

Assessment of Bias in Measurement of Mercury Emissions from Coal Fired Power Plants – Comparison of Electronic CEMS and Sorbent Traps

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Abstract

Mercury emissions from coal fired power plants are generally measured using one of two methods - electronic Continuous Emission Monitoring Systems (Hg CEMS) that most commonly use atomic fluorescence, or sorbent traps. Electronic Hg CEMS are often compared against sorbent traps using EPA's Method 30B Relative Accuracy Test Audit (RATA). Because sorbent traps include mercury contained in the particulate matter (PM) that escapes the boiler's PM control device, there is an expected bias of the sorbent trap indicating a higher result than the electronic Hg CEMS. For uncontrolled units this difference is normally an insignificant amount of mercury compared to the total. As will be shown, for controlled units, this difference can be more significant. Some researchers have proposed additional explanations for apparent differences in these methods, to include interference from bromine that may be present in the flue gas.

In this effort, work by others is reviewed and comparative data from electronic CEMS and method 30B RATA are presented. The data includes conditions where bromine is injected, where activated carbon is injected and where activated carbon is injected while bromine is introduced to the flue gas. This data is examined for trends in bias and is assessed statistically to determine the confidence levels in any observed trends. The results of the analysis of the data will be used to help test the various proposed explanations for the observed difference between electronic CEMS and sorbent traps and will provide practical guidance for facility owners going forward.

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Introduction

Roughly 500 coal fired units use Hg analyzers as Continuous Emission Monitoring Systems (Hg CEMS). The most common method of performing Relative Accuracy Test Audits of these systems is EPA Method 30B, which uses sorbent traps. As such, there have been hundreds of comparative measurements between Hg analyzers and sorbent traps. However, except for those units operating with Hg controls, there has been limited data at Hg concentration levels required for compliance with the Mercury and Air Toxic Standards (MATS).

Controls for Hg for bituminous and subbituminous units will reduce Hg emissions to concentrations in the range of $1.0 \mu\text{g}/\text{Nm}^3$ or even less. This is achieved by converting mercury to forms that are captured in particulate matter (PM) control devices or in scrubbers. The most common forms of Hg control include sorbent injection, such as activated carbon injection (ACI), and may also include introduction of oxidizing agents, such as bromine (Br), that improve conversion of elemental mercury (Hg^0) to particulate mercury (Hg^{P}) or oxidized mercury (Hg^{2+}). This effort was directed toward examining and understanding differences that may exist between Hg analyzers used as CEMS and EPA method 30B at MATS compliance levels when Hg emission controls are employed.

The Hg analyzers used at CEMS are primarily from two suppliers – Tekran and Thermo Fisher Scientific (hereafter referred to as Thermo). Both major suppliers were contacted to provide comparative data. Tekran agreed to provide comparative data from RATAs. Thermo did not, but perhaps may make data available in the future.

Potential Contributors to Differences in Hg Analyzers and Method 30B

Sources are required to measure the total emission of both gaseous forms of mercury, Hg^0 and Hg^{2+} , and report the total of the two. Hg^{P} is not intended to be included in the reported value, although, as will be discussed below, it often is depending upon the measurement method used.

The Tekran Hg CEMS analyzes the sample using the method of atomic fluorescence whereby Hg that is collected on a gold amalgam is then pulsed with ultraviolet light and emits a fluorescence. The Thermo Hg CEMS also uses atomic fluorescence but does not use a gold amalgam. The intensity of the fluorescence is related to the amount of mercury present. The analyzer is only capable of detecting Hg^0 , and therefore it is necessary to convert Hg^{2+} in the sample to Hg^0 prior to reaching the analyzer. Both major Hg CEMS suppliers use dry thermal conversion, where the sample is heated to convert Hg^{2+} to Hg^0 . This is to be differentiated from wet conversion systems that convert the Hg^{2+} to Hg^0 using wet chemical methods.

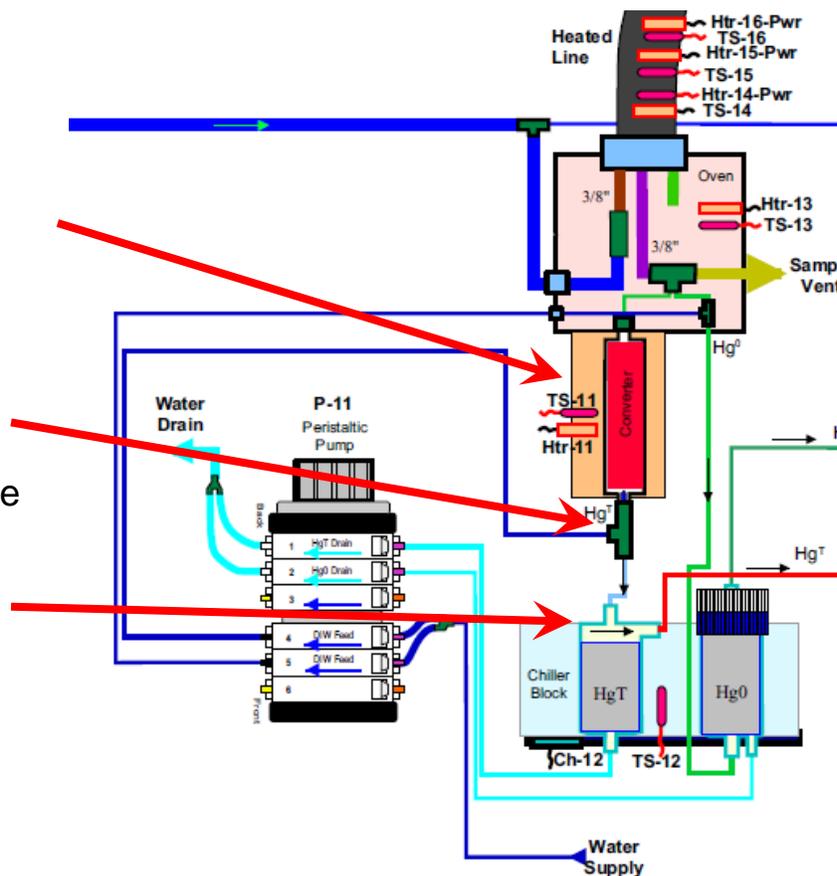
There are two places where some interferences could potentially be introduced before the analyzer.

- On the probe filter tip or other active internal surfaces – surface reactions on the filter tip or within the probe could convert gaseous Hg to Hg^{P} . To minimize potential of such reactions, Tekran’s filter is made of an inert material and blowback cleaning is performed on an hourly basis and internal surfaces are coated. Thermo takes similar measures to avoid this effect.

- The other location is the sample converter/conditioner system. Figure 1 shows a schematic of Tekran's patented converter/conditioner system. This conversion and handling system is designed to both effectively convert Hg^{2+} in the sample to Hg^0 and minimize the potential for back reactions that could reform Hg^{2+} upon gas cooling by reactive halogens, like Br. The sample probe filters the Hg^p from the sample, so no Hg^p is included in the total Hg reported. The sample is then diluted with dry zero air at a rate of 30:1 (or more). All internal surfaces are made from inert materials or coated with inert material. The internal converter material in the thermal converter is well characterized and understood. The thermal converter heats the sample to $700^{\circ}C$, where Hg^{2+} is converted to Hg^0 . The gas is then rapidly cooled with deionized water and a chilled coalescing filter to rapidly remove acid gases and any reactive halogens. As such, the effect of potential back reactions from reactive halogens can be minimized. Thermo also uses a dilution probe and dry thermal conversion system, but does not have a follow-on deionized water gas conditioner.

Figure 1. Tekran's patented flue gas converter/conditioner system.

- Proprietary thermal converter material set at $700^{\circ}C$
- DI water injected into tail of thermal converter to "fix" Hg^0 from potential back reactions and eliminate interferences
- Gas is rapidly chilled (under 0.1 sec), water condenses and removes reactive compounds



Because of its robustness, dry thermal conversion is used by both major Hg CEMS suppliers. Thermal conversion is to be distinguished from "wet" conversion systems that are not used on Hg CEMS and are not examined here because they are now rarely used and only as temporary test systems. Wet conversion systems are known to be prone to reactive halogen interferences because they depend on a

low pH, aqueous tin chloride (SnCl₂) reduction of Hg²⁺, instead of the Hg CEMS style dry thermal converter.

With Method 30B, or the sorbent trap method, a measured volume of gas is drawn through a well characterized sorbent that captures mercury. There are two sorbent sections – a primary portion and secondary portion to check for Hg breakthrough. There is mineral wool at the inlet, between, and at the exit of the traps. Hg captured in the mineral wool is included in the total mercury measured, and this will therefore include any Hg^P that is captured by the trap. For this reason Method 30B states that the method should only be used for gas streams that are low in PM concentration.

Contributors to differences in the results from these methods can therefore be:

- Hg on PM that is in the gas stream that is included in Method 30B but not in the Hg CEMS analysis
- Reactive halogens (such as Br) that might interfere with the sample capture or conversion
- Other random or systematic errors that may be introduced.¹

Impact of Hg^P

Data were reviewed from US EPA's 2001 Information Collection Request (ICR) that included mercury measurements from about 240 *uncontrolled* units. This data showed stack outlet Hg^P ranging from non-detectable to 0.93 µg/Nm³ with only 41 having Hg^P greater than 0.10 µg/Nm³. Even the highest Hg^P values were low enough compared to the total Hg that they would not have a large impact on total Hg. However, none of these units were operating with activated carbon injection (ACI) at the time. Had they been operating with ACI, higher Hg^P would have been expected along with much lower total Hg.

Br is known to be an important participant in the capture of Hg using ACI or in a wet scrubber, as it participates in the oxidation reaction necessary to bind Hg to the surface of the ACI, to fly ash or to put the Hg in a water-soluble form for capture in the scrubber. If there is not sufficient Br (or other reactive halogens) available in the coal, Br is typically added to the fuel or is included in the activated carbon. Figure 2 illustrates what happens when ACI and Br are used in combination to reduce Hg emissions. The ACI and Br converts Hg⁰ into Hg^P and Hg²⁺. Br may also be added without ACI to convert Hg⁰ into Hg^P, with the Hg collecting on fly ash. The Hg^P is removed from the ESP or baghouse (or other PM control device). If there is a scrubber, that will remove much of the Hg²⁺. However, as a result of the mercury control, the fly ash will have higher mercury content than if there were no controls and, although the total Hg emissions will drop, the Hg^P will actually increase versus the uncontrolled condition.

Br is sometimes added alone to the flue gas (normally as a fuel additive) upstream of a scrubber and this will convert much of the Hg⁰ to Hg²⁺ (which is removed by the scrubber) and will likely increase Hg^P as well.

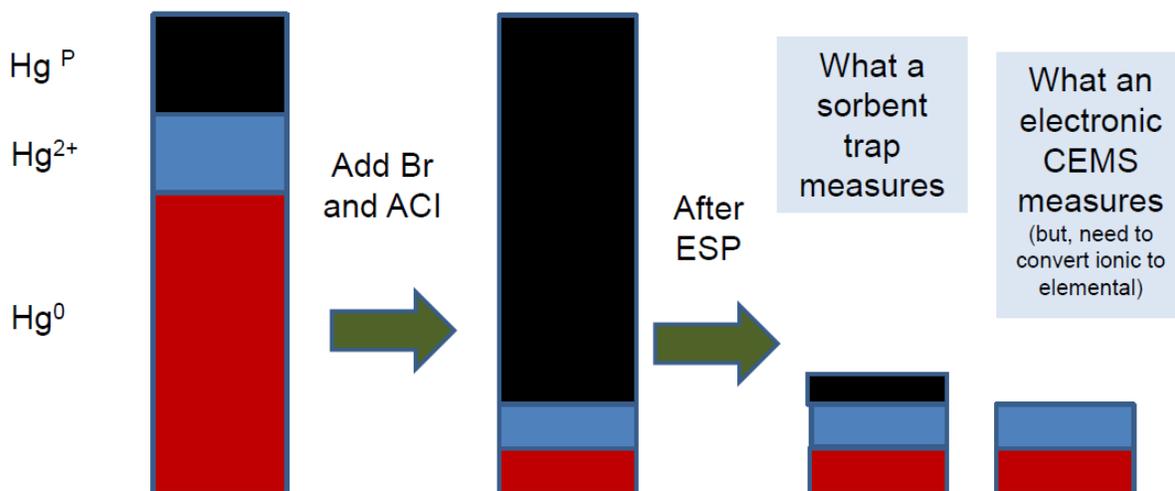
¹ This paper does not explore the analytical methods used for Method 30B, which might also introduce differences in the measurements.

Moreover, because the sorbent trap includes Hg^P that makes it past the ESP, but the electronic CEMS does not, a sorbent trap should in general indicate a somewhat higher result because it includes the Hg^P . The degree to which there is a difference depends upon:

- The PM concentration in the exhaust gas at the stack
- The mercury concentration in the PM

According to EPA's monitoring requirements, only the gaseous components of Hg are of concern and need to be reported, and the presumption is that Hg^P is sufficiently low after the PM control device that its contribution to the result of Method 30B can be ignored. However, this is not really the case at MATS compliance levels, and especially when ACI is used.

Figure 2. Fate of Hg constituents when controlling Hg with ACI and Br and what is measured by sorbent traps and electronic CEMS.



The concentration of Hg in the fly ash of coal power plants will vary based upon the coal characteristics and the characteristics of the plant. Researchers have found that the Hg in fly ash tends to be higher in concentration in the finest size fractions. The Hg concentration in the fly ash also is higher at the exit of an ESP than in the inlet.² This seems reasonable. Smaller size fractions have greater surface area per unit mass and are more likely to adsorb Hg and Br. Smaller size fractions are also more likely to pass through an ESP or other PM control device than larger size fractions. Researchers found Hg concentrations on fly ash at the exit of an ESP without ACI in the range of 5-10 ppm (mg/kg).³ Nevertheless, use of activated carbon to capture Hg will certainly result in an increase in the

² Jedrusik, M., and Swierczok, A., "The influence of unburned carbon particle on electrostatic precipitator collection efficiency", 13th International Conference on Electrostatics, Journal of Physics: Conference Series 301 (2011) 012009

³ This does not mean that 5-10 ppm (mg/kg) is typical, but it seems reasonable under some conditions. For uncontrolled facilities with low Hg content coal and low intrinsic capture, the value could be much less.

concentration of Hg^P exiting the ESP.⁴ It can be shown with some calculations that the average concentration of Hg on activated carbon used to capture Hg may be on the order of 100 ppm – sometimes higher. The finer size fractions, which are most likely to pass through a PM control device will also tend to have the highest Hg concentrations. The activated carbon should only increase the quantity of fly ash by a small amount; but, the much higher concentration of mercury in the activated carbon combined with the fact that activated carbon – especially the finest fraction - is not as effectively captured as fly ash, should result in significantly higher concentrations of Hg in the fly ash exiting the PM control device.

The contribution of Hg^P to total Hg concentration will cause there to be a difference between total Hg and gaseous Hg and this difference can be estimated using a few reasonable assumptions, such as typical gas flow rates per unit heat input and typical PM emission rates. Figures 3 and 4 show the results of these calculations. As shown, if the concentration of Hg in the PM exiting the control devices is somewhat under 10 ppm, at a PM emission rate of 0.015 lb/MMBtu this equates to about 0.20 µg/Nm³. If Hg concentration in the PM is increased to 25 ppm, then this increases to over 0.50 µg/Nm³. And, under the right conditions with respect to PM emission rates and Hg content of the fly ash, Hg^P at the exit could be several µg/Nm³.

These Hg^P concentrations are not a major concern from the perspective of measurement error at total Hg emission rates that are typical of many uncontrolled units, but for most units compliance with MATs will entail emission rates in the range of 1.0 µg/Nm³ or less. As shown in Figure 5, at these MATS compliance emission levels the contribution of Hg^P to total Hg emissions will be very significant portion of total emissions and will result in significant differences between the results achieved with Method 30B and electronic CEMS (although it should not be enough to fail a RATA).

⁴ Clack has investigated this, see Clack, H.L., “Particulate carbon emissions from electrostatic precipitators used for mercury emissions control: operational factors and implications”, *Air Quality, Atmosphere & Health*, 2014, pp. 1 - 9

Figure 3. Estimate of difference between total Hg and gaseous Hg as a function of PM emission rate and Hg concentration in PM (up to 10 ppm Hg in PM).

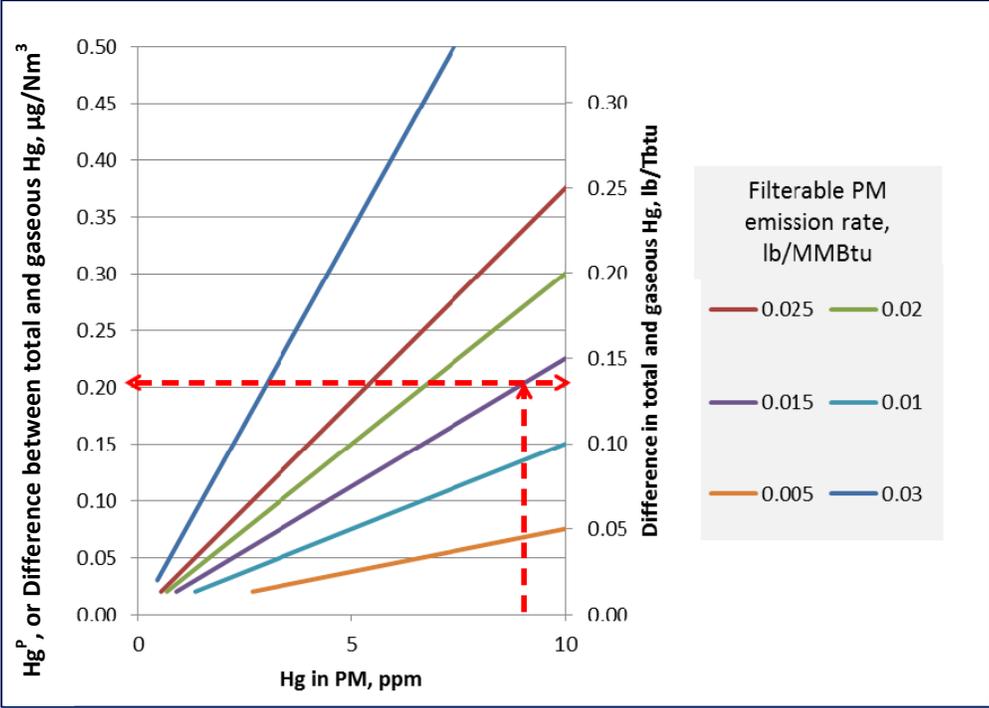


Figure 4. Estimate of difference between total Hg and gaseous Hg as a function of PM emission rate and Hg concentration in PM (up to 50 ppm Hg in PM)

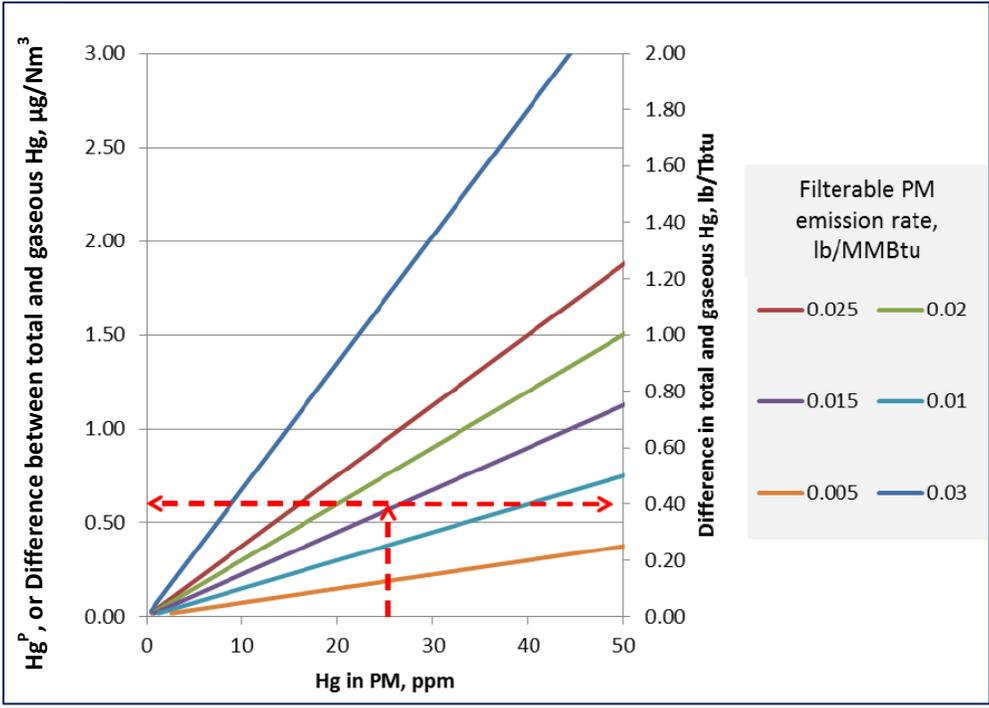
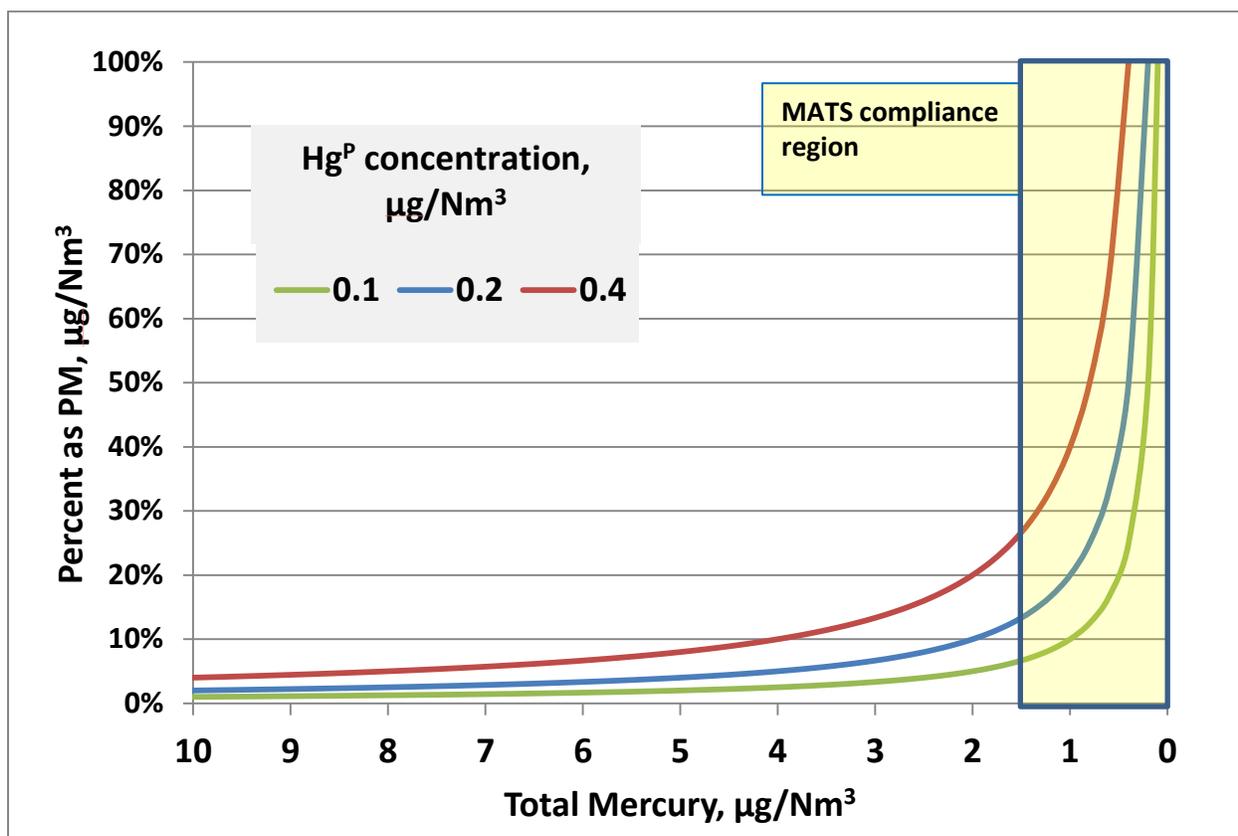


Figure 5. Potential impact of Hg^P at different total Hg concentrations.



Interference from Br or other reactive halogens

As noted earlier, reactive halogens have the potential to impact the measurement of gaseous Hg. There are a few possibilities:

- Br or other reactive halogens might increase conversion of gaseous Hg to Hg^P on the probe filter or on other reactive surfaces.
- It has also been suggested by some that the Br could interfere with the conversion of Hg²⁺ to Hg⁰ in the CEMS, which would result in a lower reported total gaseous Hg concentration.⁵

Br reactions with Hg⁰ are most rapid on a reactive surface, such as activated carbon, fly ash or another reactive site. The filter probes are made from a material that is intended to be inert and the filters are cleaned with reverse-flow dry air. However, if impurities collect or corrosion forms on the filter or other surfaces and provide reactive surface, Br reactions with Hg⁰ to form Hg^P may occur and reduce the reported total gaseous Hg from what is actually in the flue gas.

⁵ Dombrowski, K., "Bromine Interference with Hg Measurements; Field Experience", July 12, 2013

Interference in the conversion system has also been proposed. Both major suppliers of Hg CEMS use dry conversion systems that thermally convert Hg^{2+} to Hg^0 . At the temperatures of the thermal converters, Hg^{2+} should be quickly converted to Hg^0 regardless of the presence of Br. Tekran's converter takes the additional step of removing reactive halogens immediately after the converter to avoid reformation of Hg^{2+} when the gas cools on its way to the analyzer by taking advantage of Hg^{2+} 's high solubility in water.

URS has observed differences in Method 30B and electronic CEMS in cases when Br is added.⁶ They found that this is a particular concern for wet-conversion systems that are not used for compliance CEMS, but they did find a difference on a scrubbed boiler when using a dry conversion system.⁷ It is also noteworthy that the mercury concentrations that for the dry-conversion system were measured were on the order of 10-15 $\mu\text{g}/\text{Nm}^3$ (suggesting a high Hg coal) and the differences in measurement were on the order of a few $\mu\text{g}/\text{Nm}^3$ to 10 $\mu\text{g}/\text{Nm}^3$.

For the dry conversion system, URS' testing on a boiler with cold-side ESP and wet FGD without Br addition showed differences between the Hg CEMS and Method 30B – with Method 30B typically higher on the order of 2-3 $\mu\text{g}/\text{Nm}^3$ - confirming a likely Hg^p contribution to the difference. Data when testing on the same boiler with Br also showed differences, sometimes much greater; however, the data on plant load and other information that might impact PM emission rate were not available. Moreover, it seems that the wet scrubber would be expected to remove available Br from the flue gas prior to the analyzer. Therefore, the data indicates that increased Hg^p is likely at least a *partial* contributor to the difference, but the difference when Br was added may not be fully explained by Hg^p . It is also possible that some amount of HBr that escapes the wet scrubber interacts with particulate matter on the probe filter or other probe surface to remove gaseous Hg from the sample. Br interference with the conversion system has also been suggested by URS. The difference may also be the result of another effect that we don't have the information to assess.

URS also found that when injecting brominated ACI, (as opposed to adding Br to the fuel or flue gas), some Br does off-gas, but the measurements indicated HBr concentrations under 1.0 ppmv HBr at the PM control outlet. These results suggest the *possibility* of Br interactions; however, research by EERC is also helpful in evaluating the practical implications of these results.

⁶ Dombrowski, K., "Bromine Interference with Hg Measurements; Field Experience", July 12, 2013

⁷ Thermo and Tekran both use dry conversion systems with dilution air downstream of a filter, although there are some differences in their approach. URS was contacted for the name of the CEMS supplier, but declined to provide it. However, they did note that there have been changes in the company's probe design since that time that were unrelated to halogen impact needs.

EERC has conducted a pilot-scale examination of the measurement of low concentrations of Hg with and without Br present. Their results found that:⁸

- Without Br injection, the Tekran CEMS was accurate to levels well below 1.0 ug/Nm³. The Thermo unit initially did not perform well at low levels, but after some changes to the Thermo unit, the performance was improved.⁹
- With Br injection at a concentration of 5 ppmv to flue gas (outlet HBr measured at over 1.0 ppmv), there was no adverse impact of Br for either the Tekran or Thermo units, whether using coal or gas flames or whether or not ACI was used)
- With Br injected at 25 ppm to flue gas (outlet HBr at 8-10 ppmv) there was an apparent difference between Method 30B and the Hg CEMS for both gas and coal flames on the Tekran unit. The difference was greater with ACI, suggesting a possible Hg^p contribution to the difference. The Thermo unit did not seem to be impacted by the HBr.
- When injecting brominated ACI, no significant difference was observed for either the Thermo or Tekran units.

Br is, of course, highly reactive, which explains why the exit concentration is much lower than what is injected into the flue gas. Br will react with surfaces within the system, including fly ash.

When Br is injected, it is only at the highest injection rate where an impact was observed on Tekran's instrument. According to EERC:

“The bias only became significant (RA >20%) when the HBr injection was at the higher level (25 ppmv). Most likely these HBr concentrations would not be used in full-scale applications.”

The effect was also more pronounced under conditions where natural gas was burned. The reason for this was not examined in the study, but natural gas produces much more moisture than a coal flame, which participates in and may have a positive effect on the HgBr₂ reaction.

The reason for the effect on the Tekran instrument at high Br rates is unknown. A likely cause is a surface reaction, which is the fastest and therefore the most common reaction pathway for Hg and Br. This would point toward either the probe filter or a surface on the probe.

As noted, EERC also tested a Thermo Hg CEMS and did not observe a significant change in performance during Br injection. The Thermo unit also uses a dry conversion system and atomic fluorescence, and no reason could be determined to explain why the Tekran conversion system or analyzer should be more

⁸ Laudel, D., Tompson, J., Jones, A., Dene, C., “Determining the Variability of Continuous Mercury Monitors (CMMs) at Low Mercury Concentrations”, 9th IEA Mercury Emission from Coal Workshop, May 22–23, 2012, St. Petersburg, Russia

<http://mec9.coalconferences.org/idocument/atom/cview.aspx?LogDocId=92140&PhyDocId=1272>

<http://mec9.coalconferences.org/idocument/atom/cview.aspx?LogDocId=92140&PhyDocId=1303>

⁹ Jeff Thompson, Dennis Laudal, John Pavlish, Chuck Denek “Determining the Variability of Continuous Mercury Monitors (CMMs) at Low Mercury Concentrations with the Addition of Bromine”, AIR QUALITY VIII, International Conference, October 24–27, 2011, Arlington, Virginia

affected by Br than the Thermo conversion system or analyzer.¹⁰ This suggests that a surface reaction on the Tekran instrument probe was the most likely cause of the Br effect that was observed when injecting at very high Br rates.

The EERC testing also demonstrated that brominated activated carbons do not appear to have an adverse impact on the performance of either the Tekran or Thermo Hg CEMS. The URS study indicated that HBr off gas measured at the exit remained under about 1.0 ppmv, and the EERC Br injection tests at 5 ppmv injected (over 1 ppmv at the exit) did not have a significant impact on either Thermo or Tekran analyzers – which suggests that Br off-gassed from brominated ACI is not expected to impact the analyzer performance.

Comparison of RATA Data

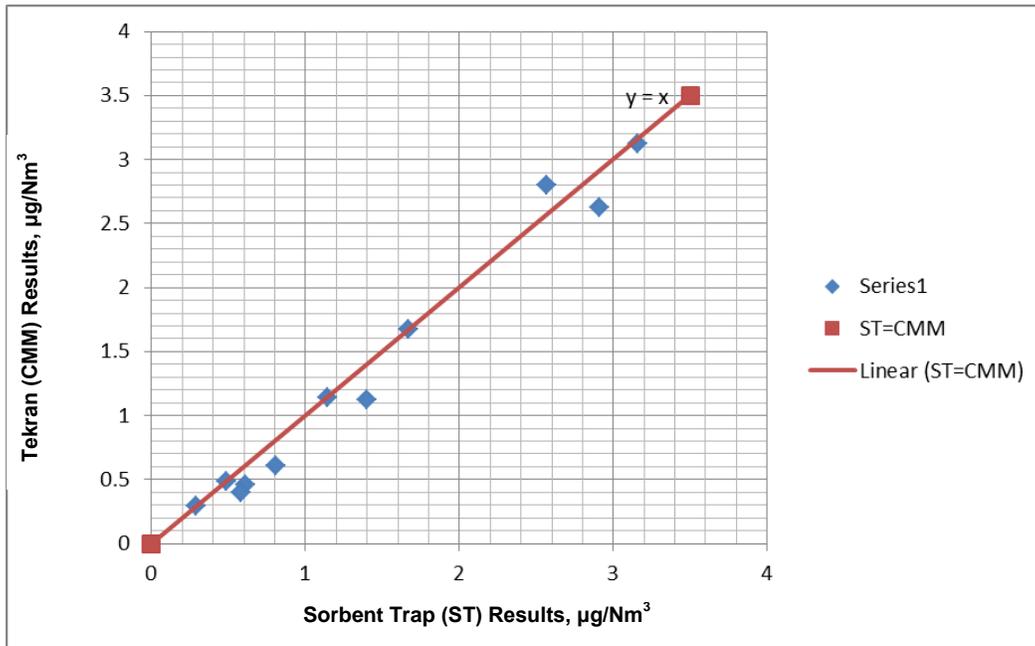
Tekran provided comparative data between Method 30B and Hg CEMS. In some cases this data was from units injecting Br. In some cases Br was not injected.

No Br injection

Figure 6 shows the results of comparative data between sorbent traps and Hg CEMS for coal fired power plants. As shown, the data (blue dots) generally track the red line that shows where the sorbent trap results would equal the Hg CEMS (or, the Continuous Mercury Monitor, or CMM). However, many of the data points fall below the equality line by an average difference of 0.20 $\mu\text{g}/\text{Nm}^3$. This difference is consistent with what might be expected for Hg^P. However, it is important to note that the results of most interest from the perspective of MATS compliance are those in the range of about 1.5 $\mu\text{g}/\text{Nm}^3$ and below. At these levels, a difference of 0.20 $\mu\text{g}/\text{Nm}^3$ from Hg^P would be significant, but would not be enough to impact whether or not a RATA was passed.

¹⁰ There are some differences in the conversion system and analyzer. But, those differences do not help explain the difference in Br effect. Moreover, because a surface reaction is the fastest and easiest reaction between Hg and Br under the conditions available, it is the most likely route.

Figure 6. Tekran CMM versus Sorbent Trap data for a coal-fired boiler without Br addition.¹¹



With Br Injection

A Tekran client provided data from RATA's over a four-year period on four units. All four units are equipped with a wet scrubber for SO₂ and PM control. The four units also used ACI and a Br additive for Hg control. Over this period Br additive injection varied. ACI rate may have varied also, but we don't have that data. It is not possible to determine the Br concentration in the flue gas because the chemical content of the Br additive was proprietary. On the other hand, because the same chemical additive was used over the four-year period and the rate of addition is known, it is possible to compare the Br additive injection rates on a relative basis, normalizing against the lowest relative injection rate (determined by comparing unit capacity and additive injection rate).

Figures 7a through d show comparative RATA data for units, 1 through 4, respectively (each point being one Method 30B and the average Tekran Hg CEMS result over the 30B sampling period), with a minimum of nine data points for each year and each unit. As shown here, with only a few exceptions, the Tekran analyzer indicated similar or somewhat lower mercury levels than Method 30B.

The effect of Br addition for all four units is shown in Figure 8, which shows the average difference between Method 30B and the Tekran Hg CEMS for the RATA plotted against the normalized Br injection rate. So, Figure 8 shows the average difference of the nine or more RATA data points in Figures 7a-d and the standard deviation. As illustrated by Figure 8, except for one of the RATAs for Unit 2, which is also at the highest normalized Br injection rate, all of the differences between Method 30B and the Tekran Hg CEMS fall within a similar range with no trend. The one point showing the difference between Method 30B and the Tekran Hg CEMS for unit 2 that is higher than the others is within two

¹¹ data provided by Tekran

standard deviations, but more than one standard deviation, of the closest point (one of the points for unit 3). This means that there is a significant difference, but not necessarily at a very high confidence level from the other, closest point.

However, if the unit 1 & 2 difference data is represented separately from the unit 3 & 4 difference data (units 1 & 2 are similar and units 3 & 4 are similar) as in Figures 9a and b, the one unit 2 difference data point at the highest Br injection rate appears to have a much more significant difference from the rest of the unit 1 & 2 data. This one data point of the difference between Method 30B and the Tekran Hg CEMS for unit 2 is different from the other unit 1 and 2 data at a high confidence level, as demonstrated by measuring two standard deviations from the mean and observing no overlap with the other data points. The data from units 3 & 4 shows no trend at all in the difference between Method 30B and the Tekran Hg CEMS, with all data points scattered over a similar range.

So, it is possible that at the highest Br injection rate that was experienced on unit 2, some additional effect associated with Br is occurring. However, especially with field data, it is always important to remember that a statistically significant difference that can be associated with a parameter does not necessarily mean causation. In this case it was not possible to conduct a careful experiment under well-controlled conditions. The wet scrubber would have certainly removed a significant amount of Br from the flue gas prior to the analyzer. PM data and samples were not available, ACI rate data was not provided, all of which would have been very helpful, and without additional information it is not possible reach a definitive conclusion about this one set of data on unit 2 for the highest Br rate.

The differences measured in this situation for the most part appear to be well within the range of values that can be explained by the Hg^p that makes it past the PM control device (in this case a wet scrubber). The one set of RATA data at the highest Br rate shows a difference between Method 30B and the Tekran Hg CEMS that is also potentially within the range of high Hg^p , but nevertheless is significantly different than the other data and there is a possibility that there are other factors at play at this highest Br addition rate.

Figure 7a. Unit 1

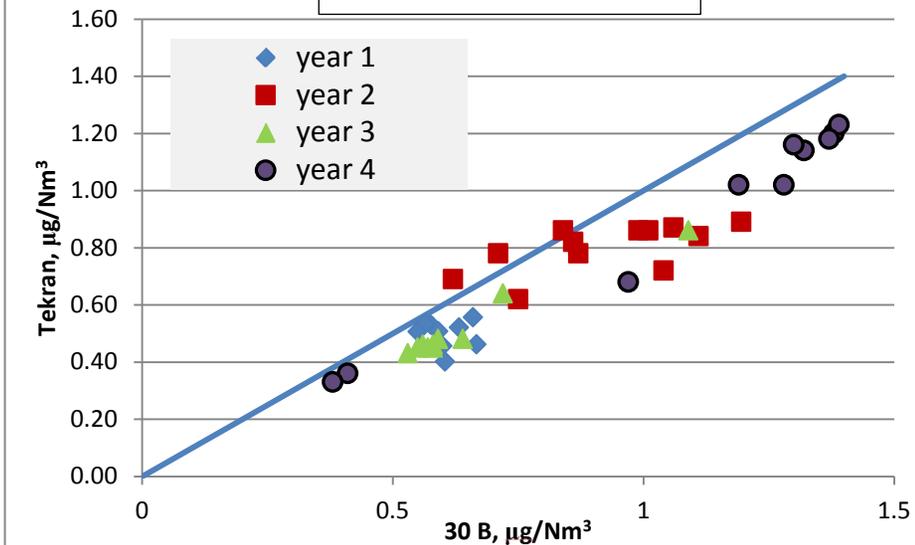


Figure 7b. Unit 2

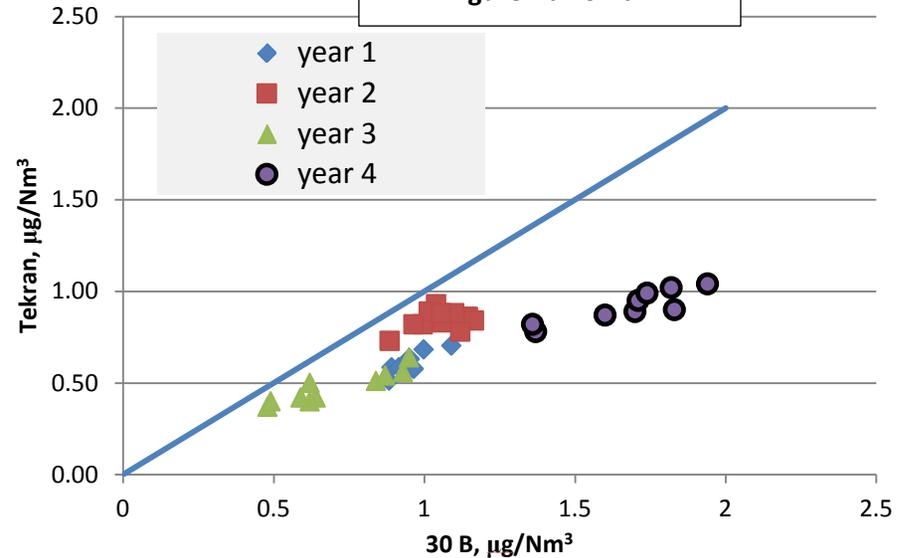


Figure 7c. Unit 3

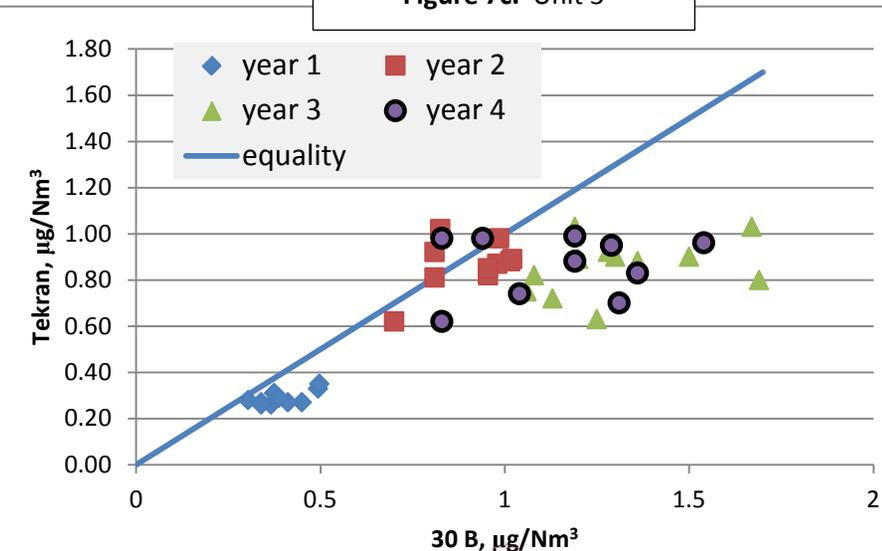


Figure 7d. Unit 4

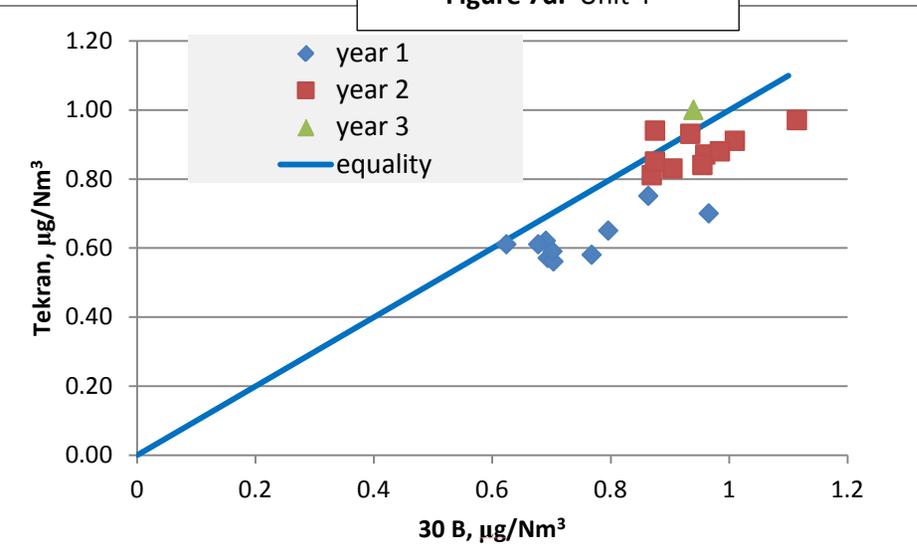


Figure 8. Method 30B minus Tekran for four units, average and standard deviation shown

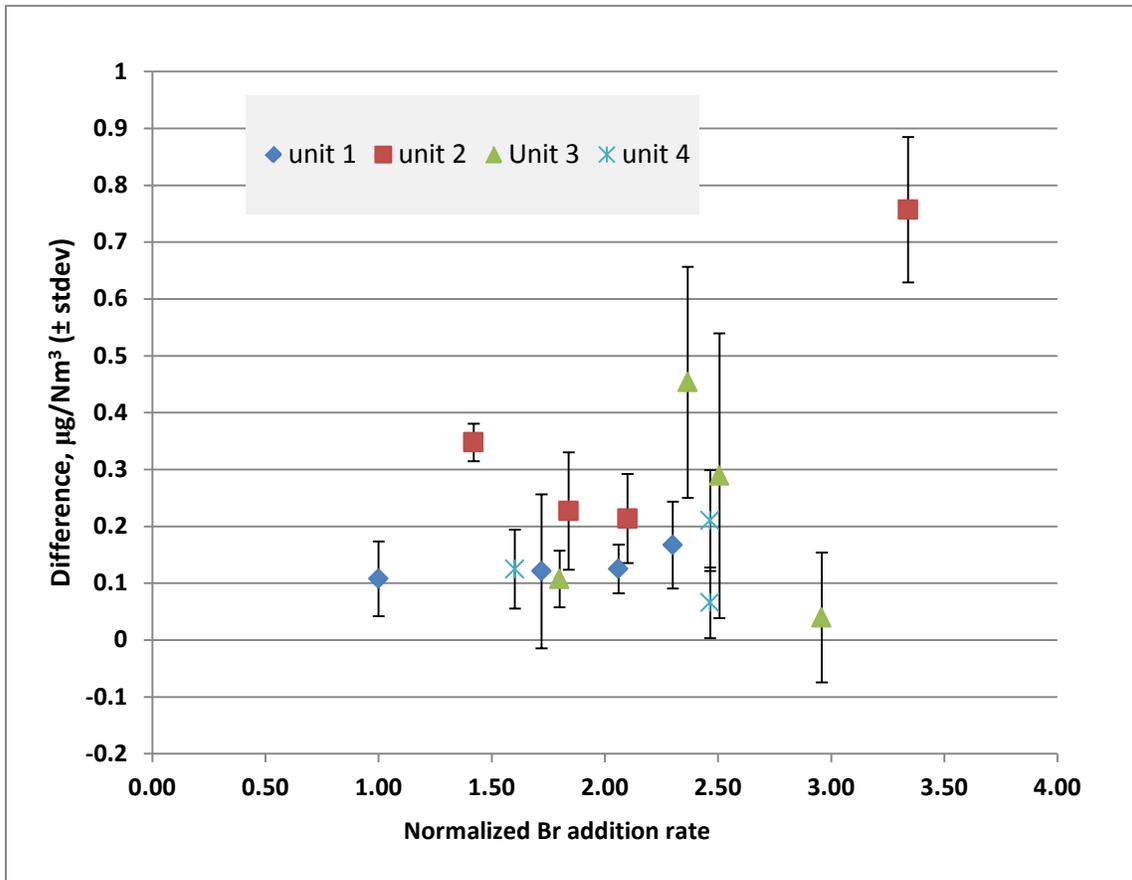


Figure 9a. Method 30B minus Tekran for units 1 & 2, average and standard deviation shown

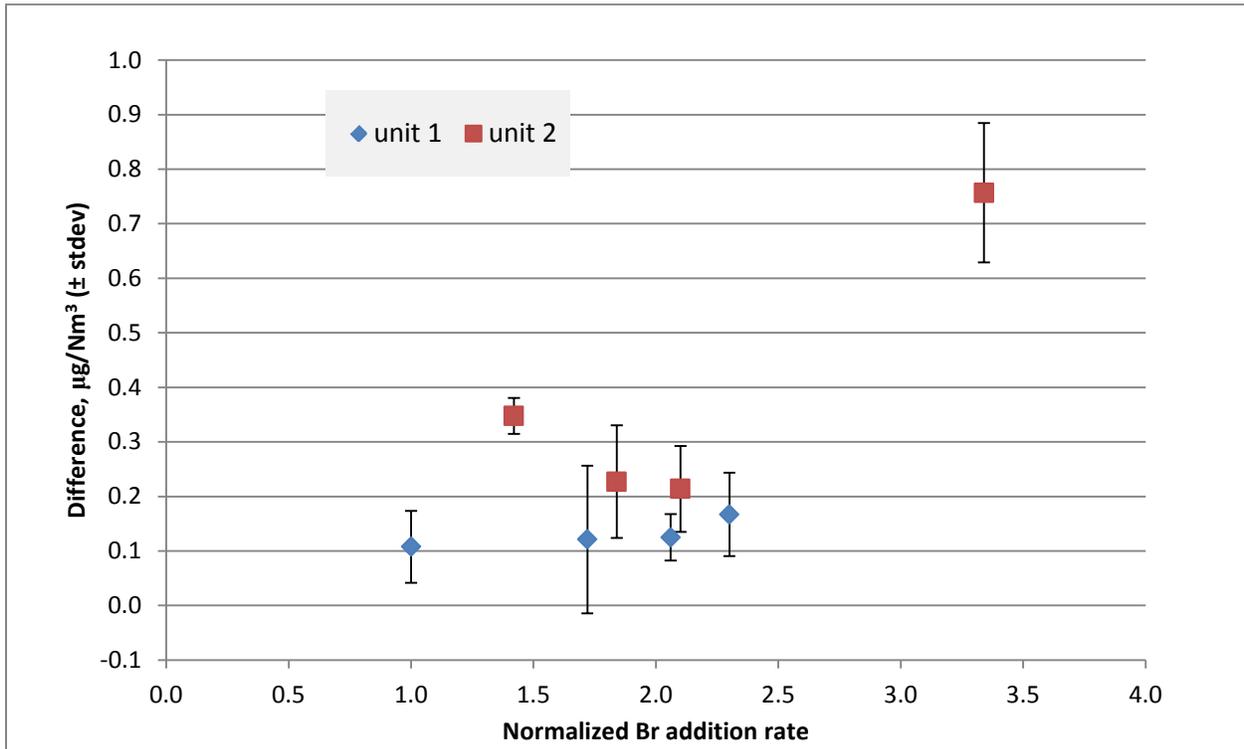
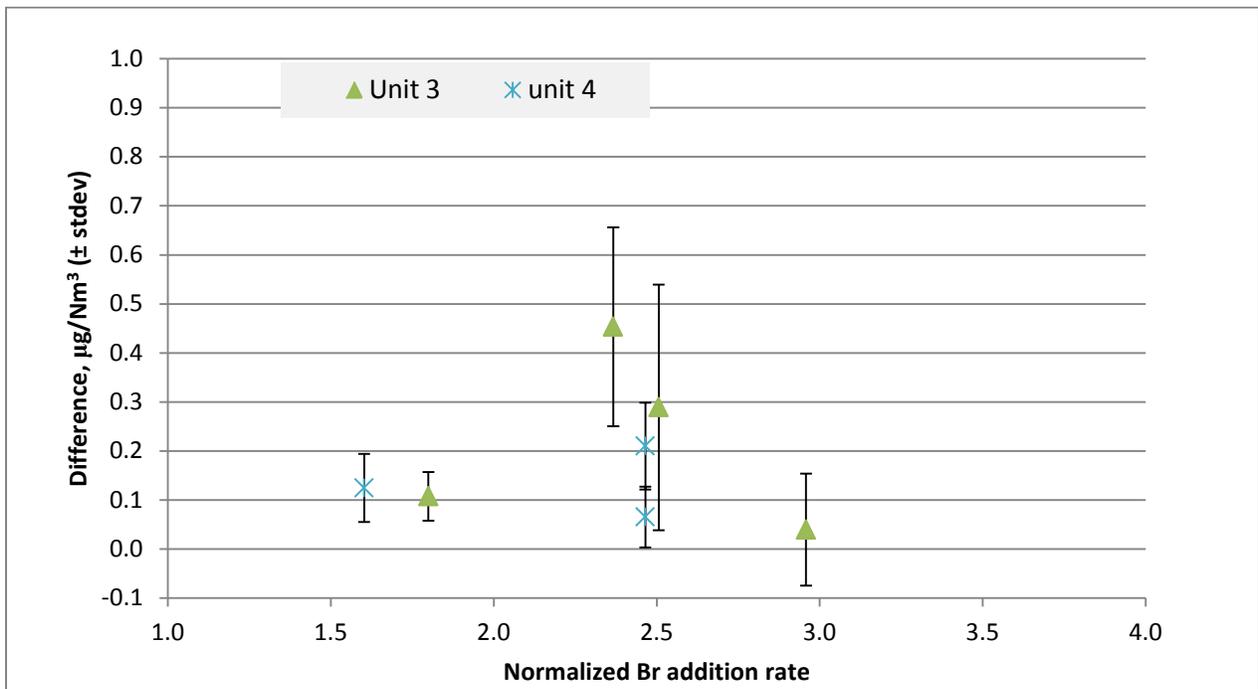


Figure 9b. Method 30B minus Tekran for units 3 & 4, average and standard deviation shown



Conclusions

This study examined some of the factors that could contribute to differences between Method 30B Hg measurements and those that result from Hg CEMS.¹² The following conclusions can be drawn:

- When Hg is not controlled, the contribution of Hg^P is generally not enough to result in a significant difference between Method 30B and electronic Hg CEMS.
- ACI and Br addition for Hg control will increase Hg^P. When Hg is controlled to MATS control levels, Hg^P that makes it past the PM control device may be sufficient to cause Method 30B to overestimate the gaseous Hg emissions by a significant degree, but typically not enough to impact whether or not a RATA is passed.
- At sufficiently high Br levels, there is a *potential* for Br to contribute to differences between Method 30B and Hg CEMS that are not explained by Hg^P alone. One possible mechanism is the reaction of Br on the probe filter (or other surface) with gaseous Hg. This will be exacerbated if the probe or filter surfaces are reactive (ie., not adequately coated), if the filter condition has deteriorated or if material with reactive surface has accumulated on the filter. Others have also suggested that interference with the sample conversion system may contribute to this difference. For most Br addition rates expected under practical conditions, this potential effect is not expected to be significant.
- The use of brominated activated carbon will impact the difference between Hg CEMS and sorbent traps due to formation of Hg^P as a direct and intended result of controlling Hg. The increased Hg^P that makes it past the PM control device will contribute to a difference between Hg CEMS and Method 30B. On the other hand, Br released from brominated activated carbon does not appear to impact gaseous mercury measurements to any significant degree.
- This paper explored some key factors that might impact the difference between Hg CEMS and Method 30B; however, there are other factors for both of these procedures that could potentially introduce differences in the measurements.

The following are some practical considerations of these conclusions:

- Method 30B (sorbent traps) includes Hg^P, which may result in an overestimation of gaseous Hg that may be significant at MATS Hg levels
- Differences in Hg^T typically up to about 0.50 µg/Nm³ may be explained by Hg^P when controlling Hg with ACI and/or Br, although higher Hg^P concentrations have occasionally been measured after PM control devices.
 - This effect will vary somewhat by coal Hg levels, PM emissions, ACI injection, etc.
- Br “interference” should not be a concern except possibly for extremely high furnace Br injection rates and is not a concern when using brominated activated carbon.
- Differences may also result from other effects that are not explored here, which are of particular concern with field data.

¹² These conclusions will apply for either of the two major suppliers, who both use CVAF analyzers and dry conversion systems. For other electronic Hg CEMS technologies, there may be other issues that are not discussed in this paper.