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Collection and Thermal Evolution Behaviors of Different Mercury Species Captured with Gold

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The effects of temperature on the collection and evolution of different mercury (Hg) species captured with gold were investigated to help determine if temperature control could be used to provide Hg speciation information in gaseous effluents. Elemental mercury, dimethyl mercury, and mercuric chloride were loaded onto a gold trap (one Hg species per test) at temperatures of 25−375 °C. The Hg was then evolved (in argon) at 900 °C. In other tests, Hg was loaded onto the trap at 25 °C and then heated (in argon) at 50−1000 °C to release Hg. The argon streams were analyzed using cold vapor atomic fluorescence to obtain information on Hg collection and evolution as a function of temperature. The Hg was released from the gold entirely as elemental mercury, regardless of the Hg species collected. Temperatures of about 250 °C were required to release the Hg, and there were no differences among Hg species with respect to the temperatures necessary to evolve the Hg. Results of the tests on Hg collection efficiency versus the temperature of the gold trap indicated that proper selection of the collection temperature could potentially be used to provide Hg speciation information. However, refinements in the technique are necessary before it can be put into practical use.

Introduction

It has been estimated that coal combustion at electric utilities emits about 50 tons of Hg annually (*1*). In view of the toxicity and public concern over Hg, the 1990 Clean Air Act Amendments require a special study on Hg from coal-fired power plants. Roughly 90% of the Hg downstream from the boiler is typically in the vapor phase and is therefore largely uncontrolled by particulate collectors. The Hg vapors in coal combustion flue gases are generally thought to be in the form of elemental mercury (EM) and mercuric chloride (MC). Although methyl mercury (MM) was previously considered to comprise a significant fraction of the vapor phase Hg in some flue gases, it is now generally believed that MM does not exist in coal-fired flue gas streams. The relative concentrations of different Hg species in flue gases are highly variable, are difficult to predict, and are a major factor affecting Hg removal efficiencies by various pollution control devices. As one example, Hg removal by wet scrubbers can vary from 10 to 90% (*2*). Since wet scrubbers are generally effective at collecting oxidized Hg (soluble in scrubber solutions) but are generally ineffective at capturing elemental mercury (low solubility in scrubber solutions) (*3, 4*), this large variation in scrubber efficiency for Hg probably relates to the relative concentrations of each Hg species in the gas stream at a given site. Consequently, knowledge of the concentrations of Hg species present provides important information related to the abatement of total Hg emissions from coal-fired power plants and the optimization of flue gas cleanup technologies. In view of this, there is considerable interest in the development of an accurate, on-line Hg speciation monitor for environmental monitoring and process control applications. However, no such monitor for directly determining each of the Hg species of interest in flue gas yet exists.

Although Hg can be collected with numerous metals, including silver, gold, copper, platinum, tin, and zinc (*5*), the most commonly used metal for Hg collection in gaseous process streams is gold. Efforts to devise a Hg speciation system for ambient air applications have been performed by other researchers and involved the use of a series of sorption tubes containing noble metals (silver and gold) as well as chromatographic type adsorbents and solid supports (*6, 7*). In one of those studies, it was reported that dimethyl mercury (DMM) was not collected by silver but was collected quantitatively by gold (*6*). In the other study, it was reported that both silver and gold films effectively captured DMM, EM, and MC (*7*). In yet another study, it was reported that both gold and silver effectively capture EM, while only the gold was effective at capturing DMM (*8*). In that work, a Hg speciation system for ambient air was developed which employed silver and gold traps.

A variety of commercially available ambient Hg monitors employ gold traps. These include the Tekran model 2537A mercury vapor analyzer (*9*), the Jerome 431-X mercury analyzer (Arizona Instruments), and the PS Analytical Sir Galahad system. Commercially available instruments employing gold traps for possible application to coal combustion gases have also been studied recently and include analyzers sold by Perkin-Elmer and PS Analytical.

In our study, the technical feasibility of two novel approaches that could potentially be used for determining Hg species in coal combustion flue gas was investigated. Specifically, we investigated the collection and thermal evolution efficiencies of different Hg species captured with gold as a function of temperature. The two approaches investigated in this study are referred to as programmed temperature sorption (PTS) and programmed temperature evolution (PTE), respectively. This work helped assess whether there was any potential for preferential collection or evolution of a given Hg species through proper control of the gold temperature. The Hg species investigated were EM, MC, and DMM. DMM was included in this work as a form of methylated Hg since MM was once thought to be present in flue gas from coal combustion and because there may be other applications that involve DMM streams in process gases. Also, the data are still of interest from a Hg speciation standpoint, and DMM is often discussed in the literature as a possible atmospheric Hg species (*6*−*8*). The purpose of this work was to determine whether PTS or PTE has any Hg speciation potential and to document the collection and thermal evolution behaviors of various Hg species as a function of temperature for use by the scientific community.

Background

For capturing Hg in flue gas streams, gold is often the preferred metal because of its high collection efficiencies and because, unlike silver, it is not adversely affected by sulfur-containing gases (*10*). Also, it can be used repeatedly without losses in collection efficiency. At room temperature,

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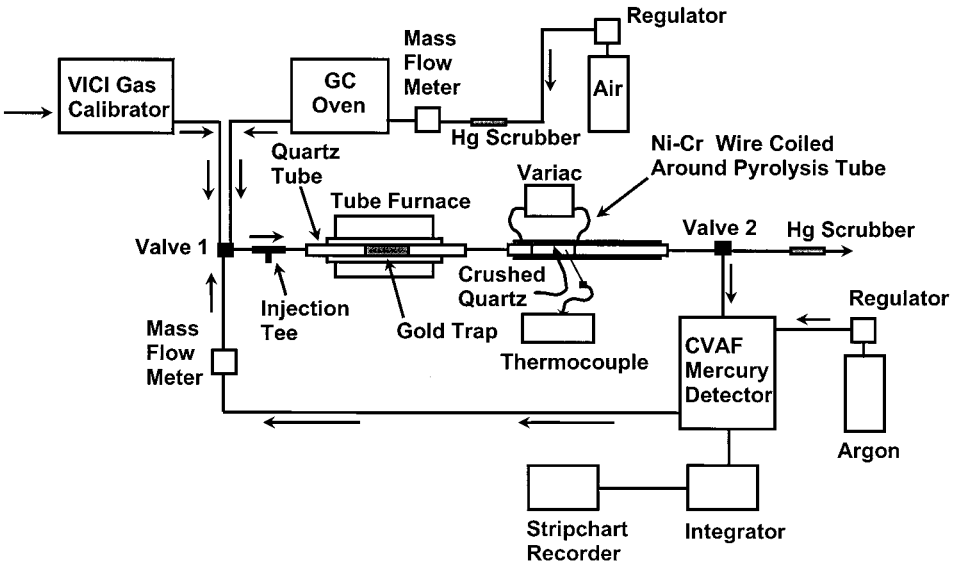

FIGURE 1. Schematic diagram of testing apparatus.

gold quantitatively collects vapor phase Hg, both in the oxidized and elemental forms (*11*−*13*). However, Hg collection efficiencies by gold can apparently vary greatly depending on the Hg species involved. For example, it has been reported that gold is much more effective at capturing EM than DMM because of different collection mechanisms involved (*12*). In other work, Hg collection capacities using gold were only somewhat lower (within a factor of 3) for DMM than for EM (*13*). The collected Hg can be thermally evolved at high temperatures (e.g., 900 °C) as EM and subsequently quantified through the use of a suitable Hg detector. At lower temperatures, little is known about the effects of thermal evolution temperature on the Hg species released from gold that was used to collect DMM or MC. However, in one study (*13*), it was reported that a thermal evolution temperature of about 700 °C completely converted DMM to EM, while there was some evidence that only about 50% of the MC was converted to EM under those conditions. If this is the case, the kinetics of converting different Hg species to EM at different temperatures could potentially be used to distinguish between those species. Also, if different sorption mechanisms are involved, different temperatures may be required to effectively thermally evolve each Hg species.

Information in the literature regarding the effects of temperature on the amount of Hg evolved from gold is sparse. However, in one study, it was noted that a minimum temperature of 500−600 °C was needed for complete evolution of Hg collected as DMM (*11*). In another study, EM reportedly was quantitatively thermally evolved from a gold trap at 300 °C (*14*). In view of the possible differences in temperatures needed for evolving the Hg, different forms of Hg could potentially be separated by using different thermal evolution temperatures for each Hg species collected. Also, for ambient air, there is evidence that EM is mainly dissolved in the gold, whereas oxidized Hg may be largely adsorbed onto the surface (*15*). If true, then it is conceivable that different temperatures could be used to preferentially evolve a given Hg species from the gold.

Another potential Hg speciation approach deals with the possible preferential collection of different Hg species on gold at different temperatures. Little or no information has been reported in the literature on Hg collection efficiencies of various Hg species versus temperature. If some of the Hg species can be preferentially collected at a given temperature, this could be used to develop a Hg speciation approach by using several gold traps at different temperatures and sequentially thermally evolving the Hg from each gold trap. The amount of Hg evolved from each trap could then be quantified using an appropriate Hg detector.

Experimental Section

Apparatus. A schematic diagram of the apparatus used for these studies is shown in Figure 1. The system shown here was used for loading Hg onto a gold trap and also for thermal evolution of the Hg into a cold vapor atomic fluorescence (CVAF) Hg detector. Unless otherwise noted, all system components that came into contact with Hg were manufactured with PTFE or PFA Teflon. The gold trap used to collect Hg was prepared by sputter-coating a thin layer of gold (approximately 50 nm) onto flattened quartz wool gauze. This wool was loosely packed into a quartz tube (12 mm o.d., 10 mm i.d.) to create a plug 2 cm in length. This gold trap was used for all of the tests performed in this study. The quartz tube was sufficiently long (80 cm) to enable it to be shifted back and forth within a preheated tube furnace (Lindberg Blue M Mini-Mite) so that the gold-coated quartz plug could be heated and cooled without the tube ever being removed from the furnace entirely. By following this procedure, the cover of the tube furnace was never opened, thus minimizing the fluctuation in temperature each time the gold trap was inserted or removed.

Initially, the use of a pyrolysis tube was envisioned in order to convert oxidized Hg species to EM for detection. The pyrolysis tube was made by using a 30-cm quartz tube (12 mm o.d., 10 mm i.d.) packed with a 10-cm section of crushed quartz. The crushed quartz was packed at both ends with quartz wool plugs. The tube was placed in a coil of nickel−chromium wire and then wrapped with Fiberfrax insulation. The heating coil was connected to a variable transformer, and the pyrolysis tube was heated to a steady temperature of 900 °C by applying approximately 23 VAC to the heating coil. Other researchers have reported that DMM is completely disassociated at 500 °C, while MC requires a temperature of 900 °C for complete conversion to EM (*7*). The temperature of our pyrolyzer was measured with a type K (chromel−alumel) thermocouple inserted into a narrow well on the center of the pyrolysis tube.

A VICI Metronics model 340 Dynacalibrator was used with a DMM permeation wafer (supplied by VICI Metronics) to generate continuous gas streams containing known concentrations of that Hg species. The room air used as the carrier gas was scrubbed with activated carbon (inside the

Dynacalibrator) prior to entering the glass chamber containing the permeation devices, thus ensuring that ambient Hg levels did not increase the Hg content of the calibration stream.

For EM, gas-tight syringes were used to withdraw Hg-saturated air above a pool of elemental mercury contained in a flask fitted with a septum. By measuring the room temperature and pressure, the Hg concentration in the air above the pool was calculated using known Hg vapor pressure parameters, and the amount of Hg in a given volume of air could be calculated. Those volumes of air containing EM vapor were then manually injected into the carrier gas stream (via a Teflon injection tee) just prior to the gold trap.

For MC, a permeation tube from VICI Metronics was used to deliver MC streams to the trap. However, due to reported problems involving condensation and sublimation of MC emitted from those permeation tubes, a separate system was used to deliver this Hg species in order to prevent contamination of the VICI Metronics calibrator. This system consisted of a compressed air cylinder connected to a glass "U-tube" (containing the permeation device) that was heated inside the oven of a gas chromatograph (GC). By using the temperature control of the GC oven, the emission rate from the permeation tube was regulated with sufficient accuracy and precision for the purposes of our work.

When loading either DMM or MC, gases from either the VICI Metronics calibrator or the GC oven were connected to valve 1, depending on the species being loaded (see Figure 1). Those gases were then directed (via valve 1) to the gold trap. Valve 2 was switched so that the gases exiting the gold trap passed into an activated carbon Hg scrubber rather than to the CVAF detector. Theoretical amounts of DMM and MC delivered to the gold trap were calculated using the nominal Hg emission rates from the permeation tubes and the exposure time of the gold to the Hg-containing streams. When loading EM, argon from the CVAF Hg detector was used as the carrier gas stream and was directed to the gold trap with valve 1. As was the case with DMM and MC, valve 2 was switched to the Hg scrubber while loading EM onto the gold trap.

For the thermal evolution step in which the gold was heated to release the collected Hg, valve 1 was switched to send argon (from the CVAF detector) to the gold trap, and valve 2 was switched to divert gases exiting the gold trap into the CVAF detection cell. Before heating the gold trap to thermally evolve any collected Hg, the argon was allowed to flow through the system for about 10 min.

Since the purpose of the research was to observe general trends in collection and evolution behaviors of different Hg species as a function of temperature, a high degree of accuracy in the amounts of Hg delivered to the gold trap was not necessary for this work. For EM, the amount of Hg injected is estimated to be accurate to within 20%. For DMM, a certified permeation device was used that had emission rates estimated by the manufacturer to be accurate to within 10% of the theoretical rates. No certified permeation device for MC was commercially available. Although a theoretical emission rate was provided for the MC permeation tube, no emission uncertainties were provided by the manufacturer for that tube. However, the tube manufacturer estimated that the nominal emission rate was probably accurate to within a factor of 2.

Unless otherwise noted, a Tekran model 2500 CVAF Hg detector was used. This instrument provided an excellent detection limit (below 0.2 pg of Hg), a wide dynamic range ($>10^5$) and excellent baseline stability following routine changes in gas flow rate. A small portion of the high-purity argon supplied to the CVAF detector was split off inside the unit and served as a detector purge gas. The remaining argon exited the analyzer and was used for the sample carrier gas into the detection cell. This sample carrier gas stream was used while loading EM onto the gold trap and during all of the thermal evolution steps in which Hg released from the trap was measured. CVAF detects only Hg in the elemental form, and it was not known at the start of the study whether the oxidized Hg species collected by the gold would be released entirely as EM. Therefore, as noted above, a pyrolysis tube containing crushed quartz was initially used with the system in order to convert any oxidized Hg to EM for detection by CVAF. Research grade argon (99.9995% minimum purity) was used as the carrier gas during Hg evolution from the gold to avoid sensitivity loss due to quenching effects from molecular gases in the sample cell. A strip chart recorder and a peak integrator were connected to the CVAF unit to record the detector signal.

Preliminary Tests. Calibration studies were performed to assess the consistency of the output from the calibrators and memory effects of the apparatus. For this work, various volumes of calibration gases of each Hg species were passed over the gold at room temperature. The collected Hg was then thermally evolved at 900 °C and detected by CVAF. Plots of the detector signal versus the theoretical amount of Hg entering the gold trap were then prepared. Two calibration curves were prepared in this manner for each of the three Hg species investigated in this work.

Although it has been reported that Hg can be thermally evolved from gold as EM at high (e.g., 900 °C) temperatures, regardless of the Hg species collected, it was necessary to confirm this before performing any PTS or PTE tests. Since the CVAF instrument detects only EM, several tests were performed to ensure that the Hg released from the gold during heating at high temperatures was present as EM, regardless of the Hg species collected. If not, then a pyrolysis tube might be necessary to serve as a converter to help ensure that the Hg is in the proper form for detection. These tests focused on MC, since it is more difficult to pyrolyze than DMM and because of concerns about the possible recombination of Hg with Cl if those species are both present as the Hg (collected as MC) is evolved from the gold. On the basis of the calibration curves obtained using DMM, EM, and MC, no tests were performed to ensure that there was no recombination of DMM after being released from the gold (see Results).

The gold trap was loaded with 24 ng (nominal) of Hg (as MC) over a period of 3 min. The Hg was subsequently thermally evolved at 900 °C. During the Hg evolution step, the carrier gas stream passing over the trap was bubbled into two 10-mL absorbing solutions for a period of 8 min (trap heated during the entire sampling period). The absorbing solutions were used to measure the amount of Hg released and to determine whether it was elemental or oxidized Hg. Deionized (DI) water was used to preferentially collect oxidized Hg forms, since only oxidized Hg species have an appreciable solubility in water. After sampling using the DI water, the water was immediately acidified to minimize Hg losses onto the container walls. Acidified potassium permanganate solutions were used to collect total Hg (i.e., both oxidized and elemental forms). In similar tests using 24 ng of EM, quantitative recovery (110%) of the Hg was obtained in acidified potassium permanganate solutions using the above sampling procedure. Conventional cold vapor atomic absorption (CVAA) analyses were used to quantify the amount of Hg in each collection solution.

Programmed Temperature Evolution. A technique referred to as programmed temperature evolution (PTE) was used to determine whether the Hg species collected affects the temperature at which it can be thermally evolved from the gold. About 10 ng of Hg (present as EM, DMM, or MC) was passed over the gold by measuring the length of time the calibration gases (airstream containing Hg) passed into

the gold trap (for DMM and MC) or by injecting 10 ng of EM (calculated from vapor pressure data) into the carrier gases upstream from the gold trap. A gas flow of 300 mL/min was used for this loading step, which was performed at room temperature. The gold trap was then inserted into a tube furnace that was preheated to various temperatures ranging from 50 to 1000 °C. The apparatus was purged for about 3 min with research-grade argon flowing at about 350 mL/min before the collected Hg was thermally evolved into the argon stream maintained at that flow rate. Due to the possibility that some of the Hg was retained by the gold at low thermal evolution temperatures, precautions were taken to ensure that the gold used at each collection temperature contained no residual Hg from the previous test. To prepare the gold trap for each new evolution temperature, the gold trap was heated to 900 °C for 10 min after each evolution temperature was studied.

Evolution efficiencies for EM, DMM, and MC at each evolution temperature were calculated using peak height and peak area. A 100% evolution efficiency was defined as the maximum peak height (or peak area) that was observed for each Hg species over the range of 25−1000 °C. In addition to determining evolution efficiencies, the times required to observe the peak maxima during Hg evolution were measured.

Programmed Temperature Sorption. To investigate whether different Hg species have different collection efficiencies at different temperatures at a fixed carrier gas (air) flow rate, a technique referred to as programmed temperature sorption (PTS) was employed. The Hg loading was performed in the same manner discussed above for the PTE work. As with the PTE tests, Hg loadings of about 10 ng were used. The air flow rate from the calibration systems and the argon flow rate used during the thermal evolution step were also the same as that used in the PTE work. The gold trap was preheated to various temperatures ranging from 25 to 375 °C by inserting it into the tube furnace and allowing the temperature to stabilize prior to collecting Hg. To determine the Hg collection efficiency at each of these temperatures, the portion of the quartz tube containing the gold (loaded with Hg) was first slid out of the tube furnace. The tube furnace was then heated to 900 °C. Although the temperature of the gold trap was not measured during this period, the trap was withdrawn from the furnace far enough (about 2 in. upstream from the furnace) such that it was only slightly warm to the touch, even when the furnace was at 900 °C. After the furnace equilibrated at 900 °C, the gold trap was reinserted into the furnace to evolve the collected Hg, which was swept from the quartz tube into the CVAF detector using a stream of high-purity argon. As with the PTE work, the quartz tube and the detector were thoroughly purged with argon prior to thermal evolution of Hg from the gold trap.

Collection efficiencies for EM, DMM, and MC at each collection temperature were calculated using peak height and peak area. A 100% collection efficiency was defined as the peak height (or peak area) of the detector response obtained by thermally evolving (at 900 °C) the Hg that was captured by the gold at room temperature. Although a small portion of each Hg species was probably lost during sample transport due to sorption effects, the definition of 100% collection efficiency was accepted as a valid approximation of the actual collection efficiency at room temperature in view of the accuracy requirements for this study.

Results and Discussion

Preliminary Studies. In the calibration studies, a reproducible linear calibration graph of detector signal versus theoretical Hg quantities was produced for each Hg species. Typical calibration curves for each Hg species are shown in Figure 2. Because the DMM curve was close to the EM curve,

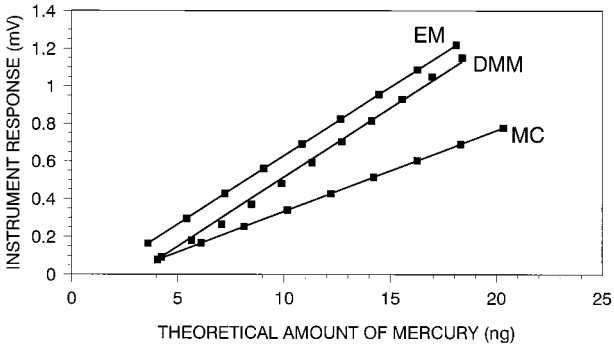

FIGURE 2. Typical calibration curves obtained for EM, DMM, and MC.

there was not a significant (if any) degree of DMM recombination after being released from the gold. If there were a substantial amount of recombination to an oxidized Hg species, the DMM calibration curve would be shifted downward to a much greater extent. The MC curve has a substantially different slope than the other two curves. This is probably primarily related to the uncertainty in the MC emission rate provided by the vendor (estimated to be accurate to within a factor of 2). Alternately, recombination of MC after release of the Hg from the gold must be considered a possibility. To a lesser degree, difficulties in transporting MC may also be partially responsible. For each Hg species, results were generally reproducible (based on duplicate tests) to within ±5% for DMM and within ±10% for EM and MC. Exceptions were noted for the lowest amounts (e.g., less than 5 ng) of Hg, in which case results were reproducible to within ±15−30%. These data showed that the concentration of Hg in the gases from the calibrator (DMM and MC) or syringes (EM) as well as the losses due to wall effects were consistent from trial to trial (but different for each Hg species). Thus, for the purposes of this study, consistent Hg loadings onto the gold could be attained. This experimental verification of consistent Hg loadings was an important quality control measure prior to proceeding with other testing.

For the CVAA analyses on the solutions used to assess the need for a pyrolysis tube downstream from the gold trap, the detection limit of the analytical method was about 2 ng of Hg. Thus, for a 10-mL solution, this corresponds to a detection limit of 0.2 ng/mL. If all of the Hg (using nominal values) in the MC tests were collected in a single absorbing solution, this would give a Hg concentration of 2.4 ng of Hg/mL, which is about 12 times the detection limit. However, it is of interest to note that the total Hg recovered was only 45−60% of the amount anticipated based on the nominal MC emission rate from the permeation tube. This is in good agreement with Figure 2, which indicates that the MC results are typically 40−50% lower than expected based on the calibration curves prepared using gold traps for collection and evolution of Hg. As noted earlier, there were no emission uncertainties provided by the manufacturer of the MC permeation tube, although it was expected to be accurate to within a factor of 2. Because MC loadings were only roughly half of the nominal values, the actual Hg level in an absorbing solution (if all of it was collected in a single solution) would be about six times the detection limit of the analytical methodology used. Peak-to-background ratios of roughly 10:1 were observed for the analyses, and analytical results were typically reproducible to within ± 10%.

In an expanded study, it would be desirable to repeat these tests using larger Hg loadings. However, conclusions can still be drawn from the CVAA data despite the analytical uncertainties associated with the MC tests. Results of the CVAA analyses indicated that the large majority of the Hg loaded onto the gold (as MC) was collected by the acidified

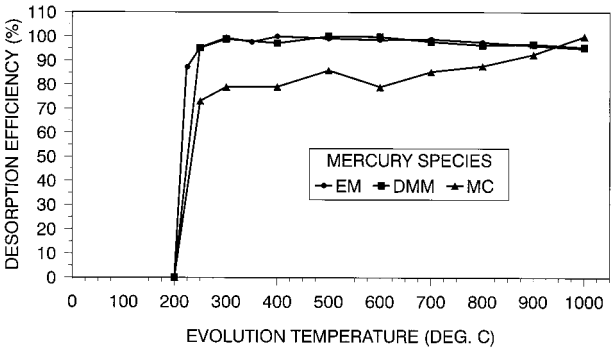

FIGURE 3. Mercury evolution vs evolution temperature.

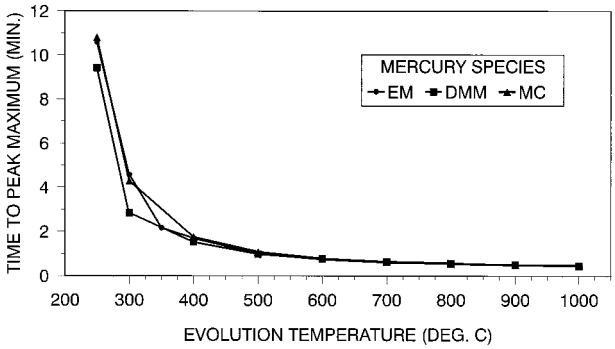

FIGURE 4. Mercury retention time vs evolution temperature.

permanganate solution after subsequent thermal evolution of the Hg, while little or no Hg was found when the tests were repeated while bubbling the gases into DI water. This indicates that the Hg collected as MC was thermally evolved at high temperatures predominantly (if not entirely) as EM. In view of the analytical uncertainties, it cannot be concluded that 100% of the Hg collected as MC was released from the gold as EM. However, it is clear that 75% or more of the Hg was released as EM in those tests. We viewed this as acceptable for the purposes of our feasibility study involving the effects of temperature on the collection and evolution of Hg. This is particularly true in view of potential problems involved with the pyrolysis of MC and the relatively large surface area of the packing material in the pyrolyzer, which could in turn increase unwanted memory effects. Also, similar tests were not performed at this time to ensure that Hg collected as MC is released as EM using thermal evolution temperatures of less than 900 °C. Those tests were postponed pending results from the PTE tests (see below), which supported the lack of a need for a pyrolysis tube. Consequently, a pyrolyzer was not used for any of the PTE or PTS tests because our results showed that (i) Hg collected as MC is evolved from the gold mostly (if not entirely) as EM, and (ii) MC is not reformed to a significant degree (if at all) downstream from the gold under the experimental conditions used in this study.

Programmed Temperature Evolution. Results obtained using the PTE approach were analyzed by preparing graphs of evolution efficiency versus evolution temperature. All tests were performed in triplicate or quadruplicate, and the evolution efficiency for a given Hg species typically differed by 5% or less among tests. These plots, which are based on data from peak areas, are shown in Figure 3. In addition, the times required to reach maximum peak height (i.e., retention times) were graphed as a function of evolution temperature (see Figure 4). This, in essence, is an indicator of peak broadening.

For all three Hg species, an evolution temperature of 200 °C (maintained for 20 min) was found to be insufficient for the evolution of Hg from the gold. At a temperature of 250 °C, however, evolution of Hg was easily detected for each species. The rate of Hg release increased with temperature. Consequently, peak heights also increased with increasing temperature. The increase in Hg evolution rate with increased temperature is also reflected in Figure 4, which shows that the time necessary to reach the peak maximum decreases rapidly as the temperature is increased above 250 °C. The plots of peak height versus temperature were nearly identical for each Hg species. However, it must be noted that using a different gold trap containing a different amount of gold or a different substrate material may shift these curves.

The evolution efficiencies that were calculated using peak areas also revealed a similarity between the thermal evolution behaviors of EM, DMM, and MC as a function of temperature (Figure 3). Results showed that, for temperatures of 250 °C or more, the temperature generally was not an important factor in the amount of Hg released. Thus, the Hg evolution rates increased with increased temperature, but the evolution was generally complete regardless of temperature once a critical temperature of about 250 °C was reached. For both EM and DMM, 95% or more of the Hg collected as EM and DMM was released, while about 75% of the Hg collected as MC was released. For EM and DMM, the amount of Hg evolved changed only slightly at higher evolution temperatures. For MC, increasing the evolution temperature from 250 to 1000 °C improved the evolution efficiency by about 25% (absolute). However, because of difficulties in working with MC, it is not certain whether this is actually related to the increased evolution temperature or whether it is related primarily to sample transport considerations or other experimental variables. Similarly, the small deviations from a smooth curve in the evolution efficiency of MC as a function of temperature in the temperature range from 250 to 1000 °C may reflect sample transport problems or slightly variable MC output from the calibration system.

The PTE data show that the Hg was completely released from the gold as EM at temperatures of 900 °C, regardless of the form of Hg when it was collected. Even at 250 °C, Hg collected as DMM was released entirely as EM, while most of the MC was clearly released as EM at that temperature. As noted above, difficulties in working with MC preclude drawing definitive conclusions with respect to whether 100% of the MC was converted to EM at relatively low temperatures. The DMM and MC may have been converted to elemental mercury prior to evolution. One possible mechanism for this reduction involves the stripping of the methyl ligands of DMM and the chlorine ligands of MC during collection (*16*). In one study, it was reported that DMM is demethylated to EM as it is removed from gold during heating (*6*).

It was hoped that different forms of Hg collected with gold would be bound differently, and that this could subsequently result in different temperatures necessary to evolve all of the Hg. However, this does not appear to be the case. On the basis of the results of this work, using the PTE approach does not appear to be a viable Hg speciation method.

Programmed Temperature Sorption. As with the PTE work, three to four replicate tests were performed under each set of experimental conditions, and results for a given set of conditions were generally reproducible to within 5%. The data obtained using the PTS approach were summarized by plotting collection efficiency versus collection temperature. For PTS, the trends in the curves obtained using peak areas were nearly identical to those obtained with peak heights. Results obtained by using peak areas are shown in Figure 5. As noted with the PTE work, it is possible that using a different gold trap containing a different amount of gold or another type of substrate material may very well shift each of these curves.

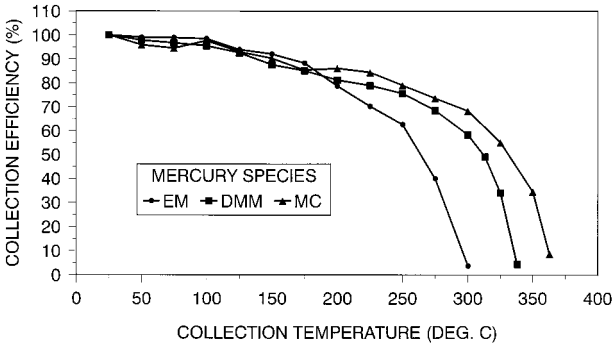

FIGURE 5. Mercury collection efficiency vs collection temperature.

A comparison of the Hg collection efficiencies as a function of collection temperature revealed important differences among EM, DMM, and MC. In the case of EM, the quantity of Hg captured at 200 °C was approximately 80% of the Hg captured at room temperature, and this percentage diminished rapidly as the collection temperature increased until, at a temperature of 300 °C, only 3% of the Hg was successfully captured. For DMM, this rapid decrease in collection efficiency began with a collection of about 85% of the Hg at a temperature of 225 °C and ended with only a 3% collection at a temperature of 335 °C. Thus, the "collection curve" for DMM was shifted to higher temperatures. The collection efficiency of MC was observed to follow a similar trend, but the curve was shifted to still higher temperatures.

Although the differences in the collection efficiencies of EM, DMM, and MC as a function of temperature are not major, there nonetheless exists the possibility for separating these Hg species using the PTS approach. Also, it is important to note that each of the Hg species can be collected at elevated (e.g., 150 °C) temperatures. This is important for flue gas sampling applications, where sampling temperatures on the order of 150 °C are likely. However, before this technique can be considered further for separating different Hg species, the baseline must be made more horizontal and the slope of the Hg collection curve in the 200−400 °C region must be made steeper. It is likely that improvements can be made in these areas through proper modification of the experimental design and experimental procedures. For example, a different gold trap design (size, shape, and type of Hg collection material) or altered gas flow rates may significantly affect results.

Once the shapes of the curves are improved, multiple traps could potentially be used to provide Hg speciation information. In one possible approach, side-by-side traps could be used. During Hg collection, each gold trap would be maintained at a suitable temperature (determined by the Hg collection curves, which are not yet sufficiently refined). With suitable refinement in the PTS curves, the lowest collection temperature would be used to collect EM and MC (as well as DMM if present) while the highest temperature would be used to capture only MC. If DMM were suspected to be present, an intermediate temperature could potentially be used to collect only MC and DMM. In this scenario, the Hg captured at each temperature would be thermally evolved (one at a time) into a suitable Hg detector, and each oxidized Hg species would be determined by difference (i.e., high collection temperature captures MC only, intermediate temperature captures MC + DMM, and low temperature captures MC + DMM + EM).

In cases where DMM is probably not present, such as in coal combustion gases, this approach would add an alternative to using a pyrolyzer in front of a CVAA detector. In that approach, the coal combustion gases are passed directly into the CVAA detection cell (no gold trap). Since the detector measures only EM, the EM fraction of the total Hg in that gas stream is measured while the oxidized Hg fraction is excluded from analysis. When the coal combustion gases pass through the pyrolyzer prior to the detector, the oxidized Hg is converted to EM (while the EM originally present is unchanged), and the detector therefore measures the total gaseous Hg present since all of the Hg is now in the form necessary for detection by CVAA. The oxidized Hg fraction is then determined by difference (i.e., total Hg minus EM).

For analyzing coal combustion gases, another consideration is that difficulties involving diminished CVAF detector signals have been noted while using such traps for Hg preconcentration in the presence of simulated and actual coal combustion streams, even though the trap is subsequently heated in argon. However, proper operation of the analyzer is apparently restored by scrubbing HCl (without affecting Hg) from the gases prior to the gold trap (*17*).

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