Determination of Mercury concentration in the sediment and blood samples of fuel stations area using cold vapor atomic absorption spectrometry

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Abstract

A cold mercury vapor atomic absorption spectroscopy (CVAAS) Technique has been used for the determination of mercury in both of blood and sediment samples. After the blood Samples were digested in a mixture of (3:2:1) [Nitric, Perchloric and sulfuric concentrated acids] respectively and a sediment samples were digested in a mixture of (1:1) [Nitric and Hydrochloric concentrated acids] , a 25% (W/V) of Tin Chloride has been added as a reduction agent also a 1% (W/V) of Potassium dichromate have been added in order to improve sensitivity of measurements.

The results show that average of mercury contents in the fuel stations worker blood samples are in range [22-36] ng/ml; whereas its contents in the fuel station area sediment samples are in range [30-48] ng/g.

الخلاصة

تم استخدام طريقة الامتصاص الذري بتوليد بخار الزئبق البارد في تقدير محتوى الزئبق في عينات من الدم للعاملين في محطات تعبئة الوقود وكذلك والرواسب الترابية في محطات التعبئة. بعد عملية هضم عينات الدم بمزيج من (3 : 2 :1) من حوامض النتريك , البركلوريك والكبريتيك المركزة على التوالي , وهضم عينات الرواسب الترابية بمزيج من (1:1) من حامضي النتريك والهيدروكلوريك المركزين تم اضافة 25 % من مادة كلوريد القصديروز كعامل مختزل كما اضيفت 1 % من مادة داي كرومات البوتاسيوم لتحسين حساسية القياس.

اظهرت النتائج بأن معدلات محتوى الزئبق في نماذج الدم للعاملين في محطات تعبئة الوقود تتراوح ضمن المدى (22-36) نانوغرام/ مليلتر بينما تكون معدلات المحتوى للزئبق في نماذج الرواسب الترابية تتراوح (30-48) نانوغرام /غرام.

***Key Words**: Mercury, Sediment, Blood, Cold Vapor, Atomic Absorption.*

Introduction

With its interesting physical and chemical properties, high toxicity and wide usage in various industrial sectors, mercury has become one of the most studied pollutant (1,2).

Mercury has long been recognized as a serious global pollutant that has a significant impact upon our ecosystem. Unlike most other pollutants, it is highly mobile, non biodegradable, and bio-accumulative and as a result has to be closely monitored to ensure its harmful effects on local populations are minimized. Approximately 50 tons of mercury particulates are emitted into the atmosphere every year by a variety of different man-made and natural sources including coal-fired power plants, solid waste incineration plants, volcanoes and forest fires. When the mercury falls back to earth it is deposited on the land and gets into the soil, river sediments and water ecosystems, where it is converted into the highly toxic organo mercury compound, methyl mercury (CH3Hg+). This toxicant enters both the plant and aquatic system food chain, and eventually ends up in the crops, vegetables and seafood we consume. In addition to being ingested via the food we eat, mercury can also enter the human body through contact with the skin and by inhalation into the lungs, where it can eventually end up in the bloodstream [3].

Several methodologies are currently used for the determination and speciation of mercury (4) but continuous flow cold vapor atomic absorption spectrometry (CV-AAS) has been continuously gaining in popularity in the last decades because of its high sensitivity and selectivity (5). It has been demonstrated recently that the replacement of stannous chloride by sodium tetrahydroborate as a reducing agent could present several advantages, including reduced costs on chemical reagents, elimination of the degassing step and prevention of SnO2 precipitation inside the gas/liquid separator (6).

Experimental

1- Apparatus:

The mercury content in the samples achieved by means of cold mercury vapor atomic absorption spectrometry (CVAAS) using shimadzu atomic absorption spectrophotometer model (AA-360-12) has been used. A (17 × 0.8) cm silica tube has been used as an absorption cell. (99.99%) pure Argon gas was used as a carrier gas for transferring the forming mercury vapor from the reduction vessel to the absorption cell.

2- Reagent:

- **1000 ppm Mercury (II) solution**: (1.3535) g of mercuric chloride was dissolved in 1 litter by deionized water (fluka).
- **Tin(II) Chloride solution**: a (25% W/V) of $SnCl_2$ dissolved in 50 ml of concentrated HCl then diluted using deionized water , freshly prepared. (Merck).
- **Potassium Dichromate solution**: a (1%W/V) of $K_2Cr_2O_7$ was prepared by dissolving in deionized water.
- **Hydrochloric acid**.
- **Nitric acid.**
- **Perchloric acid.**
- **Sulfuric acid.**
- **Hydrofluoric acid.**

3-Preparation of sample solution

a- blood

A 1ml of whole blood is mixed with approximately 3 ml of a 5:2:1 mixture of 70% (w/w) nitric acid, 70% (w/w) perchloric acid and 98% w/w sulfuric acid in a 10 ml nominal volume graduated polyethylene test tube. The digestion mixture is warmed to 40 °C for 60 minutes and the heated at 90 °C for at least 60 minutes with frequent mixing until the brown fumes of oxides of nitrogen dissipate and the remaining liquid is golden yellow in color. It is important to control the liquid's temperature so that boiling any stronger than could be described as effervescence is precluded. Make up to 5.0 ml with reagent water [7].

b- Sediment

A 1g of dry sediment is mixed with 6 ml of a 1:1 mixture of 70% (w/w) nitric acid and 37% w/w hydrochloric acid in a polyethylene test tube. The digestion mixture is warmed up to 80 °C until it getting dry, then a 4 ml of 1: 1 mixture of Perchloric and hydrofluoric concentrated acid have been added and the mixture warmed to 75 °C until it getting dry. The rest of solution dissolved in 5 ml (0.5 N) of HCl.

4-Procedure:

One ml of digested samples were introduced in the reduction vessel, 1ml of $SnCl_2$ solution was added and mixed using magnetic stirrer for 90 second then the formed mercury (I) vapor transferred to the absorption cell using (99.99 %) Argon gas at flow rate 250 ml/min.

5-The direct method

The calibration graph for mercury was prepared by using different concentrations (10, 20,40,60,80 and 100 ng/ml) of mercury standard solution.

Table -1 : calibration curve of Mercury ng/ml.

No.	Hg Concentration ng/ml	Absorbance
1	10	11
2	20	20
3	40	45
4	60	70
5	80	90
6	100	110

Table - 2: Hg ng/ml concentration in the fuel station blood samples comparable with the control samples.

	Hg Concentration in blood ng/ml	
No.	Fuel station workers	Control samples
1	***22***	***12***
2	***29***	***18***
3	***26***	***19***
4	***36***	***11***
5	***27***	***18***
6	***28***	***16***
7	***28***	***16***
8	***36***	***16***
9	***24***	***19***
10	***35***	***12***
11	***24***	***16***
12	***22***	***18***
13	***26***	***16***
14	***22***	***11***
15	***28***	***16***

Table - 3: Hg ng/g concentration in the fuel station sediment samples comparable with the control sediment samples.

	Hg Concentration in sediment ng/g	
No.	Fuel station sediment	Control sediment samples
1	***33***	***5***
2	***38***	***8***
3	***42***	***11***
4	***44***	***8***
5	***48***	***4***
6	***30***	***10***
7	***42***	***8***
8	***44***	***6***
9	***46***	***6***
10	***32***	***2***
11	***36***	***8***
12	***32***	***9***
13	***42***	***10***
14	***30***	***6***
15	***28***	***6***

Results and discussion

1-Calibration

Figures [1] show the calibration graph for mercury. It appears as a straight line passing through the calibration points which indicate an excellent precision and reproducibility of the process.

2-Absolute Sensitivity, Detection limit and linearity

Absolute sensitivity (IUPAC characteristic concentration) for example nanograms of Mercury giving absorbance value(0.0044) was found to be 0.01 ng/ml injected standard solution.

Detection limit was determined by submitting 10 replicates of (2 ng/ml) injected standard solution to analytical procedure.

Limits of linearity ranged between [0.5-120 ng Hg /ml] .

3- Variation of Mercury contents

Table [2] shows that the mercury content in the fuel station blood samples are in the range of [22-36 ng/ml], Whereas its content in the control people blood samples are in the range of[12-19 ng/ml].

Table [3] shows that the mercury content in the fuel station sediment samples are in the range of [30-48 ng/g], whereas it's content in the control sediment samples are in the range of [2-10 ng/g].

Both of Blood and sediment mercury content in the fuel station comparable with those samples in the normal area make clear evidence that fuel stations have a strong contribution on the atmosphere mercury pollution Fig.[2] and Fig[3].

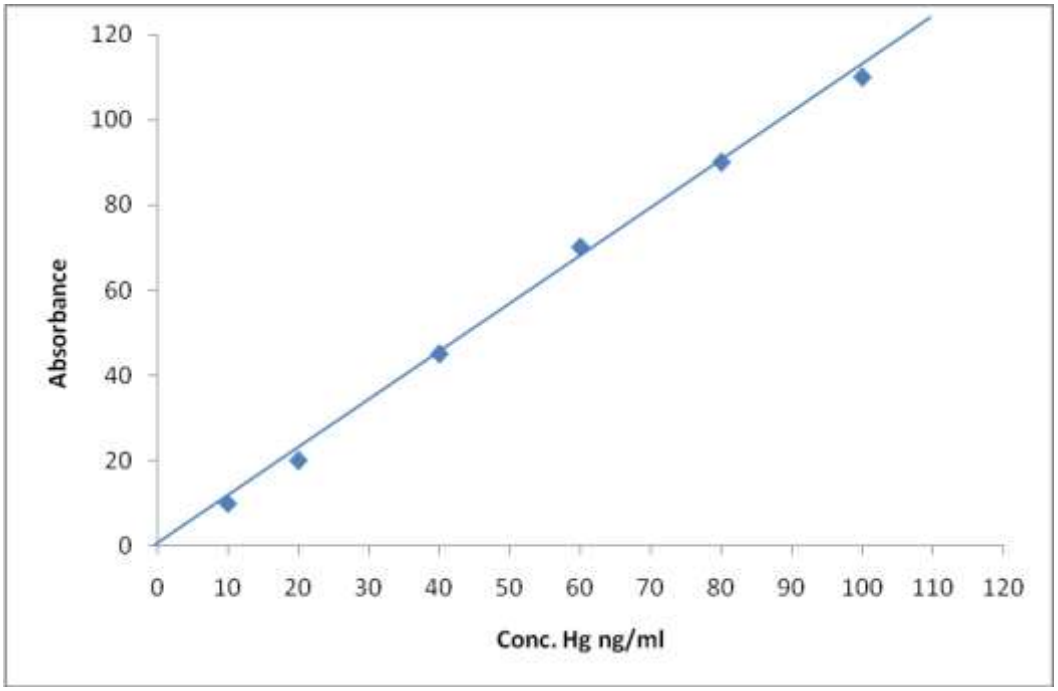

Fig.[1] Calibration graph for mercury.

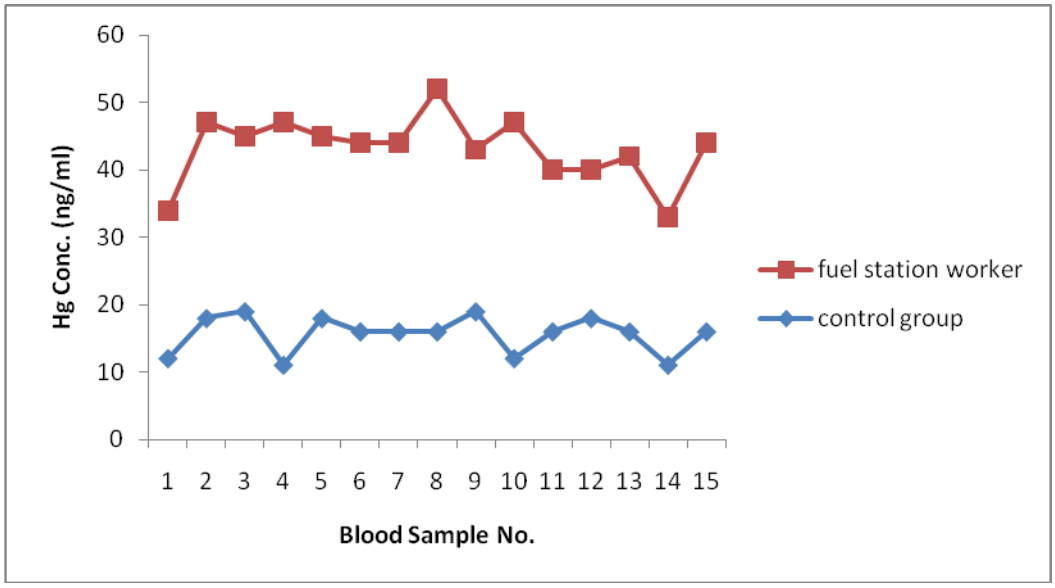

Fig.[2] Hg ng/ml concentration in the fuel station blood samples comparable with the control samples.

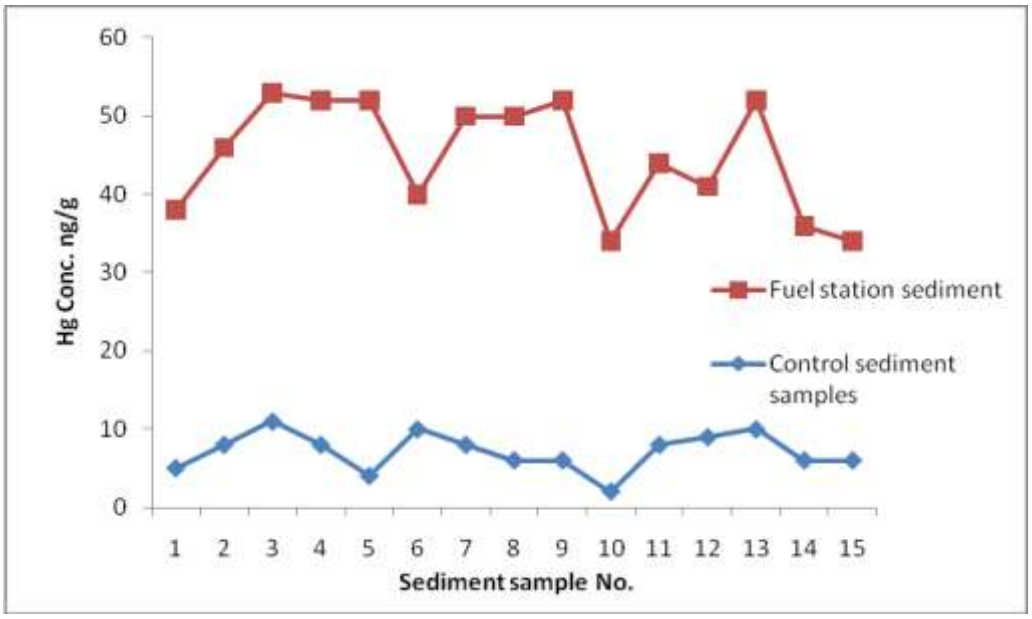

Fig.[3] Hg ng/g concentration in the fuel station sediment samples comparable with the control sediment samples.

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