Applicability of Atomic Fluorescence and Atomic Absorption Spectroscopy for On-Line Analysis of Mercury in Coal Combustion and Gasification Effluents

Authors:

G. A. Norton
D. E. Eckels

Contractor:

Iowa State University
Ames Laboratory
Ames, Iowa 50011

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Abstract

With the passage of the Clean Air Act Amendments of 1990, the on-line monitoring of mercury in effluents from coal combustors and gasifiers is receiving considerable interest. In this study, the applicability of using atomic fluorescence and atomic absorption techniques for on-line monitoring applications is discussed. Laboratory data obtained with two sensitive commercial mercury detectors (one fluorescence and one absorption unit) are presented to demonstrate general instrumental and analytical capabilities. Differences in instrument sensitivity, detection limits, dynamic range, quenching effects, and interferences are discussed.

Introduction

The concentration of Hg in coal can range from about 20 to 2000 ppb_w, with a mean value on the order of 200 ppb_w being reported\(^1\). Coal combustion in the U.S. emits on the order of 100 tons or more of Hg annually. The Clean Air Act Amendments (CAAA) of 1990 require that the EPA study the potential deleterious health effects anticipated to occur from emissions of hazardous air pollutants, including Hg, from coal-fired power plants. In view of the toxicity and public concern over Hg, that element was singled out by the CAAA for special study. As a result of concerns that Hg emissions may be regulated, there has been a heightened interest in on-line analysis of Hg emissions from coal-fired power plants.

One of the most common laboratory methods for determining Hg is cold vapor atomic absorption spectroscopy. Cold vapor atomic fluorescence spectroscopy is another analytical technique for determining Hg and has been gaining in popularity in recent years. In this paper, the potential use of atomic absorption (AA) and atomic fluorescence (AF) spectrosopies for on-line analysis of Hg at coal gasification facilities and conventional coal-fired power plants is discussed.
Principles of Operation

Atomic Absorption

Atomic absorption spectroscopy involves free neutral ground-state atoms absorbing light energy that is characteristic of that particular element. Light at the characteristic energy with a given incident intensity, $I_0$, will be absorbed by the analyte in the sample cell and produce a decrease in the transmitted intensity, $I_t$. The transmitted intensity is related to the incident intensity by the Beer-Lambert Law,

$$I_t = I_0 10^{-abc}$$  \hspace{1cm} (1)

where "a" is the absorptivity of the analyte, "b" is the pathlength of absorption, and "c" is the concentration of the analyte. The absorbance, $A$, of the analyte is given by

$$A = -\log \frac{I_t}{I_0} = abc$$  \hspace{1cm} (2)

and is linear with analyte concentration. A Hg lamp is usually employed to generate the characteristic radiation for Hg. The most common wavelength to use for analysis is 254 nm, since absorption is strongest at this wavelength. For the Hg detector used in this study, both a sample beam and reference beam are used. The radiation intensity passing through the analyte-free reference cell represents the incident intensity, while the radiation intensity passing through the sample cell represents the transmitted intensity. For the measurement of Hg, the Hg must be present in the elemental vapor phase and not combined with other elements in a molecular form. Problems which are of special concern for AA include spectral interferences from molecules such as hydrocarbons, H$_2$S, and SO$_2$.

Atomic Fluorescence

Atomic fluorescence, which is a type of photoluminescence, is similar to atomic absorption in that both involve the absorption of light energy that is characteristic of a particular element by a free neutral ground-state atom. However, the desired signal for atomic fluorescence is the emitted or luminesced light energy from the excited atom and not the transmitted light. If the luminesced radiation is the same frequency as the absorbed light, then resonance fluorescence occurs. The AF detector used in this study measures the resonance fluorescence of elemental Hg at 254 nm.

The fluorescence light intensity, $I_f$, is directly proportional to the absorbed light using Eq. 3,

$$I_f = K(I_0 - I_t)$$  \hspace{1cm} (3)

where "K" is a constant of proportionality which depends on the element and its environment. If a substitution is made for the transmitted intensity, $I_t$, then Eq. 4 results:

$$I_f = KI_0(1 - 10^{-abc})$$  \hspace{1cm} (4)
Deviations of the fluorescence signal from Eq. 4 can be due to either primary or secondary absorption effects. The primary absorption effect is absorption of the incident radiation before it reaches the portion of the sample cell observed by the detector. The secondary absorption effect is absorption of the fluorescence signal before reaching the detector and is usually due to self-absorption by the analyte. Combining Eq. 4 with the absorption effects gives Eq. 5,

$$I_f = K I_o 10^{-apc(1 - 10^{-abc})10^{-asc}}$$

(5)

where "p" and "s" are the pathlengths for the primary and secondary absorption effects, respectively.

For small absorbancies (abc < 0.01 with p + s < b), Eq. 5 can be approximated by using Eq. 6,

$$I_f = 2.303K I_o abc$$

(6)

and the fluorescence intensity is directly proportional to the concentration of the analyte.

In addition to absorption effects, the intensity of the fluorescence signal can be decreased significantly due to "quenching" of the signal from certain other atoms or molecules in the sample. Quenching occurs when the excited analyte atoms transfer their excitation energy via collisions with other atoms or molecules. To avoid this problem, Hg is normally collected on gold and then thermally desorbed into an Ar carrier gas. Because even trace amounts of impurity gases can decrease sensitivity, ultra high purity Ar is preferred.

Compared to AA, where numerous compounds interfere at the absorbing wavelength, AF is less subject to false positives. This results from the fact that the observed signal of AF is the characteristic emission (rather than absorption) from the analyte.

**Experimental**

**Mercury Determinations**

The AA and AF units used in this study are described separately below. Both instruments were designed to operate with gases known to have negligible absorption at the excitation wavelength of 254 nm. Consequently, neither instrument provides a background correction for other gases which can have substantial absorptions.

**Atomic Absorption.** A Thermo Separation Products Model 3200 mercury detector was used for the AA analyses in this study. Data were collected on a strip chart recorder connected to a 10 mV full-scale output jack on the instrument. The range for the output is selected on the instrument by the user and varies from 0.0005 to 2.0 absorbance units (AU). Mercury responses were obtained by measuring peak heights on the recorder output. In all cases, the instrument was set for a one-second response time.
**Atomic Fluorescence.** For AF analyses, a Tekran Model 2500 Fluorescence Mercury Detector was used. Most tests were performed with the external sensitivity setting on the instrument adjusted to the maximum value of 10.0. The PMT voltage in the detector can be increased to further increase the sensitivity of the instrument, although baseline noise would also be increased. As with AA, data were collected on a strip chart recorder and the Hg responses were obtained by measuring peak heights.

**Mercury Standards**

**Manual Injections.** Known amounts of vapor phase elemental Hg ranging from 3 to 50,000 picograms (pg) were collected with gas-tight syringes by withdrawing Hg-saturated air above a pool of Hg in an Erlenmeyer flask fitted with a septum. At known temperature and pressure, the Hg concentration in air was calculated from known Hg vapor pressure parameters. The smallest injection volume that could be reliably withdrawn was about 0.2 μL of Hg-saturated air, which corresponds to about 3 pg of Hg at room temperature. For comparative purposes, a series of injections were performed with the AF detector in which Hg vapor was collected from the flask containing an Ar atmosphere rather than air, thereby eliminating any potential quenching effects from the air being injected along with the Hg. For a given injection volume, three to six injections were made and the average peak intensities and relative standard deviations (RSDs) for those injections were calculated.

Gases entering the detectors were spiked by injecting known amounts of Hg into the gas stream through a septum in a 1/8" Teflon union tee. All lines downstream from the point of injection were 1/8" OD Teflon. For the AA work, the carrier gas was either Ar or zero air. Research grade (99.9995% minimum purity) Ar was always used in the AF instrument to provide a continuous purge of the optical path. Research grade Ar was also generally used as the carrier gas for the AF tests. However, a series of tests was performed with the AF detector in which a variety of gases other than Ar were used for the carrier gas. These gases, which included CH₄, CO, CO₂, O₂, H₂, and N₂, were used to study the fluorescence quenching effects to determine whether it might be possible to pass conditioned sample gases directly into the detection cell for analysis. It should be noted that the instrument is not intended to be operated with carrier gases other than Ar, and that passing other gases through the detector is an aberration from specified procedures in the instrument manual.

Flow rates for the carrier gases varied, but were consistent within a given series of tests. For the AA tests, gas flow rates were typically 100-200 mL/min. For the AF detector, the flow rate was 115 mL/min unless otherwise noted.

**Permeation Tubes.** In addition to manual injections of Hg vapor into the carrier gas, a VICI Metronics Model 340 Dynacalibrator with elemental Hg permeation tubes was used to provide a continuous flow of gases containing known concentrations of Hg. Nominal permeation rates from the tubes ranged from 0.02 to 195 ng/min. Certified permeation tubes were not used in this study since a high degree of accuracy was not required to evaluate the AA and AF technologies for flue gas monitoring applications. According to the manufacturer, the tubes were generally accurate to within 15-30%. The flow rate through the permeation chamber was fixed at
170 mL/min, which provided nominal Hg concentrations ranging from about 0.1 to 960 ppb, in air. All of the AA tests were performed using zero air for the carrier gas, except for one series of tests in which Ar was used as the carrier gas to allow better comparisons with data obtained by AF. Because of fluorescence quenching effects from molecular gases, Ar was used as the carrier gas for all of these tests with the AF detector. For the AA and AF tests, three sequential signals at each Hg concentration were recorded and averages and RSDs were then calculated from those data.

Results

Atomic Absorption

For the AA tests, baseline drift was typically about $5 \times 10^{-5}$ AU/hr and was always less than $1 \times 10^{-4}$ AU/hr. An AU reading of $1 \times 10^{-4}$ is roughly equivalent to a Hg concentration of about 0.5 ppb, in air or an injection of several pg of Hg.

Minimal baseline noise was observed even for flows up to 1000 mL/min. However, changes in the gas flow rate into the detector for gas flows ranging from 200 to 1100 mL/min caused significant changes in baseline absorption values, which often required five minutes or more to stabilize. The amount of change in the baseline for a given flow rate adjustment was erratic. However, the magnitude of change in baseline absorption values for a flow rate adjustment of about 200 mL/min was typically equivalent to a signal that would be observed from a Hg concentration of 1 ppb, or less in a continuous gas stream.

Results from Hg injections indicated that the detector could easily detect less than 3 pg Hg. A theoretical detection limit of 0.3 pg Hg was calculated from the recorder data by multiplying the Hg concentration (ppb) by the quotient of three times the noise divided by the peak height, where the noise is defined as half of the approximate peak-to-valley baseline signal. The instrument response showed good linearity in the range of 3 to 50,000 pg, as shown in Figure 1. The RSDs were typically $\pm 1$-5% for injections of 25 pg or more and were typically $\pm 10$-15% for injections of lesser amounts.

The AA detector was designed for cold vapor AA analysis of liquid samples. Consequently, a magnesium perchlorate trap is normally used near the detector inlet. This trap constitutes a large "dead volume." For the Hg injections, the detector sensitivity increased by a factor of five with the perchlorate trap bypassed.

Results of tests with the permeation tube calibrator using air as the carrier gas are shown in Figure 2. The dynamic range was excellent and spanned at least four orders of magnitude in Hg concentration. A typical signal for a Hg concentration of 0.5 ppb, is shown in Figure 3. As can be seen, an excellent signal is obtained at that concentration. The amount of baseline drift over a period of about 15 minutes was negligible relative to the magnitude of the signal, as evidenced by the change in baseline for zero air before and after a gas containing 0.5 ppb, Hg. When a 0.1 ppb, (0.01 ppb, Hg stream, which is near the minimum detectable concentration, was passed
through the detector, a distinct signal was observed. For Hg concentrations ranging from 0.1 to 1000 ppb, RSDs for the sequential measurements at a given concentration were ± 5% or better. For concentrations above 10 ppb, RSDs did not exceed ± 2%.

**Atomic Fluorescence**

The baseline drift for the AF unit was typically on the order of 0.5 mV/hr. A signal of 0.5 mV is roughly equivalent to the signal produced from injecting about 1 pg Hg. After allowing the baseline to stabilize, flow rate changes for gas flows in the range of 10-1000 mL/min generally didn't affect the baseline signal level or baseline noise.

The instrument response showed good linearity over at least two orders of magnitude in the amount of Hg injected, as shown in Figure 4. Over a wider range, the non-linearity may be largely a result of quenching effects related to the increased amount of air associated with the increasing amount of Hg injected into the detector. It may also be partially attributable to peak broadening with increasing Hg quantities and the fact that Hg signals were quantified using peak heights, although peak shapes generally did not appear to be affected substantially by the amount of Hg injected. The non-linearity could also be partially due to self absorption from the analyte (see Eq. 5), but this probably had a minor effect on the results. Decreasing the instrument's external sensitivity adjustment did not increase the linear range based on analyses using peak heights.

Excellent peaks were observed for 3-pg injections of Hg. A theoretical detection limit of 0.1 pg was calculated in the same manner discussed above for the AA detector. This is in excellent agreement with the detection limit reported by the instrument manufacturer. The RSDs were ≤ 5% for injections of 25-5,000 pg and 5-25% for injections of 2-25 pg.

When Hg was collected in an Ar atmosphere rather than in air, virtually no differences in peak heights were observed for injections less than about 300 pg Hg. However, for injections of about 300 to 5000 pg, peak heights for a given amount of Hg increased by up to 40%, which improved the linearity of the curve somewhat. It is suspected that the collection flask may still have had low concentrations of air. Consequently, those tests will be repeated with a different experimental setup to help ensure that the atmosphere in the collection vessel does not contain air.

When studying quenching effects from molecular carrier gases, a decrease in the peak height for a given Hg injection in Ar was noted after each use of either O₂ or CO. In each case, the peak heights for Hg injected into Ar carrier gas decreased by 20-30% from the peak heights that were initially observed using Ar as the carrier gas. Instrument sensitivity was not recovered even after purging the sample cell for up to 24 hours with Ar. However, it was later observed that the sample cell had a large number of black specks of unknown origin. When the specks were removed by washing the sample cell, the instrument was restored to its original sensitivity. Although this complicated assessing the magnitude of quenching effects, conclusions could still be drawn from the data. No quenching effects were observed for CH₄, substantial quenching was observed for N₂, and severe quenching was observed for O₂, H₂, CO, and CO₂. For the latter gases, a signal reduction (compared to signal levels with Ar as the carrier gas) of 95% or more
was observed for Hg injections of 2500 pg or less. For Hg injections of 500 pg or less, the decrease in signal strength was roughly 75% for nitrogen and was 99% or more for O

2, CO

2, CO, and H

2. The most severe quenching was observed for O

2. The degree of quenching generally appeared to decrease as the amount of Hg injected increased in the range of 2 to 5,000 pg, as shown in Figure 5. It is also interesting to note that negative peaks were observed for O

2 and H

2. This was repeated several times for confirmation. The reason for the negative peaks is uncertain at this time, but may be related to the possible formation by photochemistry of Hg compounds that strongly absorb the excitation radiation and do not fluoresce at the excitation frequency.

When the permeation tube calibrator was used, the detector could easily see an emission of about 20 pg/min of Hg into an Ar stream flowing at about 170 mL/min. In Figure 6, results obtained using the permeation tubes are shown and compared to data obtained under identical conditions using AA with the Hg-containing Ar carrier stream. As noted above, the sensitivity of the AF unit decreased when carrier gases other than Ar were introduced and did not recover after extensive purging of the sample cell with Ar. In order to better compare the AA and AF sensitivities, the AF data were "corrected" to the original sensitivity observed for the AF detector prior to the introduction of molecular carrier gases. For this purpose, a correction factor of 3.5 was used to adjust the AF data. For instruments used as they were received from the manufacturers, comparable sensitivities were observed for AA and AF. However, because of uncertainties in the corrections to the AF data, the actual magnitude of the relative sensitivity between the AA and AF units can not be made with certainty.

Discussion

Concentrations of Hg vapor in combustion or gasification effluents are anticipated to range roughly from 1 to several hundred ppb, w. For most coals, it is anticipated that both techniques would have sufficient sensitivity to measure total vapor phase Hg emissions after all of the Hg has been converted to the elemental form for detection. This conversion is probably particularly important for coal combustors, where significant amounts of mercuric chloride and possibly some methyl mercury species are present. In coal gasification effluents, smaller amounts of mercuric chloride (as a percentage of the total vapor phase Hg) are expected, but there may be significant amounts of methyl mercury present since levels of methan

o can be as high as 15% (molar).

For many coals, it appears that the AA and AF units have a low enough detection limit that stream dilution (e.g., 10:1) could be used to lower the dew point of water in the sample gas to room temperature. This is particularly true for coal combustors, where moisture contents are lower than those found in gasifiers. In coal gasifiers, moisture contents can be as high as 50% (molar) and a higher dilution ratio may be required to lower the water dew point to room temperature. Consequently, in that situation, the instruments probably would not have adequate sensitivity. In this event, the moisture will either need to be selectively removed from the gas stream or a heated sample cell would be needed. Alternatively, the Hg could be captured by gold amalgamation and thermally evolved into a suitable dry carrier gas for detection.
Although the linearity of the AF calibration curves based on Hg injections did not appear to be as good as those obtained with AA, nearly identical linearity was observed between AF and AA when the permeation tube calibrator was used (see Fig. 6). The use of the permeation tubes eliminated numerous concerns, including peak broadening, potential problems with using only peak heights, variable injection times, and quenching effects from air in the injected volumes.

Also, in view of the changing sensitivity of the AF detector during the testing program, it is difficult to compare accurately the responses of the AA and AF detectors for various amounts of injected Hg. It should once again be emphasized that the AF detector was operated in a manner for which it was not intended and that our introduction of carrier gases other than Ar into the detection cell is a highly abnormal procedure for the AF unit.

Both detectors are compact, have minimal baseline noise, and offer rapid analysis, high sensitivity, low cost, and simplicity. The AF unit exhibited less baseline drift than the AA unit, although the amount of drift in the AA baseline was still acceptable in view of the concentrations of Hg anticipated to be present in coal gasification or combustion gases. Unlike AA, the AF baseline was not significantly affected by flow rate changes. Thus, small changes in flow rate during sampling would be less problematic with the AF unit than with the AA detector. In addition, instrument calibration for low Hg concentrations is simplified by the absence of flow rate effects on the baseline. For Hg concentration measurements below 10 ppb, the flow rate effects for the AA detector studied in this work could be a problem.

An advantage of using AA is the potential for passing conditioned effluent gases directly into the absorption cell. Also, the instrument does not have the requirement for a high purity Ar purge or carrier gas. Disadvantages of using AA include interferences from hydrocarbons and other molecular gases, including SO$_2$ and H$_2$S. For passing gases directly into the AA cell, background corrections for those gases will be required if they cannot be selectively removed. Coal tars from coal gasifiers are anticipated to be a particular problem and will have to be removed prior to analysis of the gas stream for Hg.

As a result of the high sensitivity of the AF unit, the possibility existed that extensively conditioned effluent gases could be directly analyzed by passing those gases into the AF detector cell. The gold amalgamation or similar collection step would be eliminated along with the need for high purity Ar. Unfortunately, the extent of the quenching from most of the major gases in a combustor or gasifier stream precludes the possibility of direct analysis at the anticipated Hg concentrations.

**Conclusions**

Both the AA and AF detectors used in this study are excellent units. They are compact and have adequate sensitivity to determine vapor phase Hg in coal combustion and gasification effluents.

Due to substantial quenching effects from matrix gases, Hg cannot be adequately determined by passing conditioned sample gases directly into an AF detection cell. However, AF can still be
used for effluent monitoring if the Hg is first collected by gold amalgamation or other suitable collection material and then released into a high purity Ar stream, which is the procedure for which the instrument was designed.

Performing Hg determinations by direct analysis of effluent gases in an AA detection cell may be possible, although extensive gas conditioning and an instrument employing spectral background correction may be required, particularly for effluents from coal gasifiers. Gas conditioning is anticipated to be less problematic with AF using gold amalgamation collection than with AA employing direct analysis. However, an amalgamation step for AA may be desirable for preconcentration or for avoiding interferences.

For total Hg determinations by both AA and AF, some sort of mechanism will be required to convert all of the Hg species to the elemental form.

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References


Figure 1
AA Calibration Curve for Hg Injections

MERCURY (pg)

1000000

1000

100

10

1

0.1

1

MILLILAMBARBANCE UNITS
Figure 3
AA Signal Observed for 0.5 ppb$_w$ Hg in Air Using a Permeation Tube Calibrator
Figure 4
AF Calibration Curve for Hg Injections
Figure 5
Quenching Effects for Various Gases vs. Amount of Hg Injected
Figure 6
Comparison of AA and AF Calibration Curves Obtained with a Permeation Tube Calibrator