

A JOINT STUDY EMPLOYING EPA METHOD 29 FOR THE CAPTURE
AND ANALYSIS OF MERCURY SPECIES CONDUCTED BY
ADVANCED TECHNOLOGY SYSTEMS, INC. AND THE UNIVERSITY OF NORTH
DAKOTA'S ENERGY AND ENVIRONMENTAL RESEARCH CENTER

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BACKGROUND

The capture and analysis of mercury and its associated compounds from coal-fired boiler flue gas streams is of interest due to the potential regulation of this utility industry sector under the Clean Air Act Amendments of 1990. The desired method should not only capture, exhaustively, the mercury and compounds present but should be capable of identifying and quantifying the various species detected. In emission studies commissioned by the U. S. Department of Energy's Pittsburgh Energy Technology Center (DOE-PETC) in 1991 and conducted by five contractors, EPA Method 29 was the principal method used for the assay of mercury and associated compounds. Advanced Technology Systems, Inc. (ATS), as a secondary DOE contractor on this project, evaluated the results of these studies and determined that inconsistencies existed in the mercury levels found. Some of these discrepancies could be traced back to the sampling methodology applied.

Therefore, DOE-PETC requested ATS to develop new methodologies for determining the chemical species of mercury in coal flue gas, either by the modification of existing ones or by the introduction of novel methods, with the final validation of acceptable methods. ATS's approach to these method development studies has been to first test the existing methods under ideal laboratory conditions, with the philosophy that if the methods cannot perform as designed under ideal laboratory conditions, there is little chance that they would produce desired performance results at plant site environments.

INTRODUCTION

As a prelude to these method development studies, ATS examined EPA Method 29 as a mercury speciating sampling method. The sampling train consists of Greenburg-Smith or modified Greenburg-Smith impingers containing various capture solutions. The first two impingers contain acidified hydrogen peroxide solution (H_2O_2/HNO_3), proposed to capture only oxidized (ionic) mercury (Hg^{2+}), followed by an empty impinger called a "knock-out" impinger. This is followed by two impingers, containing acidified potassium permanganate ($KMnO_4/H_2SO_4$) solution shown by EPA (Method 101A) to capture all forms of mercury, which are utilized here to capture the remaining reduced (elemental) mercury⁰(Hg

In these experiments, known amounts of mercuric chloride were spiked into the first H_2O_2/HNO_3 impinger. The train was then assembled and sampling was performed by drawing laboratory air through a heated probe

into the sampling train. The essential goal was to determine if mercuric chloride spiked into the mercury capture solutions remained there during the course of the sampling.

The results of these EPA Method 29 tests, that were reported previously¹, showed varying degrees of migration of low level mercuric chloride spikes (usually approximately 3 ug per impinger representing 1 ug/Nm³ in the flue gas) from the acidified hydrogen peroxide solution to the acidified potassium permanganate solution. Also, Maskew and coworkers² reported an almost even distribution of mercury between the peroxide and permanganate impingers for sampling performed at a pilot plant in which the flue gas was spiked with HgCl

As a consequence of ATS's findings, DOE-PETC requested a "round robin" testing in which ATS and three other laboratories [Research Triangle Institute (RTI); the University of North Dakota's Energy and Environmental Research Center (EERC); and Radian Corporation] performed bench scale air sampling tests using EPA Method 29 and following ATS's sampling and analytical protocol. The results, presented elsewhere³, showed considerable variation in total amounts of mercury recovered from each train. However, the greatest variability, from lab to lab, was in the loss of mercury from the peroxide impingers with the consequential "carry-over," which represented the corresponding amount found in the permanganate impingers even though it had not been placed there as a "spike." Results from the work at ATS showed the most overall loss along with the largest migration.

It is important to note that another method was evaluated in the "round robin" testing albeit only by ATS and EERC. As a sampling technique, the Ontario-Hydro Method is very similar to EPA Method 29 with a potassium chloride solution replacing the acidified peroxide in the ionic mercury capture impingers. "Round robin" results from both ATS and EERC confirmed results from earlier work by ATS that showed little migration of mercury with the Ontario-Hydro impinger solutions and close to 100% total mercury recovery of the spiked mercury.

To resolve this inter-laboratory discrepancy with respect to the Method 29 results, DOE-PETC requested that ATS and EERC perform identical, side-by-side, laboratory-scale experiments to determine the reasons for the conflicting results. The design of this experimental plan was intended to address the following issues:

- 1) Did the ATS operator overlook some steps in the procedures that resulted in the inordinate migration of mercury from the peroxide impingers?
- 2) Were there equipment differences between ATS and the other laboratories?
- 3) Were there differences in the chemicals, reagents and standards used by ATS compared to those used by the other labs?

EXPERIMENTAL

The following descriptions of equipment and procedures apply to the experimental work performed at the ATS laboratory by ATS and EERC personnel. Sampling equipment, including impinger glassware and sampling probes, were independently specified by each of the two laboratories. All analyses, performed in these studies, were carried out at ATS. Previous comparison of analytical results from the two laboratories had shown that there were no significant differences in analytical performance by the two labs.

Reagents and Equipment

Chemicals used in this work were of analytical reagent grade quality with certified maximum mercury content. Deionized water and trace metal grade acids were used in preparing solutions. Glassware was cleaned following a lengthy procedure, developed by ATS, which included extensive rinsing to insure removal

of mercury from impinger surfaces after sample solutions were recovered from trains. Standard solutions were prepared using class A volumetric glassware. Impinger contents were determined gravimetrically. An automatic pipette with certified precision and accuracy was used to spike mercury standard solutions into the desired impingers.

Air sampling was performed using Nutech 2010 Stack Samplers. Although the ATS and EERC standard sampling train assemblies were identical past the first impinger, they varied considerably between the probe nozzle and the connection to the first impinger. ATS utilized a full-size (6 ft) heated probe, followed by a quartz-fiber filter within a heated filter chamber (250 °F) with the chamber connected to the first impinger by a short (several inches) section of glass. EERC, on the other hand, utilized a short (≈12 inch), unheated narrow (I.D. ≈0.19 inch) piece of glass tubing as a probe. EERC's filter box was heated to the same temperature as that of the ATS system, but it was connected to the first impinger by a long (≈3 feet) and unheated section of flexible tubing with an internal coating of Teflon.

Mercury analyses were carried out utilizing a Bacharach Model MAS-50B CVAAS Mercury Analyzer System. The mercury analyzer has a lower detection limit of 0.010 ug. Detection limits for impinger solutions ranged from 0.025 to 0.15 ug depending upon sample dilution, as prescribed in the sampling train cleanup procedure, and the size of the aliquot taken for analysis as indicated in the analytical procedure.

Procedures

The sampling performance evaluation tests were conducted in accordance with EPA methodology. Filter weights, and the weights and volumes of the impingers and their contents were recorded before and after each sampling run. In all the sampling runs performed, a total volume of 3.06 cubic meters of ambient laboratory air was collected over a period of approximately 3 hours. In addition, temperatures and vacuum pressures were carefully monitored and recorded every 30 minutes.

Upon completion of each sampling run, the train was disassembled, and the filter and impinger solutions were recovered following the appropriate EPA methodology. The impinger solutions were analyzed for mercury as described in EPA SW 846 Method 7470. Briefly, this method involved reducing the mercury collected (in the mercuric form) to elemental mercury, which was then aerated from the solution into an optical cell and measured by atomic absorption spectrophotometry. Calibration of this unit was based on a five point-calibration curve.

Experimental Plan

Blank tests were performed for the purpose of determining the ambient level of mercury in the laboratory. In these experiments, sampling trains were set-up to sample laboratory air, after which they were broken down and the impinger solutions were recovered in the manner prescribed by EPA Method 29. However, impinger solutions were not spiked with mercury; therefore, any mercury found represented mercury present in ambient air.

Mercury spiking experiments were performed by introducing known volumes of a mercuric chloride standard solutions directly into the acidified peroxide impingers using a repeater pipette. The mercury spike concentrations were based on the lowest expected concentrations of mercury in coal flue gas.

Sampling trains were run simultaneously, in pairs, and side by side on the same laboratory bench. Paired trains, identified as "a" and "b," were identical in every way. A chemist from the ATS laboratory operated one train (a) while his counterpart from EERC operated the other (b).

In the first three (3) experiments, the six (6) trains were ATS trains configured in the typical manner and employing ATS glassware and reagents with the exception of trains 3a and 3b in which the EERC's mercury

spiking solution was utilized. The first peroxide impinger of each train was spiked with 2.9 ug of mercury as mercuric chloride in experiments No. 1 and No. 2. This corresponded to 0.95 ug/Nm³ of mercury in 3.06 Nm³ of sampled air collected in a 3 hour period. In Experiment No. 3, 3.2 ug of mercury, equivalent to 1.02 ug/Nm³, was spiked into the first acidified peroxide impinger. In Experiment No. 4, EERC trains, glassware and reagents were utilized in both runs. The first peroxide impinger of each train was spiked with 2.9 ug of mercuric chloride. In Experiment No. 5, the complete ATS system employed in experiments No. 1 and No. 2 was again utilized; however, the first peroxide impinger of each train was spiked with 22.0 ug of mercury, equivalent to 7.19 ug/Nm³ of mercury in flue gas.

RESULTS AND DISCUSSION

The results from blank train runs have been reported elsewhere^{1,2}. The results of these experiments indicated mercury present in the laboratory air to be below the detection limit of approximately 0.1 ug/Nm

The results for the five (5) experiments [ten (10) EPA Method 29 sampling trains] are presented in Table 1. The average percent total mercury recovery for the six (6) spiked trains in experiments numbered 1, 2, and 3 was 90.5% with a standard deviation of 5.0% (90.5 ±5.0%), and the average percent recovery from the peroxide impingers was 81.0 ±4.6%. Differences in results between the two operators (a and b) in total mercury recoveries and in carry-over to both the second peroxide impinger and the permanganate impingers were statistically insignificant. The results from Experiment No. 3, the only two runs utilizing ATS equipment with EERC's mercury spiking reagent, were not statistically distinct from the results from Experiments No. 1 and No. 2 in which a typical ATS system was used. This was evidence that the ATS operator was performing in the same way as the EERC operator using the ATS sampling assembly. Also, the change in the mercury standard used did not alter the outcome of the sampling.

The average percent total recovery for Experiment No. 4 was 105 ±2.7%, and the average percent recovery from the peroxide impingers was 93.8 ±2.2%. Again, there were no differences in the results that could be attributed to the different operators. Total recovery in Experiment No. 4 (105%), which was purely an EERC system, was greater than that of the average of the first three experiments (91%), while recovery from the peroxide solutions in Experiment No. 4 (94%) was greater than the average recovery from the peroxide solutions in Experiments 1 through 3 (81%).

The average percent total recovery for Experiment No. 5 was 93.3 ±1.0%, and the average percent recovery from the peroxide impingers was 88.2 ±3.3%. In this experiment, with mercury solution spikes approximately ten times greater in mass than in all the others, total mercury recovery (93%) was greater than in the experiments utilizing the smaller amounts spiked for the ATS sampling system (90%) but less than those of the low level spikes used with the EERC system(105%). This same pattern was seen in the recoveries from the peroxide impingers. Recovery of mercury from the peroxide solutions (88%) was greater than in the experiments utilizing the smaller spike amounts for the ATS sampling system (81%) but less than those of the low level spikes used with the EERC system(94%). Again, there were no differences in the results that could be attributed to the different operators.

CONCLUSIONS

Several observations can be made from the results presented. Firstly, no significant differences in recoveries of mercury from peroxide impingers, total mercury recoveries and thus mercury migration through the system could be attributed to idiosyncracies in sampling train operation by either ATS or EERC personnel. Secondly, there was no evidence that different chemicals, reagents and standards had any effect on results. Thirdly, total mercury recovery was considerably higher and loss from the first peroxide impinger was less with the EERC sampling system than with ATS 's system. Finally, the use of larger mercuric chloride spikes appeared to slightly improve total mercury recovery and the retention of the spike in the peroxide impinger with the ATS train although it did not match the low level spike recoveries and the retention observed with the EERC assembly.

This study also confirmed that the lower total mercury recoveries and the greater amount of mercury migration from the first peroxide impingers demonstrated by ATS were real and most likely resulted from sampling system differences. This is more likely to be equipment related rather than due to the chemical reagents used. However, the ATS sampling system, compared to EERC 's, is more representative of those used in actual field work.

The speculation is that since ATS uses a probe which is heated and much longer than EERC 's and that the heated filter is connected by a much shorter length of tubing to the first impinger, the contents of that impinger are subject to a higher temperature than the corresponding impinger in EERC 's system. We believe that this additional heat promotes the migration of mercury species in some form or another from the peroxide impingers. This phenomenon is unique to the peroxide solution medium since no significant difference in total mercury recoveries and in the retention of Hg^{2+} spiked into the KCl impinger solutions was shown in the Ontario Hydro test results presented by ATS and EERC from the round robin³ study

The confirmation from this study of the previous findings by ATS, regarding low level mercury migration from the peroxide impingers to the permanganate impingers and the absence of this migration when KCl impingers are involved has spawned further investigations that are currently focused on the identification of more robust and reliable mercury capturing and speciating solutions.

REFERENCES

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3. R. O. Agbede, A. J. Bochan, J. L. Clements, R. P. Khosah and T. J. McManus, "A Comparative Evaluation of EPA Method 29 and the Ontario-Hydro Method for Capture and Analysis of Mercury Species by ATS and Three Other Research Laboratories," in preparation for The Air and Waste Management Association's 89th Annual Meeting and Exhibition in Nashville, TN, June 23-28, 1996.

Table 1. ATS/EERC Joint Study: EPA Method 29 results.

Test No.	Hg Spike in first H ₂ O ₂ Impinger (ug) ²	Train, Glassware and Spiking Reagent	Operator	Hg Recovered in first H ₂ O ₂ Impinger (ug)	Hg Found in second H ₂ O ₂ Impinger (ug)		Hg Found in KMnO ₄ Impingers (ug)		Total Hg Recovery (ug)	% Hg Found in first and second H ₂ O ₂ Impinger	% Hg Found in KMnO ₄ Impingers	% Total Hg Recovery
					#1	#2	#1	#2				
1a	2.9	ATS	ATS	2.26	0.23	0.23	0.06	2.78	85.9	10.0	95.9	
1b	2.9	ATS	EERC	2.13	0.19	0.32	<0.025	2.64	80.0	11.0	91.0	
2a	2.9	ATS	ATS	2.30	<0.15	0.32	<0.025	2.62	79.3	11.0	90.3	
2b	2.9	ATS	EERC	2.29	<0.15	0.32	<0.025	2.61	79.0	11.0	90.0	
3a	3.2	ATS ³	ATS	2.52	0.27	0.23	<0.025	3.02	87.2	7.2	94.4	
3b	3.2	ATS ³	EERC	2.22	0.18	0.21	<0.025	2.61	75.0	6.6	81.6	
Average									81.0		90.5	
Standard Deviation									4.6		5.0	
4a	3.2	EERC	ATS	3.05	<0.15	0.33	0.040	3.42	95.3	11.6	106.9	
4b	3.2	EERC	EERC	2.95	<0.15	0.28	0.068	3.30	92.2	10.9	103.1	
Average									93.8		105.0	
Standard Deviation									2.2		2.7	
5a	22.0	ATS	ATS	18.87	<0.15	1.42	0.077	20.37	85.8	6.8	92.6	
5b	22.0	ATS	EERC	19.90	<0.15	0.69	0.077	20.67	90.5	3.5	94.0	
Average									88.2		93.3	
Standard Deviation									3.3		1.0	

1. Lower detection limits are 0.15 and 0.025 ug per impinger for the H₂O₂ and KMnO₄ impingers, respectively. These are based on the volume fraction of the impinger solution taken for analysis and the instrument detection limit of 0.010 ug.
2. Based on a total volume of air sampled equal to 3.06 Nm³ 2.9 ug spike corresponds to 0.95 ug/Nm³ of mercury in air, and a 22.0 ug spike corresponds to 7.19 ug/Nm³.
3. ATS's train and glassware with EERC mercury spiking reagent.