Study of Cationic Interference in the Determination of Mercury By Cold Vapor Atomic Absorption Spectroscopy

Rashida Parveen1*, Sheikh Mohiuddin1, Rajkumar Dewani1 and Iftikhar Imam Naqvi2

1Department of Chemistry, University of Karachi
2Department of Chemistry, Jinnah University for Women Karachi, Pakistan

ABSTRACT
The interference due to different Cations in the analysis of Mercury by Cold Vapor Atomic Absorption Spectroscopy (CVAAS) at trace levels has been investigated and presented in this report. There is always a chance of interference due to several factors in a quantitative analysis. Different cations (Na+, Fe2+, Zn2+, Cr3+, Co2+, Ni2+, Cu2+) were examined as possible interferents in the analysis of mercury by CVAAS under specific conditions. Some cations did not have any impact, while present in the detection of mercury, whereas others had a marked influence on the analytical results and can be suggested as possible interfering agents for this method of Hg analysis. Using single standard calibration with a 10ppb Hg solution, varying concentrations of different metal solutions, having same Hg concentrations as those of the standard solution, have been analyzed by CVAAS. The cations that interfered in the quantitative determination of mercury were further checked, by employing finer differences concentrations of the interferent. Sodium concentration was checked up to 50,000ppm because it is present in marine samples in higher concentrations.

Keywords: Mercury, Cold vapor atomic absorption spectroscopy, metal ions.

1. INTRODUCTION
Mercury is so volatile that it could be exposed easily to human environment. It would cause a neurological damage and even result in death. Generally, the concentrations of Hg in environmental samples are relatively low unless they originate from some industrial area. Total mercury concentrations in natural waters ranges from 0.2 to 100 ng/L1,2 while methylmercury levels were known to even lower around 0.05 ng/L.3 However, mercury in contaminated environmental materials may exist at levels of micrograms per liter. Recently Puri et. al, found total mercury Hg content in Futala (0.018 mgL-1 to 0.042 mgL-1), Ambazari (0.019 mgL-1 to 0.044 mgL-1) and Gandhisagar (0.012 mgL-1 to 0.046 mgL-1) in Indian lakes4. A validate a method for organic Hg determination extracted with dichloromethane in acid medium in sediment has been studied by CVAAS. The quantification limit of 3.3 µg kg-1 was found for organic Hg by CVAAS5. Simple and convenient methods are required to permit the determination of Hg(II) in the contaminated samples. Techniques which can determine low concentration of mercury in water and biological materials have been developed, including inductive coupled plasma mass spectrometry,4,5 inductive coupled plasma atomic emission spectrometry,7,8 cold vapor atomic absorption spectrometry12,13 and anodic stripping voltammetry14. In some techniques, the preconcentration is desirable to facilitate ultra trace level determination of Hg. However, these procedures may reduce the accuracy of the determination and require a longer handling time. Among these preconcentration techniques, cold vapor atomic absorption spectrometry has widely been used12,13 with merits such as high sensitivity and little interference effects on the cost poor precision and accuracy14. Inductive coupled plasma atomic emission spectrometry and inductive coupled plasma-mass spectrometry are useful in determining ultra trace Hg without preconcentration15,16. However, these instruments are very expensive and costly to maintain. The method has simplicity, high sensitivity and the non requirement preconcentration and relative freedom of interferences.
owing to trace amounts of copper(II) in aqueous solution cold vapor atomic absorption spectrometry (CVAAS) has generally been used for determination of mercury in natural water samples. Several different approaches for determining methylmercury and inorganic cations in aqueous solution are in practice. In order to improve the limit of detection limits of mercury in aqueous solution coprecipitation, noble metal amalgamation, solvent extraction, ion exchange and chelating sorbents have been proposed for the preconcentration of mercury in natural waters.

This study is confined to chemical interference experienced in the analysis of mercury by cold vapor atomic absorption Spectroscopy. The interference could be cationic or anionic and it may also pertain to improper reduction of mercury or hindrance in its transfer to the cell.

2. EXPERIMENTAL

All atomic absorption measurements were made on a double beam atomic absorption spectrophotometer. (Model: Perkin-Elmer AA3100) equipped with MHS-10 system for use with a nitrogen gas cylinder.

Chemicals used were of “AR” grade of Merck. NaBH₄ (>96 %) (Fine granulated product for synthesis). Hg Standard Solution AAS reagent. Contents: 1000+ 5 ppm Hg, 4.98 mmol/litre mercuric nitrate in 5M HNO₃. 1000 ppm of Hg stock solution was diluted up to 1 ppm with 0.001 M solution of K₂C₂O₇, along with the addition of 5 ml of concentrated HNO₃ for preservation.

Stock solutions of 1000 and 100,000 ppm Na were prepared in 1000ml volumetric flasks. 0.2548 gm of NaCl salt was accurately weighed and transferred to a 100 ml volumetric flask and made up to mark with deionized water to give a 1000 ppm Na solution. Likewise a 100,000 ppm Na solution was prepared.

Stock solutions of 2000 ppm concentration of other metal ions such as K, Fe, Zn, Cr, Co, Ni, Cu were prepared in a similar fashion from their stable salts mentioned in Table 1. 5.0 mL of 37 % concentrated HCl solution was added to all the metal ion solutions prior to making up their volumes to avoid hydrolysis.

A sample solution in this study refers to a solution composed of standard amount of Hg (II) along with specific concentration of the metal ion whose interference is under investigation. Dilutions of 1.0 ppm, 50 ppm, 300 ppm and 1000 ppm were prepared from the previously prepared 2000 ppm stock solutions along with one drop of 5 % KMnO₄ solution and 1 mL of 1 ppm standard Hg solution using a micropipette, to give a final solution of 10 ppb in Hg concentration. The solutions were prepared in 100 mL volumetric flasks, with deionized water. 10 ppb Hg standard solution was also prepared in a similar fashion.

3. RESULTS AND DISCUSSION

The determination of the smallest traces of mercury has been of importance in toxicology for many years. Increasing fears of widespread environmental pollutions and stringent regulations covering the quality of surface waters and rivers, drinking and wastewaters, soil and air and meat, fish, beverages and other foodstuffs have made the determination of mercury a major priority.

Besides mercury leaves many toxic affects on human health specially the methyl mercury, the exposure to which causes severe affects on nervous system. Interference in an analysis is as important as the analysis itself. The interference effect of several anions and cations was also tested. The method was used to determine mercury in water samples by Afkham et al. The determination of mercury in the presence of matrix substances (such as inorganic cations and anions, and organic compounds) was studied by cold vapor atomic absorption spectrometry with “completely continuous micro flow”, using tin(II) chloride in sodium hydroxide solution as reducing reagent. A method was developed for determination of total Hg in seafood using 10% w/v SnCl₂ ⋅ 2H₂O and continuous flow CVAAS. Average recoveries of inorganic and organic Hg added to seafood were 102% and 99%, respectively. Hagemann has reported the amalgamation of mercury with metal
that stabilize it in the solution. It may be a possible reason for the interference due to Cobalt\(^{31}\).

Our results are being reported pertaining to particular conditions as depicted in Tables 2 and 3 in which the interference of particular cations can minimize. The concentration of sodium was scanned from 0.1 to 10,000 ppm, and potassium form 1pp-100 ppm with 10ppf of Hg(II). No evidence was found for any interference offered by Na(I), K(I) at these concentration levels (Tables 4, 5). Among the transition metals Fe(II) and Zn(II) having concentration range of 1-1000 ppm, as represented by Table 6 and 7 did not interfere in Hg(II) determination. In case of Cr(III) the % recovery of Hg(II) decreases with the increase of Cr(III) concentration from 1ppm to 1000 ppm (Table 8). Initially there is rapid decrease in Hg signal as a function of increasing Cr(III) concentration but after 100 ppm gradual decrease was observed. The results for Co(II) are similar to that for Cr(III) but the % recovery significantly lowered. At 50 ppm of Co(II) Hg (II) signal has been reduced to half and b beyond 100 ppm insignificant signals for Hg(II) was recorded (Table 9). The maximum interference was observed for Ni (II) in which mercury concentration was reduced to zero at 30 ppm (Table 10). Among all cations Cu (II) showed unique pattern. Initially the recovery of Hg(II) is gradually lowered as that of Co(II), but after 300 ppm Cu(II), the Hg(II) signal gets increased again forming a overall curve (Table 11). A number of possibilities that may be responsible in the lowering of Hg (II) signals are as under.

1. The reduction in Hg (II) to atomic mercury vapors.
2. Transportation of mercury vapors to the cell.

There is a possibility that interfering cation interferes due to one of the following steps. Interfering cation inhibits the reduction Hg(II) ions or it reacts with or binds with reduced form of Hg , blocking its delivery to the absorption cell.

It may also happen that the interferent is preferentially reduced prior to Hg(II) ions because of being present in greater concentration. If such is the case then the Hg(II) signal should be inversely proportional to the interferent’s concentration which is clearly observed in case of Co(II), Cr (III) and Ni(II)

But there is also a possibility maybe that if the experimental conditions mention in Table 1 and 2 are varied interference ought to be observed. The above mentioned results are thus valid only for the conditions mentioned in Table 1 and 2.

---

**Table 1: Stable salts of metal ions used for determination interfering effect**

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Metal Ions</th>
<th>Salts of Metal ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Na</td>
<td>NaCl</td>
</tr>
<tr>
<td>2</td>
<td>K</td>
<td>KCl</td>
</tr>
<tr>
<td>3</td>
<td>Fe</td>
<td>(NH(_4))(_2)SO(_4), FeSO(_4), 6H(_2)O</td>
</tr>
<tr>
<td>4</td>
<td>Zn</td>
<td>Zn(_2)(PO(_4))(_3), 4H(_2)O</td>
</tr>
<tr>
<td>5</td>
<td>Cr</td>
<td>CrCl(_3), 6H(_2)O</td>
</tr>
<tr>
<td>6</td>
<td>Co</td>
<td>CoSO(_4), 7H(_2)O</td>
</tr>
<tr>
<td>7</td>
<td>Ni</td>
<td>NiSO(_4), 6H(_2)O</td>
</tr>
<tr>
<td>8</td>
<td>Cu</td>
<td>CuSO(_4)</td>
</tr>
</tbody>
</table>

**Table 2: Instrumental variables used for mercury analysis**

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Lamp current</td>
<td>6 mA</td>
</tr>
<tr>
<td>2</td>
<td>Integration time</td>
<td>25 s</td>
</tr>
<tr>
<td>3</td>
<td>Calibration</td>
<td>Linear</td>
</tr>
<tr>
<td>4</td>
<td>Measurement type</td>
<td>Peak Area</td>
</tr>
<tr>
<td>5</td>
<td>Wavelength</td>
<td>253.7 nm</td>
</tr>
<tr>
<td>6</td>
<td>Slit band width</td>
<td>0.7 nm</td>
</tr>
<tr>
<td>7</td>
<td>Slit height</td>
<td>Low</td>
</tr>
<tr>
<td>8</td>
<td>Nitrogen gas pressure</td>
<td>3 bar</td>
</tr>
<tr>
<td>9</td>
<td>Plunging time</td>
<td>5-10 s</td>
</tr>
</tbody>
</table>
Table 3: Concentrations and volumes of different solutions used in experiments

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Concentration of Hg (II) standard solution.</td>
<td>10 ppb</td>
</tr>
<tr>
<td>2</td>
<td>Volume of sample solution</td>
<td>10 mL</td>
</tr>
<tr>
<td>3</td>
<td>Concentration of NaBH₄</td>
<td>3% in 1% NaOH</td>
</tr>
<tr>
<td>4</td>
<td>Stabilizing agent</td>
<td>1 drop of 5%</td>
</tr>
<tr>
<td>5</td>
<td>Volume of acid mixture</td>
<td>KMnO₄</td>
</tr>
<tr>
<td>6</td>
<td>Concentration of HCl</td>
<td>10 mL</td>
</tr>
</tbody>
</table>

Table 4: Effect of concentration of sodium ion on % recovery of mercury

<table>
<thead>
<tr>
<th>S.No</th>
<th>Concentration of Na⁺ (ppm)</th>
<th>% recovery of Hg(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>101.00 ± 5.76</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
<td>92.00 ± 5.71</td>
</tr>
<tr>
<td>3</td>
<td>0.3</td>
<td>105.00 ± 13.22</td>
</tr>
<tr>
<td>4</td>
<td>0.4</td>
<td>98.00 ± 8.88</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>108.00 ± 11.88</td>
</tr>
<tr>
<td>6</td>
<td>0.6</td>
<td>92.00 ± 7.72</td>
</tr>
<tr>
<td>7</td>
<td>0.7</td>
<td>102.00 ± 14.29</td>
</tr>
<tr>
<td>8</td>
<td>0.8</td>
<td>125.00 ± 13.56</td>
</tr>
<tr>
<td>9</td>
<td>0.9</td>
<td>108.00 ± 15.60</td>
</tr>
<tr>
<td>10</td>
<td>1.0</td>
<td>90.00 ± 0.90</td>
</tr>
<tr>
<td>11</td>
<td>2.0</td>
<td>89.00 ± 1.03</td>
</tr>
<tr>
<td>12</td>
<td>3.0</td>
<td>89.00 ± 1.02</td>
</tr>
<tr>
<td>13</td>
<td>4.0</td>
<td>92.00 ± 2.47</td>
</tr>
<tr>
<td>14</td>
<td>5.0</td>
<td>92.00 ± 1.14</td>
</tr>
<tr>
<td>15</td>
<td>6.0</td>
<td>91.00 ± 3.64</td>
</tr>
<tr>
<td>16</td>
<td>7.0</td>
<td>91.00 ± 1.68</td>
</tr>
<tr>
<td>17</td>
<td>8.0</td>
<td>92.00 ± 1.01</td>
</tr>
<tr>
<td>18</td>
<td>9.0</td>
<td>92.00 ± 1.93</td>
</tr>
<tr>
<td>19</td>
<td>10.0</td>
<td>90.00 ± 0.92</td>
</tr>
<tr>
<td>20</td>
<td>100</td>
<td>95.00 ± 10.88</td>
</tr>
<tr>
<td>21</td>
<td>500</td>
<td>116.00 ± 14.84</td>
</tr>
<tr>
<td>22</td>
<td>1000</td>
<td>96.00 ± 18.12</td>
</tr>
<tr>
<td>23</td>
<td>10000</td>
<td>83.00 ± 19.09</td>
</tr>
</tbody>
</table>

Table 5: Effect of increasing concentration of Potassium on % recovery of mercury

<table>
<thead>
<tr>
<th>S.No</th>
<th>Concentration of K⁺ (ppm)</th>
<th>% recovery of Hg(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0</td>
<td>95.00 ± 5.95</td>
</tr>
<tr>
<td>2</td>
<td>2.0</td>
<td>98.00 ± 4.79</td>
</tr>
<tr>
<td>3</td>
<td>3.0</td>
<td>108.00 ± 3.24</td>
</tr>
<tr>
<td>4</td>
<td>4.0</td>
<td>98.25 ± 2.16</td>
</tr>
<tr>
<td>5</td>
<td>5.0</td>
<td>104.50 ± 13.72</td>
</tr>
<tr>
<td>6</td>
<td>6.0</td>
<td>109.16 ± 2.48</td>
</tr>
<tr>
<td>7</td>
<td>7.0</td>
<td>99.00 ± 13.58</td>
</tr>
<tr>
<td>8</td>
<td>8.0</td>
<td>99.87 ± 7.81</td>
</tr>
<tr>
<td>9</td>
<td>9.0</td>
<td>95.40 ± 11.87</td>
</tr>
<tr>
<td>10</td>
<td>10.0</td>
<td>105.10 ± 8.47</td>
</tr>
</tbody>
</table>
Table 6: Effect of concentration of iron (II) on % recovery of mercury

<table>
<thead>
<tr>
<th>S.No</th>
<th>Concentration of Fe^{2+} (ppm)</th>
<th>% recovery of Hg(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0</td>
<td>89.75 ± 19.57</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>101.25 ± 14.48</td>
</tr>
<tr>
<td>3</td>
<td>300</td>
<td>88.33 ± 13.80</td>
</tr>
<tr>
<td>4</td>
<td>1000</td>
<td>88.00 ± 36.94</td>
</tr>
</tbody>
</table>

Table 7: Effect of concentration of zinc(II) on % recovery of mercury

<table>
<thead>
<tr>
<th>S. No</th>
<th>Concentration of Zn^{2+} (ppm)</th>
<th>% recovery of Hg(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0</td>
<td>93.00 ± 16.37</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>91.00 ± 9.20</td>
</tr>
<tr>
<td>3</td>
<td>300</td>
<td>106.00 ± 6.35</td>
</tr>
<tr>
<td>4</td>
<td>1000</td>
<td>122.75 ± 19.16</td>
</tr>
</tbody>
</table>

Table 8: Effect of increasing concentration of chromium (III) ion on % recovery of mercury

<table>
<thead>
<tr>
<th>S. No</th>
<th>Concentration of Cr^{3+} (ppm)</th>
<th>% recovery of Hg(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0</td>
<td>95.00 ± 0.41</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>83.00 ± 12.22</td>
</tr>
<tr>
<td>3</td>
<td>300</td>
<td>76.00 ± 2.08</td>
</tr>
<tr>
<td>4</td>
<td>1000</td>
<td>68.80 ± 20.92</td>
</tr>
</tbody>
</table>

Table 9: Effect of concentration of cobalt(II) on recovery of mercury

<table>
<thead>
<tr>
<th>S.No</th>
<th>Concentration of Co^{2+} (ppm)</th>
<th>% recovery of Hg(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0</td>
<td>119.0 ± 10.16</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>47.00 ± 3.95</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>19.00 ± 2.00</td>
</tr>
<tr>
<td>4</td>
<td>200</td>
<td>12.00 ± 2.52</td>
</tr>
<tr>
<td>5</td>
<td>300</td>
<td>7.00 ± 3.22</td>
</tr>
<tr>
<td>6</td>
<td>400</td>
<td>10.00 ± 1.00</td>
</tr>
<tr>
<td>7</td>
<td>500</td>
<td>8.00 ± 2.64</td>
</tr>
<tr>
<td>8</td>
<td>600</td>
<td>7.67 ± 1.53</td>
</tr>
<tr>
<td>9</td>
<td>1000</td>
<td>0.75 ± 2.99</td>
</tr>
</tbody>
</table>
Table 10: Effect of increasing concentration of nickel (II) on % recovery of mercury

<table>
<thead>
<tr>
<th>S.No</th>
<th>Concentration of Ni²⁺ (ppm)</th>
<th>% recovery of Hg (II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0</td>
<td>84.75 ± 14.06</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>33.00 ± 1.45</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>9.00 ± 1.93</td>
</tr>
<tr>
<td>4</td>
<td>30</td>
<td>0.01 ± 1.70</td>
</tr>
<tr>
<td>5</td>
<td>40</td>
<td>ND</td>
</tr>
<tr>
<td>6</td>
<td>50</td>
<td>ND</td>
</tr>
<tr>
<td>7</td>
<td>300</td>
<td>ND</td>
</tr>
<tr>
<td>8</td>
<td>1000</td>
<td>ND</td>
</tr>
</tbody>
</table>

Table 11: Effect of increasing concentration of copper(II) on % recovery of mercury

<table>
<thead>
<tr>
<th>S.No</th>
<th>Concentration of Cu (ppm)</th>
<th>% recovery of Hg (II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>71.00 ± 7.08</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>55.00 ± 2.43</td>
</tr>
<tr>
<td>3</td>
<td>300</td>
<td>29.0 ± 7.25</td>
</tr>
<tr>
<td>4</td>
<td>1000</td>
<td>0.01 ± 1.70</td>
</tr>
</tbody>
</table>

Fig. 1: Effect of concentration of Na⁺, K⁺, Fe²⁺, Zn²⁺ on % recovery of mercury
4. CONCLUSION
There are a number of possibilities that may have resulted in the lowering of Hg signal. After Hg is introduced in the reaction flask there are two important processes that are likely to occur. First the reduction of Hg (II) to atomic mercury vapors. Secondly transportation of mercury vapors to the cell. There is a possibility that the interfering cation interferes in one of the following or in both the steps. That is either the interferent inhibits the reduction of Hg (II) ions or it reacts with or binds with the reduced form of Hg²⁺, blocking its delivery to the absorption cell.

REFERENCES
7. Karunasagar D, Arunachalam J and Gangadharan S. Development of a collect and punch cold vapour inductively coupled plasma, mass spectrometric method for the
23. Dumarey R, Dams R and Hoste J. Comparison of the collection and desorption efficiency of activated charcoal, silver, and gold for the