FINAL REPORT:

DEVELOPMENT OF ANALYTICAL METHODS FOR THE QUANTIFICATION OF THE CHEMICAL FORMS OF MERCURY AND OTHER TARGET POLLUTANTS IN COAL-FIRED BOILER FLUE GAS DOE Contract No. DE-AC22-92PC92583--01 A

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Prepared By:	**Terence J. McManus, Ph.D.**
Approved By:	**Robinson P. Khosah, Ph.D.**
Project No.:	**ATS Project No. 93-002-P**

Advanced Technology Systems, Inc.
639 Alpha Drive
Pittsburgh, PA 15238

Telephone No.:	**(412) 967-1900**
Fax No.:	**(412) 967-1911**

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1.0   BACKGROUND, GOALS AND SUMMARY OF RESULTS

Since approximately 55% of the electrical power produced in the U. S. is generated by coal-based power utility plants, there is serious concern about the massive amounts of coal combustion products emitted into the atmosphere annually. Furthermore, Title III of the 1990 Clean Air Act Amendments (CAAA) requires the measurement and inventory of a possible 189 hazardous air pollutants (HAPs) from any stationary source producing more than 10 tons per year of any one pollutant or more than 25 tons per year of total pollutants. Although power utilities are not presently included on the list of source categories, the CAAA requires the U. S. Environmental Protection Agency to carry out a study of emissions from electricity generation using fossil fuels. Since many of these HAPs are known to be present in coal derived flue gas, coal-fired electric power utilities may be subject to regulation following these studies if Congress considers it necessary.

In a cooperative effort with the U. S. Environmental Protection Agency (EPA), the U. S. Department of Energy (DOE) through its Federal Energy Technology Center (FETC) initiated such a study in 1991. DOE-FETC commissioned five primary contractors to conduct emission studies at eight different coal-fired electric utilities. The eight sites represented a cross section of feed coal type, boiler designs, and particulate and gaseous pollutant control technologies. The major goal of these studies was to determine the sampling and analytical methodologies that could be used efficiently to perform these emission tests while producing representative and reliable emission data. The successful methodology could then be recommended to the EPA for use in compliance testing in the event the regulation of air toxic emissions from coal-fired power plants is implemented. A secondary purpose of the testing was to determine the effectiveness of the control technologies in reducing target hazardous air pollutants.

The CAAA regulations did not identify the sampling and analytical methods to be used in performing the emission tests. As such, one of the challenges facing the primary contractors was to identify methods, previously used for other applications, that could be used for emission testing at coal-fired power plants to gather accurate HAPs emission data.

In carrying out the study, the contractors tested for major and trace metals, mercury, total particulates, volatile organic compounds, semi-volatile organic compounds, aldehydes, halogens and acid gases (HF, HCl, HBr, F_2, Cl_2 and Br_2), ammonia, cyanide, phosphates, sulfates and radionuclides. Mercury testing was performed using EPA Method 29 and usually with simultaneous sampling with either the Hazardous Element Sampling Train (HEST) or the Mercury Speciation Adsorption (MESA) Method. Most of the sampling and analytical methods employed were based on existing EPA-approved methodologies or modifications of methods that had previously been approved for other applications.

Advanced Technology Systems, Inc. (ATS) as a secondary DOE contractor on this project, assessed the sampling and analytical plans and the emission reports of the five primary contractors to determine how successful the contractors were in satisfying their defined objectives. ATS identified difficulties and inconsistencies in a number of sampling and analytical methodologies in these studies. In particular there was uncertainty as to the validity of the sampling and analytical methods used to differentiate the chemical forms of mercury observed in coal flue gas. Considering the differences in the mercury species with regard to human toxicity, the rate of transport through the ecosystem and the design variations in possible emission control schemes, DOE sought an accurate and reliable means to identify and quantify the various mercury compounds emitted by coal-fired utility boilers. ATS, as a contractor for DOE, completed both bench- and pilot-scale studies on various mercury speciation methods. The final validation of the modified Ontario-Hydro Method, its acceptance by DOE and submission of the method for adoption by ASTM was a direct result of these studies carried out in collaboration with the University of North Dakota≥s Energy and Environmental Research Center (UNDEERC).

This report presents the results from studies carried out at ATS in the development of analytical methods to identify and quantify various chemical species, particularly those of mercury, in coal derived flue gas. Laboratory- and pilot-scale studies, not only on mercury species, but also on other inorganics and organics present in coal combustion flue gas are reported.

2.0 MERCURY METHODS: LABORATORY DEVELOPMENT WORK

The development of methodologies to distinguish the chemical forms of mercury in coal combustion product flue gas was the primary focus of ATS=s work contract with DOE-FETC. This following section presents the bench-scale efforts to that end while the pilot-scale work is presented in Section 3.

2.1   MERCURY METHODS-SAMPLING TRAINS

All the methodologies proposed in these studies to distinguish (speciate) the chemical forms of mercury found in coal combustion derived flue gas were based on the EPA Method 5 impinger sampling train, which is used solely to determine particulate matter in flue gas. The quintessential speciation sampling train is that prescribed by the EPA Reference Method 29 shown in Figure 2.1. In this scheme, flue gas is drawn into a heated probe and passed through a heated filter into a series of impingers, through a dry gas meter, and, finally, into and out through the exhaust of the driving pump. EPA Method 29 sampling trains were originally designed for the sampling and analysis of volatile metals in gas streams. In this scheme, an upstream filter removes non-volatile particulate matter while the impinger solutions downstream entrain the volatile, soluble metals and non-metals. This method is an expanded version of EPA Method 101A used to determine total mercury species. A schematic of the EPA Method 101A impinger sampling train is shown in Figure 2.2. Like EPA Method 101A, Method 29 utilizes impingers containing acidified permanganate solutions, which in the former are used to convert the less soluble elemental mercury to a soluble ionic form by reaction with this strong oxidizing agent. In Method 29 trains, water-soluble volatile metals are captured in the hydrogen peroxide solutions while the less soluble metals (e.g. elemental mercury, etc.) are likely to be converted to a soluble form by the strong oxidizing effect of the acidified potassium permanganate solution. Originally, the purpose of the acidified hydrogen peroxide solutions was to chemically react with the sulfur dioxide present in the flue gas preventing its reaction with and subsequent decomposition of the acidified permanganate solution. However, based on chemical knowledge and work performed here, it was proposed that this scheme might accurately differentiate oxidized forms of mercury from the elemental forms. In EPA Method 29 trains, the first two
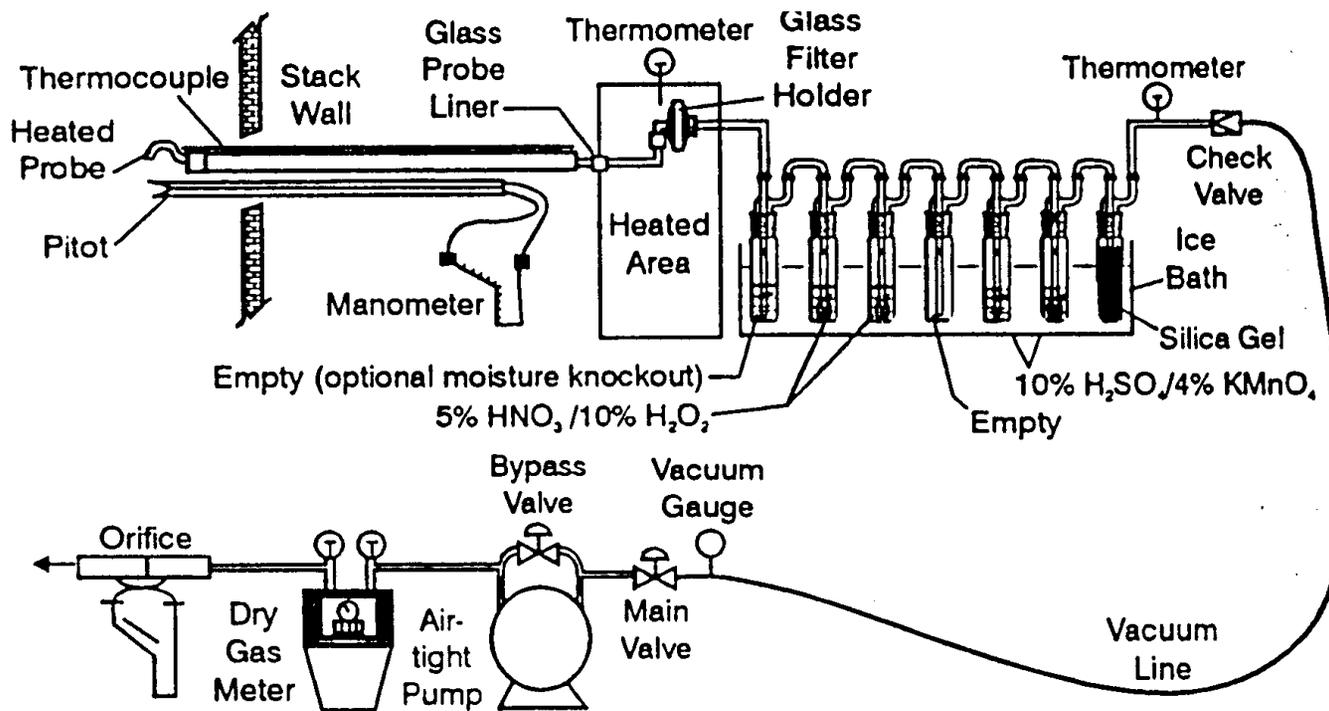
FIGURE 2.1: EPA REFERENCE METHOD 29
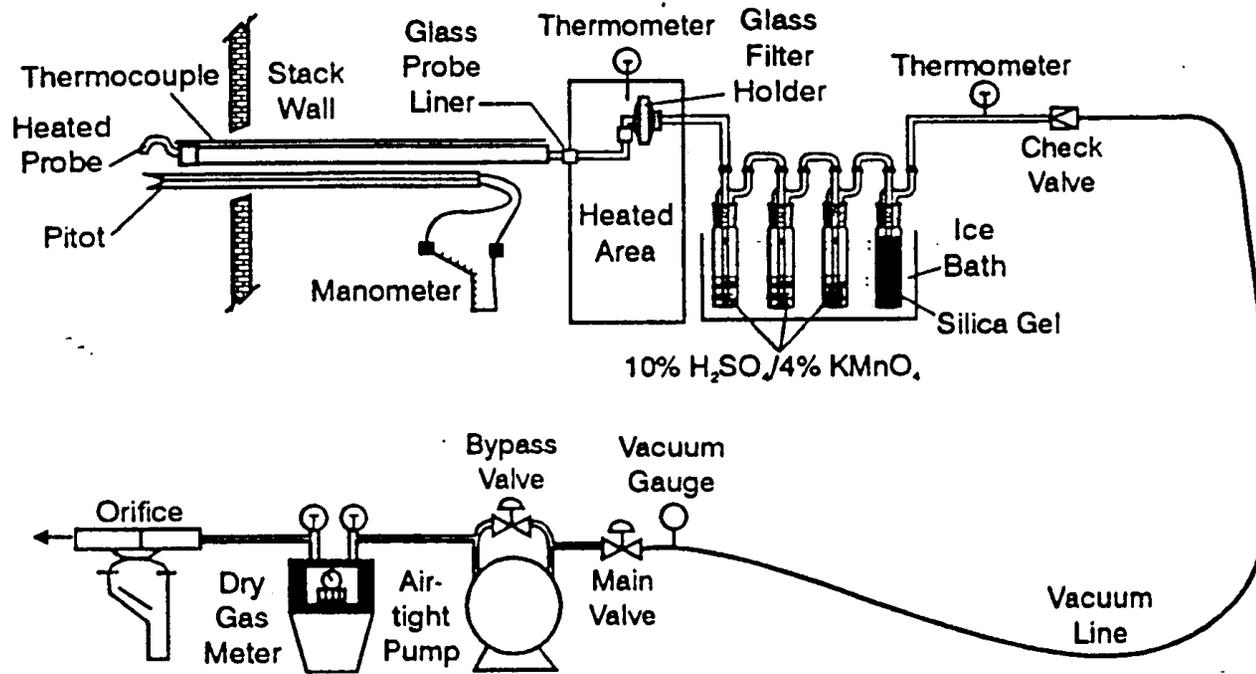
FIGURE 2.2:   EPA METHOD 101A

impingers contain acidified hydrogen peroxide (H_2O_2) followed by an empty impinger called a "knock-out" impinger and by two impingers containing acidified potassium permanganate ($KMnO_4$) solution. The proposed idea was that oxidized forms of mercury (e.g. mercuric chloride) would be readily captured in the water-based hydrogen peroxide solutions since they are soluble due to their ionic nature and that the elemental, less soluble form would pass through these solutions unchanged to be captured downstream by the permanganate solutions. Thus, upon solution analysis, mercury found in the hydrogen peroxide solutions is assumed to be of the oxidized form while that found in the permanganate impinger solutions is considered to be the remaining elemental form.

Another mercury speciation train tested and eventually modified by ATS was that of the Ontario-Hydro Method. The mercury speciation scheme utilized in the Ontario-Hydro sampling train, shown in Figure 2.3, is very similar to that of the EPA Method 29 train. Here, the first three impingers contain a potassium chloride (KCl) solution, which is intended to capture oxidized mercury. These are followed by a knock-out impinger and three impingers containing the same $KMnO_4$ solution utilized in the EPA Method 29 trains. Henceforth, acidified hydrogen peroxide impinger solutions of EPA Method 29 trains and KCl impinger solutions of Ontario-Hydro trains will be referred to as Aoxidized mercury capture solutions,@ and acidified potassium permanganate solutions will be referred to as Aelemental (or reduced) mercury capture solutions.@

The evaluation of currently used sampling and analytical methods for determining the chemical species of mercury in coal flue gas, the development of new methodologies either by the modification of existing ones or by the introduction of novel methods, and the final validation of acceptable methods were the tasks that DOE-FETC requested of ATS. ATS=s role in method development studies began with the testing of the hypothesis that these impinger solutions could effectively capture and retain these specific mercury species, and lead eventually to the modification and validation of a sampling/analytical scheme that performed as expected - the Modified Ontario-Hydro Method. ATS's approach to the laboratory-scale method development studies was to first test the existing methods under ideal laboratory conditions, with the philosophy that if the methods could not perform as designed under ideal laboratory conditions, there was little chance that they would produce desired performance results at plant site environments.
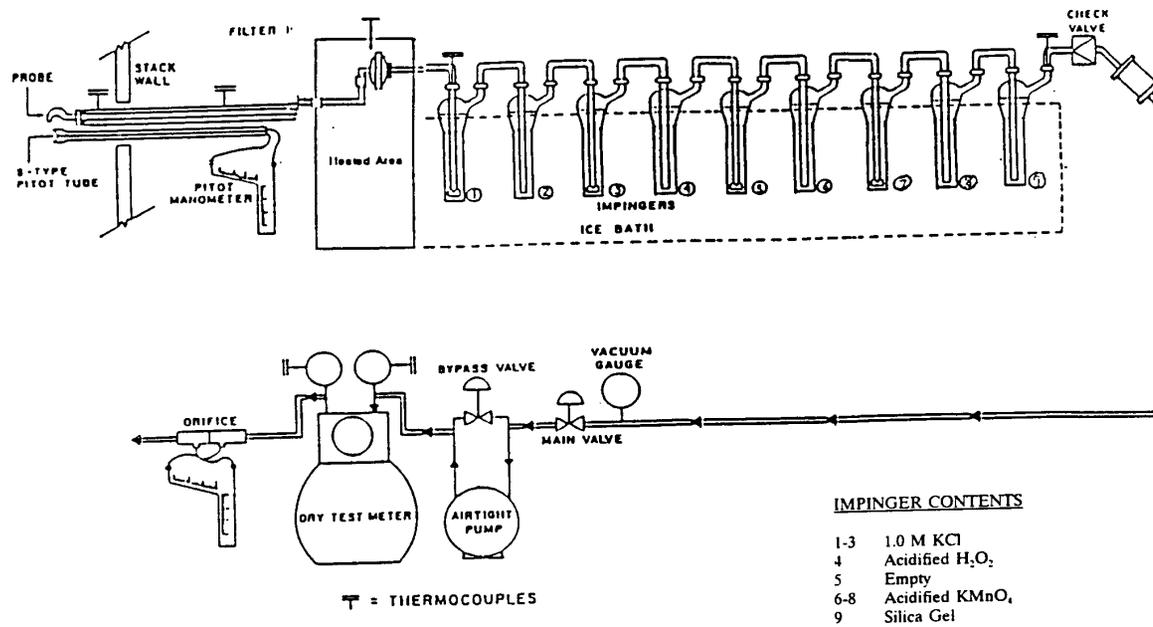
FIGURE 2.3:   ONTARIO-HYDRO METHOD

IMPINGER CONTENTS

1-3	1.0 M KCl
4	Acidified H_2O_2
5	Empty
6-8	Acidified $KMnO_4$
9	Silica Gel

T = THERMOCOUPLES

2.2 GENERAL EXPERIMENTAL: EQUIPMENT, REAGENTS AND PROCEDURES

The following general descriptions of equipment and procedures relate to the experimental work performed at ATS and apply throughout this report. Whenever appropriate, EPA sampling and analytical protocol was followed exactly as stated. Otherwise, procedures established for the non-EPA methodologies were used as prescribed unless otherwise indicated. To limit interlab variability, our sampling and analytical procedures were given to the other three laboratories participating in the ARound Robin@ Study described in Section 2.5. It can be assumed that sampling procedures varied little between laboratories; however, since each laboratory used its own analytical instrumentation, some variation in analytical procedures was to be expected.

2.2.1 Reagents and Equipment

Every effort was made to avoid contaminating the sampling and analytical systems with mercury. 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. Mercury analyses were performed 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 individual and combined impinger solutions ranged from 0.01 to 0.30 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.

2.2.2 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. A full-size (6 ft) heated probe, followed by a quartz-fiber filter within a heated filter chamber (250^0 F), was used in all experiments. 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 unless otherwise specified. In addition, temperatures and vacuum pressures were 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 or other 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 the spectrometer was based on a five point-calibration curve. Results from mercury analyses were given in concentration units of micrograms per normal cubic meter (g/Nm^3) with normal referring to 20 ^{o}C and 760 mm Hg.

A general discussion on experimental equipment and procedures has been presented in this section. In the following section, discussions of the laboratory-scale studies include experimental details specific to those studies and the associated findings.

2.3   PRELIMINARY IMPINGER SPIKING STUDIES: EPA METHOD 101A

The capture *and* retention of mercury species are both necessary conditions for the proper function of any potential impinger-based mercury speciation system. Thus, the much simpler but equally important retention studies were initiated first. These involved the addition of known amounts of mercury (mercuric chloride) to impinger solutions of trains operating under typical sampling conditions. Loss of mercury from impinger solutions during air sampling, performed as an initial simulation of flue gas sampling, in laboratory tests would indicate failure of the Aretention@ criterion and disqualify the sampling scheme from any further testing.

Blank tests were performed, for each sampling method, for the purpose of determining the ambient level of mercury in the laboratory. Mercury spiking experiments were performed by introducing

known volumes of a mercuric chloride standard solution directly into the desired impingers using a repeater pipette. The mercury spike concentrations were based on expected low to mid-range concentrations of mercury in coal-fired boiler flue gas and the volumes of the recovery solutions.

The EPA Method 101A tests were performed by spiking 5.0 ug of mercuric chloride each into the second and third impingers of a standard EPA Method 101A train. This corresponded to an equivalent concentration level of 1.63 ug/Nm^3 of mercury in 3.06 Nm^3 of air collected in a 3 hour period in each impinger. (The expected range of mecury in coal-fired boiler flue gas is approximately 2 - 25 g/Nm^3.) After spiking was completed, the sampling train was assembled and leak-checked. Sampling was performed by drawing laboratory air through the sampling train. After the completion of the sampling, the train was leak-checked, disassembled and the impinger solutions were recovered following standard EPA Method 101A procedures.

The results for the five (5) EPA Method 101A experiments are shown in Table 2.1. Mercury found in train blanks was low (<100 ng or <0.033 ug/Nm^3) compared to the amount of mercury in the spiked runs; therefore, mercury contamination was considered to be negligible. The average mercuric chloride recovery for the 5 spiked trains was 10.4 ug or 3.4 ug/Nm^3 as mercury, giving an average percent recovery of 104% with a standard deviation of 2% (104"2%). This recovery is excellent considering the small mass and low concentration of mercury present in the solutions.

This preliminary work demonstrates the following two important points:

C   The ambient mercury concentration level in the laboratory environment (from the air, reagents, glassware, bench tops, etc.) was negligible in terms of flue gas sampling techniques.

TABLE 2.1: EPA METHOD 101A RESULTS

Test No.	Hg Spike in second and third KMnO₄ Impinger (ug)[1]	Total Hg Spike (ug)	Hg Recovered in KMnO₄ Impingers (ug)	Total Hg Recovered (ug)	% Hg Recovery in KMnO₄ Impingers	% Total Hg Recovery
Blank	--	--	<0.10	<0.10	--	--
1	5.0	10.0	10.3	10.3	103	103
2	5.0	10.0	10.8	10.8	108	108
3	5.0	10.0	10.3	10.3	103	103
4	5.0	10.0	10.3	10.3	103	103
5	5.0	10.0	10.3	10.3	103	103
Average					104	104
Standard Deviation					2.2	2.2

1.   Based on a total volume of air sampled equal to 3.06 Nm^3, a 10.0 ug spike corresponds to 3.3 ug/Nm^3 of mercury in air.

C Small amounts of mercury spiked into KMnO$_4$ impinger solutions remained there throughout the laboratory air sampling procedures. This corroborated EPA=s validation of the use of acidified permanganate impinger solutions in the determination of total mercury.

2.4 IMPINGER SPIKING STUDIES: EPA METHOD 29 AND THE ONTARIO-HYDRO METHOD

EPA Method 29 and the Ontario-Hydro Method tests were performed in a manner similar to that of the EPA Method 101A tests. Since the EPA Method 101A tests demonstrated the efficacy of acidified permanganate solutions in retaining mercury spikes and since permanganate solutions are used as elemental mercury capture solutions, the next step was to test the respective oxidized mercury capture solutions of the two methods to determine their ability to retain captured mercury.

For EPA Method 29, 3.0 ug of mercury as mercuric chloride, equivalent to 0.98 ug/Nm^3 of mercury in 3.06 Nm^3 of sampled air collected in a 3 hour period, was spiked into the first acidified peroxide impinger. Also, during selected tests, 4.0 ug of mercury as mercuric chloride, equivalent to 1.31 ug/Nm^3, was spiked into the first acidified permanganate impinger. After the spiking operation was finished, the sampling train was assembled, leak-checked and air sampling was performed as previously described. When sampling was completed, the train was leak-checked and the impinger solutions were recovered following standard EPA Method 29 procedures.

Table 2.2 presents results from thirteen (13) Method 29 experiments performed by ATS in which only the first H$_2$O$_2$ impinger solution was spiked with 3.0 ug of mercury. Overall mercury recovery was 93"17%. Recovery from spiked H$_2$O$_2$ solutions was 59"18% with 34"10% of the mercury spiked into the peroxide being found in the KMnO$_4$ solutions. Noted here is the remarkably high "carry-over" of mercury from the H$_2$O$_2$ impinger solutions into the KMnO$_4$ solutions.

Table 2.3 presents results from eighteen (18) Method 29 experiments in which the first H$_2$O$_2$ and the first KMnO$_4$ solutions were spiked with 3 ug and 4 ug of mercury, respectively. (Permanganate impinger solutions were still being spiked at this time in order to absolutely assure that these

TABLE 2.2: EPA METHOD 29 RESULTS.[1]

Test No.	Hg Spike in First H_2O_2 Impinger (ug)[2]	Hg Spike in first $KMnO_4$ Impinger (ug)	Total Hg Spike (ug)	Hg Recovered in H_2O_2 impingers (ug)	Hg Found in Knockout Impinger (ug)	Hg Found in $KMnO_4$ Impingers (ug)	Total Hg Found (ug)	% Hg Recovery in H_2O_2 Impingers	% Hg Carry-over into $KMnO_4$ Impingers	% Total Hg Recovery
				H_2O_2 Only Spiking Tests						
1	3.0	--	3.0	1.99	<0.01	0.98	2.97	66.3	32.7	99.0
2	3.0	--	3.0	2.26	<0.01	1.09	3.35	75.3	36.3	111.7
3	3.0	--	3.0	1.96	<0.01	0.82	2.78	65.3	27.3	92.7
4	3.0	--	3.0	2.04	<0.01	1.01	3.05	68.0	33.7	101.7
5	3.0	--	3.0	1.59	<0.01	1.01	2.60	53.0	33.7	86.7
6	3.0	--	3.0	1.02	<0.01	1.17	2.19	34.0	39.0	73.0
7	3.0	--	3.0	0.72	<0.01	1.33	2.05	24.0	44.3	68.3
8	3.0	--	3.0	1.50	<0.01	1.20	2.70	50.0	40.0	90.0
9	3.0	--	3.0	1.30	<0.01	1.47	2.77	43.3	49.0	92.3
10	3.0	--	3.0	1.70	<0.01	0.50	2.20	56.7	16.7	73.3
11	3.0	--	3.0	1.95	<0.01	0.51	2.46	65.0	17.0	82.0
12	3.0	--	3.0	2.71	<0.01	0.81	3.52	90.3	27.0	117.3
13	3.0	--	3.0	2.25	<0.01	1.30	3.55	75.0	43.3	118.3
Average								58.9	33.8	92.8
Standard Deviation								18.1	9.9	16.5

1. Lower detection limits are 0.30, 0.01 and 0.05 ug per impinger for the peroxide, knock-out and permanganate 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 Nm^3, a 3.0 ug spike corresponds to 0.98 ug/Nm^3 of mercury in air.

TABLE 2.3: EPA METHOD 29 RESULTS[1]

Test No.	Hg Spike in First H_2O_2 Impinger (ug)[2]	Hg Spike in first $KMnO_4$ Impinger (ug)	Total Hg Spike (ug)	Hg Found in H_2O_2 Impingers (ug)	Hg Found in Knockout Impinger (ug)	Hg Found in $KMnO_4$ Impingers (ug)	Total Hg Found (ug)	% Hg Found in H_2O_2 Impingers	% Hg Found in $KMnO_4$ Impingers	% Total Hg Recovery
				H_2O_2 and $KMnO_4$ Spiking Tests						
1	3.0	4.0	7.0	1.51	<0.01	4.23	5.74	50.3	105.8	82.0
2	3.0	4.0	7.0	1.76	<0.01	5.56	7.32	58.7	139.0	104.6
3	3.0	4.0	7.0	1.28	<0.01	5.10	6.38	42.7	127.5	91.1
4	3.0	4.0	7.0	1.59	<0.01	4.89	6.48	53.0	122.3	92.6
5	3.0	4.0	7.0	1.59	<0.01	4.65	6.24	53.0	116.3	89.1
6	3.0	4.0	7.0	0.99	<0.01	4.96	5.95	33.0	124.0	85.0
7	3.0	4.0	7.0	0.51	<0.01	5.05	5,56	17.0	126.3	79.4
8	3.0	4.0	7.0	0.80	<0.01	5.25	6.05	26.7	131.3	86.4
9	3.0	4.0	7.0	1.38	<0.01	5.22	6.60	46.0	130.5	94.3
10	3.0	4.0	7.0	0.41	<0.01	5.22	5.63	13.7	130.5	80.4

1.   Lower detection limits are 0.30, 0.01 and 0.05 ug per impinger for the peroxide, knock-out and permanganate 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 Nm^3, a 3.0 ug spike corresponds to 0.98 ug/Nm^3, and a 4.0 ug spike corresponds to 1.31 ug/Nm^3 of mercury in air.

TABLE 2.3: EPA METHOD 29 RESULTS.[1] (CONTINUED)

Test No.	Hg Spike in First H_2O_2 Impinger (ug)[2]	Hg Spike in first $KMnO_4$ Impinger (ug)	Total Hg Spike (ug)	Hg Found in H_2O_2 Impingers (ug)	Hg Found in Knockout Impinger (ug)	Hg Found in $KMnO_4$ Impingers (ug)	Total Hg Found (ug)	% Hg Found in H_2O_2 Impingers	% Hg Found in $KMnO_4$ Impingers	% Total Hg Recovery
11	3.0	4.0	7.0	2.57	<0.01	4.50	7.07	85.7	112.5	101.0
12	3.0	4.0	7.0	2.19	<0.01	4.60	6.79	73.0	115.0	97.0
13	3.0	4.0	7.0	1.82	<0.01	5.63	7.45	60.7	140.8	106.4
14	3.0	4.0	7.0	2.06	<0.01	5.29	7.35	68.7	132.3	105.0
15	3.0	4.0	7.0	1.96	<0.01	4.56	6.52	65.3	114.0	93.1
16	3.0	4.0	7.0	1.32	<0.01	5.50	6.82	44.0	137.5	97.4
17	3.0	4.0	7.0	1.37	<0.01	5.35	6.72	45.7	133.8	96.0
18	3.0	4.0	7.0	1.58	<0.01	4.93	6.51	52.7	123.3	93.0
Average								49.4	125.7	93.0
Standard Deviation								18.7	9.9	8.3

1. Lower detection limits are 0.30, 0.01 and 0.05 ug per impinger for the peroxide, knock-out and permanganate 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 Nm^3, a 3.0 ug spike corresponds to 0.98 ug/Nm^3, and a 4.0 ug spike corresponds to 1.31 ug/Nm^3 of mercury in air.

solutions, in a somewhat different train than that of EPA Method 101A, would still be effective in retaining mercury.) Since overall mercury recovery was 93"8%, which was very similar to the experiments in which only the peroxide impingers were spiked, it is apparent that no loss is occuring from the permanganate impingers. Recovery from the H_2O_2 solutions was 49"19%, and 126"10% was found in the $KMnO_4$ solutions.

In these experiments the total mercury recoveries were reasonable and comparable to the control spike recoveries, but slightly less that those observed with the EPA 101A Method. However, the corresponding standard deviations were considerably large. Also, transport between the H_2O_2 and $KMnO_4$ solutions was evident with considerable variability exhibited. Considering the number of blanks analyzed and that mercury was always below the detection limit, it can be concluded that any mercury found in the permanganate impingers and not placed there as a "spike," must have originated from the first peroxide impinger.

2.5 COMPARATIVE MULTI-LABORATORY SPIKING STUDY: EPA METHOD 29 AND THE ONTARIO-HYDRO METHOD

The results of EPA Method 29 spiking tests showed varying degrees of migration of low level mercuric chloride spikes (1 g/Nm^3) from the oxidized mercury capture solution (acidified hydrogen peroxide) to the reduced mercury capture solution (acidified potassium permanganate). As a consequence of ATS's findings, DOE-FETC requested a "round robin" testing in which ATS and 3 other laboratories (Research Triangle Institute, RTI; the University of North Dakota's Energy and Environmental Research Center, UNDEERC; and Radian Corporation) performed bench-scale mercury spiking air sampling tests using EPA Method 29 and following ATS's sampling and analytical protocol. Also included in this study were similar tests performed utilizing the Ontario-Hydro Method albeit only ATS and UNDEERC participated in this part of the study.

The Ontario-Hydro Method tests were performed by adding 5.0 ug of mercury as mercuric chloride, equivalent to 1.63 ug/Nm^3 of mercury in 3.06 Nm^3 of air collected in a 3 hour period, to the first of the three impingers containing the potassium chloride (KCl) solution. In addition, for selected tests, 5.0 ug of mercury as mercury chloride was added to the first of the three $KMnO_4$ impingers. After spiking was completed, the sampling train was assembled, leak-checked and air sampling was

performed. After the completion of sampling, the train was leak-checked and the impinger solutions were recovered using a method described by Southern Research Institute[1]. The recovery procedure for the KCl impinger solutions was very similar to that of the recovery procedure for the H_2O_2 impinger solutions for EPA Method 29. However, Ontario-Hydro $KMnO_4$ impinger solutions were treated with hydroxylamine hydrochloride and dichromate solutions before they were removed from the impingers. This was carried out to dissolve the manganese dioxide precipitate and consumed the remaining $KMnO_4$, which if present would cause analytical difficulties in the EPA Method 29 procedure.

Table 2.4 shows the results for six (6) Ontario-Hydro Method "round robin" experiments performed by ATS and seven (7) performed by UNDEERC (EERC in Table). (The other two laboratories did not participate in this portion of the study.) The QA/QC information is taken from the ATS study. Mercury was found to be below the detection limit in the blank tests. Mercury recovery was approximately 97% for the control spike samples performed by ATS indicating that very good analytical procedures had been followed. The values found in the column indicated as "Hg Recovery in $KMnO_4$ Sol. %" were calculated by subtracting the amount of mercury spiked into the first permanganate impinger from the sum of the amounts in all of the permanganate impingers determined by the chemical analysis. This difference is assumed to be carry-over from the first KCl impinger.

The average total mercury recovery was 99±3% and 102±5% for the ATS and UNDEERC results, respectively. On average, for each respective laboratory, 99±2% and 101±6% of the mercury spiked into the KCl solution remained there. Mercury carry-over from the spiked KCl impinger to the $KMnO_4$ impinger solutions was 1.0±2.2% and 2.2±1.8%, respectively. The difference between any pair of these values is less than the expected experimental error.

These data, obtained with the Ontario-Hydro Method for the two laboratories, did not show significant mercury carry-over from the KCl impingers to the $KMnO_4$ solutions, and overall

TABLE 2.4: MERCURY SPIKE RECOVERY FROM ONTARIO-HYDRO TRAIN - ROUND ROBIN RESULTS

Test No.	Hg Spike in First KCl Impinger (ug)	Hg Spike in First KMnO$_4$ Impinger (ug)	Total Hg Spiked (ug)	Hg in #1 KCl Impinger (ug)	Hg in #2 KCl Impinger (ug)	Hg in #3 KCl Impinger (ug)	Hg in Dry Impinger (ug)	Hg in #1 KMnO$_4$ Impinger (ug)	Hg in #2 KMnO$_4$ Impinger (ug)	Hg in #3 KMnO$_4$ Impinger (ug)	Total Hg (ug)	Hg Recovery in #1 KCl Impinger (%)	Hg Recovery in KMnO$_4$ Sol. (%)	Total Hg Recovery (%)
EERC														
1	3.7	0	3.7	3.74	<0.03	<0.03	<0.03	0.11	<0.03	<0.03	3.85	102.5	3.1	105.6
2	3.7	0	3.7	3.92	<0.03	<0.03	<0.03	0.11	<0.03	<0.03	4.03	107.4	3.0	110.4
3	4.4	0	4.4	4.05	<0.03	<0.03	<0.03	0.12	<0.03	<0.03	4.17	92.0	2.7	94.8
4	4.4	0	4.4	4.20	<0.03	<0.03	<0.03	0.14	<0.03	<0.03	4.34	95.5	3.2	98.6
5	3.7	3.7	7.4	3.80	<0.03	<0.03	<0.03	3.64	<0.03	1.47**	7.44	104.1	-0.3	100.5
6	3.7	3.7	7.4	3.9	<0.03	<0.03	<0.03	3.80	<0.03	<0.03	7.70	106.8	4.1	104.1
7	4.4	4.4	8.8	4.3	<0.03	<0.03	<0.03	4.38	<0.03	<0.03	8.68	97.7	-0.6	98.6
										Average		100.9	2.2	101.8
										Std. Dev.		5.9	1.8	5.3
ATS														
1	5	0	5	4.85	<0.03	<0.03	<0.01	<0.03	<0.03	<0.03	4.85	96.9	0.0	96.9
2	5	0	5	4.83	<0.03	<0.03	<0.01	<0.03	<0.03	<0.03	4.83	96.5	0.0	96.5
3	7.5	0	7.5	7.40	<0.03	<0.03	<0.01	<0.03	<0.03	<0.03	7.40	98.7	0.0	98.7
4	5	5	10	5.14	<0.03	<0.03	<0.01	5.25	<0.03	<0.03	10.40	102.9	5.1	104.0
5	5	5	10	4.97	<0.03	<0.03	<0.01	5.11	<0.03	<0.03	10.08	99.4	2.1	100.8
6	5	5	10	4.97	<0.03	<0.03	<0.01	4.96	<0.03	<0.03	9.93	99.4	-0.9	99.3
										Average		99.0	1.0	99.3
										Std. Dev.		2.3	2.2	2.8

** EERC states that this value results from contamination, and it is not included in subsequent calculations.

recovery is comparable to that of Method 101A in the ATS study. Notable is the observation that when the $KMnO_4$ solutions were not spiked with mercuric chloride, analyses of these solutions for mercury gave results that were below the detection limit for the analytical method. Under these conditions, oxidized mercury is recovered where it was spiked. The second and third KCl impinger solutions and the second and third $KMnO_4$ impinger solutions were found to have mercury levels below the detection limit of the instrument. This suggests that for this method, variations between measured and originally spiked amounts are due to experimental error and not because of transport between impingers since no mercury was found in the intervening impingers.

Given in Tables 2.5(a) and 2.5(b) are the results from the EPA Method 29 experiments performed in the round robin study. The values found in the column indicated as "Hg Recovery in $KMnO_4$ Sol. %" were calculated by subtracting the amount of mercury spiked into the first permanganate impinger from the sum of the amounts in all of the permanganate impingers determined by the chemical analysis. This difference is assumed to be carry-over from the first peroxide impinger. It should be noted that in all of the sampling train experiments performed by ATS, analyses of knock-out impinger catches showed them to contain less than 0.010 ug of mercury in the several milliliters of condensate typically recovered.

Total mercury recoveries reported by all the laboratories ranged from 87% to 106%. However, reported carry-over from the peroxide impingers varied greatly between laboratories. For UNDEERC and RTI, the values were low, being 1.1% and 0.0%, respectively. Radian reported a mid-range value of 8.9%, and ATS had the highest value of 42.0%. It should be noted, however, that RTI initially reported carry-over but later explained the finding as an analytical artifact with the permanganate solution analyses. An examination of the values presented by RTI in the table suggests that they used these "rejected" values in calculating total mercury recoveries.

TABLE 2.5(A): MERCURY SPIKE RECOVERY FROM EPA METHOD 29 TRAIN — ROUND-ROBIN RESULTS

Test No.	Hg Spike in First H_2O_2 Impinger (ug)	Hg Spike in First $KMnO_4$ Impinger (ug)	Total Hg Spiked (ug)	Hg in #1 H_2O_2 Impinger (ug)	Hg in #2 H_2O_2 Impinger (ug)	Hg in Dry Impinger (ug)	Hg in #1 $KMnO_4$ Impinger (ug)	Hg in #2 $KMnO_4$ Impinger (ug)	Total Hg (ug)	Hg Recovery in #1 H_2O_2 Impinger (%)	Hg Recovery in $KMnO_4$ Sol. (%)	Total Hg Recovery (%)
Radian												
1	3	4	7	2.60	0.10	0.02	4.27	0.09	7.08	86.7	12.0	101.1
2	3	4	7	3.72	0.10	0.01	4.27	0.09	8.19	124.0	12.0	117.0
3	3	4	7	2.89	0.11	0.04	4.21	0.04	7.29	96.3	8.3	104.1
4	3	0	3	2.70	0.03	0.01	0.19	<0.01	2.93	90.0	6.3	97.7
5	3	0	3	3.08	0.06	0.01	0.17	<0.01	3.32	102.7	5.7	110.7
									Averag	99.9	8.9	106.1
									Std	14.8	3.0	7.7
EERC												
1	4	0	4	3.50	<0.03	<0.03	0.10	<0.03	3.60	87.5	2.5	90.0
2	4	0	4	3.45	<0.03	<0.03	0.02	<0.03	3.47	86.3	0.4	86.7
3	3	0	3	2.60	<0.03	<0.03	0.04	<0.03	2.64	88.1	1.4	89.5
4	3	3.7	6.7	2.13	<0.03	<0.03	3.73	<0.03	5.86	72.2	1.0	88.1
5	3	3.7	6.7	2.07	<0.03	<0.03	3.80	<0.03	5.87	70.2	3.4	88.3
6	3	3.7	6.7	2.53	<0.03	<0.03	3.63	<0.03	6.16	85.8	-2.4	92.6
									Averag	81.7	1.1	89.2
									Std	8.2	2.0	2.0

TABLE 2.5(B): MERCURY SPIKE RECOVERY FROM EPA METHOD 29 TRAIN — ROUND-ROBIN RESULTS

Test No.	Hg Spike in First H_2O_2 Impinger (ug)	Hg Spike in First $KMnO_4$ Impinger (ug)	Total Hg Spiked (ug)	Hg in #1 H_2O_2 Impinger (ug)	Hg in #2 H_2O_2 Impinger (ug)	Hg in Dry Impinger (ug)	Hg in #1 $KMnO_4$ Impinger (ug)	Hg in #2 $KMnO_4$ Impinger (ug)	Total Hg (ug)	Hg Recovery in #1 H_2O_2 Impinger (%)	Hg Recovery in $KMnO_4$ Sol. (%)	Total Hg Recovery (%)
ATS												
1	3	0	3	0.92	0.10	<0.01	0.82	0.36	2.20	30.5	39.2	73.3
2	3	0	3	0.66	0.06	<0.01	0.91	0.42	2.05	21.9	44.4	68.3
3	3	0	3	1.44	0.06	<0.01	0.79	0.42	2.71	47.9	40.2	90.3
4	3	4	7	1.27	0.06	<0.01	5.01	0.49	6.83	42.2	49.9	97.6
5	3	4	7	1.31	0.06	<0.01	4.89	0.46	6.72	43.7	45.2	96.0
6	3	4	7	1.52	0.06	<0.01	4.85	0.10	6.53	50.6	33.0	93.3
									Averag	39.5	42.0	86.5
									Std D	11.0	5.8	12.5
RTI												
1	3	0	3	2.64	<0.01	<0.01	0.85	<0.01	3.49	88.0	▉▉▉	116.3
2	3	0	3	2.85	<0.01	<0.01	0.31	0.47	3.63	95.0	▉▉▉	121.0
3	3	0	3	2.63	<0.01	<0.01	<0.01	<0.01	2.63	87.7	0.0	87.7
4	3	0	3	2.69	<0.01	<0.01	<0.01	<0.01	2.69	89.7	0.0	89.7
5	10	0	10	10.13	0.04	<0.01	<0.01	<0.01	10.17	101.3	0.0	101.7
6	10	0	10	9.97	<0.01	0.13	<0.01	<0.01	10.10	99.7	0.0	101.0
									Averag	93.6	0.0	102.9
									Std D	6.0	0.0	13.6

Table 2.6A shows results from experiments in which the first H_2O_2 impinger solution was replaced by a KCl solution in an EPA Method 29 train. This impinger was subsequently spiked with 3.0 ug of mercury. Average total mercury recovery was 116±3%. Average recovery in the KCl impinger was 106±5% and mercury found in both $KMnO_4$ impingers was approximately 9±2% of the total spike. Mercury control spike recoveries were approximately 106%.

Table 2.6B is a tabulation of results from experiments in which the second H_2O_2 impinger solution was replaced by a KCl solution in an EPA Method 29 train. The first impinger was subsequently spiked with 3.0 ug of mercury, and the average total mercury recovery was 92±9%. Average recovery in the H_2O_2 impinger was 70±21%, and mercury found in both $KMnO_4$ impingers was approximately 20±5% of the total spike. Mercury control spike recoveries were approximately 98%.

The results above indicate that the anomalies observed with the EPA Method 29 mercury recoveries can probably be attributed to the acidified peroxide impinger solutions. Mercury recoveries are variable and unpredictable when peroxide is involved.

The results from the last two experimental systems demonstrate clearly the effect of H_2O_2 compared to KCl in a proposed mercury speciation train. In the case where the KCl solution was placed upstream of the H_2O_2 solution, total mercury recovery was high with most of the spiked oxidized mercury remaining in the KCl solution during air sampling. In the case where the H_2O_2 solution was placed ahead of the KCl solution, total mercury recovery was lower with less of the oxidized mercury that was spiked into the H_2O_2 solution remaining there. However, it is worth noting that in either case the second impinger, regardless of which solution it contains, did not capture the majority of the mercury that exited the first impinger. Most of this mercury was captured by the $KMnO_4$ impingers. An explanation consistent with all of the above observations would be that part of the Hg^{2+} present was being reduced to Hg^0, which is neither captured nor held by either the KCl or H_2O_2 solutions while either form of mercury is efficiently captured and held by the $KMnO_4$.

TABLE 2.6A: MODIFIED EPA METHOD 29 RESULTS[1]

Test No.	Hg Spike in KCl Impinger (ug)[2]	Hg Spike in H$_2$O$_2$ Impinger (ug)	Hg Spike in first KMnO$_4$ Impinger (ug)	Hg Recovered in KCl Impinger (ug)	Hg Found in H$_2$O$_2$ Impinger (ug)	Hg Found in KMnO$_4$ Impingers (ug) #1	#2	Total Hg Recovered (ug)	% Hg Recovery in KCl Impinger	% Hg Found in H$_2$O$_2$ Impinger	% Hg Found in KMnO$_4$ Impingers #1	#2	% Total Hg Recovery
						#1	#2				#1	#2	
KCl First/H$_2$O$_2$ Second Tests													
1	3.0	--	--	3.34	<0.15	0.13	0.12	3.59	111.3	--	4.3	4.0	119.7
2	3.0	--	--	3.18	<0.15	0.17	0.04	3.39	106.0	--	5.6	1.3	113.0
3	3.0	--	--	3.05	<0.15	0.25	0.09	3.47	101.7	2.7	8.3	3.0	115.7
Average									106.3		6.1	2.8	116.1
Standard Deviation									4.8		2.0	1.4	3.4
Controls													
1	3.0	--	--	3.21	--	--	--	3.21	107.0	--	--	--	107.0
2	3.0	--	--	3.17	--	--	--	3.17	105.7	--	--	--	105.7

1. Lower detection limits are 0.03, 0.15 and 0.05 ug per impinger for the KCl, peroxide and permanganate 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 Nm^3, a 3.0 ug spike corresponds to 0.98 ug/Nm^3 of mercury in air.

TABLE 2.6B: MODIFIED EPA METHOD 29 RESULTS[1]

Test No.	Hg Spike in H_2O_2 Impinger (ug)[2]	Hg Spike in KCl Impinger (ug)	Hg Spike in first KMnO4 Impinger (ug)	Hg Recovered in H_2O_2 Impinger (ug)	Hg Found in KCl Impinger (ug)	Hg Found in KMnO$_4$ Impingers (ug) #1	#2	Total Hg Recovered (ug)	% Hg Recovery in H_2O_2 Impinger	% Hg Found in KCl Impinger	% Hg Found in KMnO$_4$ Impingers #1	#2	% Total Hg Recovery
						#1	**#2**				**#1**	**#2**	
				H_2O_2 First/KCl Second Tests									
1	3.0	--	--	1.17	0.18	0.73	0.32	2.40	39.0	6.0	24.3	10.7	80.0
2	3.0	--	--	2.60	<0.03	0.33	0.13	3.08	86.7	0.7	11.0	4.3	102.7
3	3.0	--	--	2.19	0.05	0.42	0.10	2.76	73.0	1.7	14.0	3.3	92.0
4	3.0	--	--	2.42	<0.03	0.35	0.04	2.81	80.7	--	11.7	1.3	93.7
Average									69.9	2.8	15.3	4.9	92.1
Standard Deviation									21.3	2.8	6.2	4.1	9.3
				Controls									
1	3.0	--	--	3.02	--	--	--	3.02	100.7	--	--	--	100.7
2	3.0	--	--	2.92	--	--	--	2.92	97.3	--	--	--	97.3

1. Lower detection limits are 0.15, 0.03 and 0.05 ug per impinger for the peroxide, KCl and permanganate 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 Nm^3, a 3.0 ug spike corresponds to 0.98 ug/Nm^3 of mercury in air.

Finally, the suggestion had been made that the typical spike of 3.0 ug was small, representing only 1.0 ug/Nm^3 of mercury in flue gas, and that if carry-over is some phenomenon with some limiting maximum quantity, using larger mercury spikes in the experiments would decrease the percentage of carry-over calculated.

A set of experiments using 22.0 ug mercury spikes was performed, and the results are shown in Table 2.7. Overall mercury recovery was 97"6%. Recovery from the H$_2$O$_2$ solutions was 93"7% with 4"0.4% being found in the KMnO$_4$ solutions. This set of experiments would point to a reduction of the carry-over effect when larger levels of mercuric chloride are involved. The explanation would be that of the existence of a limiting amount of "reductant" in the peroxide impingers which converts Hg^{2+} to Hg^o, resulting <u>in</u> a carry-over that is not dependent on the mercuric chloride spike concentration itself.

Conclusions that follow from the results of the mercury spiking experiments described in this section are as follows:

C   Transport of mercury spiked into acidified hydrogen peroxide impinger solutions to the acidified potassium permanganate impinger solution during laboratory air sampling procedures utilizing EPA Method 29 sampling trains has been observed.

C   The percentage amount of this transport (called Acarry-over@) between the four laboratories participating in this study varied greatly (0.0 - 42.0%).

C   No corresponding Acarry-over@ was seen in similar tests using Ontario-Hydro Method sampling trains by either of the two laboratories (ATS and UNDEERC) that participated in this comparison.

TABLE 2.7: EPA METHOD 29 RESULTS[1]

Test No.	Hg Spike in First H_2O_2 Impinger (ug)	Hg Spike in First $KMnO_4$ Impinger (ug)	Hg Recovered in H_2O_2 Impingers (ug)		Hg Found in $KMnO_4$ Impingers (ug)		Total Hg Recovered (ug)	% Hg Found in H_2O_2 Impinger		% Hg Found in $KMnO_4$ Impingers		% Total Hg Recovery
			#1	#2	#1	#2		#1	#2	#1	#2	
					22 ug Spiking Tests							
1	22.0	--	20.13	0.27	0.62	0.11	20.87	91.5	1.2	2.8	0.5	94.9
2	22.0	--	18.92	0.16	0.80	0.12	19.84	86.0	0.7	3.6	0.5	90.2
3	22.0	--	19.58	<0.15	0.79	0.12	20.49	89.0	--	3.6	0.6	93.2
4	22.0	--	22.53	<0.15	0.82	0.13	23.29	102	--	3.7	0.6	106
5	22.0	--	21.41	<0.15	0.79	0.09	22.29	97.3	--	3.6	0.4	101
Average								93.2	--	3.5	0.5	97.1
Standard Deviation								6.5	--	0.4	0.1	6.4

1. Lower detection limits are 0.15 and 0.03 ug per impinger for the peroxide and permanganate 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 Nm^3, a 22.0 ug spike corresponds to 7.19 ug/Nm^3 of mercury in air.

2.6 ATS/UNDEERC LABORATORIES JOINT SPIKING STUDY: EPA METHOD 29 AND THE ONTARIO-HYDRO TECHNOLOGIES METHOD

At this stage in the development of a mercury sampling and analytical scheme to distinguish the chemical forms of mercury in coal-fired boiler flue gas, two important considerations had to be addressed. First, it was apparent that for some reason and under certain specific conditions, mercury was observed to transport from acidified hydrogen peroxide impinger solutions to acidified potassium permanganate impinger solutions of EPA Method 29 sampling trains. Secondly, the extent of this reported transport varied greatly from test to test and from lab to lab. To resolve the inter-laboratory discrepancy with respect to the EPA Method 29 results, DOE-FETC requested that ATS and the University of North Dakota=s Energy and Environmental Research Center (UNDEERC) 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:

C   Did the ATS operator overlook some steps in the procedures that resulted in the inordinate migration of mercury from the peroxide impingers?

C   Were there equipment differences between ATS and the other laboratories?

C   Were there differences in the chemicals, reagents and standards used by ATS compared to those used by the other labs?

The following descriptions of equipment and procedures apply to the experimental work performed at the ATS laboratory by ATS and UNDEERC 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.

Equipment and reagents were of the type and quality previously described. Air sampling was performed using Nutech 2010 Stack Samplers. Although the ATS and UNDEERC 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 (250^0 F) with the chamber connected to the first impinger by a short (several inches) section of glass. UNDEERC, on the other hand, utilized a short (−12 inch), unheated narrow (I.D −0.19 inch) piece of glass tubing as a probe. UNDEERC=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.[7]

All sampling and analytical procedures were performed as previously described. 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 monitored and recorded every 30 minutes.

Mercury analyses were performed as previously described. As stated, the mercury analyzer has a lower detection limit of 0.010 ug. In this case, however, the lower 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.

Blank tests were performed for the purpose of determining the ambient level of mercury in the laboratory. Mercury spiking experiments were performed as previously described.

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

The results for the five (5) experiments consisting of ten (10) EPA Method 29 sampling trains are presented in Table 2.8. (In Table 2.8 AUNDEERC@ is abbreviated as AEERC.@) In the first three (3)

TABLE 2.8: ATS/EERC JOINT STUDY: EPA METHOD 29 RESULTS[1]

Test No.	Hg Spike in first H_2O_2 Impinger (ug)[2]	Train, Glassware and Spiking Reagent	Operator	Hg Recovered in first H_2O_2 Impinger (ug)	Hg Found in second H_2O_2 Impinger (ug)	Hg Found in $KMnO_4$ Impingers (ug)		Total Hg Recovery (ug)	% Hg Found in first and second H_2O_2 Impinger	% Hg Found in $KMnO_4$ Impingers	% Total Hg Recovery
						#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 H_2O_2 and $KMnO_4$ 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 Nm^3, a 2.9 ug spike corresponds to 0.95 ug/Nm^3 of mercury in air, and a 22.0 ug spike corresponds to 7.19 ug/Nm^3.
3. ATS's train and glassware with EERC's mercury spiking reagent.

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 UNDEERC≤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, UNDEERC 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.

The results of the blank train experiments indicated mercury present in the laboratory air to be below the detection limit of approximately 0.1 ug/Nm³.

Shown in Table 2.8 is a set of three (3) experiments in which only ATS equipment was utilized. The average percent total mercury recovery for all 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%) while the average percent recovery from the associated 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 in which only UNDEERC equipment was used 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%), where the UNDEERC equipment system was employed, was greater than that of the average of the first three experiments (91%), when the ATS system was tested. 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%).

In Experiment No. 5, ATS equipment was used, and mercury solution spikes were approximately ten times greater in mass than in all the other experiments. 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, 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.

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 UNDEERC 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 observed 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 UNDEERC 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 UNDEERC≡s, is more representative of those used in actual field work.

The speculation is that since ATS used a probe which is heated and much longer than UNDEERC≡s and that the heated filter was connected by a much shorter length of tubing to the first impinger, the contents of that impinger were subject to a higher temperature than the corresponding impinger in UNDEERC≡s system. We believe that this additional heat promoted 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 UNDEERC from the round robin study discussed in the previous section.

This study confirmed the previous findings by ATS regarding low level mercury migration from the peroxide impingers to the permanganate impingers in EPA Method 29 sampling trains and lead DOE-FETC to focus research on the Ontario-Hydro Method.

In the next section, laboratory work on the Ontario-Hydro method is described regarding optimization of sampling conditions to minimize the adverse effect of sulfur dioxide, which is one of several flue gas components.

2.7 MINIMIZATION OF THE EFFECTS OF SULFUR DIOXIDE PRESENT IN FLUE GAS

Previous work had been focused on a candidate speciation method≡s capacity to retain mercury spiked into an impinger solution during laboratory air sampling tests. Of the methods tested, the Ontario-Hydro Method performed well in this respect. The next step was to determine if the method was robust enough to perform effectively in the presence of flue gas components such as SO_2, NO_X, HCl and fly ash. The laboratory experiments described in this section involve the spiking of the Ontario-Hydro potassium chloride (KCl) impinger solutions with known amounts of mercury and subsequent sampling of air containing high levels of sulfur dioxide (SO_2). Initial results indicated

some loss of mercury from the mercury spiked impinger solution. Further experiments were carried out in which various parameters including flow rate, sampling time, SO_2 concentration and sulfuric acid presence in the impinger solutions were varied in order to minimize loss of mercury in these retention studies.

Reagents, equipment and procedures were described in the previous sections. It is emphasized that a full-size (6 ft) heated probe, followed by a quartz-fiber filter within a heated filter chamber (250^0 F), was used in all experiments since variation in this part of the equipment has been demonstrated to have profound effects on results in the previous EPA Method 29 tests. Also, in all the sampling runs performed in the laboratory, a total volume of 3.06 cubic meters of ambient laboratory air was collected over a period of approximately 3 hours unless otherwise specified.

Laboratory-scale experiments were performed to determine the effect of sulfur dioxide on the ability of the potassium chloride (KCl) impinger solutions in the Ontario-Hydro Method to retain mercuric chloride spikes during train operation. Gas phase spiking of SO_2 into the laboratory air being sampled was achieved by passing controlled volumes of certified concentrations of SO_2 in N_2 directly into the sampling probe during testing. Tests were performed by adding either 15.0 or 25.0 g of mercury as mercuric chloride to the first of the three impingers containing the KCl solution. (The mercury spike concentrations were based on the expected range of concentrations of mercury in coal flue gas of 4.9 - 8.2 g/Nm^3.) Then, the sampling train was assembled, leak-checked and laboratory air spiked with either 0, 1500 or 2200 ppmv of SO_2 was drawn through the sampling train. After sampling, the train was again leak-checked and the impinger solutions were recovered using the most currently accepted method. In this procedure, potassium permanganate replaced the potassium dichromate used previously in the treatment of the KCl solutions. The ensuing, more rapid chemical reaction with the permanganate insured that all of the SO_2 would have been consumed upon the development of the characteristic permanganate pink-purple color. Also, permanganate impinger solution treatment differs from the EPA Method 29 recovery procedure in that hydroxylamine hydrochloride was added directly to the impinger. This step eliminates the need to filter and treat large amounts of the brown manganese dioxide precipitate, which typically entrains most of the captured mercury. Thus, the KCl impinger solutions were treated immediately with a

minimal amount of acidified $KMnO_4$ until a pink-purple color developed. The permanganate impinger solutions were treated first with hydroxylamine hydrochloride to dissolve the manganese dioxide precipitate and to remove any remaining permanganate. Secondly, they were treated with a minimal amount of $KMnO_4$ to maintain an oxidizing solution and thereby prevent loss of mercury by its possible conversion to the less soluble and more volatile elemental form. Both KCl and permanganate impingers were rinsed with 8.0 N HCl to dissolve any brown deposits of manganese dioxide if they were evident.

Shown in Figure 2.4 is a bar graph with each bar representing the percentage of the mercuric chloride spiked into the first KCl impinger solution that remained after the completion of the experiment. In these experiments, 15 g of mercury as mercuric chloride was chosen as the spike size, and the train was operated for a sampling time of 3 hours and at a sampling flow rate of 0.6 ft^3/hr. In the first 3 experiments (left), no SO_2 was added to the sampled air; in the last 4 experiments (right), enough SO_2 was added to produce a concentration of 1500 ppm. The results were definitive with approximately 99 " 1% retention of the mercury spike when no SO_2 was added to the laboratory air and – 90 " 1 % in the case where the concentration of SO_2 was 1500 ppm in the air.

In order to investigate the effect of sampling flow rate and sampling time on mercury spike retention, experiments were performed in which these conditions were varied. Furthermore, a decision was made to increase the mercury spike from 15 to 25 g since this would be more representative of a mid-range level of mercury present in coals. The results of these experiments are presented in Figure 2.5. A trend was apparent with percent retention decreasing as sample time varied from 1 to 3 hours and with percent retention increasing as sampling flow rate was decreased from 0.6 to 0.3 ft^3/ hr.

FIGURE 2.4:

MERCURY SPIKE RETENTION (%) WITH AND WITHOUT SO$_2$

0,1500 ppm - SO$_2$
15 g   - Mercury Spike
3 hours   - Sampling Time
0.6 ft^3/hr - Sampling Rate

Legend:
- 0 PPM SO2 (red)
- 1500 PPM SO2 (green)

Values: 98, 98, 99 (0 PPM SO2); 91, 91, 91, 89 (1500 PPM SO2)

Y-axis: 80, 90, 100
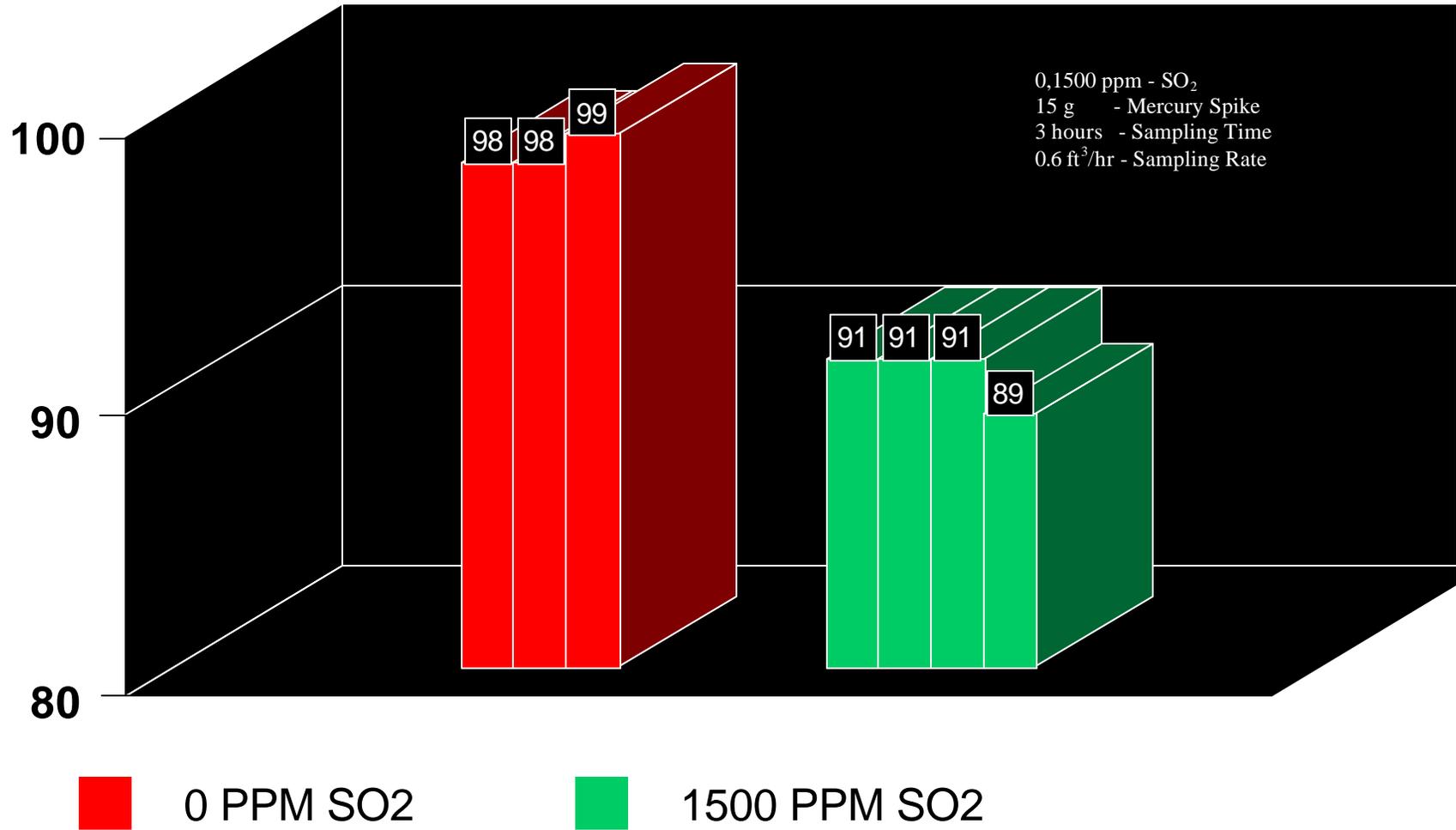
FIGURE 2.5:

MERCURY SPIKE RETENTION (%) WITH SO$_2$ AT 1500 PPM

Red bars (0.6 cu.ft./hour): 1 hour = 98, 2 hours = 97, 3 hours = 93

Green bars (0.3 cu.ft./hour): 1 hour = 99, 2 hours = 98, 3 hours = 96

0,1500 ppm - SO$_2$
25 g   - Mercury Spike
1-3 hours   - Sampling Time
0.3-0.6 ft^3/hr- Sampling Rate

0.6 cu.ft./hour   **0.3 cu.ft./hour**
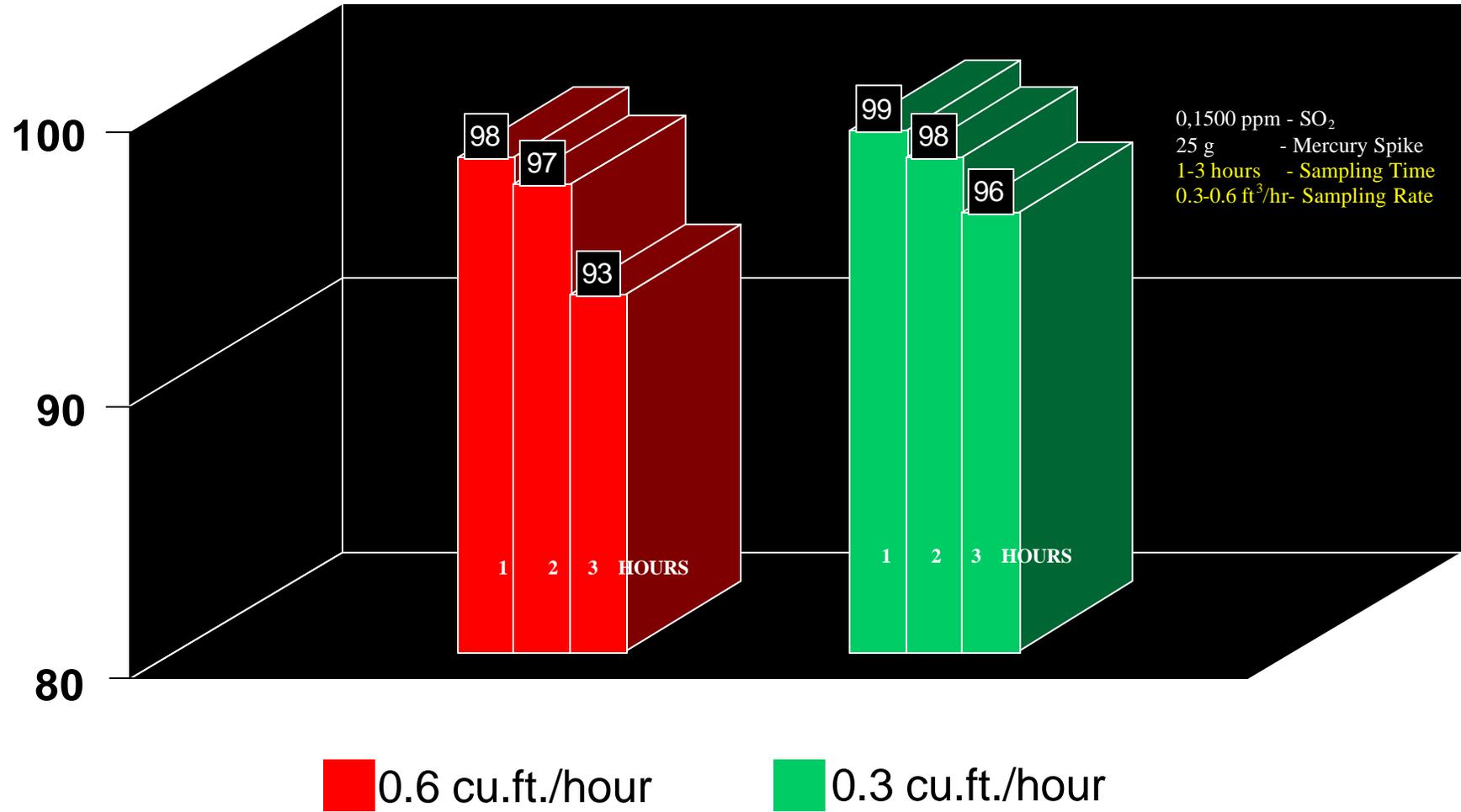
To determine the effect of increased SO_2 concentration, experiments were carried out with 2200 ppm in the sampled air. All 8 trains sampled for 3 hours, with 5 sampling at the higher flow rate and 3 at the lower sampling flow rate. These results are shown in Figure 2.6. Clearly the effect of sampling flow rate shown here is consistent with that shown in the previous figure; however, no definitive effect from the increased SO_2 concentration is apparent from the data.

Concern over the effect of sulfur trioxide (SO_3) in the flue gas prompted a final series of experiments in which sulfuric acid (H_2SO_4) was added to the KCl impinger solution containing the mercury spike. The amount of H_2SO_4 added corresponded to the amount of SO_3 that would have been absorbed based on the assumption that SO_3 is always present with SO_2 and is found at approximately 1% of its concentration. Sampling flow rate and time were varied in these experiments. Shown in Figure 2.7 are the results. Again, the effect of varying sampling flow rate and sampling time shown here is consistent with that shown in Figure 2.5; however, no definitive effect from the presence of the H_2SO_4 and consequently SO_3 is apparent from the data.

This laboratory-scale study lead to the following specific conclusions:

C   The presence of SO_2 in the sampled air reduces mercury spike retention.

C   Reducing sampling time increases mercury spike retention.

C   Reducing sampling flow rate increases mercury spike retention.

C   Increasing SO_2 concentration from 1500 to 2200 ppm has little effect on mercury spike retention.

C   The presence of H_2SO_4 in impinger solutions to simulate SO_3 in the flue gas has no apparent effect on mercury spike retention.

These conclusions provided the basis for optimizing sampling conditions to minimize the effect of SO_2 on the operation of the Ontario-Hydro Method sampling trains and led to the final validation of the methodology.

FIGURE 2.6:

MERCURY SPIKE RETENTION (%) WITH SO_2 AT 2200 PPM

2200 ppm   - SO_2
25 g   - Mercury Spike
3 hours   - Sampling Time
0.3-0.6 ft^3/hr- Sampling Rate

100

90

80

95   94   93   95   96   96   98   99

█ 0.6 cu.ft./hour   █ 0.3 cu.ft./hour
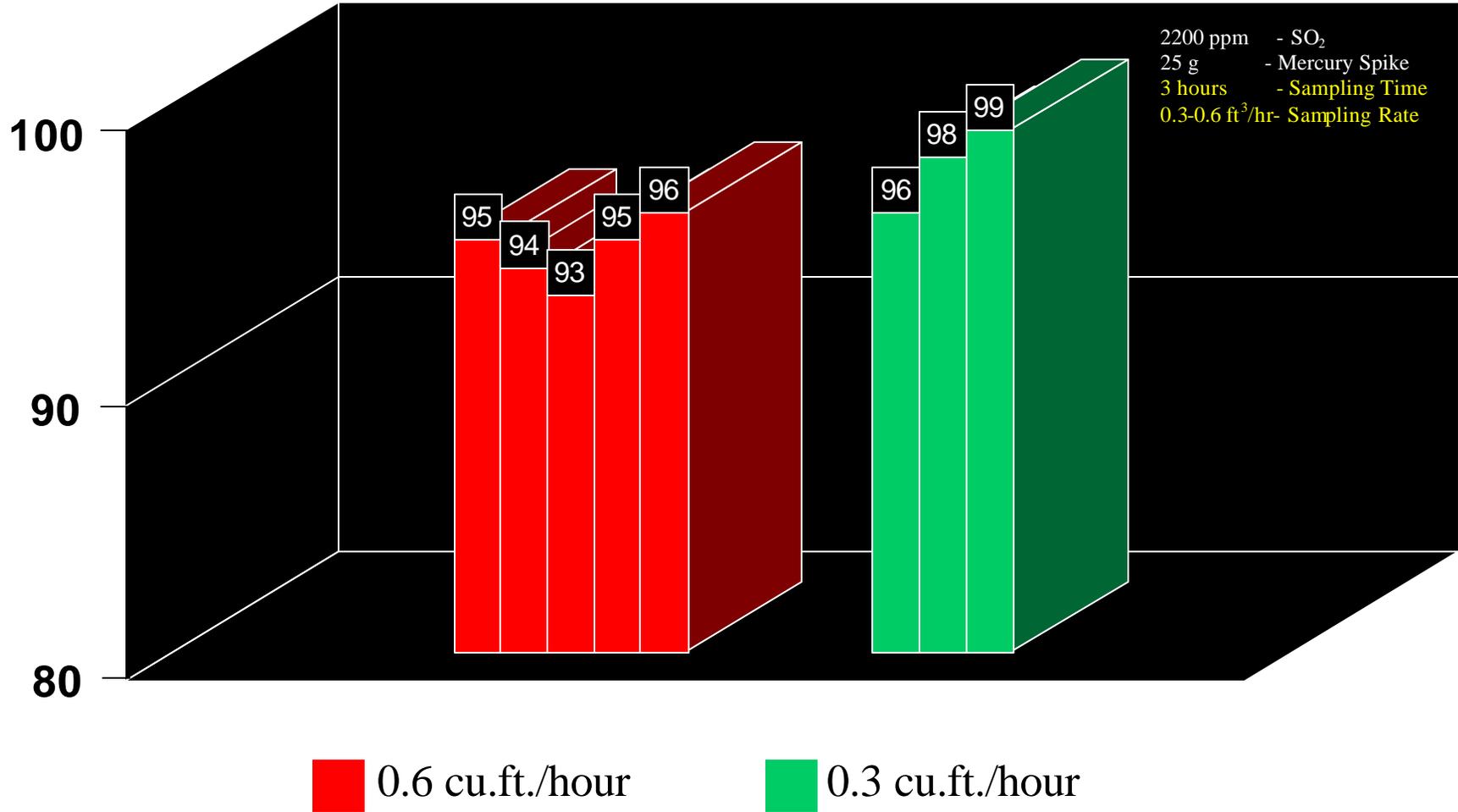
FIGURE 2.7:

MERCURY SPIKE RETENTION (%) WITH SIMULATED SO$_3$ SAMPLING
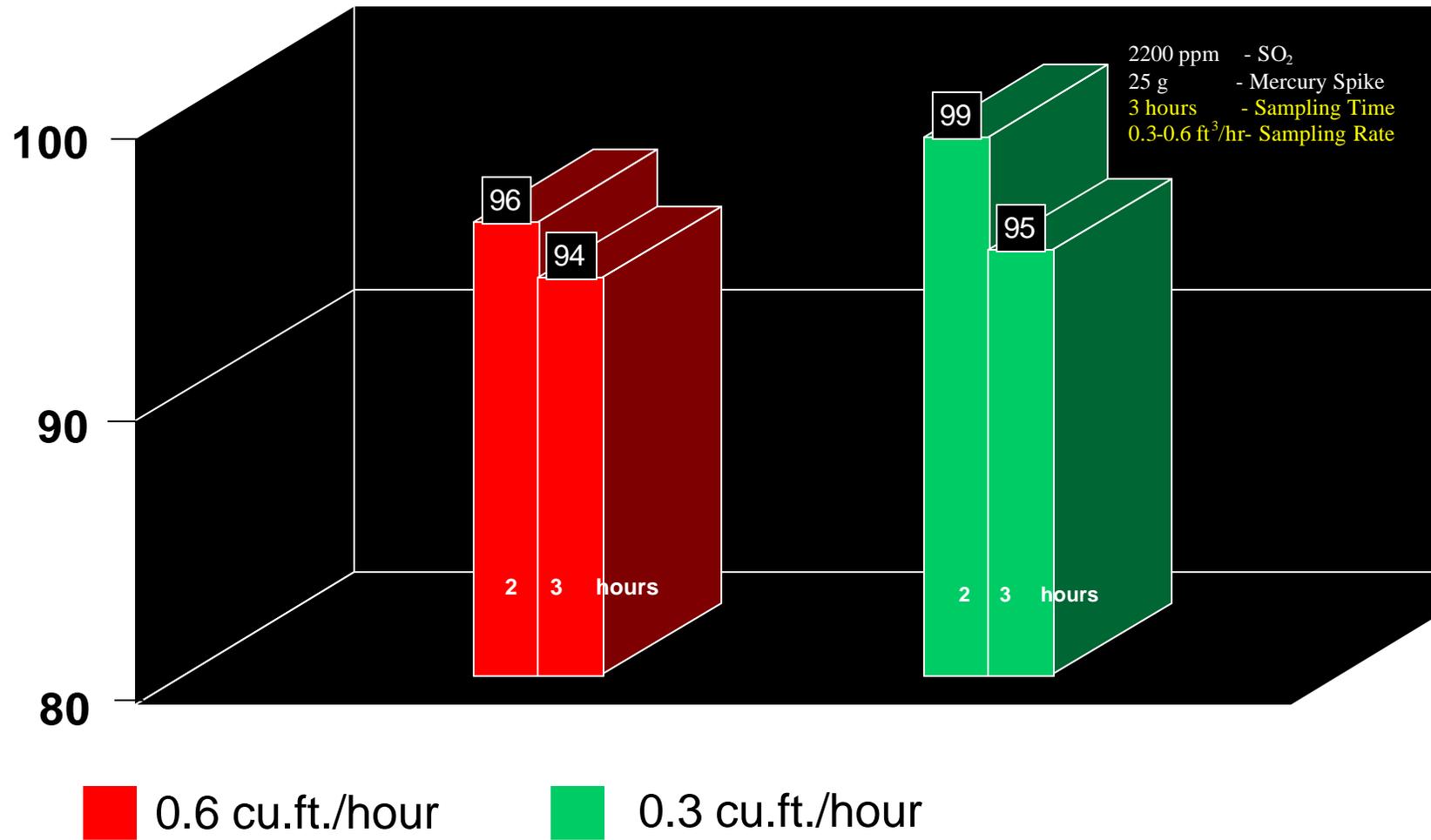
3.0 MERCURY METHODS: PILOT-SCALE SAMPLING STUDIES

A major focus in the mercury speciation development studies carried out by ATS was the evaluation of the effectiveness of the capture *and* retention of the particular chemical species of mercury by the capture solution prescribed by the method being tested. Capture without effective retention is not a sufficient criterion for a successful speciation method. Thus retention studies were a key focus in both laboratory-scale and pilot-scale studies.

In the laboratory-scale studies, presented in previous sections, acidified permanganate solutions were shown to effectively retain captured mercury. Acidified hydrogen peroxide solutions were shown not to retain mercury under even modest laboratory simulations of Areal world@ sampling. However, potassium chloride solutions were shown to be effective in retaining mercury even in the presence of realistic amounts of sulfur dioxide in the gas being sampled under controlled conditions of specified sampling time and flow rate.

In the pilot-scale studies described in this section, the Ontario-Hydro Method, which utilizes the more promising potassium chloride solution for oxidized mercury capture, was tested side by side with the EPA Reference Method 29, ATS Method 1 and ATS Method 2. The comparative tests not only evaluated mercury speciation but total mercury capture together with particulate and vapor phase metals and semi-metals determination.

In one specific study, a method utilizing carbon traps was compared to the Ontario-Hydro Method for determining total vapor phase mercury in conjunction with carbon injection testing as a means of decreasing vapor phase mercury.

Finally, pilot-scale work not directly related to the mercury methods studies was described. First, a calibration of a mercury injection system for a flue gas stream utilizing impinger methods was summarized, and, second, a study comparing the Volatile Organic Sampling Train (VOST) to a Gas Chromatography (GC) method proposed by ATS for determining organic chemical compounds in flue gas was also described.

3.1 GENERAL EXPERIMENTAL: FACILITIES AND METHODOLOGIES

Most work was performed at the DOE-FETC 500 lb/hr pulverized coal combustion unit located in Pittsburgh, Pennsylvania. The following is a general description of facilities and procedures of all pilot-scale work performed. The description of the combustor, however, applies specifically to the FETC combustion unit. Sample handling and data presentation are also presented in this section. In Section 3.2, a general discussion on ATS=s Quality Control/Quality Assurance (QA/QC) Program is given. This section immediately precedes the first pilot-scale study presented in Section 3.3.

3.1.1 Description of the FETC Pilot Plant

The pilot plant is located in Building 86 at the DOE's Federal Energy Technology Center (FETC) in Pittsburgh, Pennsylvania. The combustor is a wall-fired, dry-bottom furnace that burns pulverized coal at a nominal rate of 500 pounds per hour. The coal is fed by a screw-drive conveyor from a coal hopper to a pulverizer. At the pulverizer, the coal is crushed to a size such that 70% of it is less than 200 mesh. After crushing, the pulverized coal then enters a recycle circuit where a fast-moving stream of air keeps the coal flowing through a closed loop. A portion of the air/coal mixture is diverted to each of four burners located on the walls of the combustor. The bottom ash and slag formed during the combustion of the coal are deposited in the furnace ash pit. The fly ash and the flue gas pass through a convective section to a duct leading to a recuperative air preheater. This device is a heat exchanger which heats the secondary combustion air to a temperature of about 600 ^{o}F. After passing through the recuperative air preheater the flue gas may be treated for the removal of SO_2 by going to a lime slurry spray dryer or it may be diverted to a test duct section. After passing through the test duct section, the flue gas is transported to a fabric filter baghouse for particulate removal. In the baghouse, airjets are used to pulse the filter bags and release the filter cakes into the hoppers below. Cleaned flue gas exiting the baghouse is exhausted through the stack. When not operating on coal, the system can be operated on natural gas. A schematic of the pilot plant is presented in Figure 3.1.
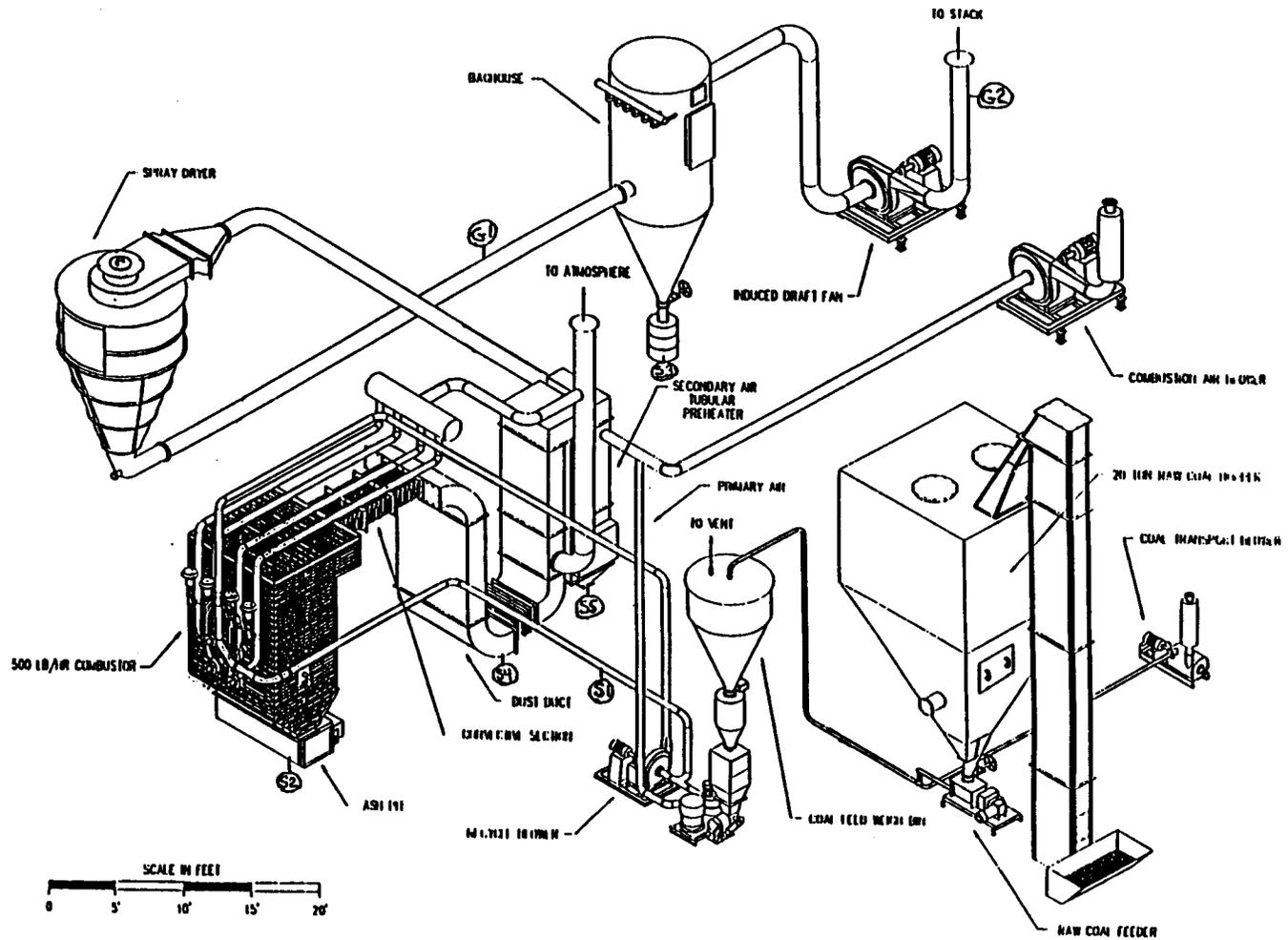
FIGURE 3.1: SCHEMATIC OF FETC'S 500 POUND PER HOUR PILOT-SCALE COMBUSTION UNIT

3.1.2 General EPA Stack Sampling Procedures

The execution of the emissions test programs required the use of several U.S. EPA-approved stack test procedures. Likewise, mercury speciation methods testing employed methods ranging from one EPA methodology approved for sampling and analysis of volatile metals to two new experimental methods developed at ATS. This section outlines the sampling and analytical procedures utilized.

3.1.2.1 Location of Traverse Points

EPA Reference Method 1 presents criteria regarding (i) the duct dimensions at the test platform level, (ii) the number of test ports installed on each duct, (iii) the distance from the test ports to the nearest upstream and downstream disturbances, (iv) the minimum number of traverse points required for isokinetic sampling and (v) the number of minutes of sampling for particulate-phase emissions at each traverse point. These data have been be presented to DOE in previously submitted reports, which will be referenced in the sections describing the specific pilot-scale studies.

3.1.2.2 Gas Stream Velocity and Volumetric Flow Rate

Gas velocities and volumetric flow rates of the process gas streams were measured using a calibrated S-type pitot tube in accordance with EPA Reference Method 2. Positive and negative pitot lines were leak-checked at the beginning and end of each test run. Gas velocity differential pressures were recorded at each traverse point. Static pressures of the process gas streams were measured with the same pitot tube. Process gas temperatures were measured with a type-K thermocouple.

3.1.2.3 Dry Gas Molecular Weight

Gas samples of flue gas were collected at appropriate locations (e.g. the baghouse inlet duct and baghouse exhaust stack in the studies where the DOE-FETC 500 lb/hr Pulverized Coal Combustor was employed). Separate, clean 5-liter Tedlar bags were utilized in accordance with EPA Reference Method 18. Analyses of the flue gas samples for fixed gas components (concentrations of carbon dioxide, oxygen and nitrogen by difference) were performed using continuous emissions monitoring techniques in accordance with EPA Reference Method 3A. The continuous emissions monitors were owned and operated by U.S. DOE-FETC and were installed as part of the 500 pound per hour combustion unit.

3.1.2. 4   Moisture Content

Percent moisture content, by volume, of the flue gas streams was measured by the weight gain of the impingers used in the isokinetic sampling trains in accordance with EPA Reference Method 4. Moisture content was calculated by knowledge of the weight gain of the sample train impingers and dry gas volume sampled.

3.1.3   Particulate Matter and Multi-Metals Sampling Procedures

EPA Reference Method 29, ATS Method 1, the Ontario-Hydro Method and ATS Method 2 were used to collect particulate matter, metals and mercury samples from the flue gas streams. Schematic drawings of the various sampling trains follow. The corresponding standard recovery procedures and especially experimental deviation from accepted procedures are discussed in the sections describing the pilot-scale studies.

3.1.3.1   EPA Reference Method 29

Particulate matter and particulate and vapor-phase metal samples were collected using EPA Reference Method 29. Sample gas was withdrawn isokinetically from the flue gas stream through a glass nozzle and a glass-lined sampling probe. A schematic of the EPA Reference Method 29 sampling train is shown in Figures 3.2.

3.1.3.2   ATS Method 1

Particulate matter along with particulate and vapor-phase metals sampling was performed using the ATS Method 1. Sample gas was withdrawn isokinetically from the flue gas stream through a glass nozzle and a glass lined sampling probe. The ATS Method I samples were recovered using the procedures developed by Keith Curtis for the Ontario-Hydro Method. A schematic of the ATS Method 1 sampling train is shown in Figures 3.3.
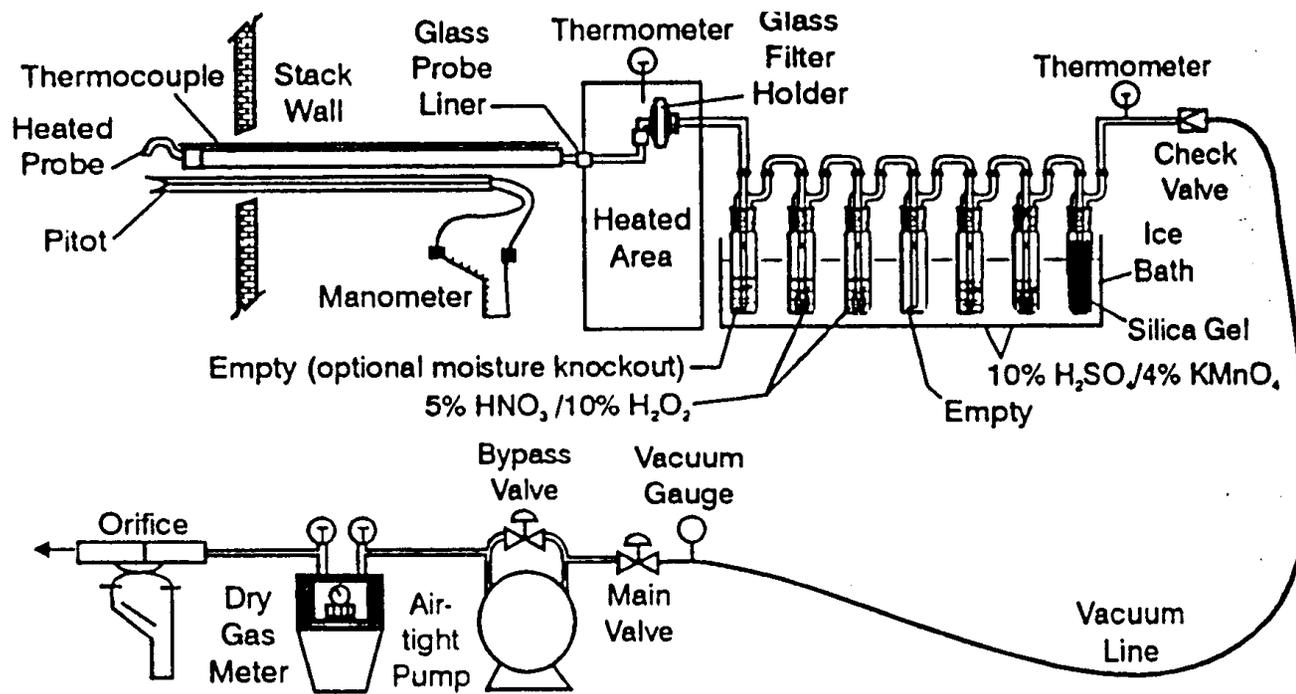
FIGURE 3.2:   EPA REFERENCE METHOD 29
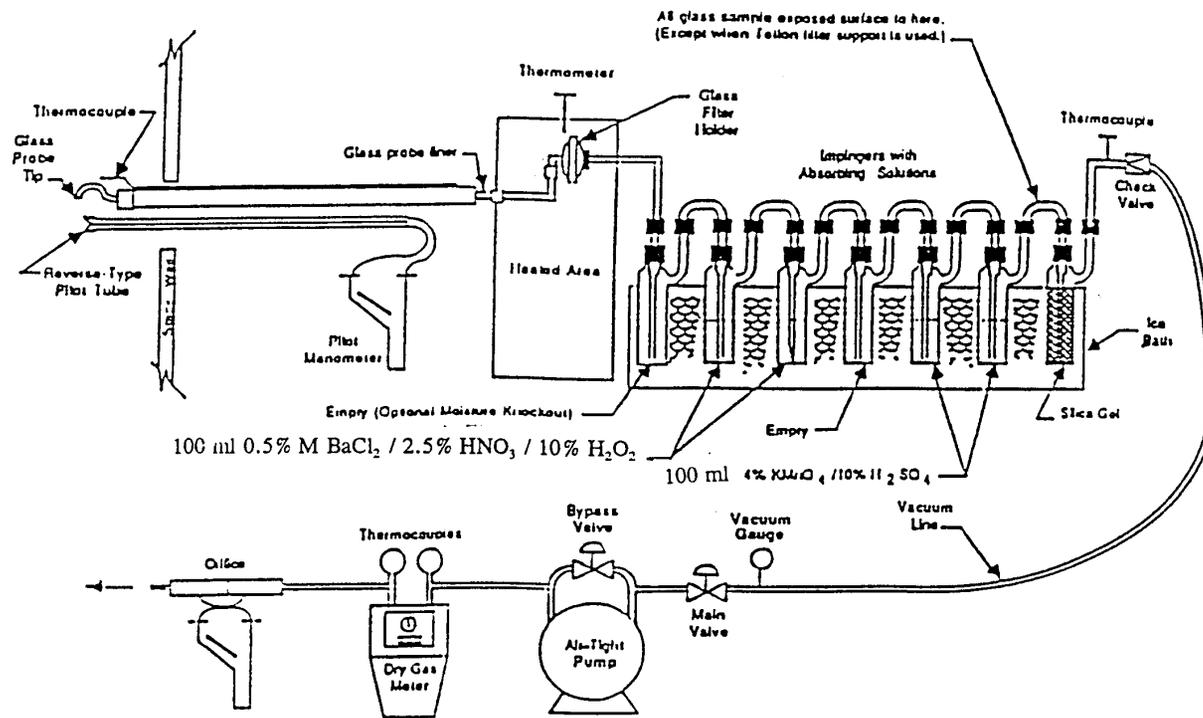
FIGURE 3.3:   ATS METHOD 1

3.1.3.3 Ontario-Hydro Method

The flue gas was also sampled for particulate matter along with particulate and vapor-phase metals using the Ontario-Hydro Method. Sample gas was withdrawn isokinetically from the flue gas stream through a glass nozzle and a glass-lined sampling probe. A schematic of the Ontario-Hydro Method sampling train is shown in Figures 3.4.

3.1.3.4 ATS Method 2

Particulate matter along with particulate and vapor-phase metals sampling was performed using ATS Method 2. Sample gas was withdrawn isokinetically from the flue gas stream through a glass nozzle and a glass-lined sampling probe. A schematic of the ATS Method 2 sampling train is shown in Figures 3.5.

3.1.4 Presentation of Data

Results from mercury analyses were given in concentration units of micrograms per normal cubic meter (μg/Nm^3) with normal referring to 20 ^{o}C and 760 mm Hg. Since the resulting dilution of flue or stack gas is effectively the same whether it results from excess air used for combustion or whether it leaks in through the flue gas duct work, gas volume and thus concentrations of flue gas species are normalized to a certain percentage of oxygen in the flue or stack gas in order to provide data comparable with that of other combustion studies. This normalization is usually to 3% or 6% oxygen and is given in the discussions on individual pilot-scale studies.

The analytical data were reduced following the specifications established by the DOE for previous work. The following explains how averages, sums and reported emission values are calculated for all species given various combinations of detected and non-detected (i.e. analytical results for which the concentration of the species of interest is below the detection limit of the method values):

In the case where all values were detected: The arithmetic average or sum was calculated, as appropriate. No special techniques were required.
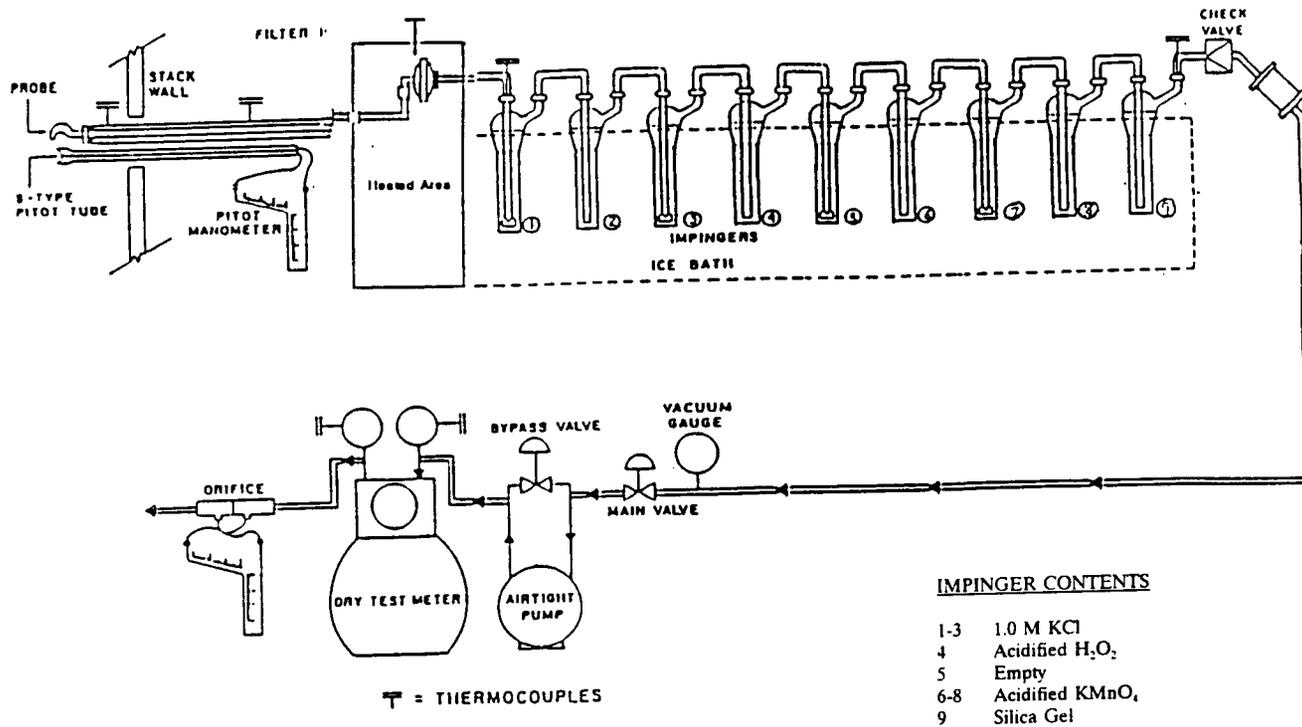
FIGURE 3.4: ONTARIO-HYDRO METHOD

IMPINGER CONTENTS

1-3	1.0 M KCl
4	Acidified H_2O_2
5	Empty
6-8	Acidified $KMnO_4$
9	Silica Gel

$\top$ = THERMOCOUPLES
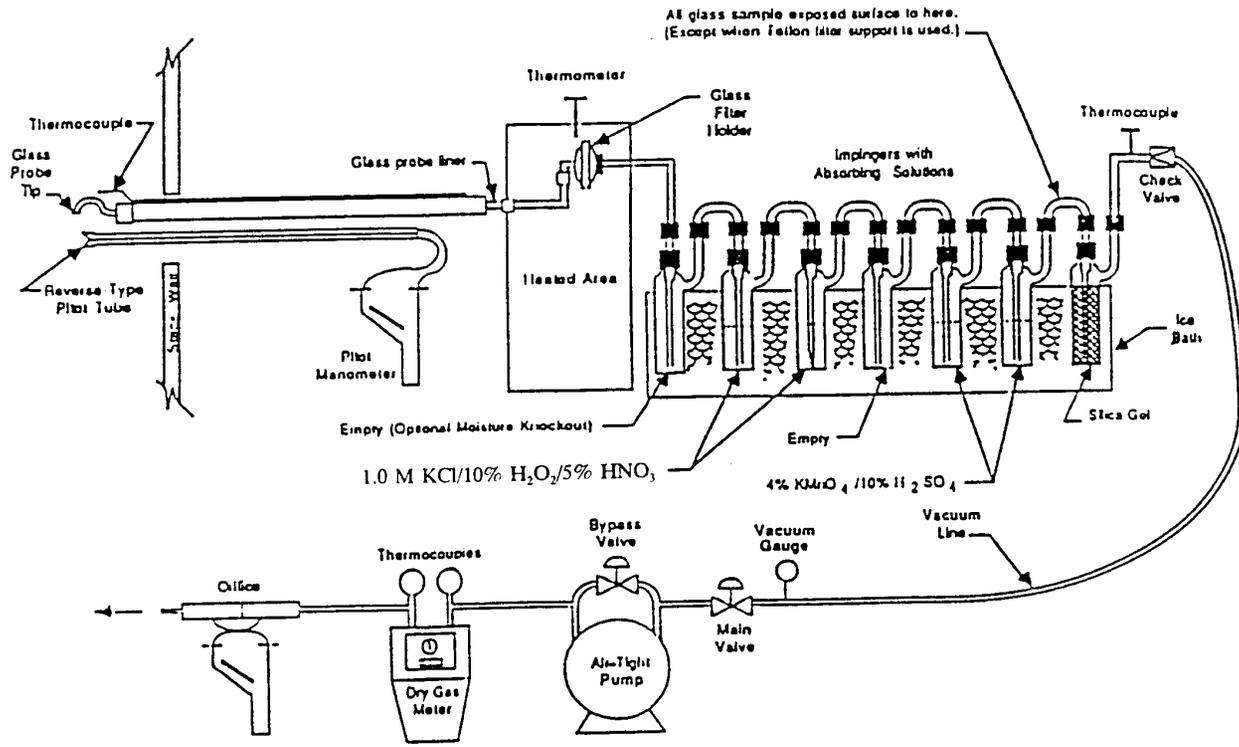
FIGURE 3.5: ATS METHOD 2

When all values were below the detection limit: For individual test runs or species, the data are reported as "ND < (detection limit)." For cases where all three runs (or multiple species) are below the detection limit, the average is reported as non-detected less than the average detection limit of the three runs (species).

In the case where some values are detected and some are non-detects: As an approximation, one-half of the detection limit for the non-detects and the actual value for the detects were used to determine reported values. As an example of averaging, an average of three test runs with results of 10, 8, and ND < 6 would be 7. As an example of summing (such as for mercury fractions) individual species values of 50, ND < 2 and ND < 1 would be summed to provide a value of 50 + 1 + 0.5 or 51.5. In reporting these values of sums or averages, no "ND <" sign is used. The only exception to this rule occurs when the average (or sum) is less than the highest detection limit of non-detected values. In this case, the averages or sums are reported as "ND < (the highest detection limit)." For example 5, ND < 4 and ND < 3 would be reported as "ND < 4."

With blank values: All values were blank corrected. In the case where the blank was below detection limits, no subtraction from the sample value was performed. When a sample value was blank corrected resulting in a value below the detection limit, it was reported as "ND < (detection limit)."

3.1.5   Sample Handling

The preservation, storage and holding time requirements for all samples are listed in Table 3.1. Samples were recovered from the sampling train at the termination of each daily run and prepared for storage and transport to ATS's laboratory. Mercury samples were fixed by addition of HCl (or other chemical agents) and stored at room temperature. All samples were transported daily to the ATS's laboratory facility in Monroeville, Pennsylvania for subsequent analysis. Completed chain-of-custody forms accompanied each shipment.

TABLE 3.1: SAMPLE PRESERVATION AND STORAGE REQUIREMENTS				
Sampling Medium	Analysis	Preservation	Storage Conditions	Holding Time
Impinger	Elements	None	Room Temp.	6 Months
Filter	Elements	None	Room Temp	6 Months
Impinger	Mercury	HCl	Room Temp	28 Days
Filter	Mercury	None	Room Temp	6 Months

3.2   QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

The purpose of ATS's Quality Assurance/Quality Control efforts was to insure that the data obtained from these test projects were scientifically sound, compatible and comparable with the results of other contractors assessing the same unit. To achieve this goal, ATS followed the quality assurance/quality control policies and procedures outlined in the ATS Quality Assurance/Quality Control Handbook. These policies and procedures included but were not limited to the following items:

3.2.1   Sample Chain of Custody

To ensure that the correct samples were analyzed, an internal sample tracking system was instituted. The following sample custody protocol was followed:

(1)   Standard Operating Procedures (SOPS) were documented to include laboratory procedures for handling, storage and preservation of samples. These procedures were posted in reagent preparation and sample recovery areas where they were easily accessible to all personnel.

(2)   A sample custodian was assigned the task of logging samples in and out. This person was responsible for verifying the receipt of samples from the field location, confirming the absence of tampering of the samples and assuring the appropriate disposition of each sample for analysis. Specific identification numbers were used for tracking all samples.

(3)   The preparation of reagents and equipment that were used for sample collection was documented.

(4)   Standard forms were used to document sampling conditions and parameters. These forms were signed by the people responsible for the sampling effort.

(5)   Pre-prepared pressure-sensitive labels were used to identify the sample containers. The time, date and responsible technician were part of the sample identification.

(6)   All shipped samples had the appropriate packing and inventory documentation.

(7)   The field blanks along with any field observations were documented in a secure and signed laboratory notebook.

3.2.2   Calibration Procedures

The sampling equipment was calibrated prior to the sampling program. Calibration checks were performed on dry gas meters, thermocouples, pitot tubes, balances, etc. used in the sampling program as close to the commencement of sampling as possible. All calibration checks were within " 5.0 % of the last full calibration. Calibration of analytical equipment was performed prior to each analysis. A correlation coefficient on a 5-point calibration of at least three nines was obtained.

3.2.3   Sampling Quality Control

To ensure that sampling was precise, accurate, comparable and complete the following guidelines were observed:

1)   Sample preparation, collection and recovery methods were available for the sampling team to review.

2)   Prior to the start of sampling activities, all of the sampling equipment was visually inspected to ensure that it was clean and operable; impinger contents were weighed; the number of traverse points was checked, all of the traverse points were located, and all appropriate gauges were checked, leveled and/or zeroed.

3)   All reagents were prepared by the same person.

In addition, the pitot tubes were leak-checked before and after each sampling run. The sampling trains were also leak-checked before and after each sampling run. During the sampling period, care was taken to maintain the proper roll and pitch axis of the pitot tube and sampling nozzle and to maintain the proper impinger temperatures. Delta P, Delta H, stack-, filter- and meter-temperatures

and vacuum pump level measurements were taken and recorded at each traverse point. Also, the flow rate was adjusted to maintain isokinetic sampling to within 10 percent.

Furthermore, the sampling trains were assembled and recovered in an environment free from uncontrolled dust, and the data sheets were checked for completeness after the end of each sampling run.

Four samples of each type were collected during most of the sampling programs. Results for these samples were used to evaluate measurement precision. Precision estimates based on the multiple samples took into account all major sources of random variability, including variability introduced during sample collection, sample storage and handling, sample preparation and sample analysis. The multiple analyses demonstrated an average precision of "10 % in these studies.

Field blanks were used as part of the sampling QA/QC effort. Field blanks were obtained by taking a sampling train to the sampling location, leak-checking the train and then recovering the train using normal recovery procedures. Field blanks were used to monitor contamination in sample handling.

Laboratory blanks on reagents were also used as part of the sampling QA/QC effort. However, they were used as a qualitative check for contamination rather than as a quantitative measure. They were obtained by exposing sampling and analytical solutions to the laboratory environment and then analyzing them for mercury.

3.2.4 Analytical Quality Control

The analytical QC effort focused on ensuring that data generated during this project met the pre-established quality objectives. To maximize comparability of measurement data, standard reference methods (EPA 101A and SW 846 Method 7470) were used to collect and analyze the flue gas samples. The analytical QC system included a variety of internal QC checks designed to assess and control data quality as the data were generated. Because feedback, in the form of analytical results, is more nearly real-time in the laboratory than is possible during sample collection, these

analytical QC checks played a more prominent role in controlling data quality than did the corresponding sampling QC checks.

3.3   DOE/FETC STUDY I

A pilot-scale mercury speciation methods comparison study was carried out at the DOE-FETC 500 lb/hr pulverized coal combustion unit located in Pittsburgh, Pennsylvania on May 7, 8, 9 and 10, 1996.

3.3.1   Background and Objectives

The purpose of this study was to compare the performance of EPA Reference Method 29, the Ontario-Hydro Method and ATS Methods 1 and 2 in not only their capacity to distinguish the chemical forms of mercury in coal flue gas but also in their potential to determine the volatile trace metals and semi-metals concurrently present. Along with these objectives, our site host (DOE-FETC) sought to characterize the combustion unit *and* the combustion coals using these methodologies. Thus, sampling locations and corresponding methodologies were chosen to accommodate both goals. Sampling was performed on the untreated flue gas at the inlet of the baghouse utilizing EPA Reference Method 29 and ATS Method 1 and at the outlet of the baghouse (directly prior to the stack) using EPA Reference Method 29, the Ontario-Hydro Method, ATS Method 1 and ATS Method 2.

3.3.2   Results and Discussion

A comprehensive report entitled AComparative Method Evaluation for the Assessment of Mercury and Other Metal Emissions at a Pilot-Scale Combustion Unit@ and dated August 1996 was submitted to DOE-FETC. All references in this Section to Tables and Figures refer to that report unless otherwise indicated.

3.3.2.1   Mercury

Given in Table 3.2 of this document are the averages of the four tests performed per method at each of the two sampling locations, the baghouse inlet and the stack (baghouse outlet).   Mercury concentrations were reported for vapor phase oxidized and elemental mercury as determined by the

sampling method. Results from mercury analyses were given in concentration units of micrograms per normal cubic meter (μg/Nm^3 or alternatively, μg/dscf) with normal referring to dry gas volume at 20 ^{o}C and 760 mm Hg. Averages were given with sample standard deviations (average $"$ -1).

Results from samples taken at the baghouse inlet showed good agreement for total mercury with 5.13$"$0.60 and 5.49$"$0.28 μg/Nm^3 for EPA Reference Method 29 and ATS Method 1, respectively. Agreement was also good at the stack with 5.43$"$0.52, 4.79$"$0.93, 4.66$"$0.40 and 5.09 μg/Nm^3 for EPA Method 29, ATS Method 1, the Ontario-Hydro Method and ATS Method 2, respectively.

TABLE 3.2 : MAY 1996 TESTS AT DOE-FETC 500 LB/HR COAL-FIRED COMBUSTOR: AVERAGE MERCURY CONCENTRATIONS FOR 4 SAMPLING RUNS.[1]

Method	Oxidized		Elemental		Total
	Vapor Phase (μg/Nm^3)	% of total mercury	Vapor Phase (μg/Nm^3)	% of total mercury	(μg/Nm^3)
Baghouse Inlet					
EPA Method 29	4.17±1.06	81	0.96±0.14	19	5.13±0.60
ATS Method 1	4.65±0.51	85	0.84±0.05	15	5.49±0.28
Average					5.31
Standard Deviation (n-1)					0.25
Baghouse Outlet (Stack)					
EPA Method 29	5.80±0.49	95	0.25±0.07	5	5.43±0.52
ATS Method 1	4.56±0.99	95	0.23±0.08	5	4.79±0.93
Ontario Hydro Method	4.10±0.21	88	0.56±0.37	12	4.66±0.40
ATS Method 2	4.77	94	0.32	6	5.09
Average					4.99
Standard Deviation (n-1)					0.34

1   Only one sampling run was performed using ATS Method 2.

The average concentration of the mercury in the flue gas at the baghouse inlet for the 2 methods was 5.31±0.25 μg/Nm^3. Because the standard deviation (n-1) of the average for the 2 methods was smaller than the standard deviation of the average of 4 runs for any individual method, we conclude that for all methods tested the reported flue gas concentrations of total mercury were the same within experimental error. This same argument applies to the 4 methods tested at the baghouse outlet where

the average of the measurements was 4.99 " 0.34   g/Nm^3. Also noted is the fact that mercury concentration measurement at the baghouse inlet and at the outlet are in good agreement. (This was not the case in DOE/FETC Study II.)

Since EPA Method 29 has been validated for quantification of total mercury, we further conclude that all methods tested measured total mercury accurately.

Interpretation on how well these methods speciate mercury compounds, based on a comparison of the percent of the total mercury that each method reported as oxidized and elemental mercury, must be done carefully since none of the methods at this point in time had been validated for speciation. The percentages of oxidized mercury at the baghouse inlet were 81 and 85% for EPA Reference Method 29 and ATS Method 1, respectively. The percentages of oxidized mercury at the baghouse outlet were 95, 95, 88 and 94% for EPA Reference Method 29, ATS Method 1, the Ontario-Hydro Method and ATS Method 2, respectively. At this time, we speculated that the concentration values of oxidized mercury were higher for the EPA Reference Method 29 and ATS Method 1 than for the Ontario-Hydro method because of the presence of hydrogen peroxide in their respective oxidized mercury capture solutions. (Although this pattern is only apparent at the baghouse outlet and we have ignored the ATS Method 2 results, it is worth noting since this was more definitively demonstrated in DOE/FETC Study II, results of which can be found in Table 3.3.) EPA Reference Method 29 and ATS Method 1 utilized impingers for the capture of oxidized mercury that contained hydrogen peroxide while the Ontario-Hydro Method did not. Other authors[2] have reported instances where it was believed that EPA Method 29 overestimated the amount of oxidized mercury in flue gas. It was hypothesized that sulfur dioxide present in the flue gas acted in conjunction with the hydrogen peroxide in the impinger solution to oxidize some of the incoming elemental mercury. Thus, we suggest the possibility that the ATS Method 1 may have overestimated the oxidized mercury as EPA Method 29 has been reported to do. Furthermore, since the Ontario-Hydro Method had performed well in laboratory evaluation tests at this time and appeared to have performed well in the field, we tentatively concluded that the Ontario-Hydro Method was giving accurate results while the other two methods were not.

3.3.2.2   Particulate Phase Metals

All sampling trains were identically configured upstream of the first impinger. Since this region contained the heated filter box, it was anticipated that all methodologies would perform similarly with respect to the capture of particulate phase metals. Results confirmed this expectation. Given in Table 3-6 are the concentrations of the particulate phase trace elements for EPA Reference Method 29 and ATS Method 1 measured at the baghouse inlet. (Comparisons between the various methods for measurements taken at the baghouse outlet are not discussed here because of the very low loadings shown in Table 3-4 resulting from concentrations values close to or below the lower detection limits of the respective analytical methods.) All concentration values for the two methods varied by less than 20% in the 0 to 10   g/dscm range and by less than 10% for those greater in concentration than 10   g/dscm with the exception of cadmium and manganese. These variations can be justified by examining Tables 3-12 and 3-13, which present concentration values for the four individual runs for EPA Reference Method 29 and ATS Method 1, respectively. Variations between the four runs (expressed as   -1) were equal to or exceeded the differences between the averages for the two methods. Thus, we concluded that the variation in results between the two methods for particulate phase metals was within the precision of the methods themselves.

3.3.2.3   Vapor Phase Metals

The determination of other vapor phase metals along with mercury was considered advantageous in the development of a mercury speciation methodology for coal-fired boiler flue gas. However, analytical limitations due to specific impinger solutions utilized in all but the EPA Reference Method 29 were shown to be problematic in this study. Graphite Furnace (GF) Atomic Absorption was the analytical method used to determine the most volatile (and also the most toxic trace elements): As, Cd, Pb, Sb and Se. Unfortunately, all the other methods utilized impinger solutions containing high concentrations of either potassium chloride or barium chloride which make GF analysis impossible except, possibly, for selenium. Inductively Coupled Argon Plasma (ICAP) Atomic Emission Spectroscopy was used as an alternative. Although this method provided reliable results, lower detection limits were not achieved as with GF analysis and interferences were always present near the detection limits regardless of the care taken by the analyst.

Table 3-18 gives vapor phase trace metal concentrations at the baghouse inlet as determined by EPA Reference Method 29. The reported presence of vapor phase aluminum and titanium, and probably

manganese, is misleading since these metals and their compounds are refractory materials and have extremely low volatilities. Their presence in the impinger solutions was undoubtably due to their relatively high concentrations in the flue gas resulting in their subsequent breakthrough across the filter medium utilized. All of the supposed volatile trace elements (As, Cd, Pb, Sb, Se and Hg) were either observed to be below the detection limit in all of the four runs or in at least two runs with the exception of selenium. This was not the case, however, with ATS Method 1 as indicated by the information given in Table 3-19. Here, all the volatile trace elements (As, Cd, Pb, Sb, Se and Hg) were reported to be somewhat above the lower detection limits even though the analyses for As, Cd, Pb and Sb were carried out using ICAP which offers considerably higher detection limits. Even the values reported for selenium, where GF was used for both methods, do not compare favorably (9.40 and 20.3   g/dscf for EPA Method 29 and ATS Method 1, respectively).

Results from the Ontario-Hydro Method and ATS Method 1 measurements taken at the baghouse outlet shown in Tables 3-15 and 3-16, respectively, were also not credible. Again, the volatile elements, determined by ICAP, were shown to be above the lower detection limit in contradiction to the EPA Reference Method 29 results utilizing GF.

It must be concluded that the EPA Reference Method 29, which utilizes GF analysis for the volatile elements and is a validated method, produced correct results which contradicted values from the other methods employing ICAP analysis.

We recommend that future work include the more sensitive and more interference-free Hydride Generation (HG) Atomic Absorption Analysis for sampling methods utilizing high ionic strength impinger solutions in order to avoid the limitations of GF analysis.

3.3.3 Conclusions

The following were the conclusions from the DOE/FETC Study I:

C   All mercury speciation methods gave comparable results on total mercury determinations.

C   Use of hydrogen peroxide as an oxidized mercury capture solution either with nitric acid, as in EPA Method 29, or with nitric acid and potassium chloride, as in ATS Method 1, probably causes overestimation of oxidized mercury in the flue gas.

C   As a consequence of the above statement, the Ontario-Hydro Method was the best candidate of the methods tested as a mercury speciation method.

C   All proposed methodologies measure particulate phase trace elements accurately.

C   Mercury, selenium and, perhaps, arsenic were the only vapor phase trace elements present at sufficiently high concentrations in coal-fired boiler flue gas to be considered in the evaluation of the proposed methodologies.

C   The Ontario-Hydro Method and the ATS Method 1 may perform well in the determination of volatile trace elements if a suitable analytical method such as Hydride Generation (HG) Atomic Absorbtion is utilized.

C   ATS Method 2 was considered no further because of analytical difficulties associated with the large amounts of barium sulfate formed as a result of the sulfur dioxide present in the flue gas.

3.4   DOE/FETC STUDY II

A pilot-scale mercury speciation methods comparison study was carried out at the DOE-FETC 500 lb/hr pulverized coal combustion unit located in Pittsburgh, Pennsylvania on July 15, 16, 17, 18 and 19, 1996.

3.4.1 Background and Objectives

The purpose of this study was to compare the performance of EPA Reference Method 29, the Ontario-Hydro Method and ATS Method 1 in not only their capacity to distinguish the chemical forms of mercury in coal flue gas but also in their potential to determine the volatile trace metals and other elements concurrently present. Along with these objectives, our site host (DOE-FETC) sought to characterize the combustion unit *and* the combustion coals utilizing these methodologies. Thus, sampling locations and corresponding methodologies were chosen to accommodate both goals. Sampling was performed on the untreated flue gas at the inlet of the baghouse utilizing EPA Reference Method 29, ATS Method 1 and the Ontario-Hydro Method, and at the outlet of the

baghouse (directly prior to the stack) also using EPA Reference Method 29, ATS Method 1 and the Ontario-Hydro Method. Blacksville coal was burned at the combustor during all four days of testing.

3.4.2   Results and Discussion

A comprehensive report entitled AComparative Method Evaluation for the Assessment of Mercury and Other Metal Air Toxic Emissions from a Pilot-Scale Combustion Unit@ and dated November 1996 was submitted to DOE-FETC. All references in this Section to Tables and Figures refer to that report unless otherwise indicated.

3.4.2.1   Mercury

Given in Table 3.3 of this document are the averages of the four tests performed per method at each of the two sampling locations, the baghouse inlet and the baghouse outlet (the stack). Mercury concentrations were reported for particulate, i.e. the material caught by the filter, and for vapor phase oxidized and elemental mercury as determined by the sampling method. Results from mercury analyses were given in concentration units of micrograms per normal cubic meter (g/Nm^3) with normal referring to dry gas volume at 20 ^{o}C and 760 mm Hg, as well as an adjustment of the values to 3% oxygen concentration in the flue gas. Averages were given with sample standard deviations (average " -1).

Results from samples taken at the baghouse inlet showed good agreement for total mercury with 8.66"0.85, 8.82"1.71 and 8.01"1.69 g/Nm^3 for EPA Method 29, ATS Method 1 and the Ontario-Hydro Method, respectively. However, at the stack there was poor agreement with 5.13"1.18, 7.04"4.80 and 3.10"0.86 g/Nm^3 for EPA Method 29, ATS Method 1 and the Ontario-Hydro Method, respectively.

TABLE 3.3.: JULY 1996 TESTS AT DOE-FETC 500 LB/HR COAL-FIRED COMBUSTOR: AVERAGE MERCURY CONCENTRATIONS IN FLUE GAS WITH STANDARD DEVIATIONS.

Method	Oxidized				Elemental		Total
	Particulate (μg/Nm^3)	Vapor Phase (μg/Nm^3)	Total (μg/Nm^3)	% of total mercury	Vapor Phase (μg/Nm^3)	% of total mercury	(μg/Nm^3)
Baghouse Inlet							
EPA Method 29	2.72±0.80	4.84±0.70	7.56±0.52	87.6±7.4	1.10±0.73	12.4±7.4	8.66±0.85
ATS Method 1	3.04±0.96	5.11±1.85	8.14±1.31	92.7±2.7	0.68±0.40	7.3±2.7	8.82±1.71
Ontario-Hydro Method	3.23±0.94	3.06±1.74	6.29±1.04	78.9±4.1	1.72±0.70	21.1±4.1	8.01±1.69
Average							8.50
Standard Deviation							0.43
Baghouse Outlet (Stack)							
EPA Method 29	0.03	4.87±1.11	4.90±1.14	95.5±1.1	0.23±0.08	4.5±1.1	5.13±1.18
ATS Method 1	0.02	6.83±4.70	6.85±472	96.9±0.8	0.19±0.08	3.1±0.8	7.04±4.80
Ontario-Hydro Method	0.02	2.67±0.78	2.69±0.79	86.8±3.4	0.41±0.13	13.2±3.4	3.10±0.86
Average							5.09
Standard Deviation							1.97

The average concentration of the mercury in the flue gas at the baghouse inlet for the 3 methods was 8.50 ± 0.43 μg/Nm^3. Because the standard deviation of the average for the 3 methods was smaller than the standard deviation of the average of 4 runs for any individual method, we concluded that for all methods tested, the reported flue gas concentrations of total mercury were the same within experimental error. Since EPA Method 29 has been validated for quantification of total mercury, we further concluded that all methods tested measured total mercury accurately.

Although the low average of 5.09 ± 1.97 μg/Nm^3, for the 3 methods at the baghouse outlet can be explained by postulating mercury removal by the baghouse, we have no satisfactory explanation for the inter-method variation in total mercury captured since the method trains were run simultaneously.

Another significant difference in the two sampling locations, apparent from the results, is the fact that at the baghouse inlet substantial amounts of mercury appear in each of the three forms, i.e. particulate, oxidized and elemental, for all three methods. It is not surprising, however, that at the stack there was very little particulate mercury since the baghouse removed most of the particulate from the flue gas stream. Also, there was no significant difference between the reported vapor phase oxidized mercury at the inlet and that at the stack; however, the data suggest that the elemental form appeared to be partially removed by the baghouse.

Interpretation on how well these methods speciate mercury compounds, based on a comparison of the percent of the total mercury that each method reported as oxidized and elemental mercury, must be done carefully since none of the methods had been validated for speciation at the time of these tests. Furthermore, the Blacksville coal used in these tests produced a higher proportion of vapor phase oxidized mercury than vapor phase elemental mercury, and an unusually large amount of mercury was associated with the particulate matter collected from the flue gas. Despite these limitations, an examination of Table 3.3 suggests adverse effects on speciation due to the presence of hydrogen peroxide when used in the oxidized mercury capture solutions. Percent concentrations of oxidized mercury are approximately 88, 93 and 79 % for EPA Method 29, ATS Method 1 and the Ontario-Hydro Method, respectively, at the baghouse inlet and 96, 97 and 87 % again for EPA Method 29, ATS Method 1 and the Ontario-Hydro Method, respectively, at the baghouse outlet. As previously stated, it is believed that EPA

Method 29 overestimates oxidized mercury due to a chemical reaction between the hydrogen peroxide present in the impinger solution with sulfur dioxide present in the flue gas. Reported concentrations of oxidized mercury for EPA Reference Method 29 and ATS Method 1 both showed higher values than for the Ontario-Hydro Method values at the baghouse inlet and at the baghouse outlet. Again, we tentatively concluded that the ratios of oxidized mercury to elemental mercury for the Ontario-Hydro Method were likely to be more accurate than for the two other methods.

3.4.2.2 Particulate Phase Metals

All sampling trains were identically configured upstream of the first impinger. Since this region contained the heated filter box, it was anticipated that all methodologies would perform similarly with respect to the capture of particulate phase metals. Results confirmed this expectation. As seen in the DOE/FETC Study I, variations between the methodologies in the determination of particulate phase trace metals measured at the inlet of the baghouse were less than those between the multiple runs for each of the methodologies. We concluded, therefore, that the variation in results between the methods tested for particulate phase metals was within the precision of the methods themselves.

3.4.2.3 Vapor Phase Metals

As stated in the DOE/FETC Study I, the determination of other vapor phase metals along with mercury was considered advantageous in the development of a mercury speciation methodology for coal-fired boiler flue gas. DOE/FETC Study II confirmed all the findings in the previous study. Although, sufficient improvement in performance of ICAP analysis was achieved such that all volatile trace elements (except As in one case) were reported below the lower detection limit, the relatively high lower detection limits of ICAP for the elements of interest again limited the usefulness of the results. Again, we recommended that future work include the more sensitive and more interference-free Hydride Generation (HG) Atomic Absorption Analysis for sampling methods utilizing high ionic strength impinger solutions such as the Ontario-Hydro Method and ATS Method 1.

3.4.3 Conclusions

The following were the conclusions from the DOE/FETC Study II:

C   All mercury speciation methods give comparable results on total mercury determinations.

C   Use of hydrogen peroxide as an oxidized mercury capture solution either with nitric acid, as in EPA Method 29, or with nitric acid and potassium chloride, as in ATS Method 1, probably causes overestimation of oxidized mercury in the flue gas.

C   As a consequence of the above statement, the Ontario-Hydro Method was the best candidate of the methods tested as a mercury speciation method.

C   All proposed methodologies measured particulate phase trace elements accurately.

C   Mercury, selenium and, perhaps, arsenic were the only vapor phase trace elements present at sufficient concentration in flue gas to permit evaluation of the methodologies being proposed.

C   The Ontario-Hydro Method and ATS Method 1 may perform well in the determination of volatile trace elements if a suitable analytical method such as Hydride Generation (HG) Atomic Absorption was utilized.

3.5   ABB STUDY

A process gas testing program was conducted at the pilot-scale power plant laboratory operated by ABB Combustion Engineering, Inc. at their research facility located in Windsor, Connecticut on May 12 through 16, 1997.

3.5.1 Background and Objectives

The ABB power plant laboratory includes a pulverized coal combustor which has a design maximum firing rate of 300 lb/hr. The flue gases from the combustor are routed through an electrostatic precipitator (ESP) for removal of particulate matter prior to release to the atmosphere.

In this study, ATS provided process gas testing and analytical laboratory services to ABB in support of their in-house engineering project. ATS=s primary contact at ABB was Dr. Srivates Srinivasachar. ATS understood that the primary purpose of the study was to evaluate the effectiveness of injecting pulverized carbon into the flue gas stream as a method for removing vapor-phase mercury from that gas stream. The effectiveness of the carbon injection was quantified by measuring the concentrations and mass flow rates of mercury in the flue gas stream. Flue gas measurements were performed simultaneously at three separate sampling locations using the following two sampling and analytical reference methods:

<   Iodated carbon solid sorbent traps and

<   The Ontario-Hydro Reference Method.

The iodated carbon solid sorbent trap reference method was developed by Frontier Geosciences, Inc. of Seattle, Washington. In short, the sorbent trap is a tube which is packed with iodated carbon. A flue gas sample stream is pulled through the tube using a pump and dry gas metering console; vapor-phase mercury in the sample stream is adsorbed by the carbon. Incidental particulate matter in the sample stream is removed by a quartz fiber plug which is inserted at the tip of the tube. Analysis of the iodated carbon for total vapor-phase mercury catch is performed using cold vapor atomic fluorescence spectroscopy.

A summary of the sampling locations and their positions relative to the carbon injection point is given in Table 3.4.

Table 3.4: SAMPLING LOCATIONS RELATIVE TO CARBON INJECTION		
Sampling Location	**Test Methods Utilized**	**Relative Position**
Inlet No. 1 to ESP	Iodated carbon traps only	Upstream of carbon injection
Inlet No. 2 to ESP	Both	Downstream of carbon injection
Outlet from ESP	Both	Downstream of carbon injection

Flue gas testing was performed during three different power plant laboratory conditions as defined by ABB. A summary of the power plant laboratory conditions is presented in Table 3.5.

Table 3.5: SUMMARY OF THE POWER PLANT LABORATORY CONDITIONS					
Process Condition No.	Test Dates (1997)	Combustor Temperature	No. Of Test Runs Without Carbon Injection	No. Of Test Runs With Carbon Injection	Carbon Injection Rate (g/hr)
1	May 12 & 13	Low	3	3	unknown
2	May 14 & 15	Low	3	3	unknown
3	May 15 & 16	High	3	3	unknown

3.5.2   Results and Discussion

At the request of Dr. Srinivasachar, no formal report was prepared by ATS for either ABB or the U.S. DOE - FETC. The following subsections summarize the major results of the study.

3.5.2.1   Effectiveness of Carbon Injection in Removing Vapor-Phase Mercury in the Flue Gas Stream

Table 3.6 presents a quantitative measure of the effectiveness of carbon injection in removing vapor-phase mercury in the flue gas stream. Average total vapor-phase mercury mass flow rates in units of milligrams per hour (mg/hr) in the flue gas stream as measured using the iodated carbon traps are listed for each power plant laboratory condition. The effectiveness of the carbon injection was quantified by calculating the removal efficiency of vapor-phase mercury in the flue gas stream by the ESP. The results show average removal efficiencies of 52, 16 and 21 percent for Process Condition Nos. 1, 2 and 3, respectively, for conditions in which no carbon is injected into the flue gas stream. In contrast, the results show average removal efficiencies of 99, 90 and 82 percent for Process Condition Nos. 1, 2 and 3, respectively, when carbon is injected into the flue gas stream. In fact, the measurements showed that nearly all of the reduction in the mass flow rate of total vapor-phase mercury occurred prior (i.e., upstream) of the ESP for conditions when carbon was injected into the flue gas stream.

Table 3.6:	QUANTITATIVE MEASURE OF THE EFFECTIVENESS OF CARBON INJECTION IN REMOVING VAPOR-PHASE MERCURY IN THE FLUE GAS STREAM					
	Average Total Vapor-Phase Mercury Mass Flow Rates (mg/hr)					
Process Condition No.	1	1	2	2	3	3
Carbon Injection	No	Yes	No	Yes	No	Yes
Sampling Location						
Inlet No. 1 to ESP *	2.27	2.78	3.02	2.88	5.10	3.91
Inlet No. 2 to ESP **	1.56	0.40	2.99	0.22	4.70	0.60
Outlet from ESP	1.09	< 0.04	2.52	0.28	3.94	0.72
Percent Reduction***	52 %	> 99 %	17 %	90 %	23 %	82 %

*:   Upstream of the carbon injection point
**:   Downstream of the carbon injection point
***:   Percent Reduction = 100 % * (Inlet No. 1 to ESP - Outlet from ESP) / Inlet No. 1 to ESP

3.5.2.2 Comparison of Total Vapor-Phase Mercury Concentrations in the Flue Gas Stream Measured Using Both Reference Test Methods

Where possible, a comparison of the total vapor-phase mercury concentrations in the flue gas stream as measured by both reference test methods was performed. The results of the comparison are presented in Table 3.7. Average total vapor-phase mercury concentrations in units of micrograms per dry standard cubic meter (ug/dscm) in the flue gas stream are listed for each power plant laboratory condition. The comparison was quantified by calculating the relative percent difference (RPD), which is defined as the ratio of the absolute difference between coincident concentrations, that were measured at the same sampling location, to the average of the coincident concentrations that were measured at the same

Table 3.7: COMPARISON OF THE TOTAL VAPOR-PHASE MERCURY CONCENTRATIONS MEASURED BY THE IODATED CARBON TRAPS AND THE ONTARIO - HYDRO REFERENCE METHODS							
		Average Total Vapor-Phase Mercury Concentrations (ug/dscm)					
Process Condition No.		1	1	2	2	3	3
Carbon Injection		No	Yes	No	Yes	No	Yes
Sampling Location	**Reference Test Method**						
Inlet No. 2 to ESP **	**Carbon Traps**	1.18	NA	1.96	NA	3.08	NA
	Ont.-Hydro	0.41	NA	1.43	NA	0.34	NA
	RPD *	97 %	NA	31 %	NA	160 %	NA
Outlet from ESP	**Carbon Traps**	0.56	< 0.02	1.51	0.18	2.56	0.51
	Ont.-Hydro	0.66	< 0.05	1.49	0.18	3.75	0.45
	RPD *	16 %	NA	2 %	2 %	38 %	12 %

*: RPD = Relative Percent Difference = 100 % * (Absolute Value of the Difference) / Average
**: Downstream of the carbon injection point
NA: Not Applicable

sampling location. The results at the Inlet No. 2 to ESP sampling location showed poor agreement between the two reference test methods - the RPDs were 97, 31 and 160 percent for Process Condition Nos. 1, 2 and 3, respectively (no carbon injection). In contrast, the results at the Outlet from ESP sampling location showed an excellent agreement between the two reference test methods - four of the five calculated RPDs were 16 percent or less. ATS submits that the iodated carbon trap reference is best suited for measuring vapor-phase mercury concentrations in Aclean@ (i.e., downstream of the particulate matter control device) flue gas streams.

3.5.3 Conclusions

The following are the conclusions from the ABB Combustion Engineering, Inc. Study:

< The test results showed that injecting pulverized carbon into the flue gas stream upstream of the primary particulate matter control device (ESP) reduced vapor-phase mercury concentrations in the flue gas stream by at least 82 percent for the three different power plant laboratory process conditions;

< A comparison of the measured vapor-phase mercury concentrations in the flue gas stream at the Inlet No. 2 to ESP sampling location showed poor agreement between the iodated carbon trap and the Ontario-Hydro reference methods; and

< A comparison of the measured vapor-phase mercury concentrations in the flue gas stream at the Outlet from ESP sampling location showed an excellent agreement between the iodated carbon trap and the Ontario-Hydro reference methods. ATS submits that the iodated carbon trap reference is best suited for measuring vapor-phase mercury concentrations in Aclean@ (i.e., downstream of the particulate matter control device) flue gas streams.

4.0 CALIBRATION OF A MERCURY INJECTION SYSTEM FOR A PILOT-SCALE COMBUSTION UNIT

A pilot-scale calibration study was carried out to evaluate the capability of a mercury injection system designed to provide known concentration levels of elemental mercury in a coal flue gas stream at the DOE-FETC 500 lb/hr pulverized coal combustion unit located in Pittsburgh, Pennsylvania on December 9, 10, 11 and 12, 1996. A comprehensive report entitled AMercury Injection Calibration for a Pilot-Scale Combustion Unit@ and dated January 9, 1997 has been submitted to DOE-FETC.

Experimental details were presented in that report. Briefly, DOE-FETC personnel passed a stream of nitrogen through a sealed container containing mercury at a temperature specified to provide a known volatility and consequently a known mass transfer to the nitrogen stream. This nitrogen was then injected into the flue gas stream of the combustion unit. This scheme was designed to produce a concentration of 10.0 g/Nm^3 in the flue gas. ATS personnel utilized EPA Method 101A to measure the resulting concentration. Results from the four tests that were carried out are presented in Table 5 of the report. The average concentration was 10.5"2.7 g/Nm^3. This result was considered by both ATS and DOE-FETC to indicate that this injection system was very accurate and reliable.

5.0 VOLATILE ORGANIC COMPOUNDS FIELD SAMPLING STUDY

A pilot-scale comparative study was carried out to evaluate methods for quantifying volatile organic compounds (VOCs) in coal-fired boiler flue gas at the DOE-FETC 500 lb/hr pulverized coal combustion unit located in Pittsburgh, Pennsylvania on November 14, 15 and 16, 1995. A comprehensive report entitled AComparative Method Evaluation for the Assessment of Organic Air Toxic Emissions from a Pilot-Scale Combustion Unit@ and dated March 7, 1996 has been submitted to DOE-FETC.

This work utilized the EPA Volatile Organic Sampling Train (VOST) in conjunction with an online Gas Chromatograph (GC). Although the VOST is a validated, accepted sampling and analytical methodology, it does not provide real-time results since each sample requires 1 to 2 hours to collect and additional time is required for subsequent laboratory analysis. On the other hand, GC methods could provide almost real-time, continuous measurements since only about 1 minute is required to collect a sample and 2 to 4 minutes are required for analysis.

Experimental details were provided in the report. The target compounds of interest, benzene and toluene, were below the lower detection limit for the GC as it was configured. The more sensitive VOST analyses confirmed this by showing very low levels of the compounds of interest. Although, the specific online GC configuration utilized failed due to insufficient sensitivity, greater sensitivity could easily be attained through various concentration techniques that could be built into a similar configuration. We recommend this approach for future work.

6.0 REFERENCES

1. <u>Southern Research Institute Emission Report: Comprehensive Assessment of Air Toxic Emissions, Draft Final Report Paradise Fossil Plant</u>, SRI-ENV-95-338-7960, Southern Research Institute, Birmingham, 1995, pp. A7-A8.

2. D. L. Laudal, K. C. Galbreath and M. K. Heidt, AA State-of-the-Art Review of Flue Gas Mercury Speciation Methods,@ EPRI Report No. TR-107080, prepared for the Electric Power Research Institute, Palo Alto, CA and for the Federal Energy Technology Center, Pittsburgh, PA, October 1996.