The Development of Iodine Based Impinger Solutions for the Efficient Capture of Hg⁰ Using Direct Injection Nebulization—Inductively Coupled Plasma Mass Spectrometry Analysis

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Inductively coupled plasma mass spectrometry (ICP/MS) with direct injection nebulization (DIN) was used to evaluate novel impinger solution compositions capable of capturing elemental mercury (Hg⁰) in EPA Method 5 type sampling. An iodine based impinger solution proved to be very efficient for Hg⁰ capture and was amenable to direct analysis by DIN-ICP/MS. Hg⁰ capture efficiency using aqueous iodine (I_3^-) was comparable to Hg⁰ capture using acidified potassium permanganate impinger solutions which were analyzed by cold vapor atomic absorption spectrometry (CVAAS), with greater than 98% capture of Hg⁰ in the first oxidizing impinger. Using DIN-ICP/MS, it was demonstrated for the first time that iodine can be generated just prior to impinger sampling for efficiently oxidizing Hg⁰ and retaining it in solution as HgI_4^{2-}. Due to the increased interest in Hg speciation from combustion sources and the potential for using DIN-ICP/MS for multiple metals analyses, an impinger sampling train for gaseous Hg speciation and multiple metals analyses using DIN-ICP/MS analyses is presented. The unique feature of such a sampling train is that each impinger solution in the series is amenable to direct analysis by DIN-ICP/MS. A bituminous coal was combusted in a bench scale coal system, and gaseous Hg species (oxidized and elemental) were determined using the proposed impinger train. The DIN-ICP/MS instrumental detection limit was 0.003 ppb, and MDLs ranged from 0.007 to 0.116 μg/L (ppb) in a variety of impinger solutions used for Hg capture.

Introduction

Mercury is a persistent bioaccumulative toxin (*1*). It is persistent in that it cannot be destroyed. Once it is introduced into an ecosystem, it stays and it bioaccumulates in the food chain. In the aquatic environment microbial action converts it to its most toxic form to humans, methylmercury. Fish may have Hg concentrations 1−6 million times higher than the surrounding water (*2*). The toxicity of methylmercury to humans, especially children and developing fetuses, is irreversible neurological damage, although Hg also has been linked to autoimmune disorders, hypertension, and cardiovascular disease (*3−5*). The U.S. Environmental Protection Agency (U.S. EPA) 1997 *Mercury Study Report to Congress* clearly supports the link between atmospheric deposition of Hg and contaminated fish (*6*). Coal utilities are the primary source of anthropogenic atmospheric Hg and have remained the last large unregulated source of Hg emissions (*7−9*). A report by the National Academy of Sciences on the science used by the U.S. EPA for establishing methylmercury toxicity was the final report required by Congress to convince lawmakers of the need to regulate Hg emissions from coal utilities (*10*).

Mercury from coal utilities is difficult to control since it eludes capture by most conventional air pollution control devices (APCDs). To develop effective APCDs it is important to know the Hg species emitted and the species transformations that may occur. Currently it is known that all the Hg in coal is converted to the elemental form (Hg⁰) in the high-temperature combustion zone and that oxidation may occur as the combustion gases cool and Hg⁰ interacts with constituent gases and particulate matter in the gas stream (*11−13*). Hg⁰ is the most difficult to capture and is involved in long-range transport and deposition. To determine the Hg species in stack gases, U.S. EPA Method 5 type sampling is used (*14*). Speciation is achieved by selective, sequential capture of the mercury in a series of impinger solutions. Current speciation methods all rely on capture of gaseous oxidized Hg in the first few impinger solutions and removal of reducing gases such as SO₂ prior to capture of Hg⁰ by oxidation in an acidified potassium permanganate solution. Once in solution, the analytical step is to convert all Hg species to Hg²⁺ followed by reduction of the Hg²⁺ species to Hg⁰ which is bubbled out of solution and detected in a dry, inert gas stream at 253.7 nm. This analytical technique is called cold vapor atomic absorption spectrometry (CVAAS).

The methods outlined in Table 1 have been or are currently used for Hg determination in coal combustion stack gases. The Ontario Hydro and the tris(hydroxymethyl)aminomethane (Tris) buffer methods have been most extensively tested and are the most promising for accurate Hg speciation (*15−17*). The limitations of these methods are that for some of these solutions there is tedious sample preparation required to ready the solution for CVAAS since all Hg species must be oxidized (Hg²⁺) and unbound. Strong ligands and organics directly interfere with analysis by CVAAS. Another limitation is that there are no methods that permit Hg speciation and multiple metals analyses. Solutions such as 1 N KCl and acidified potassium permanganate used for oxidized and elemental Hg capture, respectively, are not amenable to low-level metals techniques such as ICP-MS. The acidified hydrogen peroxide and the tris solutions are the only solutions in any of the methods in Table 1 that are completely amenable to direct analysis by ICP-MS.

The goals of this research were to (1) evaluate and select an impinger solution capable of capturing oxidized Hg that also would be amenable to direct analysis by DIN-ICP/MS, (2) develop an impinger solution to capture Hg⁰ that would be amenable to DIN-ICP/MS (since 4% KMnO₄/10% H₂SO₄ used by all sampling methods is not directly amenable to

TABLE 1. Stack Gas Emissions Sampling Methods for Mercury Determination[a]

Total Hg	Total Hg + Hg Speciation	Multiple Metals + Total Hg	Multiple Metals + Hg Speciation
EPA Method 101A[1]	*Tris Buffer Method*[2]	*EPA Method 29*[4]	None
•3 impingers of 4% $KMnO_4$/10% H_2SO_4	•2 impingers of 1.0 M tris + 2 impingers of 4% $KMnO_4$/10% H_2SO_4	•2 impingers of 5%HNO_3/10%H_2O_2 + 2 impingers of 4% $KMnO_4$/10% H_2SO_4	
	Ontario Hydro Method[3]		
	•3 impingers of 1 N KCl + 1 impinger of 5%HNO_3/10%H_2O_2 + 3 impingers of 4% $KMnO_4$/10% H_2SO_4		

[a] Key: 1, U.S. EPA Method 101A, determination of particulate and gaseous mercury emissions from sewage sludge incinerators. 2, Tris Buffer Method developed by Radian International Corporation. 3, Ontario Hydro Method, standard test method for elemental, oxidized, particle-bound, and total mercury in flue gas generated from coal-fired stationary sources. 4, U.S. EPA Method 29, determination of metals emissions from stationary sources.

DIN-ICP/MS), (3) develop an EPA Method 5 type sampling train for low-level Hg speciation that would be completely amenable to DIN-ICP/MS, and (4) to test the proposed impingers for Hg speciation against the Ontario Hydro Method in the bench scale combustion of an Ohio bituminous coal. The Ontario Hydro Method was chosen as the benchmark method because it has been extensively evaluated and reported in the literature.

Experimental Section

The DIN-ICP/MS was optimized for Hg analysis. A Hg^0 vapor generation system was built to entrain Hg^0 in a stream of air that was bubbled through a series of impinger solutions. Using the Ontario Hydro Method impinger train as the benchmark method, test impingers were evaluated for efficiency of capture and total mass captured. Percent efficiency of Hg^0 capture is defined as the ratio of the mass of Hg^0 captured in the first oxidizing impinger divided by the total mass of Hg^0 captured in all of the oxidizing impingers multiplied by 100. A novel technique to generate aqueous iodine was developed to capture Hg^0. A series of impinger solutions was devised and tested in parallel against the Ontario Hydro Method for total Hg and Hg speciation in the gaseous emissions from combustion of a bituminous coal.

Inductively Coupled Plasma Mass Spectrometry Analysis. ICP/MS is an ideal detector for Hg since ^{202}Hg is a perfectly clean mass with no isobaric or polyatomic interferences; however, long wash-out times and high detection limits (compared to CVAAS) made ICP/MS an unattractive technique for Hg analysis for many years. To overcome the problems of memory effects and high detection limits common with conventional liquid nebulization and desolvation using a spray chamber, many researchers have used cold vapor generation methods followed by introduction of Hg^0 to the plasma. ICP-MS detection can be superior to CVAAS since problematic spectral interferences from organics, water vapor, or chlorine gas are not a problem in ICP-MS detection. However, the sample preparation requirements and challenges are the same as for CVAAS since all Hg compounds must be oxidized to Hg^{2+} and in solution so that chemical reduction to Hg^0 is possible. An advance in sample introduction to ICP/MS for high memory elements such as Hg was the direct injection nebulizer (18−22). In this technique the entire liquid sample, versus a fraction of the sample aerosol, is injected directly into the plasma. Using DIN-ICP/MS, Hg can be organically bound or bound to strong ligands. Solutions such as tris+EDTA and hydrogen peroxide are easily analyzed by DIN-ICP/MS with no sample prepara-

TABLE 2. DIN-ICP/MS Conditions

Instrument

VG-Elemental PQ-3 ICP/MS equipped with a 27.12 MHz solid state RF generator

Forward Power - 1400 Watts

Coolant Flow Rate - 13 L/min

Auxiliary Flow Rate - 0.55 L/min

Nebulizer Flow Rate - 0.3 L/min

Detector Mode - pulse counting, ^{202}Hg

Acquisition - peak jumping, 3 points/peak, 45 or 90 second acquisitions

Dwell Time - 10.24 ms

Internal Standards - ^{185}Rhenium (Re), ^{193}Iridium (Ir)

DIN Nebulizer Pressure (variable) - 75-80 psi

DIN Gas Displacement Pump Pressure (variable) - 188-215 psi

Sample Delivery Flowrate (variable) - 40-50 μL/min

Platinum tipped sampling cone, nickel skimmer cone

tion other than the addition of internal standards. The benefits of using DIN-ICP/MS are high sensitivity, low required sample volume, speed of analysis, simple sample preparation, and the added benefit of being able to perform multiple metals analyses on the same solutions if desired. Limitations of ICP-MS are low tolerance for high dissolved solids and high salt matrices.

A VG Elemental PQ-3 ICP/MS (Thermo Optek Corp, Franklin, MA) was used with a Cetac direct injection nebulizer (DIN) (Cetac Technologies, Omaha, Nebraska). The DIN consisted of a high-pressure gas displacement pump for delivering liquid sample to a microconcentric type nebulizer (23). Alternatively, for some of the work, sample was delivered to the nebulizer using a Dionex microbore liquid chromatographic pump fitted with an inert pump head and PEEK tubing (Dionex Corp., Sunnyvale, CA). DIN-ICP/MS operating conditions are listed in Table 2.

A 500 μL Tefzel sample loop was used to produce 11−12 min of a steady-state signal for Hg. All analyzed solutions in this work were in the range of 0.05−3 ppb. Samples often required dilution to stay within this range. Daily calibration using five standards from 0.05 ppb to 2 or 3 ppb yielded correlation coefficients of 0.999 or better and slopes of approximately 1000−1400 counts/ppb. Standards were prepared in 2% HNO_3/1% HCl using ^{185}Re and ^{193}Ir as internal standards. New matrices were assessed for contamination and spike recovery. Spike recovery was determined by adding 1.0 ppb Hg^{2+} to the blank matrix (impinger solution). Acceptable recoveries were between 85 and 115% for iodine impinger solutions and 90−110% for hydrogen peroxide solutions.

All chemicals were ACS reagent grade or better. Water was distilled, deionized, and passed through a Waters Milli-Q system for final purification. Cleaning of glassware consisted of soaking and scrubbing with laboratory grade soap, rinsing with tap water, soaking in a mixed acid bath of 10% HNO_3 + 20% HCl, followed by rinsing with distilled deionized water, and drying at 100 °C in an oven.

Cold Vapor Atomic Absorption Analysis. Cold vapor generation techniques are rapid, simple, and sensitive. For CVAAS to perform well, however, Hg must be present in solution unbound as the Hg^{2+} ion. The sample must not contain strong oxidants or ligands that could interfere with the reduction of Hg^{2+} to Hg^0 or contain volatile organics that interfere spectrally. These conditions require samples to be acid digested if high organic content is suspected and neutralized if strong oxidants are present (24). The acidified
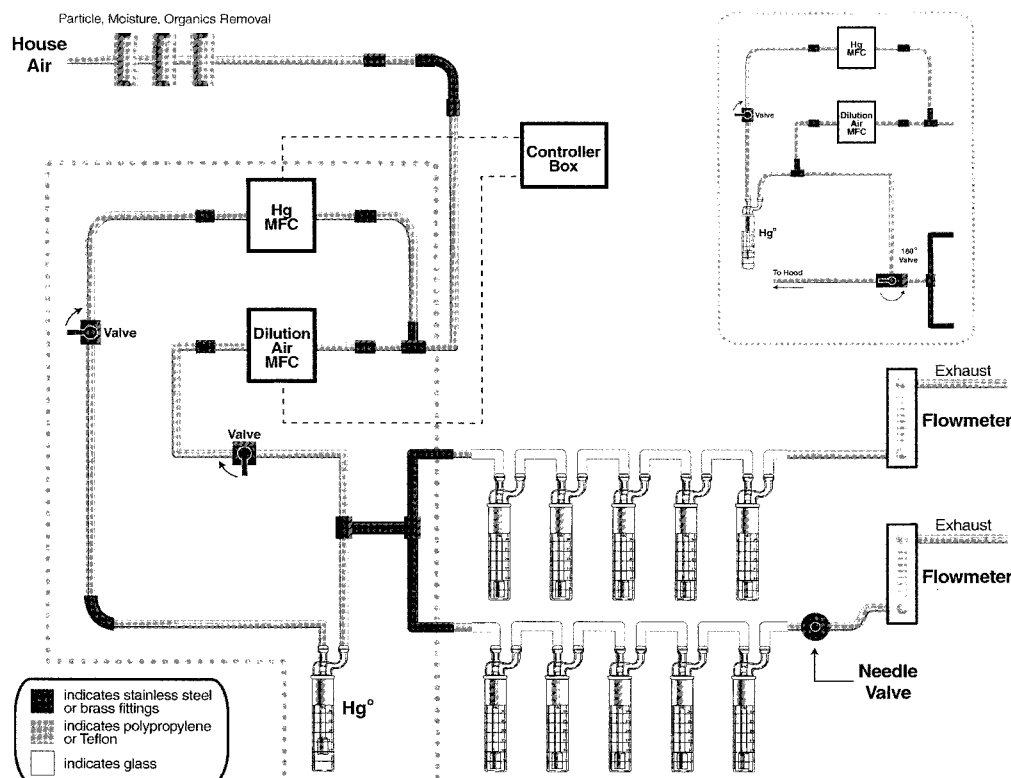
FIGURE 1. Schematic of Hg vapor generation system.

hydrogen peroxide, used in three of the four coal combustion emissions sampling methods listed in Table 1, is particularly difficult to analyze by CVAAS since the hydrogen peroxide requires a tedious and time-consuming neutralization. The solution, 1.0 M tris(hydroxymethyl)aminomethane (tris) + ethylenediaminetetraacetic acid (EDTA), used for capture of oxidized Hg in the Tris Buffer Method, requires that the tris+EDTA be preserved and oxidized using hydrogen peroxide and acid, making analysis of the tris+EDTA equally time-consuming to analyze by CVAAS. Strong ligands, such as iodide, directly interfere with Hg analysis by CVAAS. Research in the late 1960s using iodine monochloride (ICl) for the capture of organic and inorganic Hg compounds in air halted primarily due to the inability of CVAAS methods to work in the presence of iodide (25).

An automated LDC Analytical Mercury Module (Thermo Separation Products, Riviera Beach, FL) was used for CVAAS analyses. Calibration was performed daily using the same standards and quality control procedures as used for DIN-ICP/MS. Spike recoveries were acceptable at 90–110% for acidified potassium permanganate and 1 N KCl. The reducing solution consisted of 5% stannous chloride, 3% sodium chloride, and 10% sulfuric acid. The potassium permanganate solutions were neutralized with 50% aqueous hydroxylamine.

Hg Vapor Generation System. Compressed house air (HEPA filtered, purified by a 75-62 FT-IR purge gas generator, Balston Filter Products) was passed above liquid Hg⁰ contained in an impinger bottle at room temperature and mixed with dilution air prior to the gas stream being split and passed through a series of three to five impinger bottles (Figure 1). Twenty-five milliliter Midget bubblers (Ace Glass, Louisville, KY) with sintered glass filter tips were used with 15 mL of test solution in each bottle. Air (0.12 lpm) was passed over the liquid Hg and combined with 1.88 lpm dilution air at a t-connection before being split into two streams of 1.0 L per stream. Mass flow controllers (MKS Mass-Flo Controller, MKS Instruments, Inc.) were used to regulate the air flow,

and flow meters were used to regulate the flow at the outlet of the impingers. A modification was made to the system mid-way through this project that improved precision between split streams and is indicated in the Figure 1 insert. Installation of a bypass valve made it possible to purge the Hg vapor that accumulated/concentrated above the liquid Hg between runs and permitted the air flow through the impinger bottles to be balanced using Hg-free air before Hg⁰ was introduced. Once the flow was balanced at 0.94 Lpm/stream, the Hg⁰-containing air was added bringing the total flow rate to 1.0 L/min per stream. Total sampling time was always 20 min. These conditions resulted in a final Hg⁰ concentration of 100–150 μg Hg/m³, which resulted in a first Hg⁰ capture impinger concentration that was approximately 100–200 ppb. For most impinger experiments, one stream of the split stream was in the Ontario Hydro Method configuration so that total Hg captured could be compared to total Hg captured in the test impinger stream. The only modification to the Ontario Hydro Method was that 0.4% KMnO₄ was used instead of 4% KMnO₄. This was confirmed to have no detrimental effect on Hg capture since there were no reducing gases present, i.e., SO₂, in the gas stream to consume the permanganate. Blank air (no Hg⁰ introduced into the system) was routinely sampled using test impinger solutions to assess contamination which was always negligible.

Coal Combustion System. The system consisted of a screw coal-feeder, a tubular reactor, a Mark III cascade impactor, and a sample collection system (26). A pulverized Ohio, bituminous coal, with a mean particle size of 50 μm, was fed into the reactor by the screw coal feeder (Figure 2). The coal was entrained in a compressed air stream and carried into the alumina tubular reactor, which was 91 cm long, 2.54 cm inside diameter, and electrically heated. At the end of the reactor, a dilution apparatus was designed and constructed to introduce particle free nitrogen into the reactor. The nitrogen gas quenched the aerosol dynamics and chemical
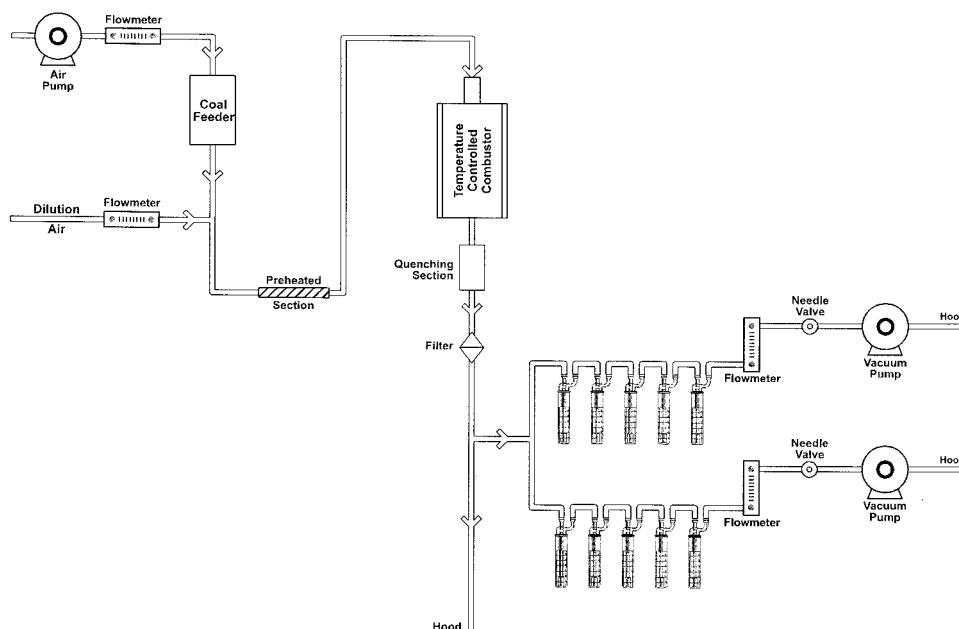
FIGURE 2. Bench scale coal combustor with impinger sampling.

Results And Discussion

reactions. A filter assembly was installed after the quenching section to remove particulate matter. A volume of the exiting gas stream was sampled using vacuum pumps attached to the outlet of two parallel impinger trains containing five impinger bottles per stream. Rotameters were installed at the vacuum pumps to control flow to 1 lpm per impinger stream. Sampling time was 60 min in all experiments.

Optimization of the DIN-ICP/MS. Initial work focused on choice of internal standards, short and long term stability, method detection limits (MDLs), and determination of blank concentrations. Hg, with seven isotopes, is an ideal element for an isotope dilution technique; however, it does add substantial expense to a method. We demonstrate here that the use of carefully selected internal standards yielded more than adequate precision for the effects we were observing. Ideally, internal standards should have a similar ionization potential (IP) and mass-to-charge ratio as the analyte of interest and be mono-isotopic. The IP for Hg is 10.4 eV. Initially, bismuth ([209]Bi, IP = 7.3), platinum ([195]Pt, IP = 9.0), and gold ([197]Au, IP = 9.2) were evaluated as internal standards. Bismuth worked well in ideal solutions but was ruled out because it is a volatile metal in coal. Platinum worked well in ideal solutions but had to be abandoned when a platinum tipped sampling cone was installed. A Pt tipped sampling cone was installed so that oxygen could be added to the nebulizing gas to combust organics. Gold is monoisotopic and has a high IP so it was thought that it would be a good internal standard. Gold, however, is also a strong ligand for Hg which might explain why the ratio Au/Hg was not always consistent. Hg contamination was particularly high in Au standards. For those reasons Au was not used as an internal standard. Rhenium ([185]Re, IP = 7.88) has been used by other researchers and was tested along with iridium ([193]Ir, IP = 9.1). Both gave acceptable results and were used in subsequent work.

Short- and long-term stabilities were evaluated by monitoring [202]Hg, [185]Re, and [193]Ir in a 2% HNO₃/1% HCl for 10 min and for 3 h, respectively. As a prerequisite for daily operation it was decided that short-term stabilities should be less than 2% RSD for 10 60-s acquisitions. For short-term stability a plot of normalized integrated counts for Hg, Re, and Ir versus time revealed a definite slope toward increasing signal, but

the short term precision criterion was acceptable (<2% RSD). However, when the relative response of Hg to Re and Ir was plotted as a function of time (Figure 3A), statistical analyses of the slopes of the internal-standard-corrected-Hg-response indicated that the slopes were not significantly different from zero at α = 0.01. Similarly, Figure 3B is a plot of 3 h stability determined by spacing four 10-min stability injections over the course of 3 h. The slope for the Ir:Hg relative response was significant at α = 0.01; however, the Durbin–Watson statistic did not indicate a time series trend. Relative percent standard deviation of the counts for each isotope was less than 2% over 3 h and % RSDs for the ratio of IS/Hg were also less than 2% over the 3 h.

Once iodine solution chemistry was developed for Hg⁰ capture, a thorough investigation was undertaken to ascertain the maximum KI concentration that could be introduced into the plasma since concomitant salts suppress element ionization (*27, 28*). Ten ppb Hg and Ir and 1 ppb Re were added to 2% HCl solutions of varying KI concentration and analyzed for three 15-s integrations. The ratio of internal standard (IS) response to Hg response was plotted (Figure 4A). From 0.0001 to 0.001 M KI, the Hg signal was low causing the ratio of IS/Hg to be high. As the KI concentration was increased the Hg signal increased, causing the IS/Hg ratio to decrease. At approximately 0.005 M KI the Hg response mirrored the responses observed for the internal standards. This phenomenon of decreasing IS/Hg ratio with increasing KI concentration to approximately 0.001 M KI is believed to be due to the formation of HgI₂ since HgI₂ has a low solubility in dilute KI solutions. As the KI concentration was increased, the HgI₂ may have been solubilized as HgI₄²⁻, causing an increase in the Hg response thus a decreasing IS/Hg ratio response. From 0.005 M KI to 0.10 M KI, the IS/Hg ratio stabilized. Figure 4B is a plot of relative Hg response versus KI concentration from 0.005 to 0.10 M KI. The slopes of the lines are not equal to zero, the ideal case for internal standardization, yet the results are acceptable, with ratios of IS/Hg at 0.1 M KI between 82 and 90% of the ratios at 0.005 M KI. At 0.05 M KI, suppression of the internal standards was approximately 50%. Since ionization suppression increases detection limits, it was estimated that 0.005 M was the lowest KI concentration that could be used to minimize signal suppression, while maintaining HgI₂ soluble as HgI₄²⁻.
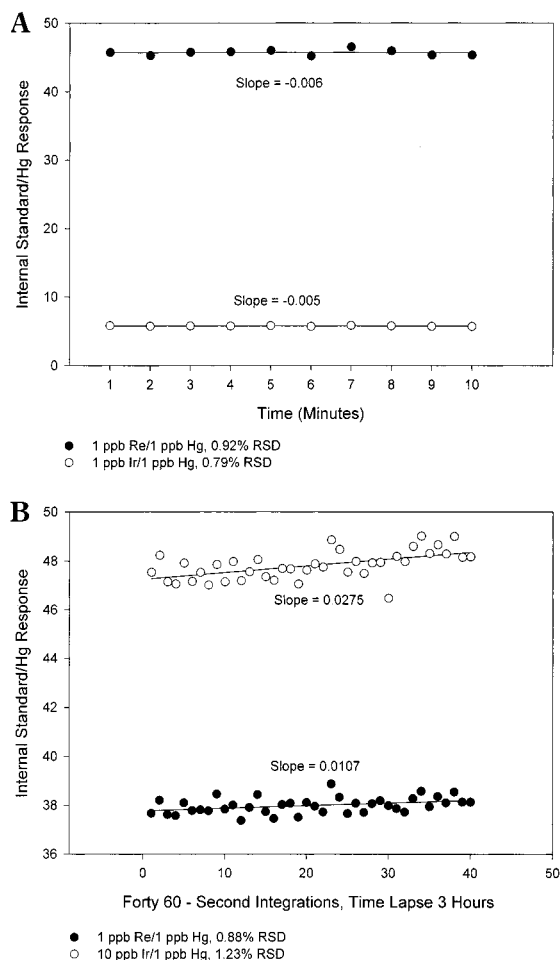
FIGURE 3. (A) Short term stability drift correction with internal standards. (B) Three hour stability drift correction with internal standards.

FIGURE 4. A. Hg response relative to internal standards (0.0001–0.10 M KI in 2% HCl). B. Hg response relative to internal standards (0.005–0.10 M KI in 2% HCl).

TABLE 3. EPA Method Detection Limits

matrix	typical blank concn (ppb)	MDL (ppb)
2% HNO_3/1% HCl[a]	0.010	0.007
10% H_2O_2/2% HNO_3[a]	<0.010	0.034
0.2% HI	0.100	0.019
0.005 N KI/1% HCl[a]	0.025	0.087
1.0 M Tris buffer[a]	<0.010	0.116
1 N KCl[b]	<0.010	0.022
4% $KMnO_4$/10% H_2SO_4[b]	0.055	0.044

[a] DIN-ICP/MS. [b] CVAAS.

Method detection limits and blank concentrations were determined for a variety of solution matrices used for Hg^0 capture. Table 3 contains EPA MDLs (*29*) and typical measured blank concentrations calculated by calibration in 2% HNO_3/1% HCl. The EPA's definition of MDL is the minimum concentration of an analyte detectable in a given matrix with 99% confidence that the concentration is greater than zero.

Impinger Solution Studies. The Hg vapor generation system in this work did not permit the accurate calculation of Hg concentration using the vapor pressure of Hg^0 and temperature. Instead, Hg^0 was determined directly by measuring the mass captured in impinger solutions at the outlet of the system. Impinger-based methods that were evaluated were EPA Method 101A (*30*), the Ontario Hydro Method (*16*), EPA Method 29 (*31*), and a method used by University of Cincinnati researchers (*32*). The first three rows of data in Table 4 summarize the results. Note that all impinger schemes yielded similar results for total Hg with acceptable precision. The Ontario Hydro method impinger scheme was chosen as the benchmark method for comparison of test impingers. To obtain the best comparisons possible, the flow from the Hg vapor generation system was split into two streams (Figure 1). Typically, one stream contained the Ontario Hydro Method impingers, and the other stream was the test stream. Total mass captured in a test stream was then compared to total Hg captured in the Ontario Hydro impinger stream. In addition to total mass captured, an important point of comparison was the ef-
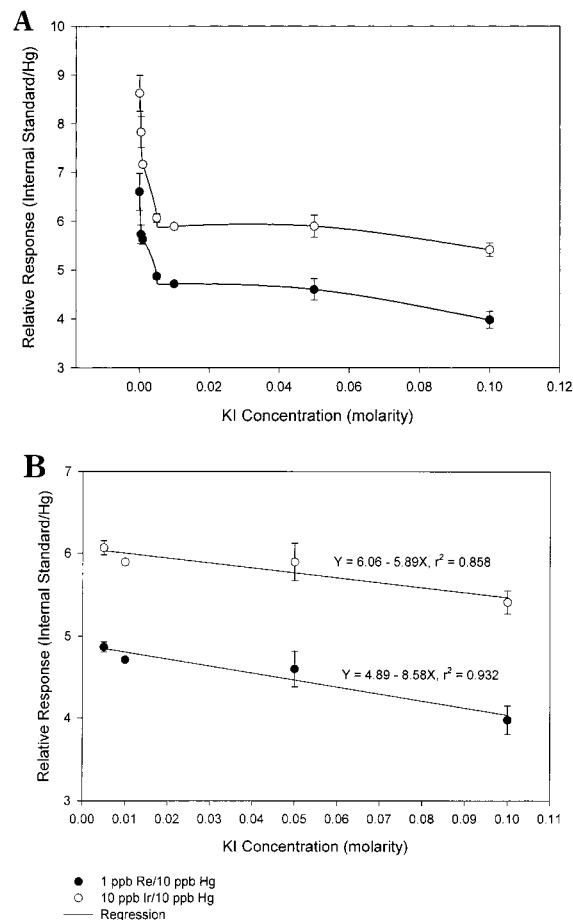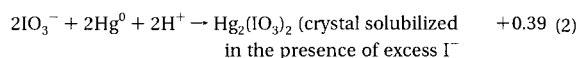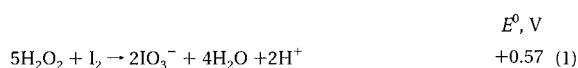
ficiency of capture in the *first* impinger designed to capture elemental Hg. Ninety-eight percent (98%) or greater capture of total Hg in the first impinger designed to capture Hg^0 would indicate that the chemical reaction was thermodynamically favored and *not* rate limited. The first oxidizing impinger varies in the order of appearance in Table 4. For example, Method 101A for total Hg determination has the first impinger containing acidified potassium permanganate designated for Hg^0 capture, whereas the first oxidizing impinger in the Ontario Hydro Method is the fourth one. An example of inefficient capture is seen with the use of chloric acid. Chloric acid was examined based on results from the literature (*33*). There was between 24% and 32% oxidation of Hg^0 in the first chloric acid impinger (Table 4, row 6). The second chloric acid impinger captured approximately 20% of the Hg and the backup impinger of acidified permanganate captured most of the Hg. Under the conditions in this work, chloric acid did not appear to be very efficient for Hg^0 capture.

TABLE 4. Various Impinger Solutions for Hg⁰ Capture[a]

Row#	Method Type		Impinger[2] 1	2	3	4	5	Total Hg Avg (µg)	N (Runs)	%RSD[3]
1	EPA Method 101A	Solution	0.4%KMnO₄ 10%H₂SO₄	0.4%KMnO₄ 10%H₂SO₄	0.4%KMnO₄ 10%H₂SO₄	0.4%KMnO₄ 10%H₂SO₄		2.29	4	6.9
		%Hg Captured	>99	<0.5	<0.5	ND				
2	Ontario Hydro[4]	Solution	1 N KCl	1 N KCl	10%H₂O₂ 5% HNO₃	0.4%KMnO₄ 10%H₂SO₄	0.4%KMnO₄ 10%H₂SO₄	2.93	4	1.1
		%Hg Captured	0.1-0.5	0.04-0.4	1-1.5	98-99	<0.1			
3	EPA Method 29	Solution	10%H₂O₂ 5%HNO₃	0.4%KMnO₄ 10%H₂SO₄	0.4%KMnO₄ 10%H₂SO₄	0.4%KMnO₄ 10%H₂SO₄	0.4%KMnO₄ 10%H₂SO₄	2.49	2	7.1
		%Hg Captured	2.9	96	<0.6	<0.02	<0.02			
4	Wu, et al.[5]	Solution	1% HNO₃	0.4%KMnO₄ 10%H₂SO₄	0.4%KMnO₄ 10%H₂SO₄	0.4%KMnO₄ 10%H₂SO₄	0.4%KMnO₄ 10%H₂SO₄	2.36	2	2.4
		%Hg Captured	0.59	99.4	<0.02	<0.02	<0.02			
5	10% Chloric acid	Solution	1N KCl	10%H₂O₂ 5%HNO₃	10% ClO₃	10% ClO₃	0.4%KMnO₄ 10%H₂SO₄	2.59	2	2.4
		%Hg Captured	<0.3	<0.01	31.7	22	46			
6	20% Chloric acid	Solution	1N KCl	10%H₂O₂ 5%HNO₃	20% ClO₃	20% ClO₃	0.4%KMnO₄ 10%H₂SO₄	1.96	2	10.3
		%Hg Captured	<0.2	<0.6	24	17	57			

[a] Key: 1, test conditions: Hg vapor generation system at room temperature, 24−27 °C. Hg vapor air flow, 0.06 L/min. Dilution air flow, 0.940 L/min. Total air flow through impingers, 1.0 L/min, temperature not controlled. 2, Twenty-five milliliter glass Midget bubblers with sintered glass filter tips (A- porosity, Ace Glass). Fifteen milliliters of test solution per impinger. 3, Percent relative standard deviation for $N \geq 3$, relative percent difference for $N = 2$ for total Hg captured. 4, Modifified by using 0.4% permanganate solution with no detriment to Hg capture efficiency. 5, Ref 32.

Iodine Impinger Solution Studies. The research presented in this section focuses on the use of iodine based impinger solutions for capture of Hg⁰ since iodide is a very strong ligand for Hg²⁺. Aqueous potassium iodide was initially chosen as a candidate for capture of oxidized Hg because of the high formation constant and low vapor pressure of HgI₂; however, significant capture of Hg⁰ was observed using a 1.0 N KI solution. In the first row of data in Table 5, note that ∼70% of Hg⁰ was captured in the first two 1 N KI impinger solutions. The percent of Hg⁰ captured in the first KI impinger increased to 96% when the KI impingers were used downstream of an acidified hydrogen peroxide impinger (Table 5, row 2). When the KI was acidified *and* followed a hydrogen peroxide impinger, capture of Hg⁰ increased to 99% in the first KI impinger (Table 5, row 3). Several mechanisms for Hg⁰ capture were hypothesized: (1) was iodate (about 3 ppm IO₃⁻ by the manufacturer's assay) in the KI solutions oxidizing the Hg⁰, with an increase of IO₃⁻ arising from the carryover of peroxide to the KI impingers (oxidization of I₂ to IO₃⁻ according to eq 1), (2) was iodine monochloride (ICl) being formed by reaction of excess iodide with HCl in the presence of trace IO₃⁻ with subsequent oxidation of Hg⁰, or (3) was iodine, present at varying concentrations in all KI solutions, oxidizing Hg⁰?

$$5H_2O_2 + I_2 \rightarrow 2IO_3^- + 4H_2O + 2H^+ \qquad +0.57 \quad (1)$$

$$2IO_3^- + 2Hg^0 + 2H^+ \rightarrow Hg_2(IO_3)_2 \text{ (crystal solubilized} \qquad +0.39 \quad (2)$$
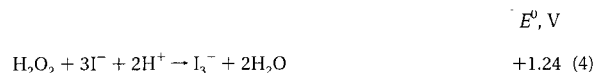$$\text{in the presence of excess } I^-$$

It was noted that capture efficiency always increased when the KI impinger followed a hydrogen peroxide impinger whether or not the KI was acidified with HCl, indicating that ICl was *not* being formed since HCl was absent in these experiments. To test if IO₃⁻ was oxidizing Hg⁰, according to eq 2, acidified KIO₃ was placed as the first impinger (row 11 of Table 5). Capture efficiency was only 27% in the first impinger of acidified KIO₃. Therefore, it was concluded that

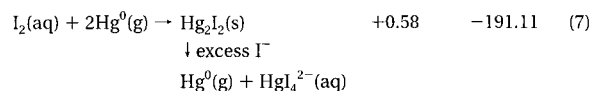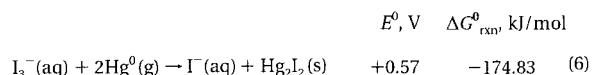iodate oxidation of Hg⁰ was not occurring, or did not occur at a practical rate.

UV scans of KI solutions that followed peroxide impingers revealed large absorption peaks at 290 and 350 nm. Absorption at these wavelengths is indicative of triiodide ion (I₃⁻). According to the well-known Dushman reaction (eq 3), iodate acts as an oxidant of iodide in the presence of acid to form triiodide.

$$IO_3^- + 8I^- + 6H^+ \rightarrow 3I_3^- + 3H_2O \quad \text{Dushman reaction} \qquad (3)$$
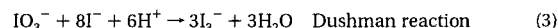
Triiodide is dissolved iodine (I₂), taking the form I₂−I in solution. Iodine, then, could be present at varying concentrations in 1 N KI solutions (due to O₂ oxidation of I⁻), acidified KI solutions containing trace amounts of iodate (the Dushman reaction), and in 1 N KI impinger solutions that followed acidified hydrogen peroxide impingers, formed according to the following proposed reactions (eqs 4 and 5):

$$\qquad\qquad\qquad\qquad E^0, V$$

$$H_2O_2 + 3I^- + 2H^+ \rightarrow I_3^- + 2H_2O \qquad\qquad +1.24 \quad (4)$$

$$H_2O_2 + 2I^- + 2H^+ \rightarrow I_2 + 2H_2O \qquad\qquad +1.23 \quad (5)$$

Possible reactions of iodine with Hg⁰ in solution are proposed in eqs 6 and 7:

$$\qquad\qquad\qquad E^0, V \qquad \Delta G^0_{rxn}, \text{ kJ/mol}$$

$$I_3^-(aq) + 2Hg^0(g) \rightarrow I^-(aq) + Hg_2I_2(s) \qquad +0.57 \qquad -174.83 \quad (6)$$

$$I_2(aq) + 2Hg^0(g) \rightarrow Hg_2I_2(s) \qquad\qquad +0.58 \qquad -191.11 \quad (7)$$
$$\downarrow \text{excess } I^-$$
$$Hg^0(g) + HgI_4{}^{2-}(aq)$$

Hg₂I₂ disproportionates in the presence of excess I⁻ to give HgI₄²⁻ and Hg⁰. The Hg⁰ is then oxidized again as shown in

## TABLE 5. Summary of Iodine Based Impinger Experiments for Hg⁰ Capture[a]

Row #	Method Type		Impinger[2] 1	2	3	4	5	Total Hg Avg (µg)	N (Runs)	%RSD[3]
1	1 N KI	Solution	1 N KI	1 N KI	10%H₂O₂ 5% HNO₃	0.4%KMnO₄ 10%H₂SO₄	0.4%KMnO₄ 10%H₂SO₄	3.53	3	11.6
		%Hg Captured	40.1	29.2	21.8	8.8	<0.1			
2	1 N KI preceded by peroxide	Solution	10%H₂O₂ 5% HNO₃	1 N KI	1 N KI	0.4%KMnO₄ 10%H₂SO₄	0.4%KMnO₄ 10%H₂SO₄	2.71	2	9.2
		%Hg Captured	<0.4	96	<4	<1	<0.1			
3	acidified 1 N KI preceded by peroxide	Solution	10%H₂O₂ 5% HNO₃	1 N KI/1% or 2% HCl	1 N KI/1% or 2% HCl	0.4%KMnO₄ 10%H₂SO₄		2.85, 3.19	1, 1	NA
		%Hg Captured	0.4, 0.3	99.4, 99.7	0, 0	0, 0.03				
4	0.5 N KI	Solution	0.5 N KI	10%H₂O₂ 5% HNO₃	0.5 N KI	0.4%KMnO₄ 10%H₂SO₄		3.07	2	15.9
		%Hg Captured	46	10	37	7				
5	acidified 0.5 N KI	Solution	0.5 N KI/2% HCl	10%H₂O₂ 5% HNO₃	0.5 N KI/2% HCl	0.4%KMnO₄ 10%H₂SO₄		2.52	1	NA
		%Hg Captured	97.8	1.3	0.9	ND				
7	0.05 N KI preceded by peroxide	Solution	10%H₂O₂ 5% HNO₃	0.05 N KI	0.05 N KI	0.4%KMnO₄ 10%H₂SO₄		2.69	1	NA
		%Hg Captured	0.6	19.9	18.1	61.4				
8	acidified 0.05 N KI with preoxidation	Solution	0.05 N KI/2% HCl	0.05 N KI/2% HCl	0.4%KMnO₄ 10%H₂SO₄	0.4%KMnO₄ 10%H₂SO₄		3.57	2	8.3
		%Hg Captured	99.3	0.7	ND	ND				
9	acidified 0.05 N KI	Solution	0.05 N KI/2% HCl	10%H₂O₂ 5% HNO₃	0.05 N KI/2% HCl	0.4%KMnO₄ 10%H₂SO₄		2.78	1	NA
		%Hg Captured	91.9	2.6	5.3	0.2				
10	acidified 0.01 N KI with preoxidation	Solution	0.01 N KI/2% HCl	0.01 N KI/2% HCl	10%H₂O₂ 5% HNO₃	0.4%KMnO₄ 10%H₂SO₄		2.52	1	NA
		%Hg Captured	98.1	1.6	0.27	ND				
11	acidified 0.5 N KIO₃	Solution	0.5 N KIO₃ /2% HCl	10%H₂O₂ 5% HNO₃	0.5 N KIO₃ /2% HCl	0.4%KMnO₄ 10%H₂SO₄		3.12	1	NA
		%Hg Captured	27.1	3.0	14.7	55.3				
12	2% HI	Solution	2% HI	2% HI	10%H₂O₂ 5% HNO₃	0.4%KMnO₄ 10%H₂SO₄	0.4%KMnO₄ 10%H₂SO₄	2.25	2	18
		%Hg Captured	99	<1	<0.02	<0.05	<0.05			
13	10% HI	Solution	1N KCL	10%H₂O₂ 5% HNO₃	10% HI	10% HI	0.4%KMnO₄ 10%H₂SO₄	2.69	2	2.1
		%Hg Captured	<0.3	<0.5	95	4	<0.2			

[a] Key: 1, Test conditions: Hg vapor generation system at room temperature, 24−27 °C. Hg vapor air flow, 0.06 L/min. Dilution air flow, 0.940 L/min. Total air flow through impingers, 1.0 L/min, temperature not controlled. 2, Twenty-five milliliter glass Midget bubblers with sintered glass filter tips (A- porosity, Ace Glass). Fifteen milliliters of test solution per impinger. 3, Percent relative standard deviation for $N \geq 3$, relative percent difference for $N = 2$ for total Hg captured. 4, Modifified by using 0.4% permanganate solution with no detriment to Hg capture efficiency. 5, Ref 32. 6, NA = not applicable

eq 7. The overall reaction is believed to be according to eq 8:

$$Hg^0(g) + 2I^-(aq) + I_2(aq) \rightarrow HgI_4^{2-}(aq) \quad -156.79 \qquad \Delta G^0_{rxn}, kJ/mol \qquad (8)$$
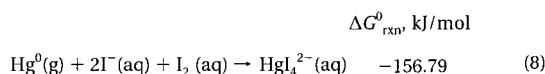
The reaction in eq 8 may be written more precisely in eq 9 to show the chemical form that iodine takes in solutions of iodide:

$$Hg^0(g) + I^-(aq) + I_3^-(aq) \rightarrow HgI_4^{2-}(aq) \quad -33.58 \qquad \Delta G^0_{rxn}, kJ/mol \qquad (9)$$
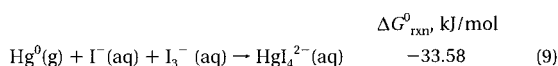
The complex, HgI_4^{2-}, in solution is stable and nonvolatile. Lower KI concentrations were explored to minimize signal suppression in the DIN-ICP/MS analyses, yet retain HgI_4^{2-} in solution. To increase the iodine concentration in low concentration KI solutions, oxidation of iodide to iodine just prior to sampling was explored. KI concentrations of 0.01 or 0.05 M still achieved greater than 98% capture in the first KI impinger (rows 8 and 10 of Table 5) when the KI solution was preoxidized by the addition of 50 µL of 10% hydrogen peroxide

per 15 mL of KI solution just prior to sampling. The generation of iodine was instantaneous and evident by formation of a orange/brown solution, characteristic of iodine solutions.

The last two rows of data in Table 5 are results using hydriodic acid (HI). The chemistry of capture of Hg⁰ with HI is the same as with the iodine solutions and proved to be as efficient; however, HI is extremely corrosive and not as easy to work with as acidified KI solutions that can be oxidized to iodine just prior to sampling.

Iodine Based Method vs Ontario Hydro Method. Figure 5 is a control chart comparing the Ontario Hydro Method results to the iodine based impinger results for total Hg capture using the Hg vapor generation system. The first sets of experiments using iodine based impingers were unusually high in Hg, probably due to an initial "cleaning" by the KI as the Hg contaminant was leached from impingers and other glassware. Results quickly returned to normal limits established by the Ontario Hydro Method.

Bench Scale Testing of Proposed Impingers in a Coal Combustion Flue Gas. The bench scale coal combustor, the operating conditions, and the feed coal chemical composition have been previously described (26). Three experiments were
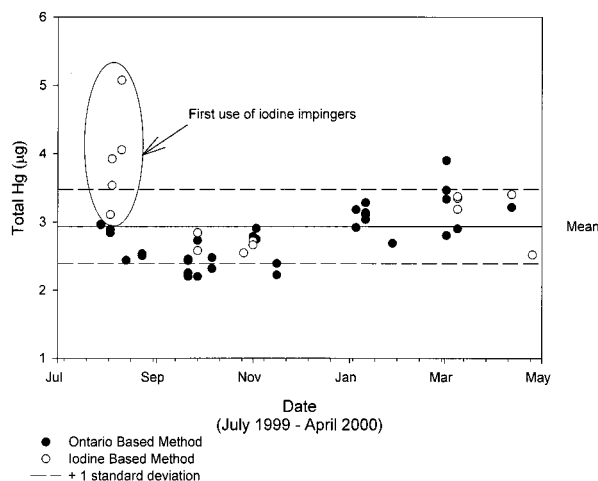
FIGURE 5. Total Hg capture, iodine method impingers compared to Ontario Hydro Method Impingers.

TABLE 6. Impinger Solutions for Bench Scale Coal Combustion Gas Sampling

Impinger #	Solution	Species Captured
1	1.0 M tris-buffer+EDTA	oxidized Hg
2	1.0 M tris-buffer+EDTA	oxidized Hg
3	10% H_2O_2/2% HNO_3	Hg^0
4	0.05M KI/2% HCl (oxidized with hydrogen peroxide to I_3^- prior to sampling)	Hg^0
5	0.05M KI/2% HCl	Hg^0

performed using this coal combustion system. The first two experiments were coal burns at two different coal feed rates with the exit gas stream split to compare the Ontario Hydro Method impingers to the proposed impingers outlined in Table 6. Results from the three experiments are compiled in Table 7. In the first experiment 4% potassium permanganate

was used, while 0.4% was used in the remaining two experiments. The 4% potassium permanganate solution, prescribed at a nearly saturated concentration in the Ontario Hydro Method, is so dense that the impinger bubbling characteristics are noticeably different when compared to less concentrated solutions. A 10-fold dilution of the potassium permanganate concentration, to 0.4%, was more than sufficient for oxidation of Hg^0 and other gases in our bench scale system, and more vigorous bubbling was observed.

Experiments were performed on different days and sampling time was for 60 min. Each train was connected to a separate vacuum pump with a volumetric flow rate of 1 lpm per stream. In the first two experiments the iodine impinger train was always connected to the same vacuum pump. The coal feed was established and allowed to burn for approximately 10 min before sampling of the gases. The iodine impinger train a vacuum pump was started first and then the Ontario Hydro impinger train. Occasionally, if the coal feeder became clogged, sampling was halted by stopping the Ontario Hydro and then the iodine impinger train. Sampling would be resumed by starting the iodine impinger stream and then the Ontario Hydro stream. In the first experiment, sampling had to be halted once. In the second experiment the coal feed rate was approximately two times faster than the other experiments and sampling was halted twice. In the third experiment sampling was not halted at all. The differences in the way sampling was started, halted, and resumed may have caused a positive bias in our split stream design with more Hg always being captured on the side that was started first. The more times an experiment was halted and resumed appeared to increase the bias. Another problem encountered were volatile losses of solution volume during the 60 min sampling time. This resulted in the volume of solution increasing from the first impinger to the last impinger. Loss/carryover was generally less than 1 mL and was accounted for in calculation of Hg mass. Concentrations of Hg in solution were generally low (0.6−3 ppb in the first Hg^0 capture impinger and 0.01−0.3 ppb in the first Hg^{2+} capture impinger).

Capture efficiency of the iodine impingers was equivalent to the Ontario Hydro Method impingers with greater than 98% capture in the first oxidizing impinger (Table 7,

TABLE 7. Bench Scale Combustion of Bituminous Coal[a]

Method Type	Impinger 1	2	3	4	5	Total Hg Nanograms (ng)
(1) Iodine Impinger Train	1 M Tris	1 M Tris	10%H_2O_2 5% HNO_3	0.05 M KI/2% HCl	0.05 M KI/2% HCl	20.3
% Hg Captured	ND	ND	0.9	99.1	ND	Train A
(1) Ontario Hydro Impinger Train	1 N KCl	1 N KCl	10%H_2O_2 5% HNO_3	4%$KMnO_4$ 10%H_2SO_4	4%$KMnO_4$ 10%H_2SO_4	15.3
% Hg Captured	ND	ND	0.6	99.4	ND	Train B
(2) Iodine Impinger Train	1 M Tris	1 M Tris	10%H_2O_2 5% HNO_3	0.05 M KI/2% HCl	0.05 M KI/2% HCl	87.2
% Hg Captured	0.2	ND	0.2	96.9	2.7	Train A
(2) Ontario Hydro Impinger Train	1 N KCl	1 N KCl	10%H_2O_2 5% HNO_3	0.4%$KMnO_4$ 10%H_2SO_4	0.4%$KMnO_4$ 10%H_2SO_4	62.9
% Hg Captured	0.4	ND	ND	99.5	0.1	Train B
(3) Ontario Hydro Impinger Train	1 N KCl	1 N KCl	10%H_2O_2 5% HNO_3	0.4%$KMnO_4$ 10%H_2SO_4	0.4%$KMnO_4$ 10%H_2SO_4	19.7
% Hg Captured	1.0	1.5	1.0	96.5	ND	Train A
(3) Ontario Hydro Impinger Train	1 N KCl	1 N KCl	10%H_2O_2 5% HNO_3	0.4%$KMnO_4$ 10%H_2SO_4	0.4%$KMnO_4$ 10%H_2SO_4	18.8
% Hg Captured	2.1	1.6	2.7	93.6	ND	Train B

[a] ND, none detected.

experiments 1 and 2). Such a high fraction of the total mercury present in the elemental form is in contrast to results of some field studies combusting similar bituminous coals where a smaller fraction has been observed in the elemental form as determined by the Ontario Hydro Method. The speciation of mercury in coal combustion emissions is dependent on several factors, and no fundamental understanding has been reported to accurately predict the speciation. While the chemical constituents in the flue gas in our bench scale system should be similar to that in a full scale system (as similar bituminous coals are being combusted), the rate of temperature decrease is higher at the exit of our combustor. This quench rate may have an important role in the ultimate speciation of the mercury, as it may halt oxidation reactions. The Tris Buffer Method solution we used to capture oxidized Hg has been demonstrated to have few biases/interferences regardless of combustion constituent gases (15). The iodine impingers used in this work consistently captured more Hg^0 than the permanganate impingers (even in percent form, Table 7); however, this phenomenon was not observed in our testing using the Hg vapor generation system (in which there was no oxidized form present). Observed biases in total Hg captured, then, may be due to our reported sampling problems. More importantly, these experiments demonstrated that the iodine impingers retained their oxidizing capacity for Hg^0 capture in real flue gas sampling.

In conclusion, DIN-ICP/MS made possible the exploration iodine based solutions for capture of Hg^0. Sensitivity and MDLs were comparable to CVAAS. The front half of the proposed impinger train consisting of Tris buffer and acidified hydrogen peroxide for capturing oxidized Hg and SO_2 gas removal was amenable to direct analysis by DIN-ICP/MS without a tedious sample preparation as required for CVAAS analysis. Using DIN-ICP/MS, we demonstrated for the first time that aqueous iodine, I_3^-, can be generated just prior to impinger sampling to efficiently oxidize Hg^0 and retain it in solution as HgI_4^{2-}.

Iridium and rhenium proved to be good internal standards (Figures 3A–4B) for Hg determination. Instrumental drift was corrected for and matrix effects accounted for in KI solutions ranging in concentration from 0.005 M KI to 0.1 M KI (Figure 4B). Below 0.005 M KI, Hg response was low, making the ratio of IS:Hg high (Figure 4A). This was believed to be due to the precipitation of HgI_2 in low KI concentration solutions. At higher KI concentrations, the HgI_2 was solubilized as HgI_4^{2-} and the ratio of internal standard response to Hg response was stabilized. A KI concentration was chosen for impinger sampling that ensures Hg^0 capture and HgI_2 solubility as HgI_4^{2-} yet minimizes signal suppression from concomitant salts in the plasma.

In two experiments of the bench scale combustion of a bituminous coal, the iodine impingers captured approximately 25% more Hg^0 than the potassium permanganate impingers in an Ontario Hydro Method train, possibly due to sampling problems. The Tris Buffer solution has already been well documented to provide accurate speciation of the oxidized forms of Hg, and the acidified hydrogen peroxide impinger solution has been well documented to remove sulfur dioxide gases. The iodine impinger solutions did not lose their oxidizing capacity in the presence of real coal combustion gases. Future research needs to be done to elucidate the chemistry of capture of oxidized Hg using the tris+EDTA buffer solution and to test the proposed iodine impinger train in real stack sampling for multiple metals analyses and Hg speciation.

Acknowledgments

Supporting Information Available

Proposed reactions for the chemistry of capture of oxidized and elemental Hg using acidified hydrogen peroxide, acidified potassium permanganate, and KCl impinger solutions and a brief discussion of the use of tris solution for capture of oxidized Hg. This material is available free of charge via the Internet at http://pubs.acs.org.

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