Fall 2012

Method for Arsenic Detection in Mine Samples from the Upper Peninsula of Michigan

Vinay Babu Yalamanchili
Governors State University

METHOD FOR ARSENIC DETECTION IN MINE SAMPLES FROM THE UPPER PENINSULA OF MICHIGAN

BY

Vinay Babu Yalamanchili

Research Project

Submitted in
Partial fulfillment of the requirements for the
Degree in Master of Science,
With a major in Analytical Chemistry.

Governors State University
University Park, IL 60484.

FALL-12/07/2012.

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Acknowledgments

Abstract

Arsenic is the 20th abundant element in the earth crust [1]. High concentrations of Arsenic is seen in mine operating countries which can affect public health and biological environment [2]. This may reach to drinking water through ground or surface run-off water. Long term exposure to arsenic causes cancer of bladder, skin, and lungs [3]. So detecting the amount of arsenic in soil and drinking has been an analytical challenge. Arsenic is found in variety of chemical forms in organic and inorganic compounds which results in chemical and physical interferences in the analysis. Graphite Furnace Atomic Absorption Spectroscopy (GFAAS) was used to measure Arsenic in environment samples from Michigan's Upper Peninsula. The best result for analysis that the standard calibration curve fit to be (R^2 = 0.996983). A calibration curve is plotted by taking concentration in the range of 0-100 ppb on x-axis and absorbance on y- axis. The Arsenic concentration in the tested samples range from 3.13 to 0.39 µg As/g sample. The values obtained after GFAAS analysis for Estuarine sediment sample is 2.16 µg As/g compared to standard NIST value 6.23 mg/kg [13]. The value obtained for Domestic sludge is 1.87 µg As/g sample compared to standard NIST value 7.82 mg/kg [12].

Introduction

Element Arsenic (As):-

Arsenic is naturally occurring material that is found in soil, water and in bed rock. It also can be released in to the environment through natural activities like volcanic eruptions, erosion of rocks and through forest fires [3]. It is odorless and tasteless and in its pure form it is silver to gray or white metal. It is used in industry, mostly as a wood preservative, also in paints, dyes and even in certain fertilizers.

Copper mines in Michigan:-

Michigan's Upper Peninsula was home to nations first mineral rush. Copper mining in Michigan originated thousands of years ago, but Cu mining became an important industry in the 19th and early 20th centuries. Native Americans were first to mine in Lake Superior and Keweenaw Peninsula of northern Michigan between 5000 and 1200BCE. This copper was used to produce tools [11].

In 1973 due to acidic run off from piles of waste rock, known as tailings, at the abandoned Dober mine on the Michigan-Wisconsin border leached in to the trout-fishing waters of the iron river, killing the aquatic life for 7-mile stretch. Today the tailings continue to contaminate the river [5].

In 1987, Torch Lake, located in the heart of U.P's old copper mining district, became a federal area of concern after fish there were discovered with tumors a decade earlier. The lake and its surrounding areas 368 square miles totally were contaminated with mercury, arsenic, copper and lead. This is the result of more than 100 years of mining in these areas. The federal EPA is now overseeing remediation efforts in these areas [5].

So detection of low levels of Arsenic has been became an challenge in mine operating areas.

Analytical Techniques:-

USEPA (US Environmental Protection Agency) Method:-

According to USEPA regulations, the level of arsenic below 10 ppb [4] is safe for drinking or for food preparation, anything above that is not recommended for drinking. Exposure to arsenic may cause skin cancer or skin changes that resemble warts called "hyper keratosis". In ground water arsenic is found in 2 forms Arsenite (As III) (AsO_3^{3-}) which is more toxic than Arsenate (As V) (AsO_4^{3-}) [4].

Method 7060A [ARSENIC (Atomic Absorption, Furnace Technique)] is an EPA method which is used for GFAAS for the determination of levels of Arsenic in mining wastes, soils and in ground water [6]. Before doing analysis samples must be converted to inorganic forms from their organic forms. Soil or aqueous samples are subjected to acid digestion procedure described in method 3050B (Acid Digestion of Sediments, Sludge and Soils) [7].

According to EPA 200.9 [3] it is used for the determination of dissolved and total recoverable elements by GFAAS in ground, surface, drinking, industrial and domestic water and even in sediment sludge's and soils.

Atomic Absorption Spectroscopy:-

The instrument used for measuring the detection limit of As is **PerkinElmer AAnalyst800**.

It has two techniques [9].

1) Flame atomic absorption spectroscopy (FAAS).

2) Graphite furnace atomic absorption spectroscopy (GFAAS).

The concentration of arsenic is very low and its limit is in parts per billion (ppb) as it is hard to find such low level using Flame Atomic Absorption Spectroscopy. So Graphite Furnace Atomic Absorption Spectroscopy (GFAAS) is used for As determination

Figure-1 PerkinElmer AAnalyst 800 At GSU.

Graphite Furnace Atomic Absorption Spectroscopy (GFAAS):-

The detection limit of GFAAS is from parts per million (ppm)- parts per billion (ppb) [9]. The working range for analysis of GFAAS is 0-5 sec on x-axis. The soil sample cannot be taken directly for the analysis as the GFAAS analysis requires an aqueous sample for doing analysis. Digestion procedure should be performed using the modified EPA method 3050B to obtain the aqueous form of sample for the analysis by autosampler.

Biology Collaborative Project:-

Mining causes wide spread metal contamination to water, soil and vegetation. Mine tailings are the waste materials left after mining process they often look like fine clay or sand and commonly contain arsenic. These tailings cause chemical pollution to the environment causing environmental hazards. Mineral processing and mineral oxidation causes chemical contamination to the environment and is distributed throughout the ecosystem by chemical, biological and hydrological interactions [9].

Upper Peninsula is one of the most important regions in 18th century for mining; the new mining companies found new metals that are trapped in bedrock containing high concentrations of sulfide ore. When these sulfide ore are exposed to air water forms sulfuric acid which poisons the ground and surface runoff water. As these mine tailings are effecting human, animal life and even making environmental pollution so biological studies of these tailings and controlling them became challenging [9].

The soil samples used in this experiment are from mines of Michigan's Upper Peninsula, samples were collected by professor Dr. John Yunger and Dr. Timothy Gsell . The biology students who helped me with project are Sandra Johnston and Felicia Krelwitz.

Figure-2 (Tailings Pond) [8]

Empire Iron Mine, Upper Peninsula, MI. These tailings are controlled and non-toxic

Materials and Method:- (Modified USEPA Method)

Chemicals used:-

- 1:1 HNO_3 (Nitric acid) [Prepared by adding 50% of ACS reagent grade water and 50% Concentrated HNO_3 by Fisher Chemicals].

- Concentrated HNO_3 (Nitric acid) [Lot # 052219 certified ACS Plus, Prepared by Fisher Chemicals].

- 30%H_2O_2 (Hydrogen peroxide) [Lot # 122112 Certified ACS, prepared by Fisher Chemicals].

- H_2O ACS Reagent Grade ASTM D 1193 Type 1 Lot # 4205360 (RICCA Chemical company Arlington Texas 76012).

Supplies and Instruments used:-

- 200 mL beakers & watch glasses.
- Pipettes, Graduated cylinders.
- Centrifugator (CRU-5000 Centrifuge).
- 50 mL Centrifuge tubes with caps and bases (Lot no#70473 by Fisher health care).
- Hot air oven (Manufacturer Precision Scientific THELCO).
- Hot pans.
- Weighing apparatus (Adventurer Pro).

Digestion procedure: - For the analysis of the samples by GFAAS the samples should undergo Modified EPA digestion procedure [6, 7].

- Weighed samples must be air dry for 2-3 days, then oven dry for 24 hours at 40^0C and weighed again and percent moisture is determined. Then 1 gm of oven dry samples are used for the digestion procedure.

- Then 10 mL of 1:1 HNO_3 is added to 1 gm of sample in 250 mL of beaker then mix the slurry and cover with a watch glass.   Further heat the sample to $95\ ^0C \pm 5^0C$ on a hot plate and reflux it for 5 minutes at $95^0C \pm 5^0C$ without boiling. After that allow the sample to cool for 5 minutes. Repeat the step.

- If brown fumes are observed, indicating that oxidation of the sample by HNO_3, repeat this step (addition of 5 mL concentrated HNO_3) until no brown fumes are produced by the sample indicating that complete reaction with HNO_3 is done. Then sample is cooled.

- Then add 2 mL of distilled H_2O and 3 mL of 30% H_2O_2. Cover the vessel with a watch glass to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to vigorous effervescence. Heat until effervescence subsides and cool the vessel. Continue to add 30% H_2O_2 in 1 mL aliquots with warming till the effervescence is minimal.

  NOTE: Do not add more than a total of 10 mL 30% H_2O_2.

- Cover the sample with a watch glass and continue heating the acid-peroxide sample until the volume has been reduced to approximately 5-10 mL or heat at $95^0C \pm 5^0C$ without boiling for 2 hours. Maintain the solution that it doesn't dry over the bottom of the vessel at all times.

- After cooling, gravimetric dilution was done using water. Quantitatively transfer the solution to 50 mL pre-weighed centrifuge vials for centrifugation (at 2,000 - 3,000 rpm for 10 minutes) and reweighed after centrifugation. The sample is finally ready for analysis by GFAAS.

Apparatus required for Analysis By GFAA:-

- Graphite Furnace Atomic Absorption Spectroscopy.(PerkinElmer AAnalyst 800).
- Argon and Compressed air cylinders.
- 200 mL Beakers.
- 100 mL volumetric flasks, Pipettes.
- Measuring cylinders
- Sampling cups.

Chemicals required for Analysis by GFAA:-

- 5%HNO_3 Lot # 27-145 AS (SPEX Certiprep).
- 2.0% (20,000ppm Mg) Mg $(NO_3)_2$. Lot # 4205048 (RICCA Chemical company Arlington Texas 76012).
- 0.2% Pd (2000 ppm Pd). Lot # 4203778 (RICCA Chemical company Arlington Texas 76012).
- Standard AS 100 mg/L With 5% HNO_3. Lot # 20-75 AS (SPEX Certiprep).
- H_2O ACS Reagent Grade ASTM D 1193 Type 1 Lot # 4205360 (RICCA Chemical company Arlington Texas 76012).

Preparation of Solutions for Analysis By GFAA:-

Preparation of Diluent (0.2%HNO_3) [Recommended by PerkinElmer].

- For this preparation 40 mL of 5%HNO_3 is taken and diluted to 1000 mL.
- This diluent is used through the entire experiment.

Preparation of chemical Modifier: [0.005 mg Pd +0.003 mg $Mg(NO_3)_2$

- Matrix Modifier, 0.2% Pd (2000 ppm Pd). Palladium metal in 5% Nitric Acid is used

- Matrix Modifier, 2.0% (20,000ppm Mg) Mg $(NO_3)_2$ Mg metal in 5% Nitric Acid is used.

- Take 3mL of Mg $(NO_3)_2$ and 0.05 mL of Pd and make up to 100 mL with diluent (0.2% HNO_3).

Preparation of AS Standard (100 ppb):- [Recommended by PerkinElmer].

- 0.1 mL (100µl) of As standard is taken and is diluted to 100 mL in volumetric flask with diluent (0.2% HNO_3).

Method for Arsenic determination using GFAAS

[Recommended by PerkinElmer].

Method Description: - Prepared as As New Method On 05/30/12 100 ppb.

Spectrometer

- Element : As
- Wavelength (nm) :193.7
- slit width (nm) :0.7L

Signal

- Type: AA - BG
- Measurement : Peak area

Settings

Read Parameters:-

- Time (sec):5.0 Delay Time (sec):0.0 BOC Time (sec) : 2

- Replicates : Same for all Samples : 3

- Lamp Current : 380 µA ,Wavelength: 193.7 nm ,Slit: 0.7H

- Arsenic Electrode discharge lamp is used (As-EDL).

Principle of the gas purging system:-

(According to users guide PerkinElmer 5-18).

To prevent the oxidation of graphite tube during the atomization step of graphite furnace Analysis, an inert gas atmosphere inside and outside the graphite tube is essential.

This gas system provides 2 independently controlled flows

1) External protective flow.

2) Internal purge flow.

The furnace gas system has 2 inlets,

1) Normal gas inlet:- This inlet provides the inert gas that prevents the graphite tube and the Sample from oxidizing at high furnace temperatures.

2) Special gas inlet: - this is optional but useful for particular applications; for example, air may produce more effective ashing of organic materials.

NOTE:- As we are not using a special gas, we are connecting the inert gas to both inlets

using the Y-connecter, as furnace is operated if there is gas pressure at both gas inlets (users guide PerkinElmer 5-8).

Furnace program

Table:-1

Table behind the principle of the sample in the Graphite tube (GT).

Step	Temp (^{0}C)	Action of sample in GT	Ramp Time	Hold Time	Internal Flow	Gas Type
1	110	Loss of H_2O	1	30	250	Normal
2	130	Loss of H_2O	15	30	250	Normal
3	1200	Charing	10	20	250	Normal
4	2000	Atomization of sample	0	5	0	Normal
5	2450	Burn off	1	3	250	Normal

Read Step 4 Injection Temperature (20^0C) :-

Once the sample is loaded in the graphite tube with autosampler tip, initially the GT gets heated to 110˚C where water is lost. Then when it reaches to 130˚C hidden water in the sample is completely lost. Later when it reaches to 1200˚C charing is done where metals transformed to ions and all organic matter turn to ash. At 2000˚C atomization is done where all the metals converted to elemental state. Finally at 2450˚C sample burns off so ready for next sample.

Furnace Autosampler:-

- Locations of the Solutions in the auto sampler.

    81 - Diluent (5% HNO_3).

    82 - Matrix modifier. [0.005 mg Pd +0.003 mg Mg $(NO_3)_2$].

    83 - Distilled water.

    84 - As standard.

- Add 5 µL of diluent and 5 µL of Matrix modifier.

    To calibration blank and standards

    To reagent blank and samples

- Volume of sample taken is 20 µL during the process.

Autosampler and Furnace Sequence:-

In the first step pipette diluent modifier 1 + spike + sample/std.

Run all the steps till the end.

Calibration equation and units:-

Equation: Linear, Calculated intercept.

Maximal places: 3.

Maximum significant figures: 4.

Calibration units: µg/L.

Sample units: µg/L.

Calibration Standard Concentrations:-

Table:-2

Table for determining calibrated standard dilution of Autosampler.

	ID	Concentration in ppb	A/S loc	Stock (µL)	Diluent (µL)
Calibration blank	Distilled H_2O		83	20	5
Reagent blank	0.2 HNO_3		81	20	5
Standard 1	10 ppb	10	84	2	23
Standard 2	25 ppb	25	84	5	10
Standard 3	50 ppb	50	84	10	15
Standard 4	100 ppb	100	84	20	5

Initially when opening this method manually do not use the calibration curves in memory. When using this method in a multimethod sequence start by constructing new calibration curves. Correlation coefficient checking is not enabled in this method. No periodic recalibration or Precision is enabled in this method. Samples over 130% are recalibrated.

Take the prepared samples and load the sample cups in the autosampler and label the cups. Fill the cups 81, 82, 83, 84 with the diluent, prepared modifier, Distilled water and standard respectively. Turn the compressed air and argon gas on. Then turn the AA on and the software the Winlab 32 on. Later on turn the lamp allow sufficient time for the As electrode discharge lamp to warm up and observe the energy of the lamp should be constant. Condition the tube and flush the sampler. Make sure that the mirrors don't obstruct the light passing through the graphite tube.

Then select a validated Method that is required as said above. Create a sample info file and fill table with the labeling as mentioned on the cups. Then open the tabs for autosampler, results display, calibration curve, transient peaks. Make sure everything is on then rebuild the list and then start the calibration.

A calibration curve is plotted taking concentration on x-axis (0-100ppb) and absorbance on y-axis.

The best result for analysis that the standard calibration curve fit to be (R^2 = 0.996983).

Checks to be performed before autosampler analysis:-

Fill and flush the rinsing system. Align the autosampler arm. Adjust the penetration depth of the pipette tip in the graphite tube. Adjust the immersion depth of the pipette tip in the sample Cup. Check the delivery of solution droplet.

NIST Standards:-

- NIST Standard Reference Material 1646a Estuarine sediment [13].

  BY U.S Department Of Commerce National Institue Of Standards And Technology Gaithersburg, MD 20899.

- NIST Standard Reference Material 2781 Domestic Sludge [12].

  BY U.S Department Of Commerce National Institue Of Standards And Technology Gaithersburg, MD 20899.

Results and discussion:-

Results of 05/30/2012 [14]:-

The Table-3 shows the results from the analysis performed on May 30th 2012.

Method Name :- As New 05/30/12 100 ppb.

When graph plotted taking concentration (µg/l 0-100 ppb) on X-axis and Absobance on Y-axis.

The Correlation coefficient observed during analysis of 10, 15, 25, 100 ppb solutions was
 0.996983 µg/L.

Before this an initial calibration,one more calibration was performed on 05/16/12 but the
correlation coefficient obtained was 0.977299 µg/L which is not as appropriate than the other.

Figure:-3

This figure represents the calibration performed on 05/30/12 from 10-100 ppb, showing the

- Slope 0.00228.
- Intercept 0.01010.
- correlation coefficient 0.996983 µg/L.
- Limit of detection also called the lower limit of detection [16].
- Signal detection limit: $Y_{dl} = Y_{blank} + 3s$.

$$=0.0007+3(0.0002) = 0.0013.$$

- Detection limit: Minimal detectable concentration = 3s/m

$$=0.0006/0.0101 = 0.059 \ µg/L.$$

- Lower limit of Quantification is the signal that is 10 times greater than the noise , or the smallest amount that can be measured with reasonable accuracy.

  Lower limit of quantification = 10s/m [16].

$$=0.002/0.0101 = 0.02 \ \mu g/L.$$

Calibration Curve $y = 0.0023x + 0.0101$ $R^2 = 0.994$
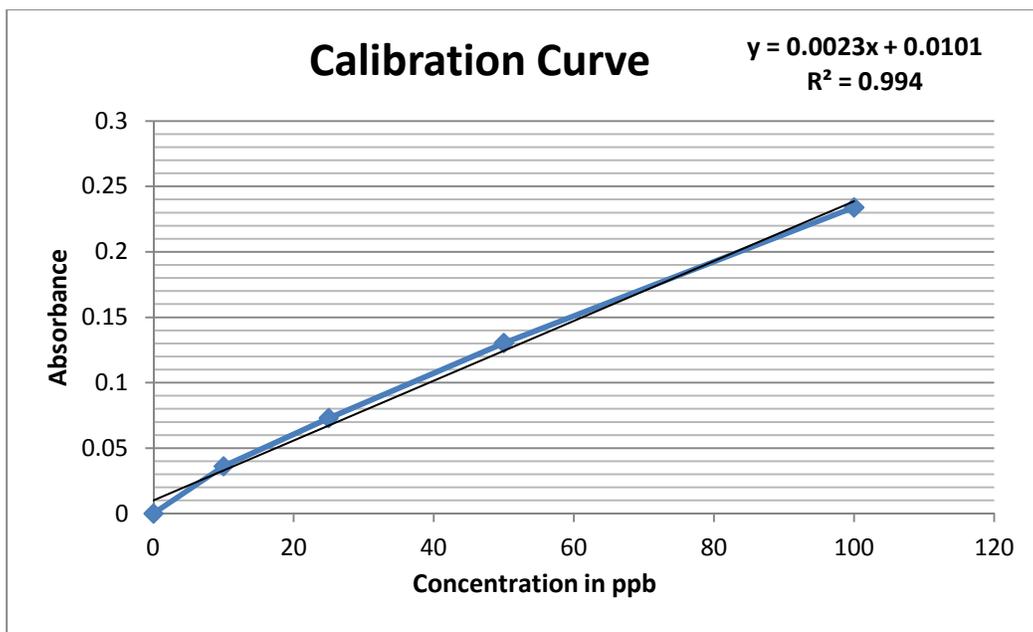
The results obtained in the table 3 below are compared with the standard NIST values.

Table:-3

This table provides the information of the soil samples of Michigan upper peninsula, weight of the air dried and digested material, RSD values of Arsenic and µg As/g sample as listed below.

UP Soil Samples	Sample taken in gm	Gravimetric diluted material	Absorbance RSD As	µg As/ g sample
Estuarine sediment	1.023	29.2392	4.50	2.16
Domestic sludge	1.0013	30.8203	9.72	1.87
Phoenix above 1	1.0372	24.9834	7.65	1.09
Phoenix side 1	1.0275	22.2747	8.89	1.04
C Falls above 1	1.021	40.3447	10.26	0.46
C Falls below 1	1.0422	38.1927	591.6	0.92
Delaware above	1.07	36.2581	230.3	0.75
Delaware on tail	1.0381	43.9924	11.62	0.47
Delaware side	1.019	40.5594	3.10	1.72
Delaware below	1.0262	39.3984	4.92	0.46
Clark 1	1.0436	27.148	127.5	2.05
Delaware 1	1.0778	40.3369	4.42	0.39
Gay sands 3	1.0372	28.9692	4.42	1.24
Cliff above	1.0237	27.004	2.02	1.43
Cliff below	1.0152	29.1858	1.44	1.59
Cliff away	1.0649	29.8054	6.95	3.13
Blank 1		19.8176		
Blank 2		18.3808		

Discussion:-

The results in the table -3 are compared with the NIST values.

- The NIST standard value of the Estuarine sediment was 6.23 mg/kg but the value obtained in the results during the experiment was found to be 2.16 µg As/g sample.

- The NIST standard value of the Domestic sludge was 7.82 mg/kg but the value obtained in the results during the experiment was found to be 1.87 µg As/g sample.

- so we observe only 34.6% of the result is obtained for Estuarine sediment and only 23.9% result is obtained for Domestic sludge (reference-14).

So to confirm these results recovery studies are made further. These recovery studies include spiking of the samples.

Results of 10/23/2012 (reference-15):-

The Table-4 shows the results from the analysis performed on october 23rd 2012.

Method Name :- As 10/23/12 100ppb recover.

When graph plotted taking concentration (µg/l 0-100 ppb) on X-axis and Absobance on Y-axis.

The Correlation coefficient observed during analysis of 10, 15, 25, 100 ppb solutios was

 0.999581 µg/L.

<u>Figure:-4</u>

This figure represents the calibration performed on 10/23/12 from 10-100 ppb, showing the

- Slope 0.00202.

- Intercept 0.00256.

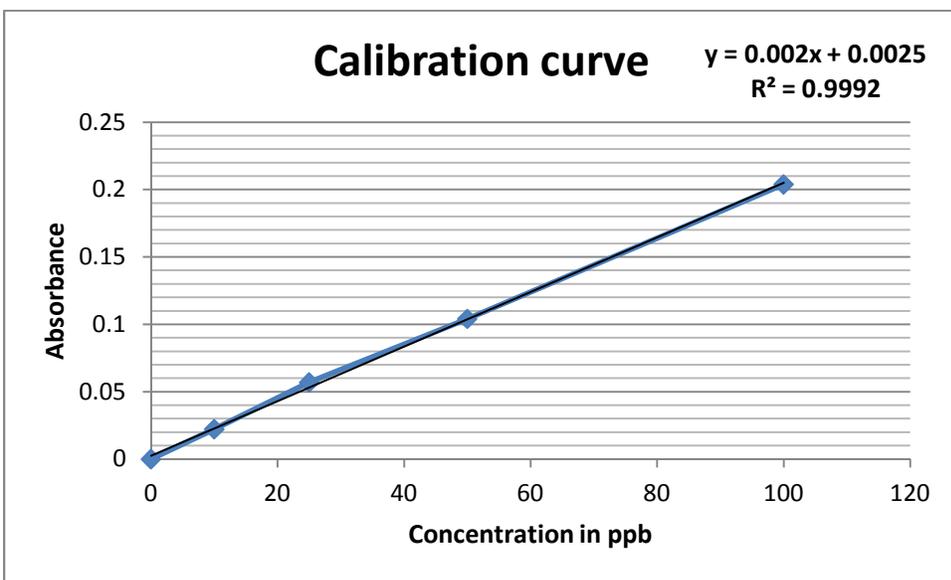- correlation coefficient 0.999581 µg/L.

Table:-4

This table provides the information of spiking and non spiking of Domestic sludge and Estuarine sediment samples weights of digested materials, RSD values of Arsenic and µg As/g, g As/g sample as listed below.

Samples taken	Gravimetric Diluted material	Absorbance RSD AS	µg As/ g sample	Mean µg As/ g sample	Mean SD
D.sludge NS-1	29.5684	3.75	1.42	1.53	0.11
D.sludge NS-2	39.889	1.579	1.53		
D.sludge NS-3	39.3842	3.399	1.64		
D.slud7 µg As/L-1	26.2237	3.288	1.56	1.69	0.141
D.slud7 µg As/L-2	41.69	3.557	1.84		
D.slud7 µg As/L-3	33.5722	1.857	1.67		
D.slu14 µg As/L-1	31.7007	1.407	1.61	1.67	0.095
D.slu14 µg As/L-2	39.8819	5.062	1.62		
D.slu14 µg As/L-3	38.8257	4.563	1.78		
E.sed NS-1	30.0142	7.382	3.91	1.32	5.70
E.sed NS-2	30.4433	42.81	0.041		
E.sed NS-3	32.9185	5.138	0.016		
E.sed 6 µg As/L -1	30.9683	8.772	4.43	3.15	2.72
E.sed 6 µg As/L -2	28.2952	94.96	0.027		
E.sed 6 µg As/L -3	31.7989	3.435	5.013		
E.sed12 µg As/L 1	32.8951	4.515	4.282	3.01	2.59
E.sed12 µg As/L-2	31.639	18.28	0.03		
E.sed12 µgAs/L -3	37.0168	1.428	4.72		

Domestic sludge:-

- Totally nine samples are used for this 3 of them are non spiked samples
- 3 of the samples are spiked with 3.5 µL (7 µg As/L) Arsenic standard.
- Last 3 samples are spiked with 7 µL (14 µg As/L) of Arsenic standard.

Estuarine sediment:-

- Totally nine samples are used for this 3 of them are non spiked samples
- 3 of the samples are spiked with 3 µL (6 µg As/L) Arsenic standard.
- Last 3 samples are spiked with 6 µL (12 µg As/L) of Arsenic standard.

Discussion:-

The results from the (table-4) recovery studies show that the spiked samples have better values when compared to earlier studies. For example the result of D.sludge 7 µg As/L -2 show 1.84 µg As/g sample compared to standard NIST value 7.82 mg/kg (reference-12). For E.sed 6µg As/L-3 show 5.01 µg As/g sample compared to standard NIST value 6.23 mg/kg (reference-13). But these results are not constant in any 3 respective samples. This difference when compared to NIST standards might be due to As lamp failure which is not showing constant energy level. This may also be due to evaporation of Arsenic as Arsine (AsH_3). The Arsenic evaporation to be verified in the future studies. (reference-15).

Conclusion:-

The atomic absorption spectrometer with Graphite furnace and furnace autosampler using Modified EPA methods 7060A and 3050B is success in determining the low (ppb) levels of Arsenic in Samples of upper Peninsula of Michigan. From the results obtained, there is a loss of Arsenic content which might be due to evaporation of Arsenic as Arsine (AsH_3) (reference 6,7). The Arsenic evaporation to be verified in the future studies. The recovery study with a new lamp has to be carried in future.

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16) 5-2 Quality assurance and calibration methods page no-103-105