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Quality Assurance Plan Project for Copper Determination Using Flame Atomic Absorption Spectroscopy

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Quality Assurance Plan Project for Copper Determination using Flame Atomic Absorption Spectroscopy

Research project

By

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Submitted in partial fulfillment of requirements for
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Abstract:

This study developed a method for determination of Copper by flame atomic absorption spectrometry (FAAS) from the soil samples and mine tailings using Perkin Elmer Analyst 800 atomic absorption spectrometer. A detailed procedure has been developed with a detection limit of 0.12 mg/L. In the recent decades, pollution from heavy metals has been increased. Copper is one of the trace metals that has a significant impact and carries risk to the human health. Calibration curve was established with working range 0.1 ppm to 5 ppm with a correlation coefficient of 0.9994. Over 50 environmental samples from the historic Copper mining district of the Upper Peninsula of Michigan and the Thorn Creek watershed in Illinois were analyzed for the amount of Copper concentration. Environmental Copper levels ranged from 41mg/Kg to 2844 mg/Kg in the Michigan samples and 6 mg/Kg to 72 mg/Kg in the Thorn creek samples.

Introduction:

Determination of trace elements in the environment is more demanding, because of the presence of a large number of metals in mine samples that may interfere in the analysis has to be monitored [6]. Copper is one of the trace metals that has a great impact on regional ecology and carries risk to the human health [1, 2]. Various techniques have been developed for the determination of trace metals over a large range of concentration in environmental samples [4]. Flame atomic absorption spectroscopy (FAAS) is one of the best techniques in the determination of trace metals because of its high selectivity, speed and low operational cost [6].

The analysis of Copper (Cu) in environmental samples can be achieved by Flame atomic absorption spectroscopy. The soil and plant samples must be digested and transformed into aqueous samples allowing determination of the trace metals of interest. The digestion of the environmental sample types was performed following a detailed procedure provided by (USEPA) United States Environmental Protection Agency [7-10]. According to USEPA, soil samples can be digested using acid digestion procedure 3050B [7]. The method 3050B allowed understanding the concentrations of the Cu in the environment and their comparison to the standard permissible levels. These measurements are required for EPA, to follow necessary control measures if the Cu levels are more than the threshold permissible levels.

The intention of this work is to provide detailed instructions and required settings for the analysis of Cu by using Perkin Elmer AAnalyst 800. This

will help the researchers who were interested in detection of trace elements especially in case of the Cu in the soils, plants and animal samples. This method will help in analyzing the element Cu with required conditions and specifications.

Experimental:

Instruments and Reagents:

- AAAnalyst 800 Atomic absorption spectrometer (Perkin Elmer).
- Multi-element Ag-Cr-Cu-Fe-Ni Lumina Hollow Cathode Lamp (Perkin Elmer)
- Centrifuge (CRU 5000- Centrifuge).
- Hot air oven (Thelco).
- Disposable graduated pipettes (non-sterile) (VWR International).
- Disposable graduated Centrifuge tubes (sterile) (VWR International).
- Glass beakers and Pipettes.
- 1:1 Nitric acid (Made with equal amounts of Nitric acid and water).
- 70% Concentrated HNO₃ (Nitric acid-Fisher Certified ACS plus).
- 30% H₂O₂ (Hydrogen peroxide-Fisher Scientific).
- 5% HNO₃ (Spex Certi Prep).
- Copper in 2% HNO₃ (1000 mg/L, Lot#:17-124CU, Perkin Elmer).
- Acetylene AA grade (Fuel).
- Compressed gas zero grade (Oxidant gas).
- Water ACS Reagent grade (RICCA Chemical Company).

Procedure for the acid digestion of soil samples using modified USEPA 3050B: [7]

- ✓ One gram of each of the soil samples were weighed and were air and oven dried to remove the moisture content.
- ✓ The weighed samples were transferred to a beaker and were digested according to a modified version of USEPA method 3050.
- ✓ The soil samples were heated and refluxed for 15 min with an addition of 10 mL of 1:1 HNO₃.
- ✓ Then the samples were cooled, and 5mL of concentrated Nitric acid was added, heated and refluxed for 30 minutes and cooled.
- ✓ Acid addition procedure was repeated until no brown fumes were generated.
- ✓ The samples were cooled, and 2mL of water and 3mL of 30% H₂O₂ were added to the samples and heated until the effervescence gets subsided.
- ✓ Samples were cooled and 1mL aliquots of 30% H₂O₂ were added until the effervescence was minimal.
- ✓ Then samples were cooled and quantitatively transferred to pre-weighed centrifuge tubes with a minimum amount of distilled water and then diluted to 30mL and reweighed.
- ✓ The diluted samples were then centrifuged for 10 minutes at 2500 rpm.

The centrifuged samples were then analyzed using AAnalyst 800 atomic absorption spectrometer.

Calibration:

The calibration standards were first prepared by making serial dilutions of the Perkin Elmer Cu standard 1000mg/L using 1% HNO₃. Initial working range tested, followed the Perkin Elmer recommended conditions.

Preparation of Diluent (1% HNO₃):

100 mL of 5% HNO₃ was diluted to 500mL with Water ACS reagent grade in a measuring cylinder.

Preparation of Calibration Standards:

A 10 mg/L was prepared as an intermediate stock solution diluting 1mL of 1000 mg/L of Cu Standard to 100mL in a volumetric flask using 1% HNO₃ as diluent.

Serial dilutions of 5 mg/L, 2 mg/L, 1 mg/L, 0.5 mg/L and 0.1 mg/L were prepared from the intermediate stock solution(10 mg/L). (See Table-1 below)

Table-1: Preparation of Calibration standards from commercial stock solution 1000mg/L Cu

(Intermediate Stock Solution) 10 mg/L	1 mL of 1000 mg/L diluted to 100mL
5 mg/L	25 mL of 10 mg/L diluted to 50 mL
2 mg/L	10 mL of 10 mg/L diluted to 50 mL
1 mg/L	5 mL of 10 mg/L diluted to 50 mL

0.5 mg/L	2.5 mL of 10 mg/L diluted to 50 mL
0.1 mg/L	0.5 mL of 10 mg/L diluted to 50 mL

The Calibration standards and the digested samples were stored at room temperature until for further analysis using FAAS.

NIST Standards:

Domestic Sludge (2781) and **Estuarine Sediment (1646a)** with standard concentrations of **Cu** as 627.4 mg/Kg and 10.01 mg/Kg respectively were used as control for the soil samples[11,12].

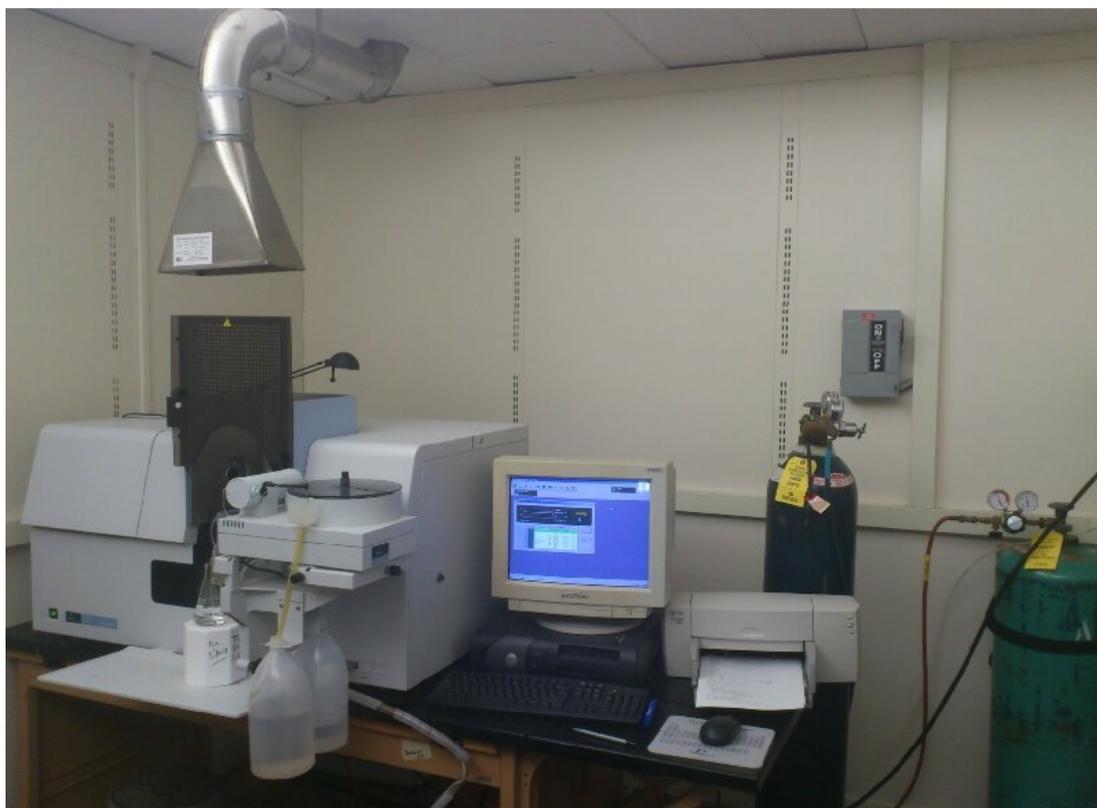
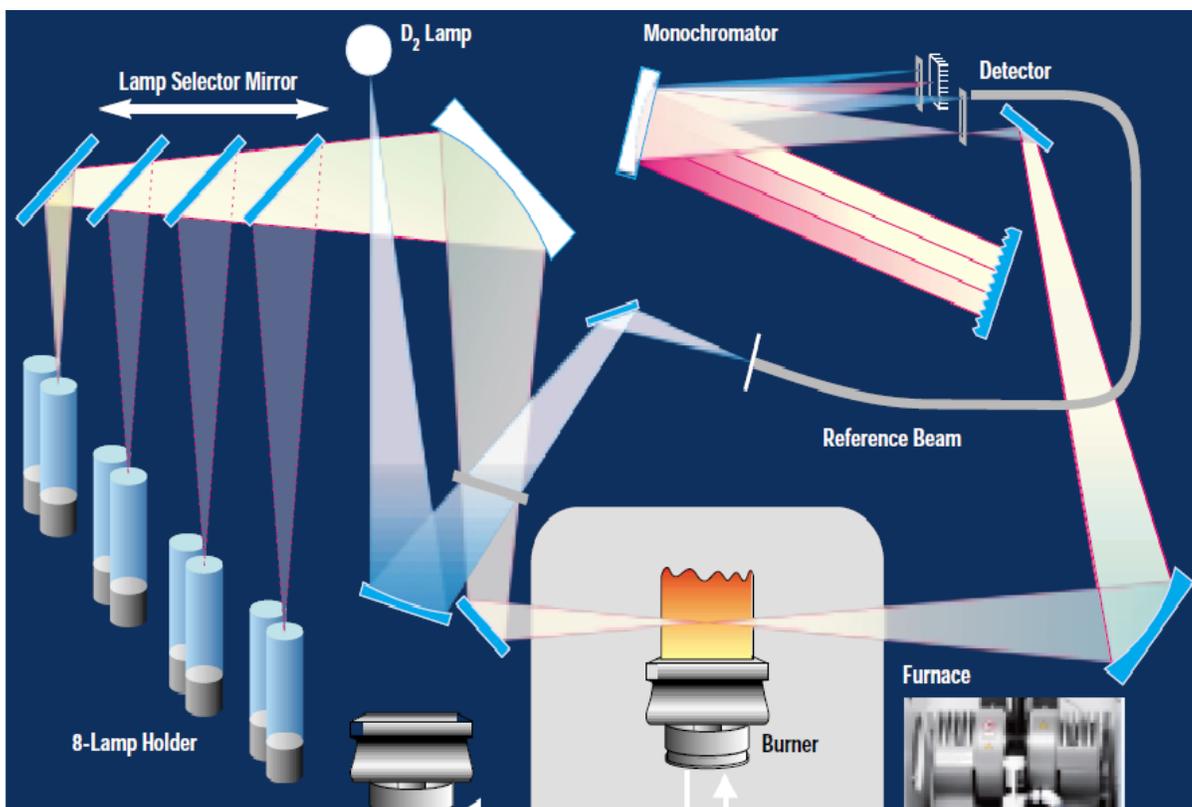


Figure-1: Perkin Elmer AAnalyst 800 in Flame Mode

Perkin Elmer **Win lab software** was used to control the spectrometer system and many quality control functions can be included. It was used in operation, data collection and preliminary analysis [8].

Figure-2: General Diagram of PerkinElmer AAnalyst 800 [8].



Conditions for Copper analysis using Perkin Elmer AAnalyst 800:

Method Development for Cu (Copper):

Atomic Absorption:

Element: Cu (Copper)

Wavelength: 324.8 nm

Oxidant flow: 17.0 L/min

Acetylene flow: 2.0 L/min

Slit width: 0.7H

Measurement: Time Average.

Flame Emission:

Wavelength: 327.4 nm

Oxidant flow: 16.0 L/min

Acetylene flow: 7.8 L/min

Settings:

Reading Parameters:

The sample was analyzed for 3 sec without any delay for 3 replicates at 72 amps.

Auto sampler was not used for FAAS.

Calibration Equation:

Equation: Linear, calculated intercept

Max. Decimal places: 3

Max. Significant figures: 4

Calibration and sample units: mg/L

Parameters	Enable	Disable
Correlation Coefficient		✓
Recalibration		✓
Precision Checks		✓
Beyond Calibration Range		✓
Matrix Recovery		✓

Results display must be included with:

- Replicate data
- Means and Statistics
- Analysis list
- Matrix Test reports
- Calibration summary and curves.

The Calibration curve was obtained using Calibration standards, and the samples were analyzed.

The results obtained were collected and further calculations were interpreted using Microsoft Office Excel Worksheet.

The experiment includes preliminarily calibration followed by working range and detection limit. The soil samples of mine tailings of Upper Peninsula of Michigan were analyzed and the Copper content in the samples were out of the calibration range. These samples were further diluted and brought into the range. Then the samples of Thorn creek analyzed, and the samples were below the range. The samples which were below the range can be further analyzed using GFAAS.

The recovery studies on the Copper in NIST standards were made due to changes in the original concentrations of the standards.

Procedure for Recovery Studies:

- ✓ Nine samples of one gram weight of NIST standards Domestic sludge and Estuarine Sediment were weighed and transferred into beakers.
- ✓ 3 replicate samples of each of the NIST standards were spiked with 5 mg and 10 mg of 1000 mg/L of Cu standard (Perkin Elmer) respectively and 3 samples were left unspiked.
- ✓ The spiking was done before the digestion procedure gets started.
- ✓ Followed by Spiking, these samples were digested in the same way as the soil samples were digested, using modified USEPA 3050B method [7].
- ✓ The digested samples were then analyzed by using FAAS.

Since the calibration range was up to 5 mg/L, the samples with high concentration were diluted and reanalyzed.

Results and Discussion:

Calibration:

Calibration curve was established with working range 0.1 ppm to 5 ppm with a correlation coefficient of 0.9994(Figure-3). The slope was found to be 0.0101, and the intercept was found to be 0.0004. The detection limit was found to be 0.12mg/L.

The results were obtained, and analysis of soil samples of Upper Peninsula of Michigan for the determination of Copper resulted in the presence of high content of Copper. The environmental Copper levels ranged from 41mg/Kg to 2844 mg/Kg in the Michigan samples and 6 mg/Kg to 72 mg/Kg in the Thorn creek samples, but the concentrations of the NIST standards, which were used as control, differed from their original concentration (Table-3). These changes in the concentrations of NIST standards may be due to loss of sample during the acid digestion procedure or cross contamination of both the standards.

Concentration of Cu in mg/L	Absorbance	SD
0	0	0.0004
0.1	0.0012	0.0004
0.5	0.0056	0.0002
1	0.0107	0.0001
2	0.0216	0.0004
5	0.0508	0.0006

Table-2: Calibration standards and their Absorbance

Signal detection line (y_{dl}) = $y_{blank} + 3s$

$$= 0.473 + 3(0.0004)$$

$$= 0.4742$$

Minimum Detectable concentration = $3s/m$

$$= 3(0.0004)/0.0101$$

$$= 0.12 \text{ mg/L}$$

Quantitation limit = $10s/m$

$$= 0.4 \text{ mg/L}$$

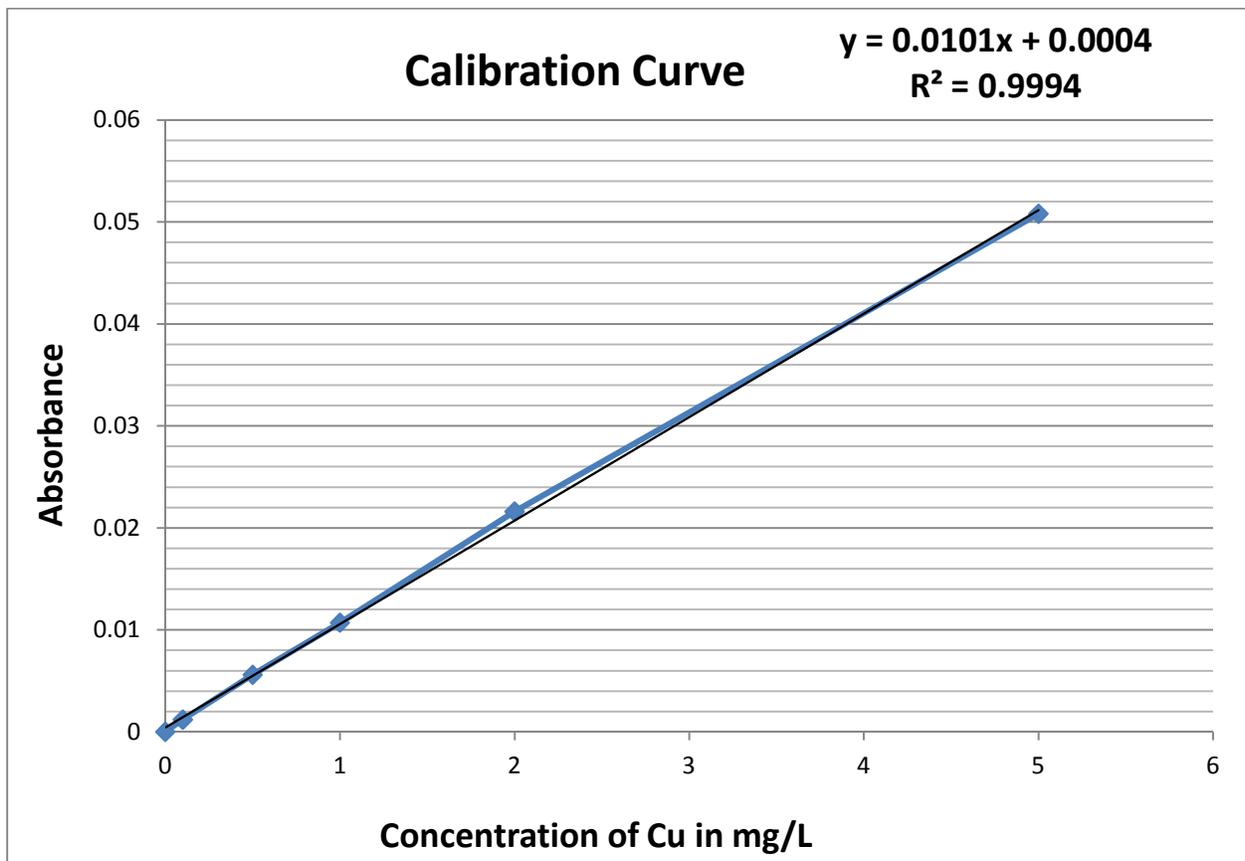


Figure-3: Calibration curve

Table-3: Determination of Copper in the Mine Samples:

UP Soil Samples	Initial sample size in g	RSD	Mean of Cu Conc. in ppm	mgCu/g sample	mgCu/Kg sample
Estuary sediment	1.023	1.427	23.9	0.683105455	683.1054545
Domestic sludge	1.0013	0.63	22.69	0.698404681	698.4046809
Phoenix below 1	1.0542	0.589	35.08	0.983158429	983.1584291
C Falls above 1	1.021	1.405	2.221	0.087762565	87.76256484
C Falls top 1	1.0756	0.778	36.28	1.467892983	1467.892983
C Falls middle 1	1.053	6.601	0.992	0.041732677	41.73267692
C Falls below 1	1.0422	0.073	43.58	1.597042666	1597.042666
Delaware above	1.07	1.128	5.774	0.195658196	195.6581957
Delaware side	1.019	0.793	9.284	0.369532355	369.5323549
Delaware below	1.0262	0.606	1.82	0.069874379	69.87437926
Delaware 1	1.0778	0.548	44.56	1.667667716	1667.667716
Phoenix E shaft 1	1.0402	0.139	95.19	2.84317211	2843.17211
Cliff below	1.0152	0.023	96.51	2.774548422	2774.548422
EP WPS	1.014	8.774	0.694	0.027978142	27.97814167
EP SS	1.093	7.765	0.327	0.013652654	13.65265389
EP RDS	0.847	4.212	0.539	0.013738981	13.73898103
EP CS	1.026	2.067	0.332	0.013035554	13.03555404
EP WDS	1.041	3.975	0.386	0.015593607	15.59360657
EP CED PARK	1.012	6.844	0.484	0.01351929	13.51929019
EP OPEN OFF TR	1.013	11.02	0.317	0.013038518	13.03851786
EP YBS	1.005	7.902	0.347	0.012372201	12.37220074
EP FS	1.086	2.644	0.745	0.022499755	22.49975495
EP SMS	1.010	7.886	0.474	0.018610013	18.61001326
A1	1.066	1.636	0.241	0.006360053	6.360052641
A2	1.061	2.905	0.247	0.006957822	6.957822199
B1	1.052	8.469	0.335	0.008083439	8.08343949
F1	1.015	6.804	0.276	0.010190213	10.19021267
F2	1.098	5.36	0.667	0.026314839	26.31483938
C1	1.028	1.926	0.299	0.012182767	12.18276663
C2 Out	1.057	8.767	0.451	0.018269041	18.26904144
C2 WF	1.032	1.271	0.309	0.013138548	13.13854826
D2	1.012	7.775	0.384	0.010754391	10.75439099
D1	0.100	5.602	0.379	0.072122717	72.12271657
E1	0.238	7.188	0.43	0.061003221	61.00322119

Table-4: Recovery studies on Copper in NIST Standards:

Soil Sample	Initial sample size in g	Mean of Cu Conc. in ppm	mg Cu/ g sample	mg Cu/Kg sample	Mean of mg Cu/Kg sample	SD of Cu
E.sed NS 1	1.0008	0.369	0.016163608	16.16360823	17.9986116	2.20123653
E.sed NS 2	0.9996	0.605	0.020439273	20.43927257		
E.sed NS 3	1.0007	0.387	0.017392954	17.39295399		
E.sed + 5mg 1	1.0037	60.56	2.742438211	2742.438211	2579.661025	141.260938
E.sed + 5mg 2	1.0041	62.64	2.507346758	2507.346758		
E.sed + 5mg 3	1.003	64.53	2.489198106	2489.198106		
E.sed + 10mg 1	1.0062	68.42	3.072877016	3072.877016	2984.024656	210.49912
E.sed + 10mg 2	1.0001	68.59	3.135529134	3135.529134		
E.sed + 10mg 3	1.0041	69.21	2.743667817	2743.667817		
D.sludge NS 1	1.0028	16.48	0.552482633	552.4826326	555.349349	3.03919573
D.sludge NS 2	1.0031	16.15	0.555029663	555.029663		
D.sludge NS 3	1.0003	16.48	0.558535751	558.5357513		
D.sludge + 5mg 1	1.0034	66.87	2.249155189	2249.155189	1383.050447	1167.59854
D.sludge + 5mg 2	1.003	55.58	1.844807149	1844.807149		
D.sludge + 5mg 3	1.003	1.254	0.055189003	55.18900259		
D.sludge + 10mg 1	1.004	68.55	3.141051125	3141.051125	2841.073022	263.56973
D.sludge + 10mg 2	1.0036	69	2.646599641	2646.599641		
D.sludge + 10mg 3	1.0028	68.93	2.735568298	2735.568298		

Recovery Studies:

The recovery studies on Copper in NIST standards were performed to find the robustness of the method and the results were found to be more precise and reproducible. The Estuarine Sediment and Domestic Sludge were found to be 18 ± 2.2 mg/Kg and 555.33 ± 3.04 mg/Kg instead of 10.01 mg/Kg and 627.4 mg/Kg respectively (Table-4). These recovery studies confirmed that the NIST standards were contaminated during the analysis of mine samples. This contamination may be at the time of transfer of NIST standards to the beakers or refluxing of soil samples during the digestion. So the results were not accurate.

During these recovery studies, the results of the NIST standards which were spiked with 5mg and 10mg to 1g of samples resulted with concentrations of 5g/Kg and 10 g/Kg instead of a target of 5 mg/Kg and 10 mg/Kg respectively which was almost 1000 times larger. This was due to experimental error. The results were inaccurate and not reproducible. The Copper content was found to be less than what they should have. This may be due to the reaction of Copper with the beakers since they were used in all Chemistry laboratories. During the acid digestion, the samples were refluxed under high temperatures, at this time there was a bumping of samples from beakers. This could be one of the reasons for the loss of Copper content.

From these recovery studies, the changes in the original concentrations of the NIST standards during analysis of Copper in mine samples were due to cross-contamination of standards and samples was confirmed.

Conclusion:

The FAAS (Perkin Elmer AAnalyst 800) used was effective in the determination of Copper in mine samples [5]. The results were more precise and reproducible. In case of sample pretreatment, acid digestion was most useful approach in the destruction of the matrix [1]. The Nitric acid was used for the acidification of soil samples, and the Hydrogen peroxide was used for oxidation of organic matter [13].

The working range for the Cu was 0.1 ppm to 5 ppm and the mine samples with high copper concentration can be diluted and reanalyzed. The method developed for Copper was optimized in such a way that the working conditions can be applied to other trace metals determined under FAAS [2].

Recommendations for future studies:

The recovery studies on Copper in the NIST standards can be done using correct spike. Use of digester during the acid digestion would reduce the loss of sample caused by bumping.

References:

[1] Sardans. (2009). Determination of As, Cd, Cu, Hg and Pb in biological samples by modern electrothermal atomic absorption spectrometry. 97-112.

- [2] Török. (2009). A study of the direct determination of Cd, Cr, Cu, Pb and Zn in certified reference materials of soils by solid sampling electrothermal atomic absorption spectrometry. 93-97.
- [3] Haroun. (2008). Analysis of heavy metals during composting of the tannery sludge using physicochemical and spectroscopic techniques. 111-119.
- [4] Hödrejärv. (1999). Pseudo-total analysis for metallic elements in siliceous soil by acid digestion and flame atomic absorption spectrometry. 293-301.
- [5] Ghaedi. (2007). Cloud point extraction for the determination of copper, nickel and cobalt ions in environmental samples by flame atomic absorption spectrometry. 533-540.
- [6] Duran. (2008). Simultaneous preconcentration of co(ii), ni(ii), cu(ii), and cd(ii) from environmental samples on amberlite xad-2000 column and determination by faas. 292-299.
- [7] (n.d.). Retrieved from <http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/3050b.pdf>
- [8] (n.d.). Retrieved from http://www.perkinelmer.com/CMSResources/Images/44-74392BRO_AAnalyst600800.pdf
- [9] (n.d.). Retrieved from [http://webs.wofford.edu/splawnbg/Chem_411_files/Atomic Absorption Spectroscopy- Analysis of Copper in Vitamins.pdf](http://webs.wofford.edu/splawnbg/Chem_411_files/Atomic%20Absorption%20Spectroscopy-Analysis%20of%20Copper%20in%20Vitamins.pdf)
- [10] (n.d.). Retrieved from http://www.uaa.alaska.edu/enri/labs/aset_lab/Methods/upload/ASET-sediment-soil-sludges-extracts-following-EPA-3050b.pdf
- [11] (n.d.). Retrieved from https://www-s.nist.gov/srmors/view_detail.cfm?srm=1646a
- [12] (n.d.). Retrieved from https://www-s.nist.gov/srmors/view_detail.cfm?srm=2781

[13] (n.d.). Retrieved from
<https://fortress.wa.gov/ecy/publications/publications/0803119.pdf>

[14] (n.d.). Retrieved from <http://www.mbanetbook.co.in/2010/05/sample-project-report-acknowledgement.html>