The Determination of Trace Mercury in Environmental Samples: A Review

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Abstract—Mercury has long been recognised as a neurotoxin element for many decades and with its compounds being extremely toxic, is ranked third in the ‘priority list of hazardous substance’ by the United States comprehensive environmental response, compensation, and liability act. In different samples, mercury can exist as either its inorganic or organic forms and this paper will review the methods for monitoring mercury in different environmental and industrial samples such as environmental waters, animals and industrial waste.

Keywords- mercury determination, atomic absorption spectrometry, detection limit.

I. INTRODUCTION

Due to the unique physio-chemical properties of Hg as a liquid metal, it is used in many industries; however its ionic and organic forms make it one of the most toxic metallic pollutants. Mercury can be found as a trace element in all environments occurring naturally or as the result of anthropogenic activity. Landfills, dental preparation, laboratory use, combustion of fossil fuel, medical waste incinerator, municipal waste incinerator, mining ore processing industries, cement industry, chlor-alkali plant, petroleum refinery, smelters and many other industrial processes are the major human made sources of mercury pollution. From this list, it can be seen that industry is the major anthropogenic source of mercury emissions [1]. Together natural and anthropogenic activities contribute to the mercury cycle in the environment. By this cycle various forms of mercury Hg (0), Hg (II), CH₃Hg⁺, (CH₃)₂Hg can interchange through atmospheric, terrestrial and aquatic environments. Anthropogenic and natural sources release mercury vapor into the atmosphere. Some of this vapor phase mercury can convert into ionic mercury by photo oxidation and return to the earth as rain water. Mercury can remain in the atmosphere for extended periods of time and can travel hundreds of thousands of miles by air currents become a threat even for those not directly exposed to this element. Currently there is an increasing international concern over the negative effects of mercury emissions on human health and the environment. After the incidence of Minamata disease, due to the consumption of methyl mercury contaminated fish in Japan 1956 [2], industrialised nations around the world began contemplating mercury emission control. In addition to local and national regulation, the United Nations has finalised the legal document ‘Minamata Convention of Mercury’ to reduce mercury emission that is signed by 140 countries [3].

Mercury is a hazardous heavy metal that can accumulate in a living body [4]. The impact of the effect of mercury on human health will depend upon factors such as dose, duration of exposure, chemical form of mercury and person’s health. Once in the body, mercury can adversely affect neurological development and functioning and can cause coronary heart disease and cardiovascular diseases [5].

With the growing awareness of the toxicity of this metal and its compounds, the adverse effects on human health and the ecosystem, many industries are paying considerable attention to its emission into the environment. The literature highlights this concern with many industries spending funds on research to minimize mercury emission into water and air [6-11]. This paper will review the different techniques for detection of mercury in various samples.

II. MONITORING OF MERCURY

The monitoring of mercury in various samples is imperative due to its toxicity, high mobility and adverse effects on human beings. For many years, researchers have constantly worked on different methods to quantify mercury in different samples. Since mercury is present in trace amount in different samples, highly sensitive and sophisticated analytical techniques are required for its measurement.

III. ANALYSIS

The required steps for analysis of mercury are; chemical vapor generation (CVG) and detection by an instrument.

A. Chemical vapor generation (CVG)

CVG has many advantages due to its capability to separate the main analyte from a complex matrix, high selectivity and easy automation. The formation of mercury vapour can be generated by any of the methods including: CVG by reductant, CVG by photoreduction, electrochemical vapour generation, and ultrasound promoted CVG.
a) **CVG by reductant:** Mercury vapour can be generated in aqueous or digested samples by using either of the two most common reducing agents, SnCl$_2$/HCl or NaBH$_4$/NaOH. SnCl$_2$ was first used as a reducing agent by Poluektovet al. [12]. Hatch and Ott [13] applied this to the analysis of soil and rock samples. Later NaBH$_4$ was used as a reducing agent due to its stronger reducing properties compared to SnCl$_2$. Despite its stronger reducing property, it has a number of drawbacks; it is non-selective and can reduce other transition metals present in the sample along with Hg, its instability and contamination from impurities in NaBH$_4$. Some samples may react to form foam with bubble formation releasing mercury giving poor precision, wrong measurements and poor reproducibility. Results using SnCl$_2$ suggest this is a more suitable digestion method. D’Uliovo et al. [14] have proposed using sodium cyanotrihydroborate(III) as a reducing agent for the formation mercury vapour and has some advantages over NaBH$_4$ as it is a milder reducing agent and works well with protic environment that makes it more specific with less interference. Despite of all these problems, CVG by reductant is still popular among many researchers [15-19] due to its reaction efficiency and its application in batch and online system.

b) **CVG by photoreduction:** This is accomplished by mixing samples with low molecular weight organic compound (such as acetic acid, formic acid, citric acid, oxalic acid, methanol, formaldehyde) followed by exposure to ultra violet (UV) radiation [20]. Some photocatalyst, (e.g. TiO$_2$) can be added to enhance the photoreduction or to improve the efficiency. A photolytic cleavage of the organic compound forms hydrogen and carboxyl radicals. These species are strong reducing agent and can reduce other transition metals present in the sample along with Hg, its instability and contamination from impurities in NaBH$_4$. Some samples may react to form foam with bubble formation releasing mercury giving poor precision, wrong measurements and poor reproducibility. Results using SnCl$_2$ suggest this is a more suitable digestion method. D’Uliovo et al. [14] have proposed using sodium cyanotrihydroborate(III) as a reducing agent for the formation mercury vapour and has some advantages over NaBH$_4$ as it is a milder reducing agent and works well with protic environment that makes it more specific with less interference. Despite of all these problems, CVG by reductant is still popular among many researchers [15-19] due to its reaction efficiency and its application in batch and online system.

c) **Electrochemical (EC) vapour generation (VG):** This technique uses electrons as a reductant and is based on the electrode reduction of Hg (II) at the cathode (graphite, glassy carbon). The efficiency of the vapor generation depends upon the cathode material and electrolyte. Electrochemical vapour generation (EC-CV) involves two processes; first, reduction on the cathode results in deposition of mercury as Hg from the soluble aqueous phase, and in the second step, generation of mercury cold vapor after removal from cathode. Zavar et al. [23] proposed a method of forming EC-CV of mercury using a graphite cathode and Pt anode in tap water and river water samples. Cerveny et al. [24] described another method for EC-CV generation using a gold wrapped graphite tube. This technique of Hg vapor generation is cost effective, shows good detection limits and is free from transition metal interference, and contamination.

d) **Ultrasound (US) promoted CVG:** In ultra sound promoted CVG, Hg vapours can be produced by mixing samples with organic acid and irradiating the mixture with ultrasonic radiation. This technique is also produces less waste compared to chemical CVG [25]. For the measurement of Hg in natural water, Gil et al. [26] proposed sono-induced CVG of Hg. They showed that sonolysis of water and its subsequent reaction with formic acid produced many gases that reduced Hg (II) to Hg$_2$.

e) **Other Miscellaneous Techniques:** Wu et al. [27] presented a technique to produce mercury vapors by dielectric barrier discharge (DBD) that produces less chemical waste than traditional CVG by reductant and applied this to the measurement of mercury in reference and mineral water samples. In this non-thermal, plasma generation method, a high energy electron stream is generated by the collision electrons with gas molecules and produces different radicals and ions to reduce mercury [28]. In another technique Hg CVG was generated by solution-cathode glow discharge (SCGD) [29]. This is a simple form of electrolyte cathode atmospheric–pressure glow discharge (ELCAD). They made a closed SCGD cell with a tungsten anode and a graphite cathode with the anode fixed a few millimetres above the sample solution. When the sample containing Hg was injected into the discharge, it was easily converted to Hg$^0$.

### B. Detection/Instrument

Many instrumental analytical methods can be employed to determine the trace level of mercury in various samples. The most prevailing techniques are: atomic absorption spectrometry, atomic florescence spectrometry, Inductively couple plasma - mass spectrometry (ICP-MS), Inductively couple plasma-atomic emission spectrometry (ICP-AES), electroanalysis, neutron activation analysis.

1) **Atomic absorption spectrometry (AAS):** This is the most commonly used method for determining mercury in different samples. This concept was first proposed by Walsh in Australia as well as Alkemade and Milatz in Netherland [30]. This technique includes the following types:

a) **Flame atomic absorption spectrometry (FAAS):** In the early stages of development, the flame was the only method for atomization. This method had very limited applications due to its poor detection limit of 0.2 mg·L$^{-1}$. A FAAS method shows only 1% characteristic absorption at a concentration of 5 mg·L$^{-1}$. Matusiewicz and Krawczyk [31] presented a method with modifications in FAAS. They demonstrated in situ trapping of mercury vapor generated by a laboratory built hydride generator and applied this method to determine total Hg in real and certified reference materials.

b) **Solid sampling-graphite furnace atomic absorption spectrometry (SS-GFAAS):** This technique utilises the possibility of solid sampling-graphite furnace atomic absorption spectrometry for the direct determination of Hg in solid samples. This method can be used as a screening method since it provides fast results without any sample treatment. Resano et al. [32] presented a method for fast and direct determination of Hg in polymers with different composition covering Hg concentrations from 20 to 1100 μg·g$^{-1}$ and a detection limit of 2.2 μg·g$^{-1}$ with modification of the high-resolution continuum source [32].
c) Cold vapor atomic absorption spectrometry (CV-AAS): This is the most successful and widely used technique for the determination of mercury due to its simplicity and good reproducibility. Mercury can stay in its atomic state at room temperature. The vapor pressure of mercury at 20 °C is 0.16 Pa that corresponds to 14 mg m⁻³ mercury concentration in air. This distinctive property of mercury allows it to be determined by AAS without any atomiser using the cold vapor (CV) technique. Atomic mercury can be released from its digested samples by reduction. The most common reducing agents are SnCl₂ and NaBH₄. Mercury vapor after volatilization is released out of the solution and carried by an inert gas to the absorption cell. The mercury absorption line is at 253.7 nm. The magnitude of the signal shows the amount of mercury present in the samples. The most decisive method for mercury determination was completely analysed by Hatch and Ott [13]. Table I presents a review of some of the CV-AAS methods.

2) Atomic emission spectrometry (AES): This technique facilitates both qualitative and quantitative measurements. The instrument consists of an emission source, an optical system to scatter the spectrum and equipment for the measurement of emitted lines. An ICP AES is the most popular plasma source for the measurement of mercury [27, 29, 33-35]. A method proposed by Zhu and Alexandratos [33] for mercury determination involved adding a mercury complexing agents (gold (III) chloride, thiourea) to reduce the memory effect. Han et al. [34] proposed a method to determine mercury in soil samples by optimising the condition of ICP AES with a detection limit of 20 µg L⁻¹.

3) Atomic fluorescence spectrometry (AFS): In AFS, the intensity of fluorescent emission is determined by the degree of atom excitation by the absorption of the radiation at the desired frequency. Due to the low background signal in AFS, this method is highly sensitive for the measurement of trace metals like mercury. Winefordner and Staab [36] in 1964 first used AFS to determine Hg. Table I summarises the literature on AFS with a brief summary of AFS methods and CV-AAS methods.

4) Inductively couple plasma – mass spectrometry (ICP-MS): The ICP-MS instrument uses high temperature argon plasma as the ionization source and a mass spectrometer (MS). In this technique, sample in the form of an aerosol is introduced into the plasma. ICP-MS has become a popular technique for mercury analysis due to its high sensitivity and wide linear range. Table I compares detection limits and reductant used for a number of ICP-MS methods in various samples.

5) Neutron activation analysis: This technique is highly sensitive and selective. This is based on the fact that when a sample (having unknown analyte) is mixed with standard materials of known elemental concentrations and irradiated with neutrons, it is converted to the radioactive isotope which emits gamma radiation. Gamma rays (γ) are indicative of specific elemental concentrations in the unknown samples. Alam et al. [37] reported a method for mercury determination using instrumental and radiochemical neutron activation analysis (INAA and RNAA, respectively) in food items. In another method, Hg has been measured along with other trace metal in curry leaves by short irradiation instrumental neutron activation analysis [38]. This technique is expensive and produces radioactive by-products.

6) X-ray fluorescence analysis: This is a non-destructive analytical method that involves bombarding of X-rays on a sample, causing excitation of the sample, which in turn emits secondary (or fluorescent) X-rays that are characteristic of the types of atoms present in the sample. It is helpful in geochemistry and forensic science in analysing a wide range of materials, including solid, liquid and powder sampling for multi element analysis. An energy dispersive X-ray fluorescence spectrometric (ED XRF) method has allowed for the measurement of mercury in polyethylene and polypropylene after xylene treatment. Xylene provides an effective homogenous element for dispersal of this element. The method has a detection limit of 12 mg kg⁻³ with 10% RSD and 81% recovery [39]. This is very fast technique with main disadvantage of loss of analyte during sample preparation step.

7) Electroanalytical method: Voltametric stripping analysis of mercury is used for the measurement of mercury in dilute aqueous solution. These methods shows detection limits as low as 10⁻¹⁴ M using differential-pulse anodic stripping voltammetry on a glassy carbon electrode [40]. Gold has a high affinity for mercury and is used in electrodes for mercury analysis – a number of gold disks or gold microelectrode arrays are described in the literature [41]. Apart from gold other electrodes used were graphite paste electrodes, modified carbon paste electrodes, glassy carbon electrodes, and platinum electrodes [42-46].

8) Mercury sensors: Researchers are also working on developing mercury sensors for fast determination of mercury. Sensors may be nanosensors, optical, chemical sensors, biosensors or apizoelectric sensors. This technique is quite new and existing literature shows its use on limited samples [47, 48].

IV. CONCLUSION

Obtaining an accurate measurement of the concentration of mercury is important due to its highly toxic and bioaccumulative nature. Due to its volatile nature, its ability to adsorb on vessel walls and its trace level in many environmental samples, the assay method must ensure that mercury is not lost during the process. The methodology of mercury determination depends on the matrix of the samples as well as the concentration and form of mercury. Techniques for solid samples are fast and simple such as SS-GFAAS and XRF but with poor detection limit and recovery, so these techniques can be used for screening of mercury in samples containing higher concentration of mercury.

Other techniques require conversion of the solid matrix to the aqueous form. AES is a good analysis technique for solution samples sample containing higher concentration of mercury. Other techniques such as CV-AAS, ICP-MS, AFS have lower detection limits making them preferred for trace determination of mercury. This sample preparation step can be performed by heating samples with concentrated acid to release mercury from solid matrix at atmospheric pressure or more efficiently at high pressure. Care must be taken in sample preparation to ensure that mercury is not lost prior to analysis.
### Table I. Comparison of some analytical techniques for mercury determination in different samples

<table>
<thead>
<tr>
<th>Method</th>
<th>Pre concentration/Cold vapor generation</th>
<th>Linear range, Detection Limit, recovery, RSD</th>
<th>Samples</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>FI–CV-AAS</td>
<td>NaBH₄ 0.4% m/v (in 0.1%NaOH)</td>
<td>0.3 ng g⁻¹</td>
<td>road dust</td>
<td>(49)</td>
</tr>
<tr>
<td>FI–CV-AAS</td>
<td>Amalgamation, 0.02% w/v (in 0.02%NaOH)</td>
<td>10 ng L⁻¹, recovery (94 - 111 %)</td>
<td>Urine, water</td>
<td>(50)</td>
</tr>
<tr>
<td>FI–CV-AAS</td>
<td>Ion exchange and reductive elution by Chelite-S⁶⁻, SnCl₂ 10% w/v in 6M HCl</td>
<td>-0.8 ng L⁻¹, (97-128 %), 5%</td>
<td>Agroindustrial sample</td>
<td>(16)</td>
</tr>
<tr>
<td>CF–CV-AAS</td>
<td>SnCl₂ 10% w/v in 12 M HCl</td>
<td>20 µg kg⁻¹, 1.2 %</td>
<td>Geological materials</td>
<td>(19)</td>
</tr>
<tr>
<td>CV-AAS</td>
<td>Amalgamation on Au-Pt trap, 2-3% NaBH₄ in 0.5% m/v NaOH</td>
<td>0.10 µg L⁻¹, recoveries = (98-101) %</td>
<td>Gasoline</td>
<td>(51)</td>
</tr>
<tr>
<td>FIMS</td>
<td>SnCl₂ 1.5 % w/v in 1% v/v HCl</td>
<td>-&lt;, recoveries = (96-100) %, 2%</td>
<td>Sewage sludge, sediment and soil samples</td>
<td>(52)</td>
</tr>
<tr>
<td>CV-AAS</td>
<td>NaBH₄ 1 % w/v</td>
<td>-0.1 ng L⁻¹, (for MeHg, 0.133 µg kg⁻¹ for Hg, &lt; 10 %)</td>
<td>Fish</td>
<td>(53)</td>
</tr>
<tr>
<td>CV-AAS</td>
<td>Amalgamation on Au coated silica powder, SnCl₂ 1% (w/v) in 3M H₂SO₄</td>
<td>-1, 1.3 pg m⁻¹ L⁻¹, recovery &gt;90%, RSD= 2.7%</td>
<td>Coal fly ash</td>
<td>(54)</td>
</tr>
<tr>
<td>AFS</td>
<td>Vapor pre concentrated by gold impregnated silica</td>
<td>Linearity up to 7200 pg, 4 pg, recovery 97%, RSD=2.5%</td>
<td>Humid air</td>
<td>(55)</td>
</tr>
<tr>
<td>ECVG-AFS</td>
<td>Electrochemical vapor generation by PANI / graphite as cathode</td>
<td>-1.4 pg m⁻¹ L⁻¹, RSD= 2.3%, recovery = 96-106%</td>
<td>Human hair</td>
<td>(56)</td>
</tr>
<tr>
<td>ECVG-AFS</td>
<td>Pt/Ti cathode in organic acid catholyte</td>
<td>-1, 1.4 pg m⁻¹ L⁻¹, RSD= 2.3%, recovery; = 96-106%</td>
<td>Traditional Chinese Medicines samples</td>
<td>(57)</td>
</tr>
<tr>
<td>IF-EC-AFS</td>
<td>Glassy carbon cathode</td>
<td>5 µg L⁻¹, 1.2 ng L⁻¹, RSD= 1.8%</td>
<td>Human hair</td>
<td>(58)</td>
</tr>
<tr>
<td>CV-AFS</td>
<td>SnCl₂ as a reductant</td>
<td>-0.01 ng g⁻¹, recovery close to 100%, RSD= 10%</td>
<td>Gasoline and other petroleum</td>
<td>(59)</td>
</tr>
<tr>
<td>CV-AFS</td>
<td>SnCl₂ as a reductant</td>
<td>13 ng L⁻¹</td>
<td>Shredded samples of fish protein certified reference material DORM-2 and marine sediment PACS-1</td>
<td>(60)</td>
</tr>
<tr>
<td>CV-ICP-MS</td>
<td>SnCl₂ as a reductant</td>
<td>0.7 ng L⁻¹, 100 ng L⁻¹, 0.7 ng L⁻¹, recovery = 94 - 109%, RSD= 2.3%</td>
<td>Humic rich natural water samples</td>
<td>(61)</td>
</tr>
<tr>
<td>CV-ICP-MS</td>
<td>NaBH₄ as a reductant</td>
<td>4.2 ng L⁻¹, (for Hg(II) and 6.4 ng L⁻¹ for total Hg, respectively RSD &lt; 5%</td>
<td>Fish otoliths</td>
<td>(62)</td>
</tr>
<tr>
<td>CV-ICP-MS</td>
<td>NaBH₄ as a reductant</td>
<td>0.006 mg g⁻¹</td>
<td>Soil</td>
<td>(63)</td>
</tr>
<tr>
<td>FI-ICP-MS</td>
<td>Amalgamation on Au-Pt gauze</td>
<td>200 pg L⁻¹, RSD= 1%</td>
<td>Sea water, fresh water</td>
<td>(64)</td>
</tr>
<tr>
<td>LC-ICP-MS</td>
<td>Cloud point extraction</td>
<td>13.8 and 6 ng L⁻¹, (for MeHg⁺, PhHg⁺ and Hg²⁺ respectively,</td>
<td>Human hair and ocean fish</td>
<td>(65)</td>
</tr>
</tbody>
</table>


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