

**Multiple Metals Stack Emission Measurement Methodology
for Stationary Sources, Current Status**

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ABSTRACT

Stack emissions of metals from stationary sources are of present interest to the United States Environmental Protection Agency (USEPA), to state and local governments, to industries, and to the public. When regulations require limitation of metals in stack emissions, it follows logically that measurement methodology is necessary for determining compliance to the established limits. This presentation presents a broad overview of measurement methodology for the purpose of determining multiple metals stack emissions of up to sixteen metals using one sampling train developed by the Atmospheric Research and Exposure Assessment Laboratory of USEPA.

Isokinetic sampling from a grid of points produces a representative sample from which the multiple emissions of up to sixteen metals can be measured in the sample from one train. Metals in the stack particulate matter and in the gases are measured separately. The samples are prepared by digestion for subsequent instrumental analysis by inductively coupled plasma or atomic absorption spectroscopy. The sixteen metals are total Cr, Cd, As, Ni, Mn, Be, Cu, Zn, Pb, Se, P, Tl, Ag, Sb, Ba, and Hg. Emission factor development, research requiring quantification of metals emissions, and determining emission compliance are important potential applications of this methodology.

This paper has been reviewed in accordance the U. S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

INTRODUCTION

Stack emissions of metals from stationary sources are of present interest to the United States Environmental Protection Agency (USEPA), to state and local governments, to industries, and to the public. When regulations require limitation of metals in stack emissions, it follows logically that measurement methodology is necessary for determining compliance to the established limits. This presentation presents a broad overview of measurement methodology for the purpose of determining multiple metals stack

emissions of up to sixteen metals using only one sampling train developed by the Atmospheric Research and Exposure Assessment Laboratory of USEPA. Previous USEPA methods exist for use when prescribed by regulations for measurement of emissions of only a single metal in one sampling train. These include a₃ separate individual train and methodology for either Pb¹, Be², Hg³, or As⁴. The multiple metals methodology is particularly useful in sampling situations in which one sampling train can be used instead of two or more trains to measure metals because of the significant potential for reduced cost and increased efficiencies in emissions measurement.

DISCUSSION

The multiple metals measurement methodology for up to sixteen metals in one train is tentatively planned by The Office of Air Quality Planning and Standards of USEPA to be proposed as Method 29, in 40 CFR 60, Appendix A⁵. The current status of this methodology is discussed in this presentation. A condensed description of the methodology is given here. A representative sample of the stack multiple metals emissions is acquired by using a single train by isokinetic sampling from a grid of sampling points. Up to sixteen metals can be measured in the sample produced by this one train. Within the sampling train a filter captures the metals in particulate matter and acidic impinger solutions capture the metals in the gases. The samples are then recovered from the train, prepared for analysis by digestion, and finally analyzed by inductively coupled plasma and/or atomic absorption spectroscopy (AAS) including Graphite Furnace AAS (GFAAS) or Cold Vapor AAS (CVAAS) as applicable. Calculations are then performed to determine concentrations of the metals in the stack effluent from which stack emissions may be determined. The sixteen metals are total Cr, Cd, As, Ni, Mn, Be, Cu, Zn, Pb, Se, P, Tl, Ag, Sb, Ba, and Hg. An important use of the methodology would occur should government entities or others develop additional regulations in the form of limitations of metals in stack emissions and determine that the methodology be used to determine compliance to the emission limits. Emission factor development and other research requiring quantification of metals emissions are other important potential applications of this methodology.

The train and methodology have undergone changes designed to increase understanding of the management of the methodology including its allowable options to yield the desired detection limits for metals concentrations in the stack effluent: these are termed in-stack detection limits as defined in the methodology. Also, changes have occurred which decrease chances for contamination of the sample, increase understanding of the measurement of metals emissions especially mercury emissions, and increase understanding of the limits to corrections allowed by the methodology for certain blank reagent values.

The methodology includes acquisition of a representative source sample from a grid of points in the sampling plane. In a

one hour sampling period at a typical average nominal stack aerosol sampling rate of 21 liters per minute, a sample of 1.25 cubic meters will be obtained which can yield the in-stack detection limits ($\mu\text{g}/\text{m}^3$) shown in Table 1. For multiple metals sampling a Method 5 type sampling train⁶ which can achieve the above described nominal sampling rates and sample volume was modified to have glass components including a glass probe tip, glass probe and glass filter holder, low metals content quartz fiber filter, Teflon filter support, and glass impingers. The modification as shown in Figure 1 of the Method 5 train was selected because of its ease of operation and availability of equipment to all source samplers, low cost, and isokinetic sampling capability. Quartz probe tips and probes are available, also, for special sampling applications. Acidic absorbing solutions for the metals are used in four of the seven impingers in the multiple metals train. As described in the method an aqueous solution of combined 5 percent nitric acid and 10 percent hydrogen peroxide is used in the second and third impingers which follow the empty first impinger, and an aqueous solution of combined 4 percent potassium permanganate and 10 percent sulfuric acid is used in the fifth and sixth impingers which follow the empty fourth impinger.

The multiple metals methodology describes how the sampler may design the sampling, digestion and analytical conditions to meet the specific needs of the test. The in-stack detection limits shown in Table 1 are for nominal sampling conditions. However, the in-stack detection limits produced in the actual test may be lowered, that is, made more sensitive than those shown in Table 1. For example, if the actual sample volume is 2.50 cubic meters instead of 1.25 cubic meters, the in-stack detection limits will be one-half those shown in Table 1. By using the other design options described in the methodology, the in-stack detection limits could be one-tenth or even much lower than one-tenth of those shown in Table 1.

If desired or required, blank corrections according to the strict guidelines/limitations described in the methodology may be performed.

SUMMARY

In summary, in its current status the multiple metals methodology allows measurement of coincidental stack emissions of up to sixteen described metals in one sampling train. The methodology describes how the sampler may adjust (design) the sampling conditions to meet the needs of the test. Preparation for sampling and the acquisition, digestion and analysis of the sample are described adequately. Blank corrections according to the strict guidelines/limitations may be performed.

REFERENCES

1. Code of Federal Regulations. Title 40 - Protection of Environment, Part 60, Appendix A, Method 12, United States Government Printing Office, Washington, DC. July 1992,

- 40 CFR 60, Appendix A, Method 12.
2. Ibid., 40 CFR 61, Appendix B, Method 104.
 3. Ibid., 40 CFR 61, Appendix B, Method 101A.
 4. Ibid., 40 CFR 61, Appendix B, Method 108.
 5. EMTIC Bulletin Board System, United States Environmental Protection Agency, Office of Air Quality Planning and Standards, Technology Transfer Network, Research Triangle Park, NC 27711, 1993.
 6. Code of Federal Regulations. Title 40 - Protection of Environment, Part 60, Appendix A, Method 5, United States Government Printing Office, Washington, DC. July 1992, 40 CFR 60, Appendix A, Method 5.

TABLE 1. IN-STOCK METHOD DETECTION LIMITS (ug/m³)
FOR TRAIN FRACTIONS USING ICAP AND AAS

Metal	Front-half Fraction 1 Probe and Filter	Back-half Fraction 2 Impingers 1-3	Back-half Fractions "Hg, only" Impingers 4-6	Total Train
Antimony	7.7 (0.7)*	3.8 (0.4)*		11.5 (1.1)*
Arsenic	12.7 (0.3)*	6.4 (0.1)*		19.1 (0.4)*
Barium	0.5	0.3		0.8
Beryllium	0.07 (0.05)*	0.04 (0.03)*		0.11 (0.08)*
Cadmium	1.0 (0.02)*	0.5 (0.01)*		1.5 (0.03)*
Chromium	1.7 (0.2)*	0.8 (0.1)*		2.5 (0.3)*
Copper	1.4	0.7		2.1
Lead	10.1 (0.2)*	5.0 (0.1)*		15.1 (0.3)*
Manganese	0.5 (0.2)*	0.2 (0.1)*		0.7 (0.3)*
Mercury	0.6**	3.0**	2.0**	5.6**
Nickel	3.6	1.8		5.4
Phosphorus	18	9		27
Selenium	18 (0.5)*	9 (0.3)*		27 (0.8)*
Silver	1.7	0.9		2.6
Thallium	9.6 (0.2)*	4.8 (0.1)*		14.4 (0.3)*
Zinc	0.5	0.3		0.8

()* Detection limit when analyzed by GFAAS.

** Detection limit when analyzed by CVAAS, estimated for Back-Half and Total Train.

Note: Actual method in-stack detection limits will be determined based on actual source sampling parameters and analytical results as described earlier in this section.

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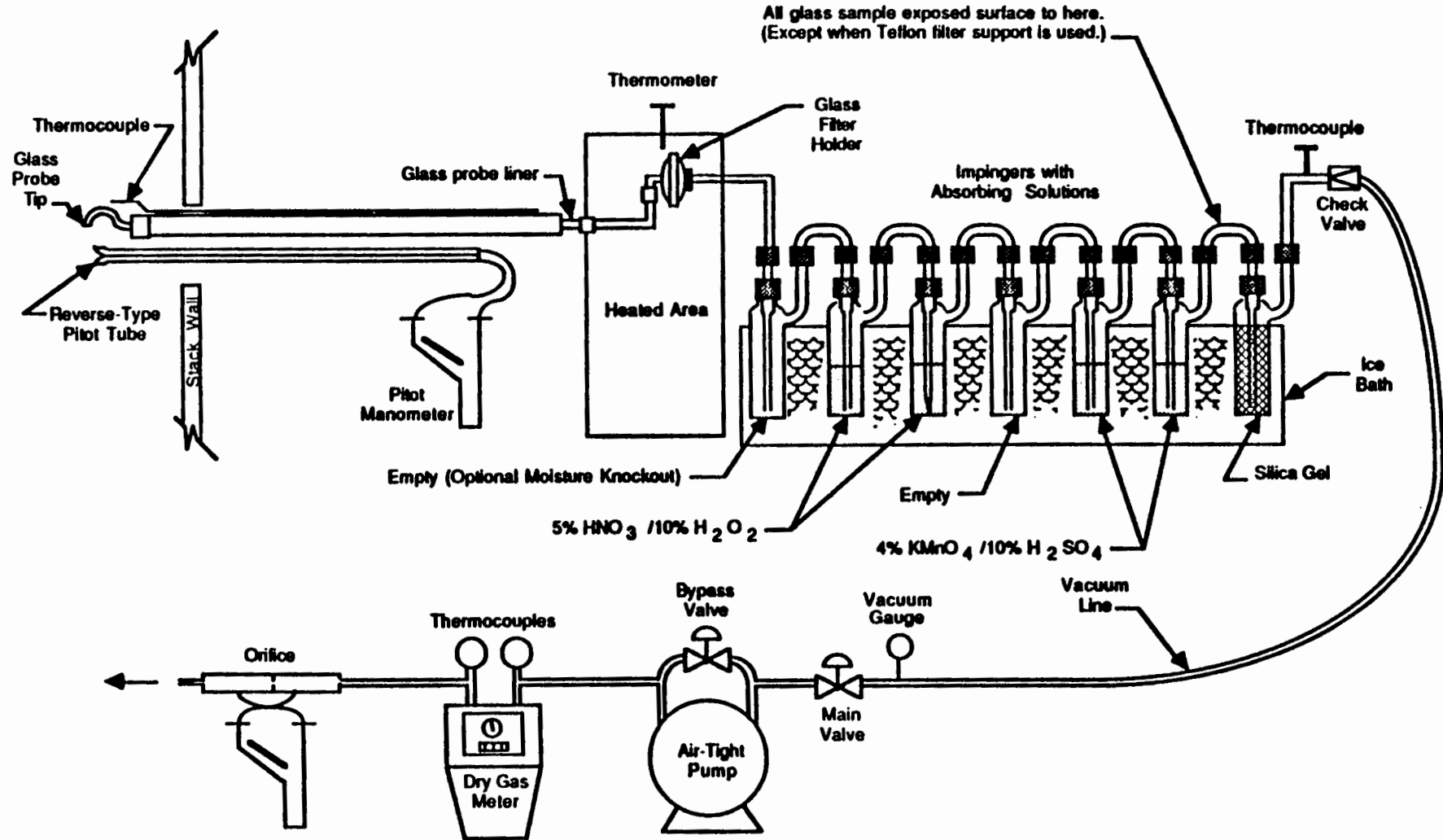


Figure 1. Schematic of multiple metals sampling train configuration.

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