Oxidised mercury determination from combustion gases using an ionic exchanger


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Abstract

Mercury displays a different reactivity and behaviour depending on its speciation. Determination of the mercury species present in combustion flue gases is important for proposing effective control technologies. The Ontario Hydro (OH) method is accepted as the only wet-chemical method suitable for measuring total and speciated mercury in flue gases. However, the continuous development of combustion technologies has the effect of modifying the operational variables and the composition of the resulting flue gases, leading to measurement biases in mercury determination. In this work, an alternative method based on the use of an ionic exchanger resin is proposed for the determination of gaseous oxidised mercury. The results show that for sampling flue gases containing reactive gases over long periods of time, the use of this resin is a suitable method for determining gaseous elemental and oxidized mercury, even in the presence of large amounts SO₂ or NO₂. Application of the OH method when elevated amounts of SO₂ or NO₂ are present in the gas composition leads to an overestimation of the amount of oxidised mercury due to the oxidation of the mercury in the KCl impinger solution.

Keywords: mercury; speciation; Ontario-Hydro, exchange resin
1. Introduction

Although mercury is present in coal in low concentrations (<1 ppm), coal-fired power plants are one of the largest sources of mercury emissions related to human activities [1]. The reduction of mercury emissions to the air is becoming mandatory due to its toxicity and persistence in the environment [2]. During combustion all the mercury present in coal is released as elemental mercury (Hg\(^0\)). When the gases cool down, not only do adsorption and heterogeneous reactions occur in the ashes, but also homogeneous oxidation may take place, giving rise to a mixture of several mercury species in the flue gas [3-4]. Because the speciation of mercury affects its atmospheric fate, the impact on health and the environment and the extent of removal by gas cleaning systems, the determination of the different mercury species in gas phase is of primary concern.

The most common method of conducting the speciation of gaseous mercury is to use a train of solutions for selective retention, followed by analysis of the liquid solutions [5]. The US EPA Method 29 (1996) allows multi-metal measurements, including mercury, from the gas phase. The metals and mercury in the gaseous emissions are recovered in a series of impingers containing aqueous acidic solutions of peroxide. The gas is passed through a further set of impingers containing acidic permanganate in which only mercury is analyzed. This method is tedious, expensive, entails the risk of contamination or even loss of mercury through the container walls and is susceptible to SO\(_2\) interference. To avoid the complexity involved in using liquid solutions, alternative methods such as the MESA method [6-7] have been developed. This method employs solid sorbent traps. A potassium chloride impregnated soda lime sorbent and iodated carbon are employed to capture Hg\(^{2+}\) and Hg\(^0\), respectively. Again, this method is greatly affected by the interaction between SO\(_2\) and NOx in the flue gas,
as a result of which the Hg\(^{2+}\) fraction is often overestimated [8-9]. There are a number of commercial sorbent traps which offer precision and accuracy in some gas compositions [10]. Most sorbent traps are able to measure total mercury, even when multiple sorbents are employed to determine mercury speciation. The U.S. EPA Method 30B (2011) is a procedure that was designed to measure total vapor-phase mercury emissions from coal-fired combustion sources using sorbent trap sampling and an extractive or thermal analytical technique. This method is only intended for use with gases with a low particulate content. After extensive reviews and evaluations [11-13], the Ontario Hydro (OH) method has finally been established as the accepted wet-chemical method for measuring total and speciated mercury in flue gases from coal combustion (ASTM D6784 (2008)). This method allows three forms of mercury to be measured: i) Hg\(^{0}\), that is separated by filtration; ii) gaseous Hg\(^{2+}\), which is collected in potassium chloride impingers, and iii) gaseous Hg\(^{0}\) that is oxidized and collected in HNO\(_3\)/H\(_2\)O\(_2\) and acidified KMnO\(_4\) solutions. Laboratory and field validations based on this method have resulted in relative standard deviations of 10-20% depending on the mercury concentration [14].

The continuous development of combustion technologies and the installation of air pollution control devices make it essential to be able to determine gaseous mercury species accurately. In recent years research has been focused on the monitoring of mercury emissions and the development of equipment – e.g. Hg CEMs (Continuous Emission Monitors) - which are nowadays commercially available. However, Hg CEMs only detect elemental mercury, although they can be adapted to measure total mercury by means of a conversion system which reduces the Hg\(^{2+}\) to Hg\(^{0}\) before it reaches the equipment. The amount of oxidised mercury can be calculated by difference. This method has an important disadvantage related with solution instability. These solutions
need to be prepared daily. In addition uncertainties due to the presence of liquid drops containing mercury in the gas phase after the impinge solution has been described in the literature [15].

Special ion exchangers are used for the purification and treatment of waters containing mercury [16-18]. It is mainly the strongly basic anion exchangers that have acquired particular importance for the removal of mercury, which in chloride-containing solutions is present in the form of complex chloromercurate ions, i.e. HgCl$_3^-$ and HgCl$_4^{2-}$ [19]. Ion exchangers are capable of absorbing not only dissolved substances but also gases. Satisfactory results have been achieved using ion exchangers as gas-phase sorbents specifically for extracting HgCl$_2$ from the gases of municipal solid waste incinerators [20]. However, there is a lack of knowledge about how effective these ion exchangers would be for determining mercury species in coal combustion atmospheres.

The aim of this study is to evaluate a procedure, using a commercial resin, for the determination of mercury species in the presence of reactive gases (SO$_2$, HCl, NO$_2$) from coal combustion. An ionic exchanger resin was used for Hg$^{2+}$ retention, while Hg$^0$ was monitored by a continuous mercury monitor. The results were compared with those obtained by the standard OH method. A tentative statistical study was carried out by means of a t-distribution test to make inferences about the differences between the means of the results obtained by both methods.

2. Experimental

A schematic diagram of the experimental device is shown in Figure 1. Essentially the device consists of three parts: i) a system to generate gaseous elemental mercury from a permeation tube (100 µg m$^{-3}$), ii) a system to produce the simulated flue
gas (SFG) (5% O₂, 1300 mg Nm⁻³ SO₂, 500 mg Nm⁻³ NO₂, 20.3 mg Nm⁻³ HCl and N₂) in which the mercury oxidation is evaluated and iii) the device to carry out the selective capture and determination of the mercury species.

The Ontario-Hydro procedure is described in the standard method ASTM D6784 (2008). Hg²⁺ is collected in impingers containing a chilled aqueous KCl solution. Hg⁰ is collected in subsequent impingers: one impinger containing a chilled aqueous solution of HNO₃/H₂O₂ and three impingers containing chilled aqueous acidic solutions of KMnO₄. ((1) in Figure 1). The solutions are then analyzed for mercury using an automatic cold-mercury analyzer (AMA 254).

The alternative speciation method proposed in this study consists in replacing the impinger solutions by an ionic exchanger resin to selectively capture Hg²⁺ ((2) in Figure 1). The resin selected was the Dowex® 1x8, which has been previously used for oxidized mercury removal in waters [16-17]. This is a strongly basic (type I) anion exchange resin for fine chemical processing. The functional group, tri-methyl ammonium, is completely converted to the chloride form by treatment with HCl. For this purpose, the resin is treated before use with a mixture of HCl:H₂O (1:1) at 90°C for 30 minutes and then filtered and dried. After gas sampling, the Hg²⁺ captured in the resin is measured by using AMA 254. Hg⁰ is determined by integrating the emission curve obtained by a continuous mercury monitor from Mercury Instruments (VM3000), which only detects Hg⁰.

3. Results and discussion

3.1. Influence of acid gases on mercury speciation analysis
Mercury speciation under different gas compositions was determined using the proposed method. The influence of different gas components produced during combustion processes was investigated. The percentage of elemental and oxidised mercury determined under each gas composition is shown in Table 1. According to the ASTM D6784 (OH), the oxidised mercury is calculated as the mercury measured in the KCl impinger solutions minus the mercury measured in the KCl blank solutions while elemental mercury is the sum of the mercury measured in the HNO₃-H₂O₂ solution plus the mercury measured in the H₂SO₄-KMnO₄ solutions minus the values corresponding to the blank solutions. Values ranging from 2 to 45 % for oxidised mercury and 98-55 % for elemental mercury were obtained by this method. When the Dowex® resin method was employed, the oxidised mercury was calculated as the amount of mercury analysed in the resin minus the amount of mercury analysed in the Dowex® resin after treatment with HCl. The elemental mercury was calculated from the signal recorded by the continuous mercury analyser. The proportions of mercury species determined in the different gas compositions by this method were 3-24 % and 97-76 % for the oxidised and elemental mercury, respectively (Table 1).

In order to ensure the reliability of the results obtained by the two methods, the apparent recovery factor of mercury was determined for each test (Table 1). The mercury apparent recovery factor is defined as the quantity of mercury selectively collected and determined by the analysis of the samples divided by the quantity of gaseous mercury emitted during each test. In general good recovery values were achieved, with values ranging from 0.99 to 1.25 and from 0.96 to 0.99 for the OH and resin method, respectively (Table 1). However a wider variability range of variability was obtained in the case of the OH method.
No differences in mercury speciation were observed by either method in a nitrogen or air (O₂) atmosphere. Even when SO₂ or HCl was present in the gas composition similar results were obtained. However, when SO₂+O₂ or NO₂ formed part of the gas composition, certain effects were observed. These effects can be attributed to liquid-phase oxidation reactions in the KCl solution resulting in an increase in oxidation. High concentrations of SO₂ or NO₂ in the presence of O₂ were dissolved in the KCl impinger solution generating sulphate and nitrate ions respectively. The elemental mercury passing through this solution was oxidised resulting in an increase of the amount of Hg²⁺ in the solution [1-2]. However, these oxidation reactions did not occur when the solid adsorbent was used for oxidized mercury capture.

\[
\begin{align*}
2 \text{Hg}(g) + 4 \text{HNO}_3 + \text{O}_2(g) &= 2 \text{Hg(NO}_3)_2(aq) + 2 \text{H}_2\text{O} \quad [1] \\
2 \text{Hg}(g) + 2 \text{H}_2\text{SO}_4 + \text{O}_2(g) &= 2 \text{HgSO}_4 + 2 \text{H}_2\text{O} \quad [2]
\end{align*}
\]

These results suggest that using Dowex® resin for capturing oxidised mercury before the mercury continuous emission monitor is an appropriate method for the determination of mercury species.

3.2. Statistical study using the t-distribution method

A set of tests was carried out to perform a statistical evaluation of the differences that might occur depending on whether the OH or the resin method is used. The t-distribution approach was employed to make inferences from the differences between the means of the results obtained by these methods. For all the statistic inferences, it was assumed that the dependent variables are normally distributed. The experiments were performed in a lab-scale reactor (Figure 1) in order to evaluate the capacity of the char samples obtained from the gasification of paper-plastic wastes to undergo mercury oxidation [21-22]. In this particular case, the OH method could not be performed long enough for the char to reach saturation capacity with the result that the data obtained
were not sufficiently accurate to allow a reliable interpretation of the results. Tables 2-3 show the results obtained with the Dowex resin. Although both methods confirm the heterogeneous oxidation of \( \text{Hg}^0 \) in the presence of char, the \( \text{Hg}^{2+} \) percentages obtained using the OH method were higher than when resin was employed. In addition, when the gas sampling time increased, a higher heterogeneous mercury oxidation was observed with the resin (Tables 2-3). Unlike the OH method, the resin approach makes it possible to evaluate heterogeneous oxidation when the sorbent is saturated, and therefore allows a better understanding of mercury behaviour in these solids [21-22]. This is because mercury oxidation continues until the sorbent reaches its maximum retention capacity (Tables 2-3). It should be added that the OH method cannot be applied for long periods of experimentation due to the instability of the solutions, especially those containing KMnO₄.

To determine whether the differences between the results (average percentage of oxidized mercury) obtained by the OH and resin methods are statistically significant, the margin of error for a pre-established interval of confidence was calculated by means of equation 1.

\[
\bar{x}_1 - \bar{x}_2 \pm t_{\alpha/2} \sqrt{\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}}
\]

(1)

where \( 1-\alpha \) represents the interval of confidence.

In equation (1) the t-distribution is an approximation, but provides good results and is relatively easy to use.

From the \( \text{Hg}^{2+} \) results in Table 4, the degrees of freedom obtained are 9 which correspond to \( t_{0.025} = 1.83 \). The estimation of the difference between the two means together with the margin of error for an interval of confidence of 95% is: \( 26.9 \pm 8.66 \).
This means that, on average, the percentage of Hg\(_{2}^{+}\) detected in the experimental conditions of this study using the OH method is 26.9 times higher than that obtained using the resin method with a margin of error of 8.66%.

The difference between the mean values obtained by the two methods was assessed using the following test statistic for the hypothesis tests (equation 2).

\[
t = \frac{\bar{x}_1 - \bar{x}_2 - D_0}{\sqrt{\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}}}
\]  

(2)

where \(D_0\) is the hypothetical difference between \(x_1\) and \(x_2\).

If it is assumed that there is no difference between the quality of the results obtained by the two methods, \(D_0 = 0\). So, in terms of the average percentages of oxidized mercury, the null hypothesis is \(H_0: \mu_1 - \mu_2 = 0\) or \(\mu_1 = \mu_2\). If the evidence collected from the analysis of several samples leads to a rejection of this hypothesis, it can be concluded that there is a difference between the mean values of the percentages obtained by the two methods. The null and alternative hypotheses in the two-tailed test are expressed as follows:

\[H_0: \mu_1 - \mu_2 = 0\]
\[H_a: \mu_1 - \mu_2 \neq 0\]

According to equation 2, the test statistic is \(t = 5.69\). For \(\alpha = 0.05\) and \(t_{\alpha/2} = t_{0.025} = 1.83\), the rule for rejecting the null hypothesis \(H_0\) is satisfied since 5.69 is greater than 1.83 which indicates that there are significant differences between the two determinations.
To explain these differences it needs to be considered that the OH method may experience some interference when reactive gases, such as SO$_2$ or Cl$_2$, are present in the flue gas [23-24]. Therefore, in the tests reported in this work, the presence of SO$_2$+O$_2$ and especially the presence of NO$_2$ in the gas composition might be the reason for the overestimation of Hg$^{2+}$. In this case interference occurred in the analysis of the potassium chloride solutions which resulted in the detection of a higher percentage of Hg$^{2+}$ with OH method than when the resin method was used.

4. Conclusions

Although both methods provide statistically accurate results leading to similar interpretations, the proposed method which is based on the use of an ionic exchanger (Dowex®) for oxidized mercury capture is less tedious, avoids problems of solution instability, allows continuous sampling over long periods of time and can be used for a wide range of concentrations. The presence of SO$_2$+O$_2$ or NO$_2$ in the gas composition leads to an overestimation of oxidized mercury when the OH method is used. This is attributed to the oxidation of mercury in the KCl impinger solution.

Acknowledgments
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References


[17] De Wuilloud JCA, Wuilloud RG, Olsinaa RA, Martinez LD. Separation and preconcentration of inorganic and organomercury species in water samples using a


<table>
<thead>
<tr>
<th>Gas composition</th>
<th>OH method</th>
<th>Dowex® based method</th>
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<tr>
<td></td>
<td>% oxid.</td>
<td>% elem.</td>
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<tr>
<td>N₂</td>
<td>4.0</td>
<td>96.0</td>
</tr>
<tr>
<td>O₂+N₂</td>
<td>2.0</td>
<td>98.0</td>
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<tr>
<td>SO₂+N₂ (1)</td>
<td>6.3</td>
<td>93.7</td>
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<tr>
<td>SO₂ + O₂+N₂ (1)</td>
<td>18.0</td>
<td>82.0</td>
</tr>
<tr>
<td>HCl+N₂ (2)</td>
<td>9.0</td>
<td>91.0</td>
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<td>NO₂+N₂</td>
<td>42.0</td>
<td>58.0</td>
</tr>
<tr>
<td>NO₃+O₂+N₂ (3)</td>
<td>45.0</td>
<td>55.0</td>
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<tr>
<td>SO₂ + HCl + NO₂+O₂+NO₂ (1,2,3)</td>
<td>41.4</td>
<td>58.6</td>
</tr>
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</table>

(1) 1300 mg·Nm⁻³SO₂; (2) 20.3 mg·Nm⁻³HCl; (3) 500 mg·Nm⁻³NO₂+5%O₂

<table>
<thead>
<tr>
<th>Oxidized Mercury</th>
<th>Elemental Mercury</th>
</tr>
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<tbody>
<tr>
<td>n=5</td>
<td></td>
</tr>
<tr>
<td>μg Nm⁻³</td>
<td></td>
</tr>
<tr>
<td>X</td>
<td>s</td>
</tr>
<tr>
<td>Ontario-Hydro</td>
<td>54.80 5.95 10.85</td>
</tr>
<tr>
<td>Resin</td>
<td>21.09 2.58 12.24</td>
</tr>
</tbody>
</table>

Table 1.- Proportions of elemental and oxidized mercury and apparent recovery factors (R) obtained using the Ontario-Hydro (OH) and the ionic exchanger resin (DOWEX®) methods under different gas compositions.

Table 2.- Results obtained from the analysis of elemental and oxidized mercury using the Ontario-Hydro method and the ionic exchanger resin method with char from paper-plastic gasification for an experimental time of 15 h (Total vapour-phase mercury: 100 μg Nm⁻³)
Table 3.- Results obtained from the analysis of elemental and oxidized mercury using the Ontario-Hydro method and the ionic exchanger resin method with a char from paper-plastic gasification for an experimental time of 48 h (Total vapour-phase mercury: 100 μg Nm⁻³)

<table>
<thead>
<tr>
<th></th>
<th>Oxidized Mercury</th>
<th>Elemental Mercury</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\bar{x}$ μg Nm⁻³</td>
<td>s μg Nm⁻³</td>
</tr>
<tr>
<td>Ontario-Hydro</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Resin</td>
<td>42.00</td>
<td>1.77</td>
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Table 4.- Results obtained from the analysis of elemental and oxidized mercury using the Ontario-Hydro method and the ionic exchanger resin method for an experimental time of 15 h (Total vapour-phase mercury: 100 μg Nm⁻³)

<table>
<thead>
<tr>
<th></th>
<th>Oxidized Mercury</th>
<th>Elemental Mercury</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\bar{x}$ μg Nm⁻³</td>
<td>s μg Nm⁻³</td>
</tr>
<tr>
<td>Ontario-Hydro</td>
<td>41.30</td>
<td>2.41</td>
</tr>
<tr>
<td>Resin</td>
<td>13.88</td>
<td>1.15</td>
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Figure captions

Figure 1. Schematic diagram of the experimental device.
Figure 1