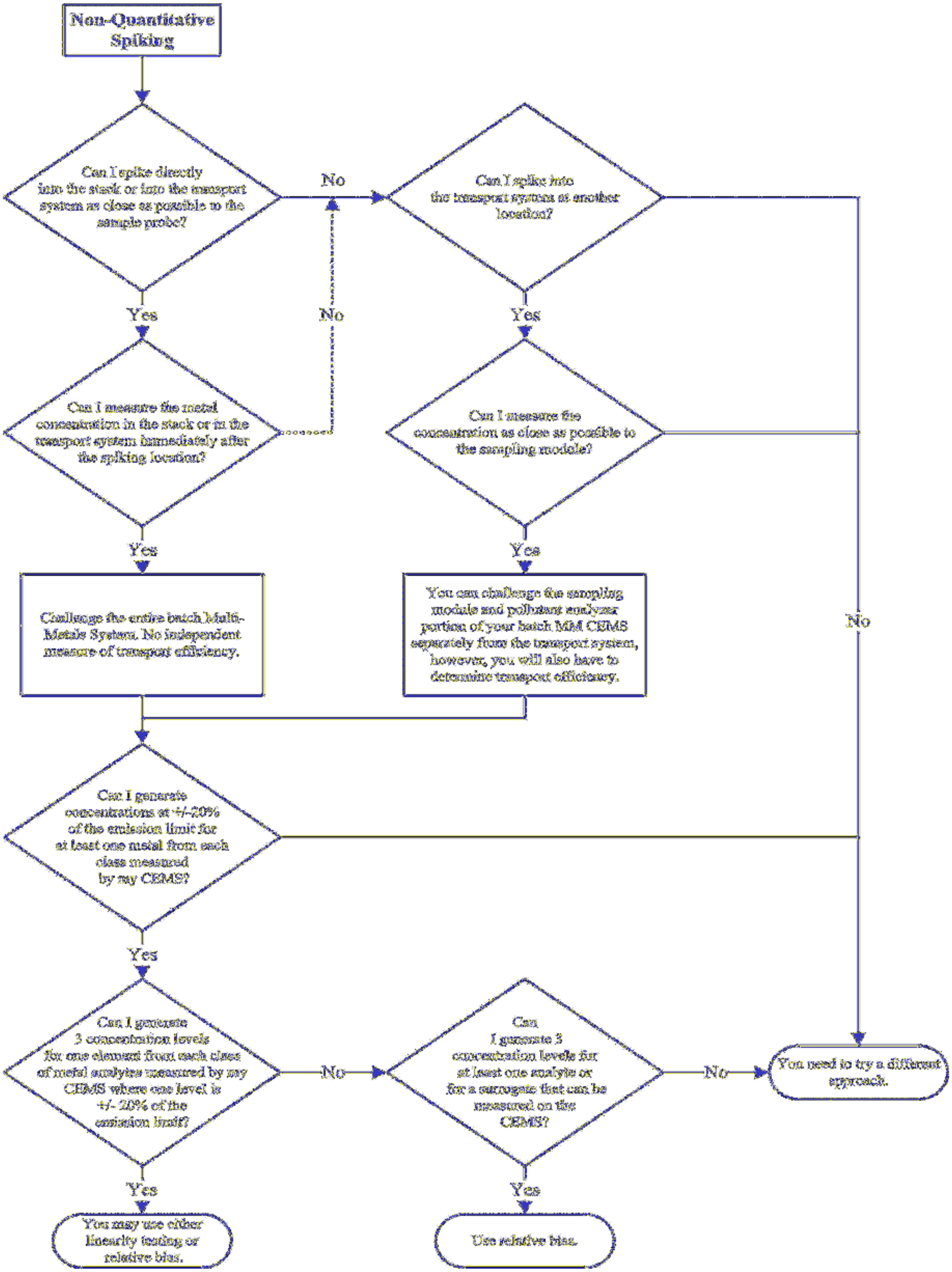

Figure 3: Flow chart for using non-quantitative spiking during the accuracy tests.

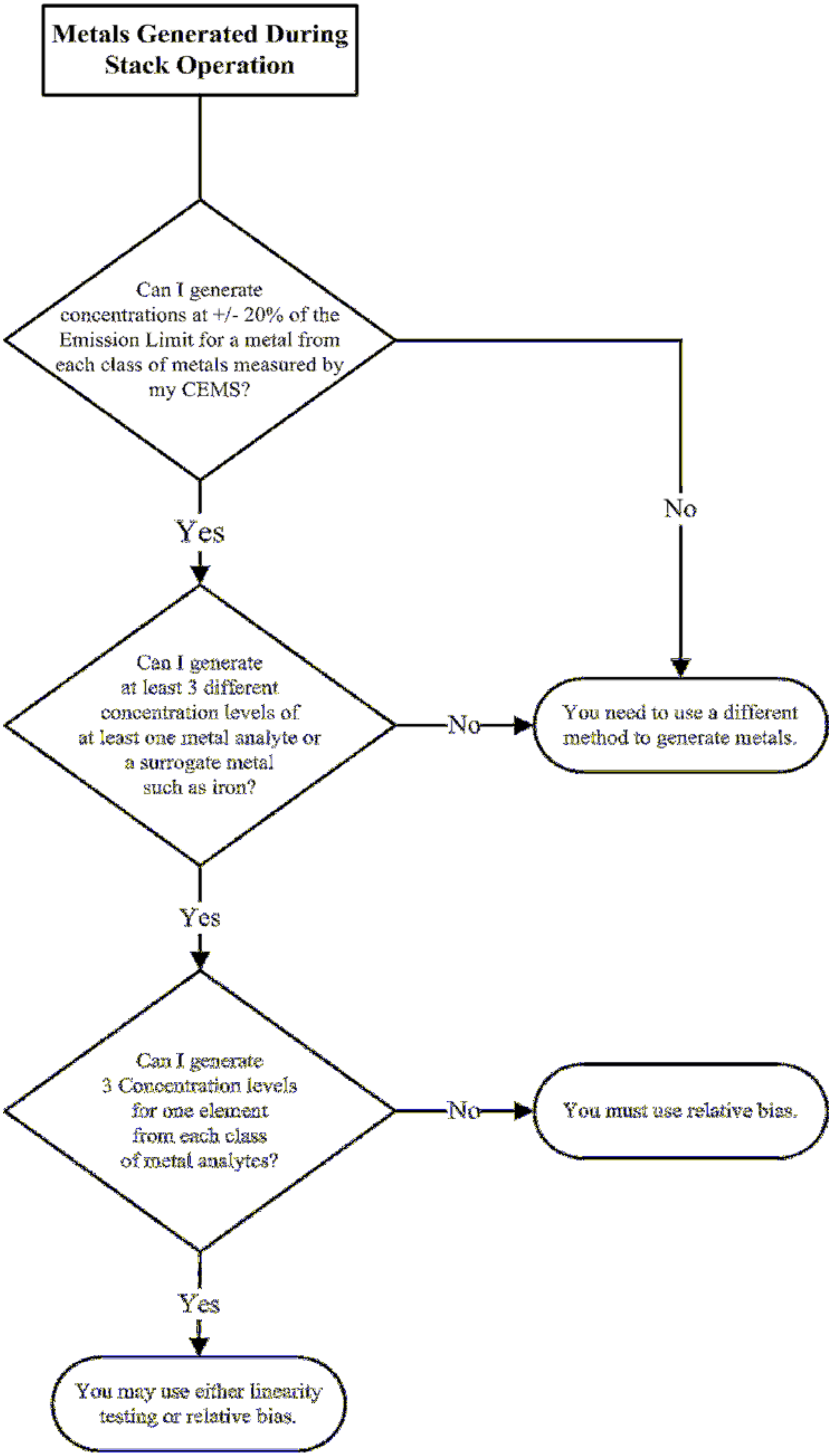

Figure 4: Flow chart for using stack operation to generate metals concentrations.

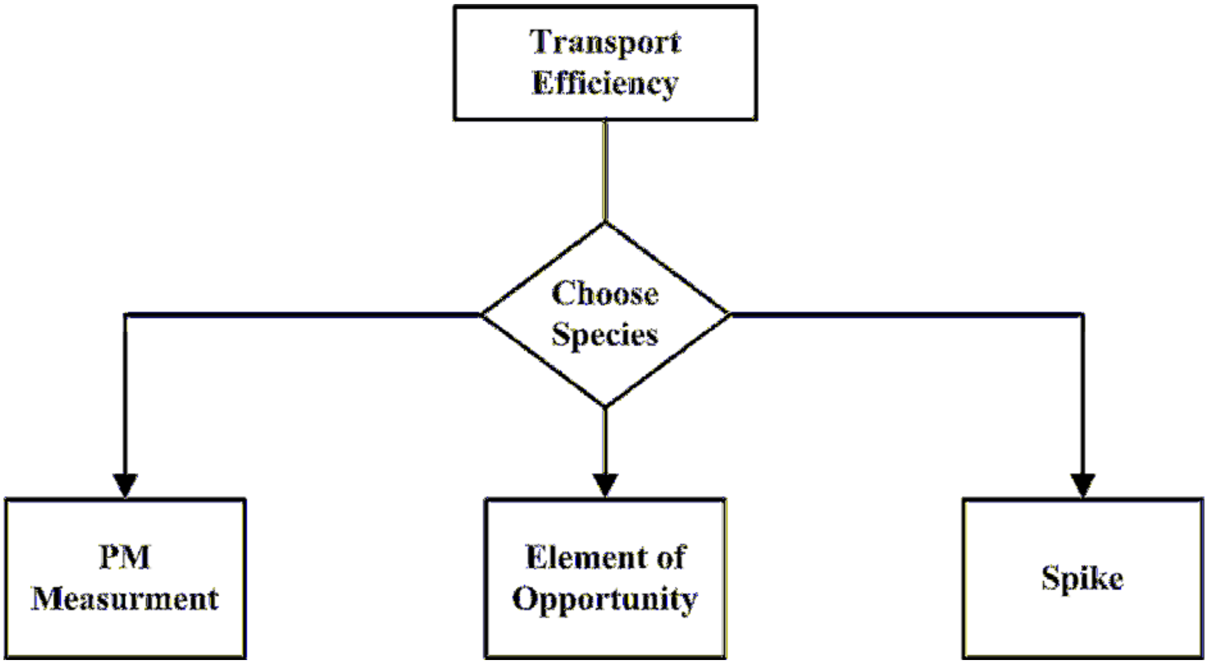

Figure 5: Species available for transport tests

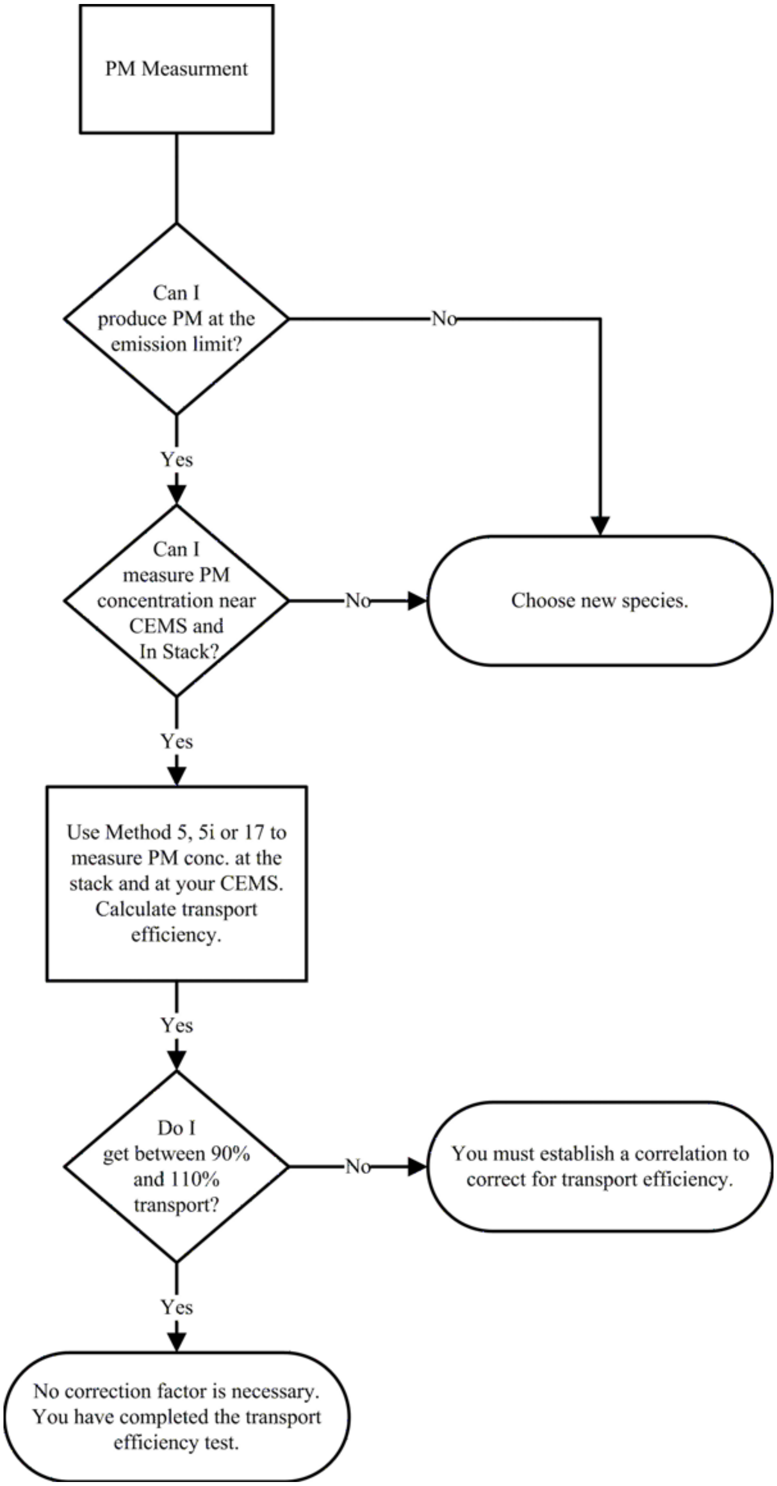

Figure 6: Procedure for percent transport using PM.

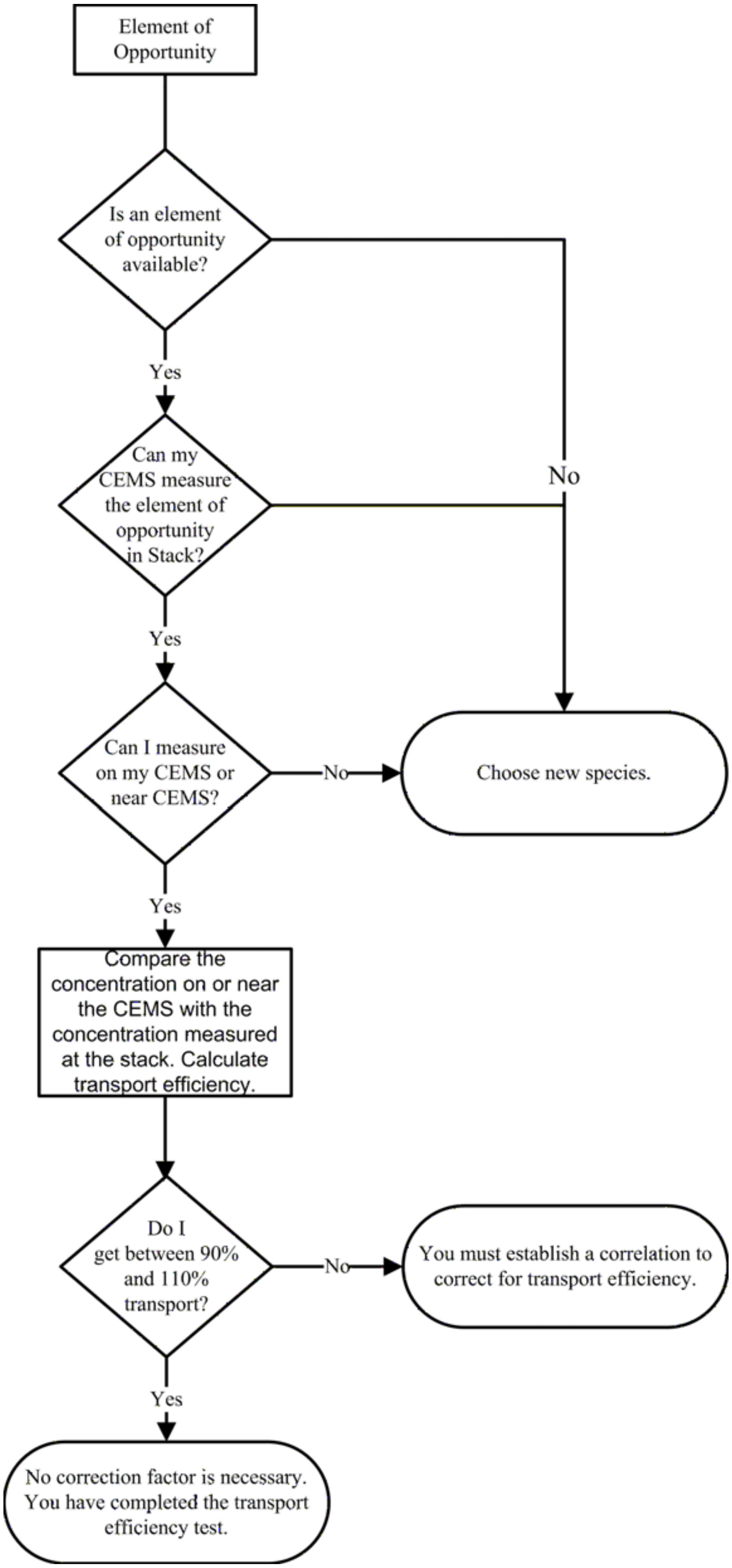

Figure 7: Procedure for percent transport determination using an element of opportunity.

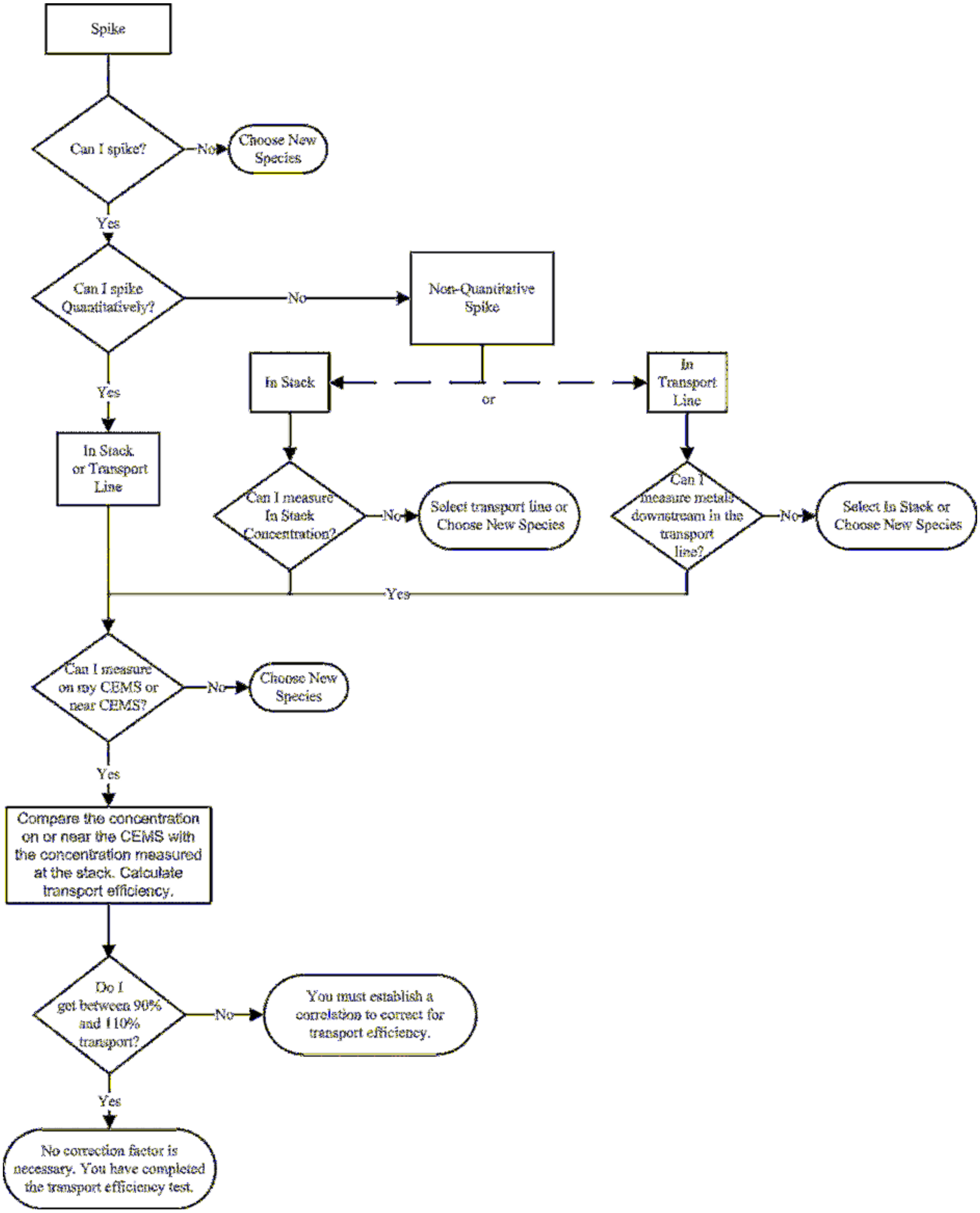

Figure 8: Procedure of percent transport determination using spiking.

5.6 What references apply to PS-YY?

1. 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.

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3. United States. Environmental Protection Agency [EPA]. Technology Transfer Network. Emission Measurement Center. Promulgated Methods. Method 5: Determination of Particulate Matter Emissions from Stationary Sources. Washington, DC: EPA; 2004. Available: http://www.epa.gov/ttn/emc/promgate/m-05.pdf via the Internet. Accessed May 10, 2005.

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5. United States. Environmental Protection Agency [EPA]. Technology Transfer Network. Emission Measurement Center. Promulgated Methods. Method 17: Determination of Particulate Matter Emissions from Stationary Sources. Washington, DC: EPA; 2004. Available: http://www.epa.gov/ttn/emc/promgate/m-17.pdf via the Internet. Accessed May 10, 2005.

6. United States. Environmental Protection Agency [EPA]. Technology Transfer Network. Emission Measurement Center. Promulgated Methods. Method 29. Determination of Metals Emissions from Stationary Sources. Washington, DC: EPA; 2004. Available: http://www.epa.gov/ttn/emc/promgate/m-29.pdf via the Internet. Accessed May 18, 2005.