



Project Summary

Laboratory and Field Evaluation of Methodology for Measurement of Cadmium in Stationary Source Stack Gases

R. F. Moseman, D. B. Bath, J. R. McReynolds, D. J. Holder, A. L. Sykes,
and T. E. Ward

An initial laboratory and field evaluation study was done to assess the usefulness of a Modified EPA Method 5 (MM5) sampling train and flame atomic absorption spectrometry for measuring cadmium in stationary source stack emissions. Field evaluations were performed at a municipal solid waste incinerator and a sewage sludge incinerator. These industrial sources are currently being evaluated by EPA/OAQPS for multiple pollutants including cadmium emissions. Also, this methodology is being developed for application, subject to verification, at other sources of cadmium emissions at or above the method detection limit. A formulation of the methodology was tested through the laboratory and field sampling validation phases to evaluate precision and accuracy of the proposed method. Collocated, quadruplicate flue gas samples of nominally 30 and 60 dscf in one- and two-hours sampling time were collected to assure an adequate cadmium content, a representative sample (including volume of stack gas and duration of sampling time), and the production of data to validate the method in terms of between-train precision. The overall accuracy and precision of the analysis procedure were 89.2% and 1.7%, respectively. The method detection limit for a 30 to 60 dscf (0.85 to 1.7 dscm) stack gas sample was found to be 0.05 to 0.025 $\mu\text{g Cd}$, respectively per dscf (1.7 to 0.88 $\mu\text{g Cd}$ per dscm). The detection limit of the atomic absorption instrument was 0.03

$\mu\text{g/ml}$. The percent coefficient of variation (precision) of between-train cadmium concentrations averaged 13.5% for the six sampling runs conducted at the municipal solid waste incinerator (Field Test #1). The precision of between-train cadmium concentrations averaged 3.8% for the four sampling runs conducted at the sewage sludge incinerator (Field Test #2). Separate analyses of the front half (probe and filter) and back half (impingers) of the field samples revealed that all of the cadmium was collected in the front half, with the exception of one sample. In this sample, a faulty filter leaked and a small percentage of the cadmium was captured in the impingers. In all of the other impinger samples, the cadmium concentration was below the detection limit. Precision of the cadmium results was not affected by varying the sample size from 30 to 60 dscf.

This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The U.S. Environmental Protection Agency (EPA) is currently investigating cadmium emissions from stationary sources as a potentially hazardous air pollutant. If EPA makes a determination to regulate cadmium emissions, appro-

appropriate methods of sampling and analysis must be available to quantify accurately the emission of cadmium in stack gases from stationary sources.

EPA's Environmental Monitoring Systems Laboratory (EMSL) in Research Triangle Park, North Carolina, is developing and validating a methodology for sampling and analysis of cadmium emissions. This report presents the results of field and laboratory studies funded by EPA and conducted by Radian Corporation. The objectives of the study were as follows:

- Determine the applicability of a Modified EPA Method 5 (MM5) train and flame atomic absorption spectrometry for measuring stationary source stack gas cadmium.
- Evaluate the precision and accuracy of the proposed laboratory analytical technique. The technique consists of sample preparation followed by analysis for cadmium using atomic absorption spectrometry.
- Assure that the method has a detection limit sufficient to measure expected cadmium in municipal solid waste and sewage sludge incinerator flue gas samples of nominally 30 to 60 dry standard cubic feet.
- Combine the results of these determinations to validate the proposed sampling and analytical methodologies.

The method validation was conducted in several stages. The initial effort focused on defining appropriate sampling and analytical procedures. The chosen procedures are discussed in Section 4 of the full report. A laboratory study was then conducted to determine overall precision and accuracy of the analytical portion of the methodology including sample preparation and analysis. The next stage of this program involved a field evaluation conducted at a large municipal solid waste incinerator and a sewage sludge incinerator.

The field evaluations were conducted according to the procedures outlined in the site-specific Quality Assurance and Project Plans, hereafter referred to as the QA Plans.

Procedures

Method Formulation and Design of Evaluation Studies

The sampling and analytical methods evaluated in this field and laboratory

study were proposed after a thorough literature search. Sampling methods, sample preparation techniques, and methods for analysis of cadmium emissions from stationary sources were reviewed. The Source Assessment Sampling System (SASS) and EPA Method 5 sampling train were reviewed as possible sampling methods. The analytical methods under consideration included amperometric titration, voltammetry/polarography, colorimetry, x-ray techniques, gamma and neutron activation, emission spectrography, mass spectrometry, inductively coupled argon plasma spectroscopy, and flame and flameless atomic absorption spectrometry. Possible sample preparation techniques included ultrasonic extraction and variations of acid digestion.

The various methods of sampling, sample preparation and analyses were then compared according to method detection limit, sensitivity, precision, speed, complexity, availability, cost, and overall practicality. After considering these factors and reviewing the literature, it was determined that sample collection using a MM5 sampling train, followed by acid digestion in a Parr Bomb and flame atomic absorption spectrometry would be used for the sampling and analysis of cadmium emissions from stationary sources.

The laboratory validation phase of this work was designed to assess the combined precision and accuracy of the sample preparation and analysis steps of the method using a National Bureau of Standards (NBS) urban particulate sample. Samples were digested using a mixture of nitric and hydrofluoric acids in a Parr bomb and analyzed in quadruplicate using three different methods: flame atomic absorption spectrophotometry (AAS), inductively-coupled argon plasma spectroscopy (ICAP) and neutron activation analysis (NAA).

A weighed amount of each particulate sample was digested along with a glass fiber filter to provide a background matrix consistent with the field samples. Following digestion, each sample was split for analysis by AAS, NAA and ICAP. The two additional analytical techniques were used to confirm the results obtained by AAS. Filter blanks were also digested and analyzed. The filter blanks were analyzed to determine the amount of cadmium present in the glass fiber filter and acid reagents.

The sampling portion of the study was designed to assess the efficiency of

the glass fiber filter for collecting cadmium from stack gases. In previous work it was common to use 0.1 N to 0.8 N (5%) nitric acid in water to attempt to capture and hold certain trace elements in solutions through which stack aerosols were passed. The concentration of 5% nitric acid in water in the impingers was chosen for this research because it is reasonable to handle and because the level necessary could be determined best in field sampling. Impingers containing 5% nitric acid or distilled water (depending on the test run) were used in the MM5 trains downstream from the filter to trap any cadmium that passed through the filter. A quad-probe was used to permit the simultaneous collection of four samples from the same nominal point in the stack (collocated samples) by a single probe. The precision of the sampling method was evaluated by determining the concentration of cadmium in each of the four samples.

Samples were collected isokinetically for periods of roughly one or two hours to yield total sample volumes ranging from 30 to 79 dscf. The sample volumes collected were chosen to demonstrate that: 1) cadmium emissions from a municipal solid waste incinerator and a sewage sludge incinerator could be measured in samples of 30 dscf and 2) increasing the size of the sample volume (above 30 dscf) would not affect the analytical precision and accuracy of cadmium concentration results.

To recover all of the cadmium from the sampling train components, the front half rinses were combined with the glass fiber filter for digestion and analysis. The impinger solutions and back half rinses were combined and analyzed to determine if cadmium was captured in the back half of the MM5 train. At the direction of the EPA Technical Project Manager, the impingers in one of the six tests of Field Test #1 were filled with distilled water in place of 5% nitric acid to assess how well distilled water could catch breakthrough cadmium and to avoid the use of acid whenever possible. (All Test #2 runs used 5% nitric acid.)

In addition to the analysis of field samples, several other analyses were performed as part of the laboratory validation procedures. Sample train component blanks (probes and nozzles) and reagent container blanks were analyzed using AAS to evaluate the quality control associated with the field sample preparation procedures.

Results and Discussion

Prior to any field sampling activities, the precision and accuracy of the proposed analytical procedures were determined. The sample preparation and AAS procedures used to analyze field samples for cadmium had an accuracy of 89.2% for analyzing known concentrations of cadmium. The precision of these procedures was 1.7%.

The precision and accuracy were determined by Parr bomb digestion of four aliquots of a National Bureau of Standards Standard Reference Material and three independent analysis techniques: AAS, ICAP spectroscopy, and NAA. Instrument detection limits for the three techniques were 0.03, 0.03, and 0.12 $\mu\text{g/ml}$, respectively.

The accuracy (% recovery) and precision (% CV) for all three analytical methods are given in Table 1. Overall average percent recoveries for each analytical method were as follows: 89.2% for AAS, 99.3% for ICAP, and 94.2% for NAA. The mean percent differences for the duplicates were 1.0% for AAS, 6.2% for ICAP, and 1.7% for NAA. In terms of standard deviation, the values were 0.84, 4.49, 1.09 $\mu\text{g/g}$ for AAS, ICAP, and NAA, respectively. The

duplicate means and the standard deviation are measures of precision for three analytical methods and serve as a basis for assessing the relative precision of the analytical methods.

The field testing portion of this study was designed to evaluate each of the following:

- The cadmium collection efficiency of the front and back halves of the MM5 train,
- The precision of the sampling and sample recovery procedures, and
- The effect of the sample volume on the ability of the method to detect cadmium.

The first field test was conducted at a municipal waste incinerator that had previously been tested for cadmium emissions. Cadmium concentrations reported during the previous testing ranged from 23 to 230 $\mu\text{g/dscm}$. Cadmium found during this study ranged from 32 to 115 $\mu\text{g/dscm}$. The second field test was performed at a municipal sewage sludge multiple hearth incinerator. The range of cadmium concentration reported for this study was 836 to 1,137 $\mu\text{g/dscm}$. Except for one run during the first field test, the sampling method employed for both tests was a

MM5 train which used nitric acid in the first two impingers instead of water. Separate analyses were performed on the front and back halves of the trains to determine the collection efficiency of each half.

To assess sampling and sample recovery precision, four "identical" samples were collected simultaneously using a quad-probe. Four simultaneous samples were collected for a total of 24 and 16 samples for Tests 1 and 2, respectively. Sampling was conducted isokinetically for all test runs.

Sample volumes collected during the field tests were nominally 30 and 60 dscf (0.9 to 1.8 dscm). The corresponding method detection limit for these sample volumes is 0.050 and 0.025 $\mu\text{g Cd/dscf}$ (1.7 and 0.84 $\mu\text{g Cd/dscm}$). Based on the previous cadmium emissions testing, cadmium detection was not expected to be a problem; however, the total volume was varied to determine the resulting effect on the cadmium analysis.

Tables 2 and 3 present the cadmium concentrations and precision assessments for the quad-train field studies. The between train pooled standard deviations were 12.39 $\mu\text{g/dscm}$ (Field Test #1) and 38.0 (Field Test #2) and represent the overall precision for the field studies. In terms of percent coefficient of variation, the pooled precision was 13.54 and 3.79, which is a measure of the precision of sampling and analysis for Tests 1 and 2, respectively.

The within-run or between-train precision shown in the tables is assessed in terms of a standard deviation and percent coefficient of variation. Contributions to these variables result from (1) differences in the sampling trains, (2) variations between trains in the sample preparation and recovery steps, and (3) analytical variability. Between-test pooled variability includes all of the above in addition to: (1) the day-to-day variability of the cadmium concentration in the feed, (2) effects of different plant operating conditions, and (3) the potential effect of within-run variability on the cadmium collection.

A second variable that was addressed was the collection efficiency of the sampling train. Except for Run 4-B in Test #2, no cadmium was detected in the back half, indicating that the filter was very efficient in preventing breakthrough. Cadmium (about 55 μg) was found in the first two impingers of the back half of Run 4-B of the second field

Table 1. Accuracy and Precision of Cadmium in NBS Standard Reference Material #1648, Urban Particulate^a

Sample ID ^b Number	AAS Accuracy ^c		ICAP Accuracy ^c		NAA Accuracy ^c	
	Individual % Recovery	Mean	Individual % Recovery	Mean	Individual % Recovery	Mean
A1	97.4	97.4	98.3	102.5	105.5	106.5
A2	97.4		106.6		107.4	
B1	84.0	84.7	107.5	104.5	92.2	91.6
B2	85.4		101.5		91.0	
C1	81.3	82.0	91.3	88.2	69.6	70.6
C2	82.7		85.0		71.6	
D1	92.0	92.7	100.1	102.2	107.5	108.0
D2	93.3		104.2		108.4	
Mean Accuracy	89.2		99.3		94.2	
% CV (Precision)	1.7		7.8		17.1	
Duplicate Differences: Mean %: ^d	1.0		6.2		1.7	
Std. Dev. of Random Error, ^{d,e}	0.84		4.49		1.09	

^aBased on an NBS cadmium value of 75 $\mu\text{g Cd}$ per gram of particulate.

^bSample A was Parr bombed once; Samples B, C, and D were bombed twice.

^cAAS, Atomic Absorption Spectrophotometry; ICAP, Inductively Coupled Argon Plasma; and NAA, Neutron Activation Analysis.

^dA measure of precision of duplicate determinations on four samples.

Youden, W.J., and E.H. Steiner, "Statistical Manual of the Association of Official Analytical Chemists," AOAC, Arlington, Virginia 22209 (1975), p. 18.

Table 2. Cadmium Concentrations and Within-Run Precision Assessments for Field Test #1

Test No.	Sample Train				Average ×	Standard ^a Deviation	Percent Coefficient of Variation (% CV)
	A	B	C	D			
1	32.2	32.8	30.4	32.6	32.0	1.10	3.4
2	96.5	85.6	87.2	104.1	93.4	8.63	9.2
3	105.5	115.5	73.5	74.9	92.4	21.36	23.1
4	76.2	88.0	101.2	76.7	84.8	11.67	13.8
5	80.0	111.5	103.3	88.3	95.8	14.24	14.9
6	101.4	328.0 ^b	93.8	95.6	96.93	3.97	4.1
					pooled	12.39 ^d	13.54 ^d

^aAll sample train results reported in micrograms cadmium per dry standard cubic meter, µg/dscm.

$$\left[\frac{\text{probe rinse} + \text{filter} + \text{impingers } (\mu\text{g})}{\text{total volume of stack gas sampled } (m^3)} \right]$$

^bThis value was excluded from the data analysis, because when subjected to a Dixon Outlier test^c for Test No. 6, it did not meet the acceptance criterion of 126.1 µg/dscm, at the 5% level of significance (i.e., 95% probability).

^cThe Dixon Outlier test may be found in Dixon, Wilford J., and Frank J. Massey, Jr., "Introduction to Statistical Analysis," McGraw-Hill Book Company, New York (1957).

$$d_{\text{pooled}} = \left(\sum_{i=1}^n \frac{s_i^2}{n} \right)^{1/2}$$

Table 3. Cadmium Concentrations and Within-Run Precision Assessments for Field Test #2

Test No.	Sample Train				Average ×	Standard ^a Deviation	Percent Coefficient of Variation (% CV)
	A	B	C	D			
1	886.2	927.8	835.5	886.6	884.0	37.8	4.27
2	1,137.1	1,133.4	1,081.9	1,081.4	1,108.5	31.0	2.80
3	989.1	1,088.0	993.6	1,057.5	1,032.1	48.7	4.71
4	1,097.8	1,041.1 ^c	1,030.9	1,081.9	1,062.9	32.0	3.01
					pooled	38.0 ^b	3.79 ^b

^aAll sample train results reported in micrograms cadmium per dry standard cubic meter, µg/dscm.

$$\left[\frac{\text{probe rinse} + \text{filter} + \text{impingers } (\mu\text{g})}{\text{total volume of stack gas sampled } (m^3)} \right]$$

$$b_{\text{pooled}} = \left(\sum_{i=1}^n \frac{s_i^2}{n} \right)^{1/2}$$

^cThe filter in this run was faulty and it leaked some cadmium to the impingers. However, only 3% of the total cadmium catch for this train was in the impingers, and 97% was in the front half.

test because gas bypassed a faulty filter. Particulate could be seen in the glass connections between the filter holder and the first impinger.

Field Test #1

A third variable evaluated in the data set of Table 2 was the length of the sampling period for each run. Tests 2, 3, and

6 were each conducted for roughly one hour while Runs 1, 4, and 5 were conducted for about two hours. An analysis of variance confirmed that there was not a significant difference in the variabilities of the cadmium concentrations of the one-hour compared to the two-hour runs at the 5% level of significance (95% probability). Thus, sampling times

of about one hour will yield concentration data equivalent to that for double the sampling time.

There were several anomalies in the cadmium concentration data set for the first field test. The average cadmium concentration level in Test #1 was much lower than for Tests 2 through 6. The cadmium concentrations reported for Tests 2 through 6 in Table 2 reflect a reasonably constant average cadmium concentration in the stack gas. However, there is no reason to suspect that the Test #1 samples were collected any differently than other test run samples. Therefore, these data were included in the data analysis. The concentration difference between Run No. 1 and the other runs is expected to be due to plant feed materials or operating conditions.

Also, Sample B in Test #6 shows an extremely high value in terms of cadmium per dscm (Table 2). Table 4 shows a comparison of cadmium in terms of gas volume sampled and the amount of cadmium per gram of particulate. Sample B, Test #6, is suspected to have been contaminated either by a large amount of cadmium after the sample was collected or by a few particles extremely rich in cadmium which may have been pulled into this particular train. The Dixon outlier test indicates that this value is an outlier (i.e., it should not be considered in the statistical analysis).

Table 4 shows a particulate value for Sample A in Test #4 which is nearly seven times higher than other values of the data set. For this particular sample, the glass probe liner broke during or just prior to sampling. A large amount of milky material was noted in the two nitric acid impingers, and the filter appeared brownish rather than white. Even though the particulate value for this sample was high, the concentration of cadmium appeared to agree with the other three runs of the test and was therefore included in the statistical analysis. Finally, the comparison of the cadmium collection efficiency of impingers containing nitric acid versus impingers containing distilled water was inconclusive. Cadmium was not detected in the train back half for any run of Field Test #1.

Field Test #2

In Field Test #2, there were no apparent outliers in the cadmium concentrations, either on the basis of mg/dscm or mg Cd/g particulate, as seen in Table 5

Table 4. Comparison of Field Test #1 Cadmium Concentrations, Particulate Concentration, Cadmium to Particulate Concentration, and Isokinetic Rates for Each Run^a

Test No.	A	B	C	D
1				
Cadmium (mg/dscm)	0.0322	0.0328	0.0304	0.0326
Particulate (mg/dscm)	^b	^b	^b	^b
Cadmium to Particulate (mg/gram)	^b	^b	^b	^b
Isokinetic Value (%)	102.2	104.1	102.6	107.6
2				
Cadmium (mg/dscm)	0.0965	0.0856	0.0872	0.1041
Particulate (mg/dscm)	^b	^b	^b	^b
Cadmium to Particulate (mg/gram)	^b	^b	^b	^b
Isokinetic Value (%)	100.8	104.2	99.9	100.4
3				
Cadmium (mg/dscm)	0.1055	0.1155	0.0735	0.0749
Particulate (mg/dscm)	38.77	38.78	49.48	36.05
Cadmium to Particulate (mg/gram)	2.72	2.98	1.48	2.08
Isokinetic Value (%)	102.8	100.0	103.5	101.0
4				
Cadmium (mg/dscm)	0.0762	0.0850	0.1012	0.0767
Particulate (mg/dscm)	224.12 ^c	34.25	33.77	32.59
Cadmium to Particulate (mg/gram)	^c	2.48	3.00	2.35
Isokinetic Value (%)	101.4	101.2	103.1	102.9
5				
Cadmium (mg/dscm)	0.0800	0.1115	0.1033	0.0883
Particulate (mg/dscm)	40.73	44.21	37.19	34.54
Cadmium to Particulate (mg/gram)	1.96	2.52	2.78	2.56
Isokinetic Value (%)	102.6	101.1	102.2	101.5
6				
Cadmium (mg/dscm)	0.1014	0.3280 ^d	0.0938	0.0956
Particulate (mg/dscm)	37.87	38.93	35.37	32.42
Cadmium to Particulate (mg/gram)	2.68	8.42 ^d	2.65	2.95
Isokinetic Value (%)	101.0	100.0	97.7	101.2

^aThe particulate emission and cadmium-to-particulate ratio values presented in this table are for information only. In any municipal waste incineration process, significant variation might be expected of particulate or cadmium emissions between tests.

^bParticulate weight was not determined.

^cNot valid for particulate concentration or cadmium-to-particulate ratio because of broken probe liner which resulted in excessive particulate weight values.

^dNot valid for cadmium, Dixon Outlier test.

Average run concentrations in mg/dscm ranged from 0.8866 mg/dscm to 1.1085 mg/dscm. An analysis of variance indicated that there was a significant difference between runs, which was not unexpected. Within-run precision, measured in percent coefficient of variation (% CV), ranged from 2.80 to 4.71, indicating consistent and precise sampling and analysis capability under the test conditions encountered in the second field test. The average cadmium concentration in Field Test #1 ranged from 32.0 µg/dscm to 96.93 µg/dscm for six runs, while in the second field test, cadmium concentrations ranged from 886.6 to 1,108.5 µg/dscm for four runs. As noted above, the precision in Field

Test #2 was consistent, exhibiting a narrow range of variability between runs. Table 2 shows the precision or between run variability for Field Test #1 to range from 3.4 to 23.1 in terms of percent CV. Runs 1 and 6 of Field Test #1 show percent CV of 3.4 and 4.1, respectively, which is in the same range of precision as the four runs of Field Test #2. These results suggest that the overall method precision (sampling and analysis) is probably not a function of the average concentration (e.g., in µg/dscm) over the concentration range from about 30 to 1100 µg/dscm. Such factors as source variability over the sampling period and quality control by the sampling and analysis personnel are proba-

bly more important than the average cadmium concentration level in determining the overall precision.

During Field Test #2, one NBS SRM urban particulate sample was analyzed for cadmium. The results showed a 5% bias (or 95% recovery) which is indicative of the accuracy of the analytical results for Field Test #2. A second in-house audit sample was prepared from a secondary cadmium standard and showed a bias of -16.6% or 83.4% recovery.

The method of addition was used to assess matrix effects for Train B of each sample run. Reanalysis of all four samples after spiking showed results within 10% of the expected values, indicating no adverse matrix effects.

For Field Test #1, the impinger solutions were adjusted to a known volume and analyzed directly. For Field Test #2, the impinger solutions were adjusted to a known volume and one aliquot was boiled to near dryness. The digested sample was then reconstituted to one-half the original volume and analyzed. The impinger solutions were also analyzed directly. Because of a faulty filter in one train of one run, cadmium reached the impingers in the amount of 3% of the total cadmium catch for that train. The analysis of the digested sample of the impingers from this train indicated that it contained about 50 µg of cadmium, while the undigested sample indicated about 60 µg.

A greenish residue was noted in most of the impingers of Field Test #2 after the nitric acid solutions had been transferred. As a check for cadmium which may not have been recovered from the impinger, the four impingers from run #2 were rinsed a final time with acetone which removed the greenish residue from the impinger. The acetone was evaporated to dryness and the residue digested with 5% nitric acid. These solutions were analyzed and found to contain no measurable cadmium.

Conclusions and Recommendations

The quantification of cadmium in stationary source stack gases consists of two portions: sample collection and laboratory analysis. The precision of the sample collection procedures was evaluated by comparing the cadmium concentrations of samples collected using concurrent quad MM5 sampling trains. The accuracy and precision of the analytical procedures, including the sample

Table 5. Comparison of Field Test #2 Cadmium Concentrations, Particulate Concentration, Cadmium to Particulate Concentration, and Isokinetic Rates for Each Run^a

Test No.	A	B	C	D
1				
Cadmium (mg/dscm)	0.8862	0.9278	0.8355	0.8866
Particulate (mg/dscm)	120.98	121.27	120.81	120.88
Cadmium to Particulate (mg/gram)	7.33	7.60	6.91	7.04
Isokinetic Value (%)	93.7	92.5	100.4	97.0
2				
Cadmium (mg/dscm)	1.1371	1.1334	1.0819	1.0814
Particulate (mg/dscm)	189.91	194.87	193.16	204.38
Cadmium to Particulate (mg/gram)	5.99	5.85	5.60	5.29
Isokinetic Value (%)	99.3	96.7	105.5	100.6
3				
Cadmium (mg/dscm)	0.9891	1.0880	0.9936	1.0575
Particulate (mg/dscm)	170.60	175.74	181.88	173.23
Cadmium to Particulate (mg/gram)	5.79	6.19	5.46	6.11
Isokinetic Value (%)	97.8	96.5	104.6	100.0
4				
Cadmium (mg/dscm)	1.0978	1.0411 ^b	1.0309	1.0817
Particulate (mg/dscm)	205.96	208.82	203.08	206.61
Cadmium to Particulate (mg/gram)	5.33	5.11	5.07	5.24
Isokinetic Value (%)	97.4	95.1	105.4	100.3

^aThe particulate emission and cadmium-to-particulate ratio values presented in this table are for information only.

^bThe filter in this run was faulty and it leaked some cadmium to the impingers. However, only 3% of the total cadmium catch for this train was in the impingers, and 97% was in the front half.

preparation steps, were evaluated by performing replicate analyses on known amounts of cadmium to determine the percent recovery and repeatability of the method. Based on this work, the following conclusions can be made:

- A Modified EPA Method 5 sampling train and flame atomic absorption spectrometry were found to be applicable for the measurement of cadmium in stationary stack gas samples.
- The overall accuracy and precision of the analytical steps were 89.2% and 1.7%, respectively. The detection limit of the analytical instrument was 0.03 µg Cd/ml of prepared sample.
- During analysis of the samples from Field Test #2, an NBS SRM urban particulate sample was analyzed and recovery was found to be 95%.
- The corresponding method detection limit for a 30 to 60 dscf (0.85 to 1.7 dscm) stack gas sample is 0.05 and 0.025 µg Cd/dscf (1.7 and 0.88

µg Cd/dscm). The determined levels of cadmium at the source tested ranged from 32 to over 1000 µg/dscm.

The percent coefficient of variation (CV) of between-train cadmium concentrations ranged from 3.4 to 23.1% for the six sampling runs conducted during Field Test #1 and ranged from 2.8 to 4.7% for Field Test #2. The pooled CVs were 13.5% and 3.8% for Field Tests 1 and 2, respectively. The method bias was not affected by total sample volume. Stack gas samples of approximately 30 to 60 dscf were collected, and the cadmium results for the two sample sizes did not differ significantly for either field test. Greater than 99.9% of the cadmium was collected in the front half of the sampling train for each run, except for the previously noted single exception caused by a faulty filter.

Therefore, based on the combined results of the method evaluation, a MM5 sampling train and atomic absorption spectrometry are recommended for measuring cadmium in stack gases. Since greater than 99.9% of the cad-

mium was collected in the front half, in these type tests analysis for cadmium in the impinger solutions (back half) at municipal and sludge incinerators may be omitted when testing conditions are not significantly different from those described in the report. When impinger solution (back half) analysis for cadmium is not performed, water as in Method 5 may be used in the impingers instead of dilute nitric acid. At least one sample from each source should be checked using the method of additions to ascertain that the chemical composition and physical properties of the sample do not cause erroneous analytical results. Finally, if a purchased stock solution of cadmium is used during analyses for preparing working standards, the concentration should be verified against an independently prepared cadmium standard.

R. F. Moseman, D. B. Bath, R. J. McReynolds, D. H. Holder, and A. L. Syke are with Radian Corporation, Research Triangle Park, NC 27709; the EPA author T. E. Ward (also the EPA Project Officer, see below) is with the Environmental Monitoring Systems Laboratory, Research Triangle Park, NC 27711.

The complete report, entitled "Field Evaluation of Methodology for Measurement of Cadmium in Stationary Source Stack Gases," (Order No. PB 87-145 355/AS; Cost: \$18.95, subject to change) will be available only from:

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650

The EPA Project Officer can be contacted at:
Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

USE YOUR COPY
OF
THIS
BOOK

United States
Environmental Protection
Agency

Center for Environmental Research
Information
Cincinnati OH 45268

Official Business
Penalty for Private Use \$300
EPA/600/S4-86/048

0000329 PS
U S ENVIR PROTECTION AGENCY
REGION 5 LIBRARY
230 S DEARBORN STREET
CHICAGO IL 60604