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Development of Method for Detection of Lead in Samples Collected from Keweenaw Peninsula Mines, Michigan in Collaboration with Environmental Biology Research Students

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DEVELOPMENT OF METHOD FOR DETECTION
OF LEAD IN SAMPLES COLLECTED FROM
KEWEENAW PENINSULA MINES, MICHIGAN IN
COLLABORATION WITH ENVIRONMENTAL
BIOLOGY RESEARCH STUDENTS

GRDUATE PROJECT STUDY

PROJECT GUIDE: Dr. Karen D'Arcy

SUBMITTED BY: Sindhu Reddy Aaireddy



SPRING 2013

Abstract:

Mining is one of the most important industries and a main cause of global pollution due to release of heavy metals into air, water, and soil. Some of these elements are persistent in the environment for years and bioaccumulation in living organisms causing toxic effects. Such elements are known as PBTs (persistent, bioaccumulate and toxic). The nature of toxicity depends on the properties, size of population exposed to it and period of exposure.¹¹ For this reason, we are interested in developing a method to detect heavy metals in soil samples, mine tailings, plant and animal samples collected from surroundings of Keweenaw Peninsula, Michigan in collaboration with the Environmental Biology department program. The collected samples are analyzed for heavy metal contamination and compared to National Institute of Standards and Technology (NIST) standards and samples collected from non-mining areas. Heavy metal concentration is determined using Atomic absorption spectroscopy (AAS). AAS is a spectroanalytical procedure for quantitative determination of metallic elements present in a sample by employing absorption of optical radiation by free atoms in gaseous state. Known concentration of lead standards were prepared to run through AAS Flame to create calibration curve. The calibration curve is used to analyze samples collected from mining areas. Unfortunately, the detection limit using FAAS was not sensitive enough for analysis of water, plant and animal samples. So, we changed the technique to more sensitive Graphite Furnace AAS to improve detection limit. The signal detection limit was found to be 21.285 m^{-1} , minimum detectable concentration is 0.894 ug/L and lower limit of detection was found to be 8.94 ug/L .

Introduction:

Lead is known to be one of the most common elements from the ancient times and is freely available in nature making up about 0.0013% of the earth's crust and can be easily mined and refined. As it is a soft, malleable and corrosion resistant material that is widely used as a covering on wires and cables to absorb vibrations and sounds and in the manufacture of ammunition. It is used in production of lead-acid storage batteries which are found in automobiles. Its high density makes it useful as a shield against X-ray and gamma-ray radiation and is used in X-ray machines and nuclear reactors.⁶ Lead is a very toxic element and has serious disadvantages in addition to its advantages. Lead poisoning occurs when humans are exposed to small amounts of lead and it accumulates in the body, causing ill health. Lead poisoning causes

malfunctioning of vital systems such as nervous system, circulatory system, digestive system, and reproductive system.^{2,7} When lead enters body it gets incorporated with bone marrow, nerve tissue, brain and kidney instead calcium as they both have similar properties¹⁰ and lead also effects the body's ability to regulate vitamin D. Lead cannot be decomposed in body and can accumulate in living organisms. Lead concentration increases as exposure to the element increases and this process of accumulation is called bioaccumulation.⁵ The half life of lead in bone is about 25-30 years and is considered a biomarker of cumulative exposure. However, some lead reenters the blood and organs from bone in certain circumstances such as pregnancy, breast feeding period, during advancing age and bone breakage. Lead is also present in an alkyl-lead form which is metabolized in the liver by oxidative dealkylation in presence of cytochrome P-450 to produce triethyllead and trimethyllead metabolites along with inorganic lead.¹¹ A part from inorganic lead, triethyllead and trimethyllead metabolites also cause toxic effects by accumulating in soft tissues particularly liver, kidneys, muscles and brain. Their accumulation can lead to vital organ disorders.^{2,7} With this study of element Lead, I decided to study about the method to detect trace amounts of lead present in samples collected from mining areas.

The two important methods to detect trace elements are Atomic Absorption Spectroscopy (AAS) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analysis. ICP-MS can analyze multiple elements at the same time whereas, Atomic Absorption Spectroscopy is specific and sensitive to a particular element. Atomic absorption spectroscopy uses the principle of absorption spectrometry to assess the concentration of an analyte in a sample. So, standards of known analyte content are prepared in order to establish a relation between the absorbance and analyte concentration, following the Beer's-Lambert Law.^{1,5} The elements that enter atomizer absorb a certain amount of energy and get excited to higher orbitals for a short span of time. The absorbance of energy at selected wavelength is particular for electron transitions in an element as a result, this technique is element selective. We used two types of atomizer in determining lead detection limits:

- 1) Flame Atomic Absorption Spectroscopy (F-AAS)
- 2) Graphite Furnace Atomic Absorption Spectroscopy (GFAAS)

Flame Atomic Absorption Spectroscopy: In this method, sample is introduced into spray chamber with pneumatic nebulizer where the sample gets desolvated leaving dry nano-particles of sample. These nano-particles are vaporized followed by atomization and ionization.^{3,5,13}

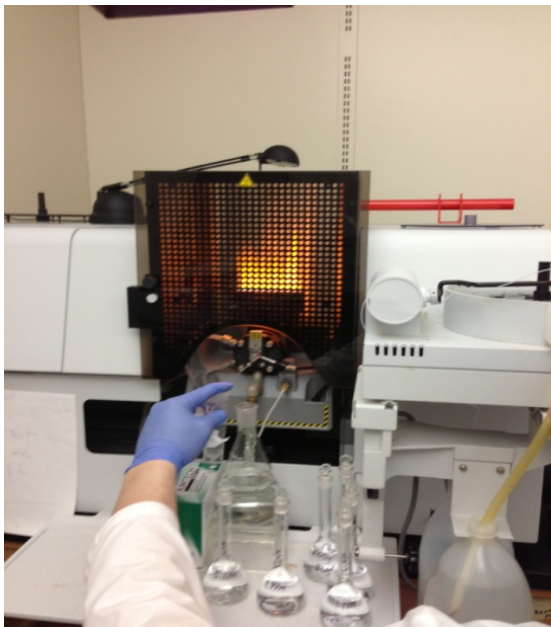


Figure 1:

FLAME AAS

Graphite Furnace Atomic Absorption Spectroscopy: This method uses graphite tube atomizers and samples are directly introduced on to graphite platform to delay atomization until atomizer reaches a stable temperature. Separation of sample components is facilitated by serial increase of temperature between the stages. When the temperature is stable evaporation of sample occurs and the matrix left after evaporation is pyrolysed followed by atomization and further temperature increases to remove carbon such that only ions of interest are present in the tube for analysis. Majority of matrix is removed at pyrolysis temperature so, chemical modifier is use to stabilize analyte at this temperature. The absorbance of energy by these ions is used for quantification.^{3,5,12}



Figure 2:
**GRAPHITE FURNACE
AAS**



Figure 3:
GRAPHITE TUBE

Sample Preparation:

USEPA 3050b method for acid digestion of sludge, sediments and soils is used.

Digestion Procedure: Samples collected are digested using Labconco digester. This digester consists of 250 mL volume long cylindrical test tubes on a holder that perfectly fits on to digestion block such that all these tubes are maintained at same temperature. Digestion tubes are washed thoroughly with 6M nitric acid to get rid of previous experiment stains. The collected sample leaves are air dried for seven days and blended to fine powder. The blended leaf powder is weighed approximately to a gram and taken into three digestion tubes, named as P1 (wt. of leaf material: 1.0004g), P2 (1.0007g) and P3 (1.0279g). Spiking was done to P1 and P2 and 10ml

concentrated nitric acid is added to all three tubes and also to standard tube. The digestion block is maintained at 110⁰C and after 10 minutes brown vapors appeared but, the volume in tube was more than 5ml so heating was continued for another 8 minutes and finally volume reached approximately 5ml. These tubes were taken off from the digestion block and set aside for cooling. After cooling, 2ml of concentrated nitric acid is added and heated for 10 minutes. When brown vapors were observed volume is checked for 5ml, if it was approximately 5ml, 2ml of hydrogen peroxide is added and same procedure was repeated for every 10 minutes by adding nitric acid and hydrogen peroxide alternatively until clear solution is obtained. The obtained clear solution is transferred to 50ml centrifuge tubes and weighed. The weighed tubes with sample are centrifuged for 10 minutes at 200 rpm. After centrifugation the sample solution is diluted with distilled water to 50ml and is used for analysis on Flame AAS and GF-AAS.⁴

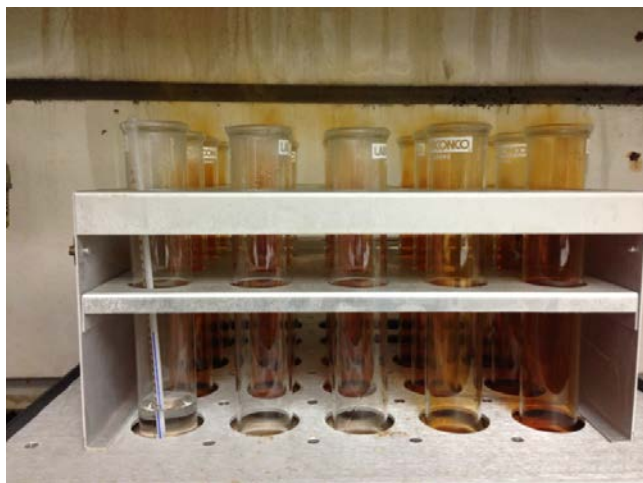


Figure: 4
LABCONCO
DIGESTER



Figure 5: Samples from mining areas after digestion



Figure 7: Practice Samples after digestion

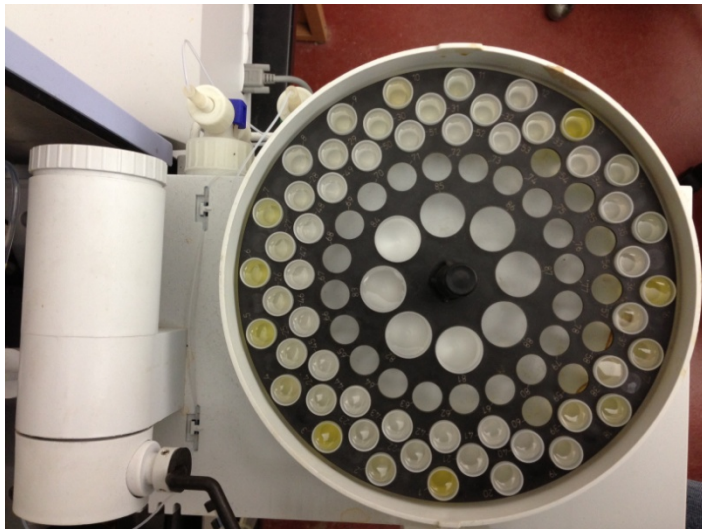


Figure 8: Autosampler in Graphite

Furnace AAS



Figure 8: Centrifuge



Figure 9: Centrifuge filled with tubes for run

Analyte Standard Preparations: Lead standards were prepared using dilution formula ($M_1V_1=M_2V_2$) from 1000ppm commercial Lead standard and 1% Nitric acid is used as diluent for flame atomic absorption spectroscopy. Whereas, for furnace lead standards were prepared using 10ppm Lead standard (Primary Drinking water, a product by SPEX CertiPrep.) using 0.2% nitric acid as diluents and chemical modifier is prepared by mixing 0.050mg Ammonium Phosphate and 0.003mg Magnesium Nitrate together.

Recommended Conditions for AA Flame:

Wave length (nm): 283.3nm

Slit width (nm): 0.7nm

Characteristic Concentration (mg/L): 0.45mg/L

Lamp Energy: 65⁰C - 75⁰C

Acetylene Flow (L/min): 2

Experimental Conditions for Flame AAS:

Wave length (nm): 283.3nm

Lamp energy: 1st run – 67⁰C

2nd run – 70⁰C

3rd run – 75⁰C

Recommended Conditions for AA Furnace:

Wave length (nm): 283.3nm

Low Slit (nm): 0.7nm

Temperature (⁰C): Pyrolysis – 800; Atomization – 1600

Lamp Energy: 65⁰C - 75⁰C

Characteristic Concentration (mg/L): 30pg/0.0044 A-s

Experimental Conditions for Graphite Furnace AAS:

Wave length (nm): 238.3nm

Lamp energy: 1st run – 70⁰C

2nd run – 73⁰C

3rd run – 75⁰C

Atomization energy: 1900

Method & Materials:

Instrument:

- Perkin Elmer AA Spectrometer- Analyst 800
- Labconco digester
- CRU-5000 Centrifuge

Materials:

- Volumetric Flasks
- Disposable cups
- Disposable beakers
- Disposable pipettes
- 50ml, 100ml & 1000ml plastic bottle containers
- Autosampler cups
- 10ml, & 100ml long necked volumetric flasks
- Glass pipettes
- Measuring cylinders
- 50ml centrifuge tubes with caps

Methods:

- 1) Flame AAS
- 2) Graphite Furnace AAS

Chemicals:

- Lead Reference Standard solution (1000ppm Pd), manufactured by Fisher Scientific, LOT# 070960
- 5% Nitric Acid manufactured by Sigma-Aldrich, LOT# BCBJ0559V
- Distilled water
- 10% Ammonium Phosphate Matrix modifier manufactured by Perkin Elmer Life and Analytical Sciences, LOT# 4-396BD

- Magnesium Nitrate Matrix modifier (2.0% Mg – Mg(NO₃)₂ in 5% Nitric Acid), manufactured by Ricca Chemicals Company, LOT# 4205048
- Lead (10mg/L) for furnace: Primary drinking water metals (10ppm of lead), manufactured by SPEX CertiPrep, LOT# 43-140AS
- NIST domestic sludge: Manufactured by U.S. Department of commerce National Institute of Standards and Technology, LOT# 2781.
- NIST estuary sediment: Manufactured by U.S. Department of commerce National Institute of Standards and Technology, LOT# 1646a.

Samples:

- Yellow Maple Leaves collected on campus,
- Cedar leaves collected from mining areas,
- Maple leaves collected from mining areas,
- Different soil samples collected from mining areas,
- Water samples collected from different taps on campus,
- Water samples collected from GSU pond

Results:

TABLE 1: 1st Run of Lead Standards on Flame AAS

Conc(mg/L)	1 st Replicate	2 nd Replicate	3 rd Replicate	Mean Absorbance	SD	%RSD
1	0.001	0.002	0.002	0.002	0.0004	22.1
5	0.009	0.009	0.009	0.009	0.0001	0.6
10	0.018	0.018	0.018	0.018	0.0002	1.0
15	0.027	0.027	0.027	0.027	0.0001	0.3
20	0.035	0.035	0.035	0.035	0.0001	0.2

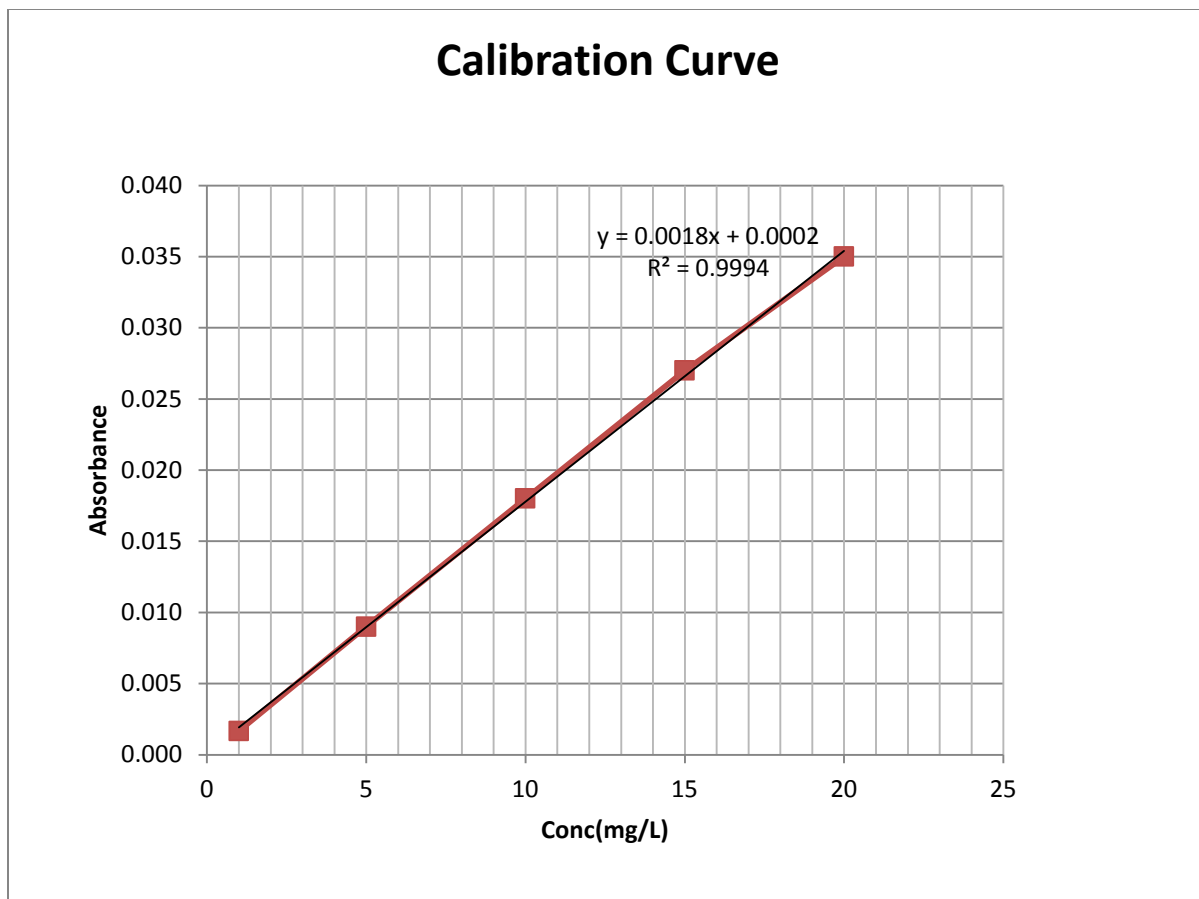


Figure 10: This run was carried out with lamp energy 67°C and the slope is 0.0018 and correlation coefficient is 0.9994.

TABLE 2: 2nd Run Of Lead Standards on Flame AAS

Conc(mg/L)	1 st Replicate	2 nd Replicate	3 rd Replicate	Mean Absorbance	SD	%RSD
0.5	0.002	0.002	0.002	0.002	0.0002	4.3
1	0.003	0.004	0.004	0.004	0.0001	3.7
5	0.015	0.015	0.015	0.015	0.0001	0.3
10	0.028	0.028	0.028	0.028	0.0002	0.6
15	0.041	0.041	0.041	0.041	0.0000	0.0

20	0.053	0.054	0.054	0.054	0.0006	1.0
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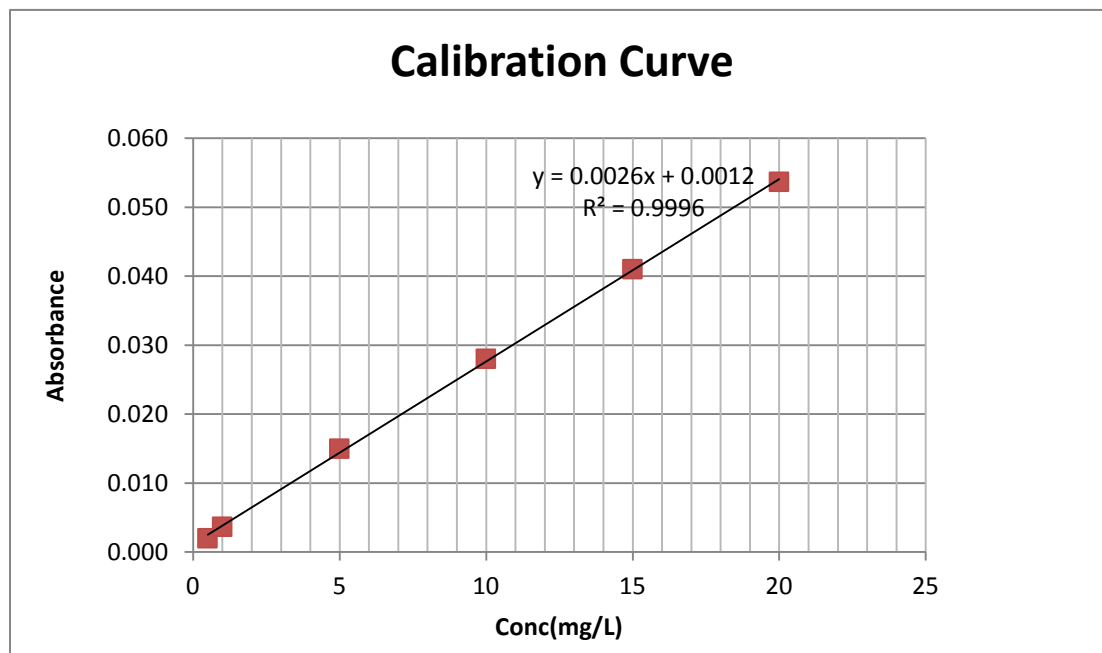


Figure 11: This run was carried out with lamp energy 70⁰ and the slope is 0.0025 and correlation coefficient is 0.9996.

TABLE 3: 3rd Run Of Lead Standards on Flame AAS

Conc(mg/L)	1 st Replicate	2 nd Replicate	3 rd Replicate	Mean Absorbance	SD	%RSD
0.5	0.003	0.003	0.003	0.003	0.0001	2.4
1	0.005	0.005	0.005	0.005	0.0001	2.1
5	0.016	0.016	0.016	0.016	0.0001	0.8
10	0.029	0.029	0.029	0.029	0.0000	0.1
15	0.043	0.043	0.043	0.043	0.0001	0.2

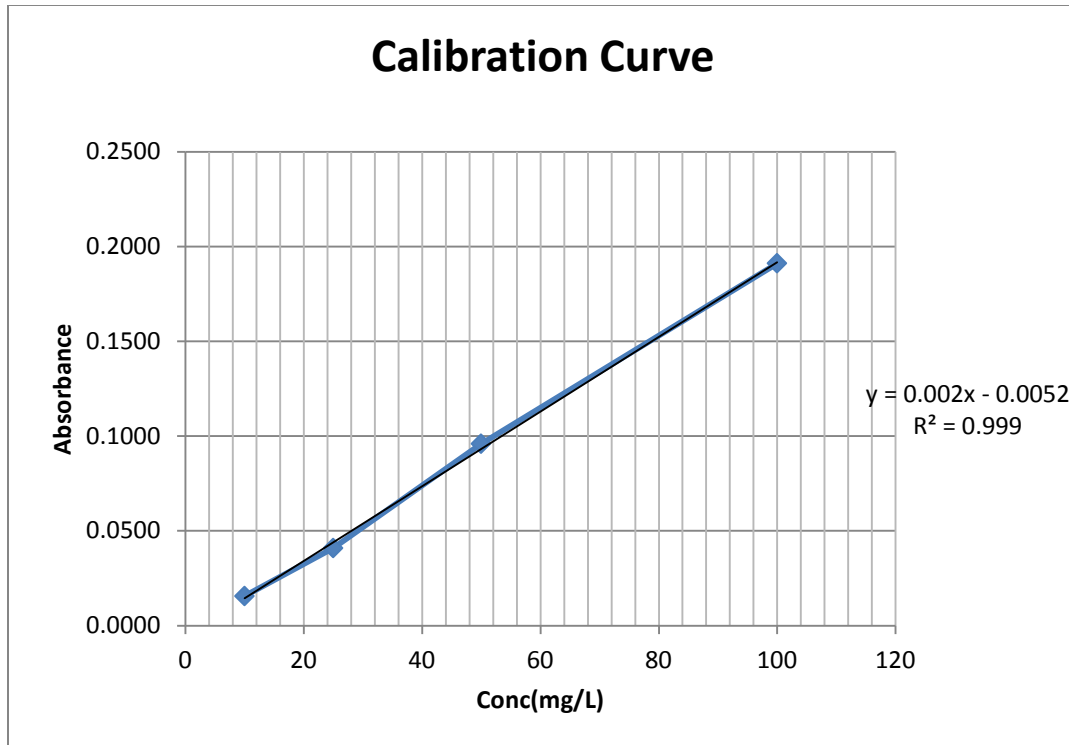


Figure 12: This run was carried out with lamp energy 75⁰ and the slope is 0.002 and correlation coefficient is 0.999.

TABLE 4: Comparison between Slopes and Coefficient relation values between three runs

Run	Date & Time	Slope	Coefficient Relation
1	10/9/2012 & 4:14pm	0.00174	0.89
2	2/20/2013 & 3:21pm	0.00272	0.99
3	2/22/2013 & 12:16pm	0.00427	0.98

TABLE 5: Run Of Preliminary Samples Collected From Mining Areas On Flame AAS

UP Soil Samples	Digested material, g	Digest sample size, g	mean Pb, mg/L	SD Pb	RSD Pb	mgPb/g sample	g Pb/g sample	% Pb
Estuary sediment	29.2392	1.023	5.969	0.113	1.894	0.170604873	0.000170605	0.01706
Domestic sludge	30.8203	1.0013	4.941	0.018	0.368	0.152085391	0.000152085	0.015209
Pheo above 1	24.9834	1.0372	-1.023	0.142	13.85	-0.02464136	-2.46414E-05	-0.00246
Pheo top 1	24.8716	1.004	-0.54	0.161	29.81	-0.013377155	-1.33772E-05	-0.00134
Pheo side 1	22.2747	1.0275	-1.16	0.096	8.265	-0.025147107	-2.51471E-05	-0.00251
Pheo below 1	29.5452	1.0542	-0.749	0.071	9.475	-0.02099161	-2.09916E-05	-0.0021
C Falls above 1	40.3447	1.021	-1.46	0.069	4.697	-0.057691736	-5.76917E-05	-0.00577
C Falls top 1	43.5189	1.0756	-1.577	0.058	3.647	-0.063805602	-6.38056E-05	-0.00638
C Falls middle1	44.2989	1.053	-1.357	0.121	8.921	-0.057087946	-5.70879E-05	-0.00571
C Falls below 1	38.1927	1.0422	-1.474	0.052	3.555	-0.054016542	-5.40165E-05	-0.0054
Delaware above	36.2581	1.07	-1.098	0.072	7.011	-0.03720691	-3.72069E-05	-0.00372
Delaware on tail	43.9924	1.0381	-0.692	0.194	28	-0.029325441	-2.93254E-05	-0.00293
Delaware side	40.5594	1.019	-1.484	0.132	8.927	-0.05906786	-5.90679E-05	-0.00591

Delaware below	39.3984	1.0262	-1.13	0.116	10.28	-0.043383543	-4.33835E-05	-0.00434
Clark 1	27.148	1.0436	-0.018	0.053	298.2	-0.000468248	-4.68248E-07	-4.7E-05
Delaware 1	40.3369	1.0778	-1.047	0.092	8.745	-0.039184203	-3.91842E-05	-0.00392
Cliff 1	25.6482	1.0085	-0.381	0.071	18.76	-0.009689603	-9.6896E-06	-0.00097
Pheo E shaft 1	31.0691	1.0402	-1.072	0.115	10.72	-0.032018915	-3.20189E-05	-0.0032
Gay sands 3	28.9692	1.0372	-1.383	0.087	6.31	-0.038627462	-3.86275E-05	-0.00386
Cliff above	27.004	1.0237	10.95	0.105	0.96	0.2888481	0.000288848	0.028885
Cliff on	29.4239	1.0069	-1.299	0.028	2.183	-0.037959724	-3.79597E-05	-0.0038
Cliff below	29.1858	1.0152	-0.032	0.055	172	-0.000919962	-9.19962E-07	-9.2E-05
Cliff away	29.8054	1.0649	0.283	0.249	88.05	0.007920864	7.92086E-06	0.000792

TABLE 6: Preliminary Flame AAS of Plants and Animals practice samples

Sample ID	Sample Prep., g	Initial Sample wt.(g)	Mean Conc mg/L Pb	SD Pb	RSD Pb	mg/Pb g sample	µg Pb/g sample	g Pb/g sample
SA	27.3854	0.9597	2.254	0.061	2.699	0.064319	64.31874	6.43187E-05

SB	26.714	0.9505	2.218	0.062	2.854	0.062337	62.33735	6.23374E-05
M1	25.818	1.0123	2.734	0.047	1.728	0.069729	69.72875	6.97287E-05
M2	25.8264	1.0327	2.547	0.033	1.302	0.063697	63.69695	6.3697E-05
M3	25.9904	0.9957	2.296	0.063	2.766	0.059932	59.93166	5.99317E-05
M4	26.4818	1.018	2.439	0.03	1.223	0.063447	63.44706	6.34471E-05
M6	26.0807	1.0401	2.863	0.036	1.263	0.07179	71.79025	7.17903E-05
M7	27.2439	1.061	2.528	0.072	2.864	0.064913	64.91289	6.49129E-05
C1	27.1987	0.9607	3.18	0.022	0.687	0.09003	90.03005	9.003E-05
C2	26.2291	1.0482	2.984	0.096	3.225	0.074669	74.66861	7.46686E-05
C3	26.1795	0.9404	3.023	0.061	2.012	0.084156	84.15635	8.41563E-05
C4	26.158	0.9004	2.807	0.058	2.074	0.081548	81.54765	8.15477E-05
C5	26.1557	0.9746	2.93	0.044	1.519	0.078633	78.63349	7.86335E-05
MA	26.9602	0.999	3.822	0.124	3.241	0.103145	103.145	0.000103145
MB	27.2131	1.0028	3.451	0.038	1.098	0.09365	93.65019	9.36502E-05
MC	26.4662	1.0328	3.296	0.052	1.59	0.084462	84.46223	8.44622E-05
MD	26.968	0.9772	3.447	0.016	0.454	0.095128	95.12761	9.51276E-05
P1	26.9437	1.0004	3.962	0.009	0.232	0.106708	106.7083	0.000106708
P2	28.0167	1.0007	3.767	0.054	1.438	0.105465	105.4651	0.000105465
P3	26.6098	1.0279	3.338	0.053	1.589	0.086413	86.4126	8.64126E-05
S1	27.6295	1.0694	4.362	0.045	1.021	0.112699	112.6986	0.000112699

TABLE 7: 1st Run Of Lead Standards on Graphite Furnace AAS

Conc(mg/L)	1 st Replicate	2 nd Replicate	3 rd Replicate	Mean Absorbance	SD	%RSD
10	0.0398	0.0386	0.0355	0.0380	0.0022	5.8
25	0.0643	0.0666	0.0644	0.0651	0.0013	2.0
50	0.1223	0.119	0.1217	0.1210	0.0017	1.4

100	0.2158	0.2105	0.214	0.2134	0.0027	1.2
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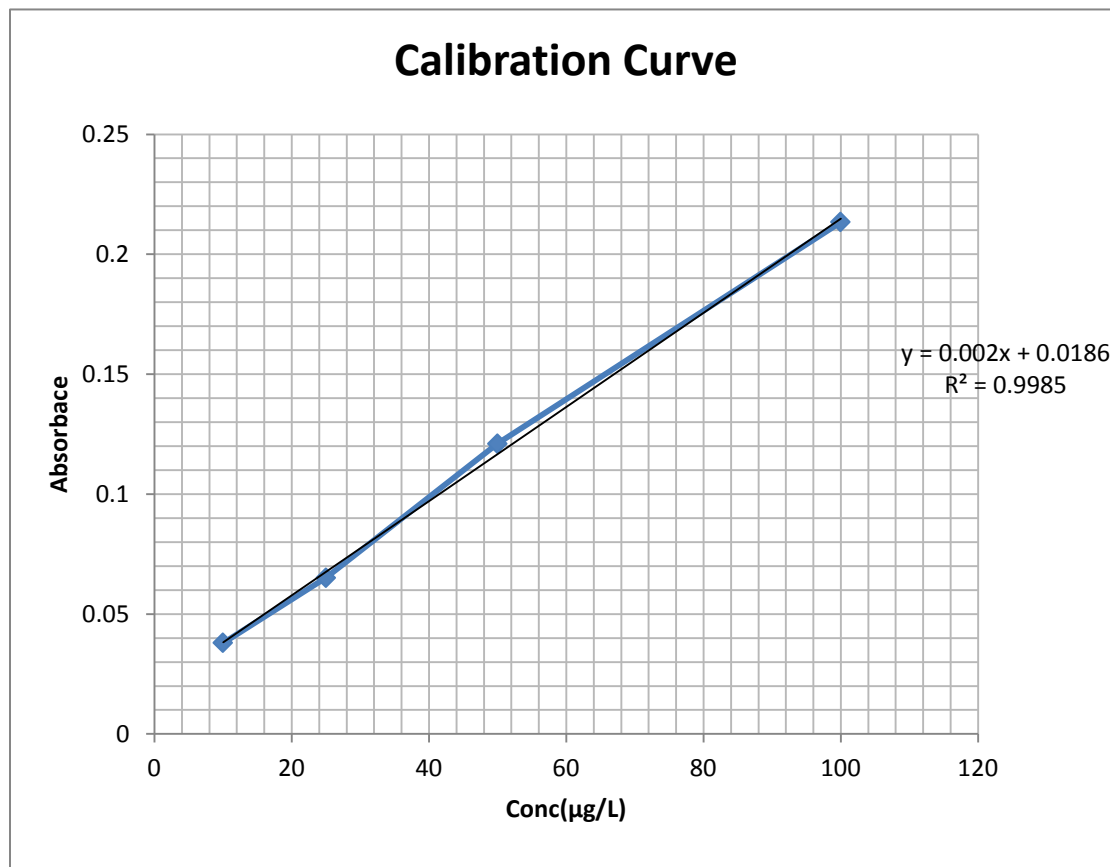


Figure 13: This run was carried out at lamp energy 70⁰ and the slope is 0.002 and correlation coefficient is 0.9985.

TABLE 8: 2nd Run Of Lead Standards on Graphite Furnace AAS

Conc(mg/L)	1 st Replicate	2 nd Replicate	3 rd Replicate	Mean Absorbance	SD	%RSD
10	0.0197	0.0215	0.0178	0.0197	0.0018	9.2

25	0.0386	0.0378	0.0469	0.0411	0.0050	12.3
50	0.0993	0.0985	0.0910	0.0963	0.0046	4.8
100	0.2025	0.1913	0.2007	0.1982	0.0060	3.0

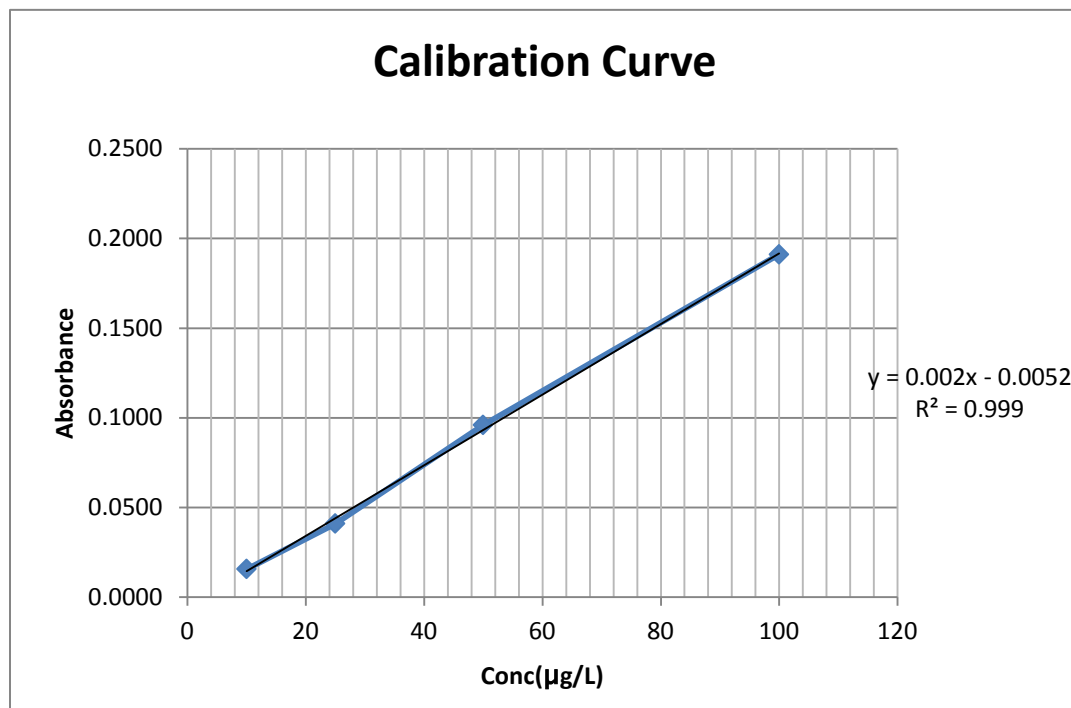


Figure 14: This run was carried out at lamp energy 73⁰ and the slope is 0.002 and correlation coefficient is 0.999.

TABLE 9: 3rd Run Of Lead standards on Graphite Furnace AAS

Conc(mg/L)	1 st Replicate	2 nd Replicate	3 rd Replicate	Mean Absorbance	SD	%RSD
10	0.0165	0.0147	0.0156	0.0156	0.0009	5.7

25	0.0422	0.0370	0.0436	0.0409	0.0035	8.5
50	0.0952	0.0956	0.0971	0.0960	0.0010	1.0
100	0.1934	0.1929	0.1870	0.1911	0.0035	1.9

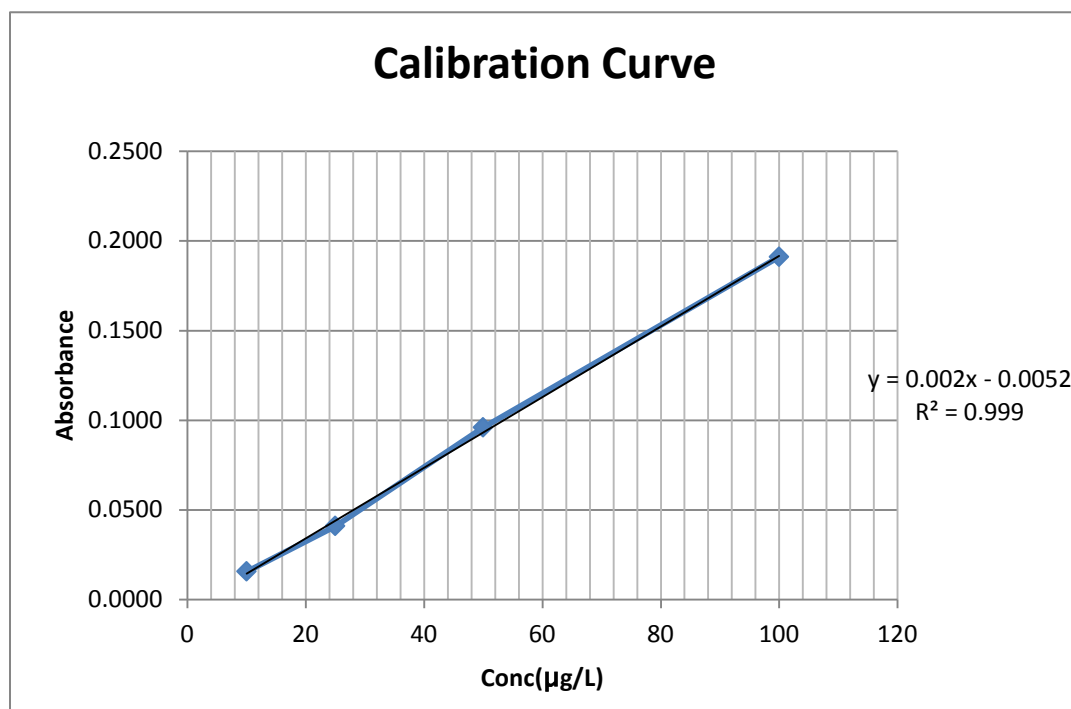


Figure 15: This run was carried out at lamp energy 75⁰ and the slope is 0.002 and correlation coefficient is 0.999.

TABLE 10: Comparison between Slopes and Coefficient relation for three furnace runs

Run	Date & Time	Slope	Coefficient Relation
1	3/26/2013 & 4:30pm	0.00207	0.99
2	5/06/2013 & 4:37pm	0.00199	0.99
3	5/07/2013 & 3:09pm	0.00194	0.99

TABLE 11: Run Of Samples Collected From Mining Areas on Graphite Furnace AAS and only few samples were qualified

UP Soil Samples	Digested material	Digest sample size	mean Pb	SD Pb	RSD Pb	mgPb/g sample	g Pb/g sample	% Pb
Estuary sediment	29.2392	1.023						
Domestic sludge	30.8203	1.0013						
Pheo above 1	24.9834	1.0372	87.95	3.203	3.641	2.118482	0.002118	0.211848
Pheo top 1	24.8716	1.004						
Pheo side 1	22.2747	1.0275	107.6	2.314	2.15	2.332611	0.002333	0.233261
Pheo below 1	29.5452	1.0542						
C Falls above 1	40.3447	1.021						
C Falls top 1	43.5189	1.0756	56.06	2.564	4.573	2.268194	0.002268	0.226819
C Falls middle1	44.2989	1.053	114.8	1.356	1.181	4.829548	0.00483	0.482955
C Falls below 1	38.1927	1.0422	67.35	1.22	1.812	2.468124	0.002468	0.246812
Delaware above	36.2581	1.07						
Delaware	43.9924	1.0381	46.93	24.47	52.15	1.98879	0.001989	0.198879

on tail								
Delaware side	40.5594	1.019						
Delaware below	39.3984	1.0262						
Clark 1	27.148	1.0436						
Delaware 1	40.3369	1.0778						
Cliff 1	25.6482	1.0085						
Pheo E shaft 1	31.0691	1.0402						
Gay sands 3	28.9692	1.0372						
Cliff above	27.004	1.0237						
Cliff on	29.4239	1.0069						
Cliff below	29.1858	1.0152						
Cliff away	29.8054	1.0649						

Table 12: Run of Samples collected from mining areas on Graphite Furnace AAS

Sample ID	Sample Prep., g	Initial Sample wt.(g)	Mean Conc µg/L Pb	SD Pb	RSD Pb	mg/Pb g sample	µg Pb/g sample	g Pb/g sample
R1 Copper Harbor, C5	27.5355	1.0048	5.985	1.057	17.65	0.164013	0.000164	1.64013E-10
R1 Copper Harbor, C8	27.0387	1.0042	9.326	0.54	5.786	0.251108	0.000251	2.51108E-10
R1 Copper Harbor, C10	26.3393	1.0049	4.264	0.129	3.032	0.111763	0.000112	1.11763E-10

R1 Copper Harbor, C12	26.1897	1.0089	7.788	0.397	5.103	0.202166	0.000202	2.02166E-10
R1 Copper Harbor, C13	26.9653	1.003	5.228	0.168	3.206	0.140553	0.000141	1.40553E-10
R1 Copper Harbor, C14	26.4399	1.0035	5.955	5.161	37.13	0.366233	0.000366	3.66233E-10
R1 Copper Harbor, C15	25.8906	1.0055	13.9	4.632	33.27	0.358426	0.000358	3.58426E-10
R2 Medora, C1	26.0531	1.0077	13.92	1.933	11.63	0.429694	0.00043	4.29694E-10
R2 Medora, C9	26.4231	1.0033	16.62	22.64	50.79	1.173804	0.001174	1.1738E-09
R2 Medora, C10	25.8729	1.0046	44.57	1.242	8.173	0.39121	0.000391	3.9121E-10
R2 Medora, C11	26.7841	1.0029	15.19	0.423	2.905	0.388849	0.000389	3.88849E-10
Kearsarge, C1	26.7433	1.0036	14.56	0.423	2.905	0.387986	0.000388	3.87986E-10
Kearsarge, C3	26.204	1.0052	26.45	3.044	11.51	0.68951	0.00069	6.8951E-10
Kearsarge, C4	26.35	1.0078	14.87	2.39	16.07	0.388792	0.000389	3.88792E-10
Kearsarge, C5	27.0867	1.0064	18.56	3.461	18.65	0.499532	0.0005	4.99532E-10
Kearsarge, C7	26.5156	1.001	16.04	1.814	11.31	0.424885	0.000425	4.24885E-10
Kearsarge, C9	26.2936	1.0007	25.05	12.61	50.35	0.658194	0.000658	6.58194E-10
Allouez, C2	26.5068	1.0071	11.24	1.54	13.7	0.295836	0.000296	2.95836E-10
Allouez, C5	26.7497	1.0073	15.66	2.502	15.98	0.415864	0.000416	4.15864E-10
STD pine needles	26.7768	1.0033	15.11	3.043	20.14	0.403267	0.000403	4.03267E-10
Blank	27.7714		13.61	0.661	4.855			

*C : capture of samples at different

Table 13: Data of replicates to calculate detection limit

Replicate No	y blank (nA)	SD of 10ppb replicates
1	23	0.0014
2	23	0.0024
3	21	0.0015
4	22	0.0047
5	21	0.0007
6	19	0.0011
7	20	0.0007
Total	149	0.0125
Average	21.2857	0.0017857

Signal detection limit:

$$y_{dl} = y_{blank} + 3s$$

$$\Rightarrow 21.28 + 3(0.00178)$$

$$\Rightarrow 21.285$$

$$\text{Minimum detectable concentration} = 3s/m = 0.00178/0.00199 = 0.894$$

$$\text{Lower limit of detection (y}_{LL}) = 10s/m = 0.178/0.00199 = 8.94$$

Discussion:

The calibration curves obtained from the flame runs of lead standards was satisfactory and from table 4 we can get know that there is an increase in slope values from 1st run to 3rd run. The slope of 1st, 2nd and 3rd were 0.00174, 0.00272 and 0.00427 respectively and coefficient relation of 1st, 2nd and 3rd are 0.89, 0.99 and 0.99 respectively. The coefficient relation for 1st run was lower than other two and this may be due to experimental errors in preparation of standard solutions or instrumental errors because 2nd and 3rd run coefficients were good. The calibration were satisfactory to do preliminary study of samples collected from mining areas but, the detection limit was observed to be too low, from table 5 we can observe that all the samples have negative percentage of lead (that is concentration was not detectable) except the standard samples Estuary sediment and Domestic sludge with lead percent of 0.01706% and 0.0152% respectively. Table 6 belong to the run of practice samples on flame AAS and S1 sample has the highest lead

concentration of 0.1127mg. The results were not satisfactory and reason might be samples were not lead contaminated or risk of interference may be high with the use of same nebulizer for all the samples though it is wiped and dipped in distilled water. So, method was changed to graphite furnace AAS as it is more sensitive and selective to elements than flame. The calibration curves for the runs of lead standards on graphite furnace were satisfactory and from table 10 comparing the slopes and correlation coefficients of the three runs, we can observe that the slope has been decreased from 1st run to 3rd run (slope of 1st run is 0.00207, 2nd run is 0.00199 and 3rd run is 0.00194) and coefficient relations are same for all three runs, it is 0.99. As calibration curves were good preliminary study of practice samples was performed (table 11) but, most of the samples were not detected and it may be due to low concentration of lead in those samples. So, another run of samples were conducted but due an error occurred with IEEE card and communication between the system and furnace lost and results were observed for very few samples. After resolving instrumental problem, the tip was manually aligned into the furnace by changing the tip of the tube as the drops of samples from autosampler are been dropped on to the walls such that reproducible results were not obtained. After alignment of tip, run of seven replicates of 10ppb and seven replicates of distilled water was performed to determine detection limit and it was successfully calculated. The signal detection limit was found to be 21.285, minimum detectable concentration is 0.894 and lower limit of detection is 8.94. Finally, a run of samples from mining areas was performed (table 12) all the samples were detectable and the sample R2 Medora C9 contained the highest concentration of lead about 0.001174ug among all 20 samples and R1 Copper Harbor C10 contained the least concentration of lead about 0.000112ug.

Conclusion:

The experiment was challenging and found that traces of lead can be detected by GF-AAS as it more sensitive and selective towards trace elements. During the experiment, we faced problems with instrument as there were errors with IEEE card and communication problems between system and furnace. When autosample is used to run more number of samples, the intensity of lamp is increased and IEEE card error is observed. We also faced problems with auto alignment of tip into the graphite tube, so, manual alignment of the tip is made such that drop is delivered on to the bottom of the tube instead on to the walls.

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