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Der Pharma Chemica, 2012, 4(6):2169-2177
(http://derpharmachemica.com/archive.html)

ISSN 0975-413X
CODEN (USA): PCHHAX

Electrothermal atomic absorption spectrometry behavior of cadmium without/with spiral tungsten filaments as platform technique and its application

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ABSTRACT

The Electrothermal Atomic Absorption Spectrophotometer (ETAAS) is one of the most important analytical techniques in the field of elemental determination owing to its high sensitivity. The graphite atomizer is a commonly used reactor where the sample undergoes various processes, leading to formation of free atoms of the anlayte. Ashing and Atomization behavior of cadmium from the pyrolytical graphite tube (conventional ETAAS) and from a new construction graphite tube mounted with spiral tungsten filaments were described, compared, discussed and applied for its determination in bovine liver. The heating program was carried out by employing a heating cycle in four steps: dry, ashing, atomization and clean. The best results were achieved by using spiral tungsten filaments-ETAAS. The new method approved by using certified standard No.1577 bovine liver. Certified standard reference materials were analyzed for the assessment of accuracy of proposed method. Calibration plots for the cadmium for both methods were achieved, as well as, the standard addition method. The calibration plot was liner from 1.0 to 13.0 ppb for the spiral tungsten filaments-ETAAS. Correlation coefficients found were at least 0.999 for direct calibration.

Keywords: Graphite furnace atomic absorption spectrometry; Cadmium standard solution; spiral tungsten filament.

INTRODUCTION

The graphite atomizer is a commonly used reactor where the sample undergoes various processes, leading to the formation of free atoms of the analyte of interest in gaseous phase. Thus atomic absorption of the cloud of atoms could be measured. This process is called atomization and depends strongly on the composition of the sample introduced into the atomizer. In graphite furnace, the sample is gradually heated according to the previously set temperature/time program so that various components of the sample could evaporate. The best conditions for atomic absorption measurements could be achieved when the matrix components evaporate before analyte atoms appear in the gaseous phase. The better the separation of the evaporation of matrix from the evaporation of analyte, less interference occurs during the measurement. It is clear that the efficiency of the separation depends on the volatilities of both matrix and analyte compounds. Generally speaking, the main aim of the modifiers is to provoke intended chemical reaction in order to enhance the separation of matrix and analyte, thus ensuring that the atomization process is free from interferences. Commonly, an excess of reagent—modifier—is added intentionally to the sample or atomizer. Its aim is to transfer the analyte into the less-volatile compounds and/or to transfer the matrix compounds to more-volatile compounds. Moreover, properly designed modification could also play its role

in the interaction of the sample with graphite surface and/or unify the atomization process of analyte being present in various species [1&2].

Although the most common atomizer in ETAAS in graphite tube, the limitations such as need for a high power supply and difficulties in the determination of elements that form refractory oxides and carbides, have led to development of many metal atomizer [3-6]. Among the metal atomizer, tungsten has been the predominant atomizer. In the recent years, tungsten coils or tubes have been used an alterative atomizer to the graphite tube in the determination of elements by ETAAS [7-10]. Their used has been extended to use as combination for vaporizer samples into inductively coupled plasma[11-16]. The tungsten devices used in atomic spectrometry as atomizers or vaporizers are summarized in recent review [17]

Tungsten coil have been used as atomizers in portable, battery powered atomic absorption spectrometers [18]. The low cost and low power requirements of these devices make them ideal candidates for field application [19]. Metals atomizer, such as molybdenum and tungsten tube are less common in atomic absorption spectrometry. These devices usually require the addition of hydrogen to argon purge gas to protect the metal from oxidation . The tungsten coil, an open metal atomizer, has been used with some success as an electrothermal vaporizer [20].

M. Masrounia [21] determined cadmium in environmental sample by electrochemical hydride generation electrothermal atomic absorption with situ trapping in graphite tube atomizer. A. Nezhadali [22] used graphite furnace atomic absorption spectrometry to determined cadmium after preconcetration and extraction by dithizone. X.wen et.al.[23] determined cadmium in rice and water using tungsten coil elctrothermal atomic adsorption spectrometry after cloud point extraction. G. Donati et.al.[24] measured cadmium in urine by cloud extraction-tungsten coil atomic absorption spectromtry.A. Salido and B. Jones [25] developed tungsten coil atomic emission spectrometry for determination Sr in soil.

The main problem in the determination of cadmium by ETAAS are tendency of these elements to form volatile compounds that can be easily lost during the ashing and atomization steps and the possible interaction of the elements with graphite furnace wall forming carbides. The use of pyrolytic graphite tube with L'Vov platform and chemical modifier that stabilizes the volatile elements until higher temperatures can avoid these problems [26].

In the present work a tungsten filaments in the graphite furnace tube for the flameless atomic absorption spectrometry is contracted and described for the study of Cadmium. This system employ a two tungsten filaments as a combination between them form a concave valley platform . The tungsten filament is extracted from a 60 Watts, 220 Volt commercial light bulb. A simple laboratory constructed was done by easily mounted of the tungsten filaments in the medial of the graphite tube and it is dose not need to realignment the optical path for the hallow cathode Lampe. The new mounting used for the determination of trace Cd in the ppb range. The behavior of this element were studied. The optimization of thermal program was carried out, such as ashing and atomization temperatures and parameters of the sampling such as the kind of the acid and the concentration were optimized in order to obtain high sensitivities. The comparative study was performed using the conventional ETAAS and spiral tungsten filaments ETAAS the new technique. The results showed from these studies when appropriate electrothermal program are used, the direct determination of Cd can be successfully performed . Finally aim of our work was to develop direct, quick and accurate method for determination of Cd in samples without using matrix modifier in inexpensive system.

MATERIALS AND METHODS

2.1. Apparatus

A Shimadzu, AA 680, Atomic Absorption Spectrophotometer equipped with Shimadzu GFA-4B Graphite furnace Atomizer, Shimadzu Autosample Changer ASG-60G and Shimadzu PR-5 Graphic printer. Argon was used to provide an inert gas atmosphere within the graphite furnace at a flow rate 1.5 l/min.. Pyrolytically graphite tubes was used. Argon gas used as sheat gas; the internal flow in the graphite tube was interrupted during the atomization step. Cadmium hollow cathode lamps were used as the spectral radiation sources. The wavelengths, spectral widths and current were set to 228.8 nm, 0.3 nm for cadmium and 4.0 mA. Deuterium background correction was used all the operation time. Peak height absorbance values were measured. The spiral tungsten filaments 1.5 cm length and 0.10 cm diameter extracted from commercial light bulb 220 volt and 100 watts.

2.2. Reagents

Reagent of analytical grad or higher quality were used from (Fluka. Riedel-de Haen AG-Fixanal, Marck and BHD) while No. 1577 bovin liver certified standard IAEA. All solution were prepared using deionized water. All glass and plastic ware were immersed in 2 M nitric acid for 24h followed by rinsing with deionized water. Several aqueous standards were used to obtained the calibration curves and the standard additions were also made. The concentrations of solution used in the calibration ranged from 1 to 13 ppb of Cd. The calibration curves were liner in the concretions ranges of these standards. The working solution were prepared daily from their stock solution (1000 mg/L, Riedel-de Haen AG-Fixanal) with distilled-deionized water.

2.3. Procedure

The analysis of certified bovine liver 1577 sample preparation was carried out by weight accurately 0.440 gram of the sample in PTFE beaker. The sample was digested by adding of 1:1 (v/v) nitric acid. The sample heated to 80^{o}C using water bath. After digestion the sample was filtered and transferred into 10 ml volumetric flask and the volume make up to 10 ml by 0.05 M HNO_3. The further dilution was carry out in the direct calibration by taken 1 ml and completed the volume to 10 ml. The standard addition method was used following the protocol of this method for preparation the standard solution. The effect of hydrochloric acid and nitric acid concentration were studied from 0.05 to 0.7 M. The graphite furnace without/with STF optimized for the determination of cadmium in the certified bovine liver No.1577.

2.4. Developed method and optimization

Fig. 1. & 2. Illustrated the laboratory set up for the mounted of spiral tungsten filaments into the graphite furnace and showed the concave valley between the two spiral tungsten filaments that can support the aliquot sample easily and steady. A 10 ul aliquot of solution was inject directly onto the spiral filaments. In this deign give privilege to the volatile elements to heat indirectly by the heat came from the wall as in the L' Vov plat form as well as the sample rise from the base of the wall of the graphite furnace. The diameter of the spiral tungsten filaments is to small that make the method to easy to handle and set up, it don't need to re-optimize the light path through the tube radiate from the hollow cathode lamp.

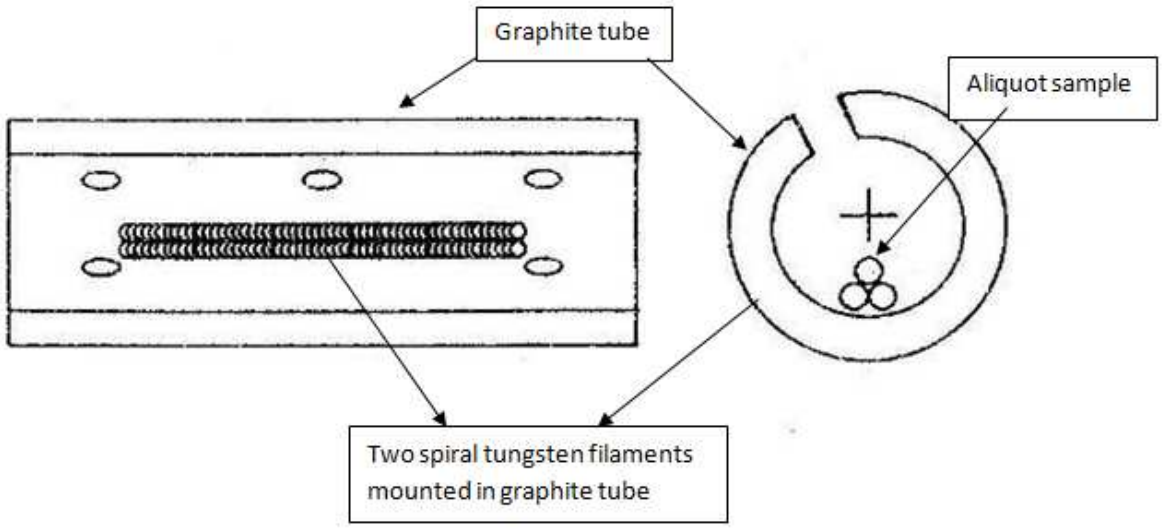

Fig. 1. Schematic diagrams of two spiral tungsten filaments mounted in graphite tube support the aliquot sample

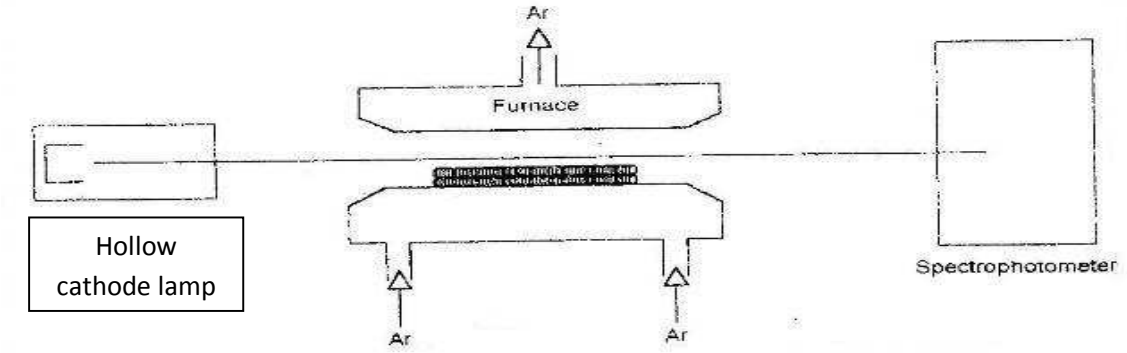

Fig. 2. Schematic diagram of spiral tungsten filaments electrothermal atomic absorption spectrometry

RESULTS AND DISCUSSION

3.1 Cadmium behavior without/with spiral tungsten filaments ETAAS.

With respect to the small concentration of Cd in set up the instrument conditions, the aqueous solution of Cd were injected duo to lower matrix load into the graphite tube, so for the starting study the aqueous solution was used. The heating program was carried out by employ a heating cycle in four steps: drying, ashing, atomization and cleaning. The drying and cleaning steps has been fixed for 150 ^{O}C ramp 30 sec., and 1400 ^{O}C / 3 sec, respectively for all the experiments. The temperature curves for ashing recorded by varying ashing temperature between 200 ^{O}C to 800 ^{O}C each step 100 ^{O}C, while keeping atomization temperature on 1200 ^{O}C. Then the temperature curve for atomization were recorded by varying the atomization temperature between 700 to 1500 ^{O}C, while fixed the ashing temperature on 300 ^{O}C. Figure 3 presented the ashing and atomization curves for the conventional ETAAS.

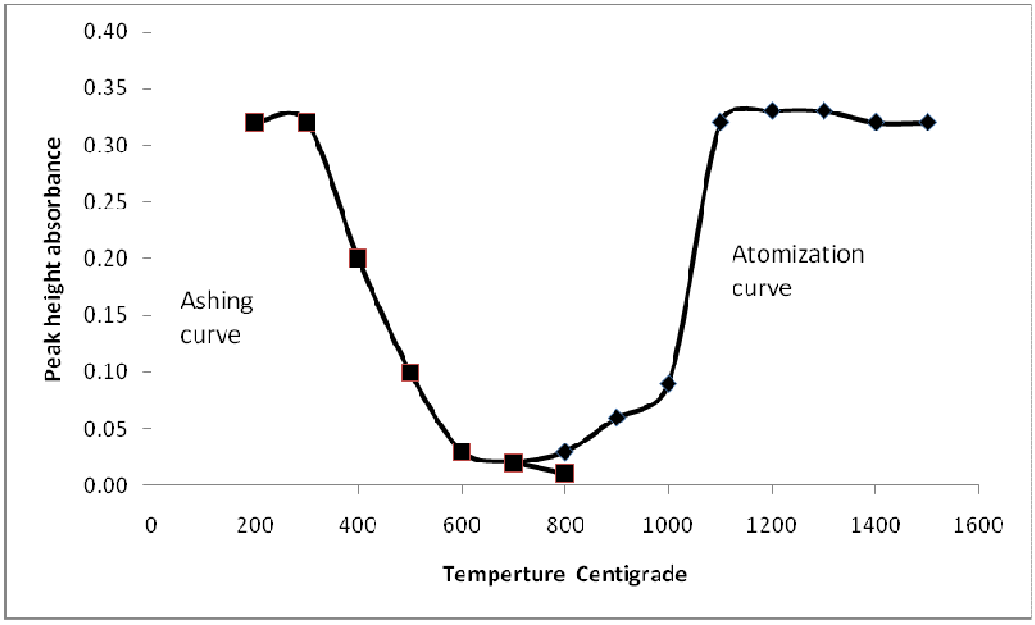

Fig. 3. Ashing and atomization temperature curves for 10 ppb Cd in aqueous solution without spiral tungsten filaments ETAAS.

Figure 4 showed the ashing and atomization curve for 10 ppb with spiral tungsten filament ETAAS implemented in the same manner as above. . Figure 3&4 showed the absorbce signal of Cd without/ with spiral tungsten filaments which indicted that the ashing temperature with spiral tungsten increased from 300^{O}C to 800^{O}C which is give privilege to this new technique a more chance to rid of all the organic compounds might present in the sample which reduce the factor of interferences, so for the samples you could applied 800 ^{O}C without loss the analyte which

is high enough to remove most of the matrix components. The results obtained were is good agreement with our expectation.

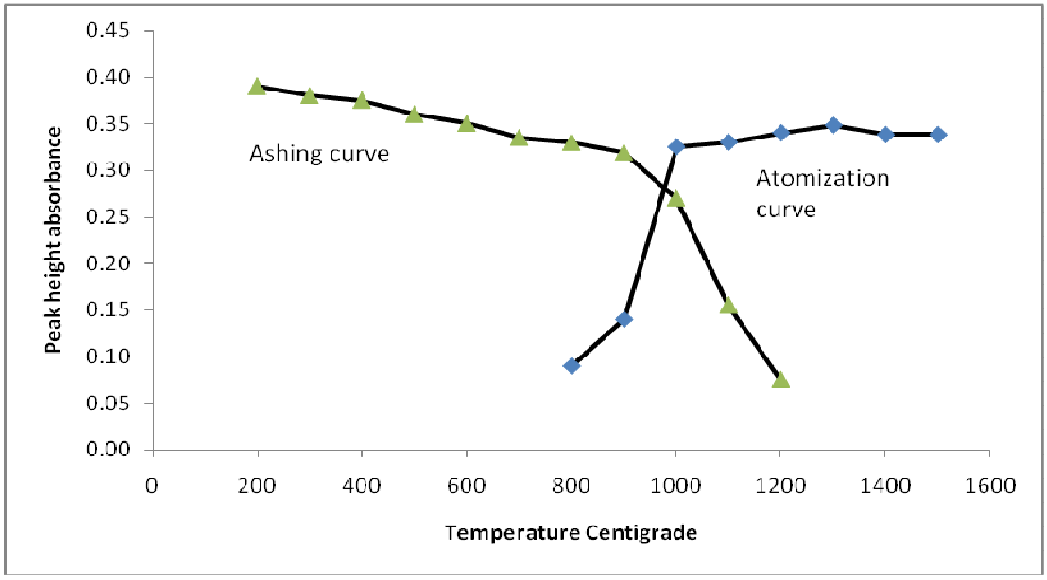

Fig. 4. Ashing and atomization temperature curves for 10 ppb Cd in aqueous solution with spiral tungsten filaments ETAAS

3.2. Effect the concentrations and acid type on the cadmium absorbance signal without/with spiral tungsten filaments ETAAS.

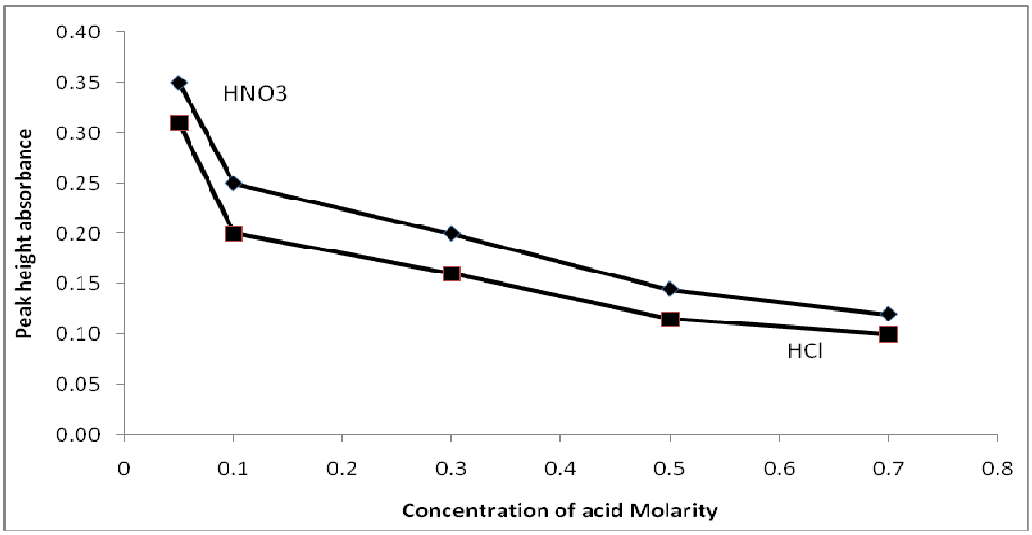

Fig. 5. Effect of different concentration of nitric acid and hydrochloric acid on the 10 ppb Cd absorbance signal without spiral tungsten filaments ETAAS

It was noted that the absorbance signal for Cd sensitive to the acid type and concentration. Hydrochloric acid and nitric are among the most acids used in digestion of the samples. Figure 5 showed the different concentration of nitric acid and hydrochloric acid (0.05-0.7 M) were tested. As shown for the figures both acid produced lower Cd absorbance signal as well as the signal with HCL give much lower absorbance signal for Cd. The same behavior of Cd with spiral tungsten filaments ETAAS but the signals was higher as shown in figure 6. It was found that the Cd signals decrease by increasing the concentration of the acid under study. There are a steady level between 0.05 to 0.3 M for the HNO_3. The use of HNO_3 was found to be effective in lowering the absorbance signal as well as HCl

with both technique (without /with spiral tungsten filaments), but with spiral tungsten filaments is less effective (lowering the absorbance signal) as seen from the figure 5 and 6. To get similarity in our study a morality of 0.05 of both acid were take as working concentration for further study.

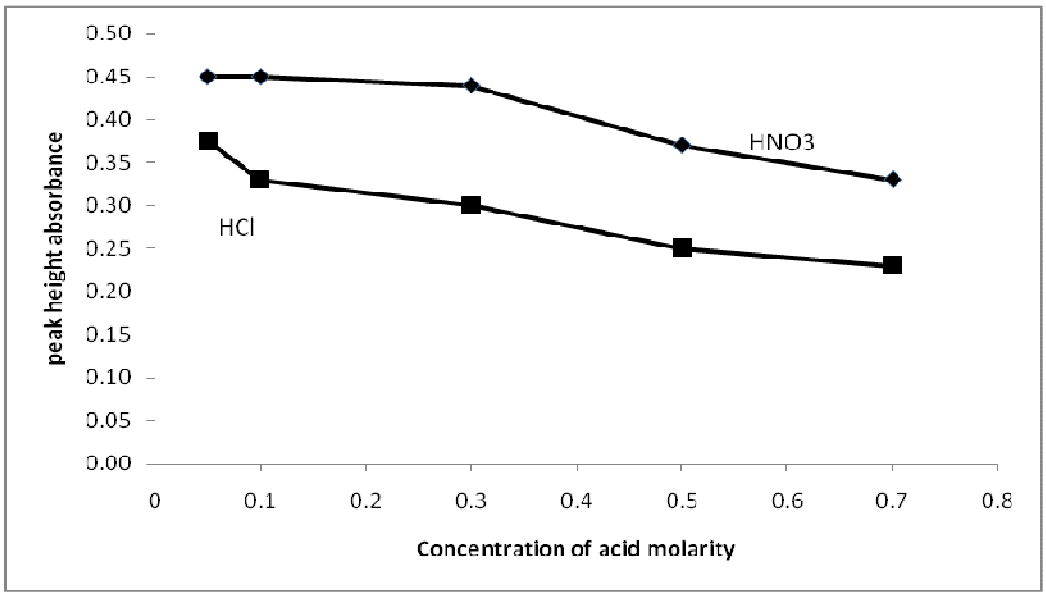

Fig. 5. Effect of different concentration of nitric acid and hydrochloric acid on the 10 ppb Cb absorbance signal with spiral tungsten filaments ETAAS.

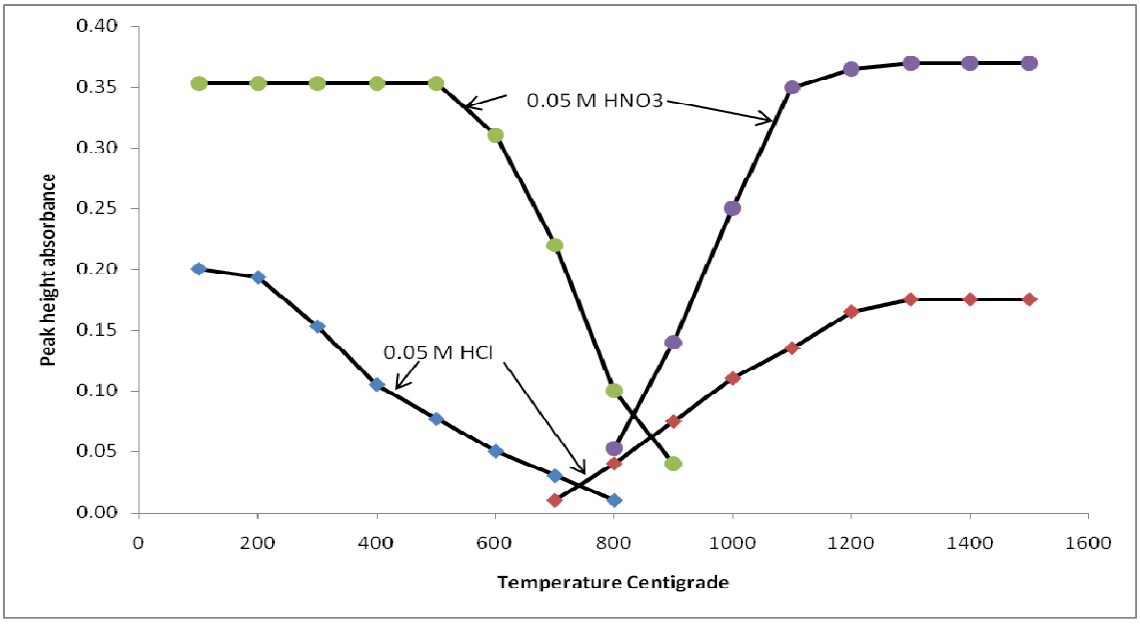

Fig. 7. Ashing and atomization temperature curves for 10 ppb Cd in 0.05 M nitric and hydrochloric acid without spiral tungsten filaments ETAAS.

3.3. Ashing and atomization temperature curves for 10 ppb Cd in HCL and HNO3 without/with spiral tungsten filaments acid type ETAAS.

Figures 7 and 8 showed the ashing and atomization curves for the 10 ppb Cd without/ with spiral tungsten filament ETAAS respectively in 0.05 M HNO_3 and HCl. The results shows for all the experiments the absorbance signal for

Cd with spiral tungsten filaments give higher responses than the conventional ETAAS which improved in sensitivity. The ashing temperature in HCl increased for 200 ^{O}C to 700 ^{O}C without /with STF respectively. Under ashing study for Cd in the 0.05 M HNO3 the ashing temperature increases form 500 OC to 800 ^{O}C which overcome the volatile elements could be loss thought the ashing stage (minimizing volatile analyte losses).The atomization temperature measurement stay on between 1100 and 1200 ^{O}C give chance to better generation of free atom as you can seen for absorbance signal. Table 1 summarized the optimum conditions heating program for the 10 ppb Cd thought the study.

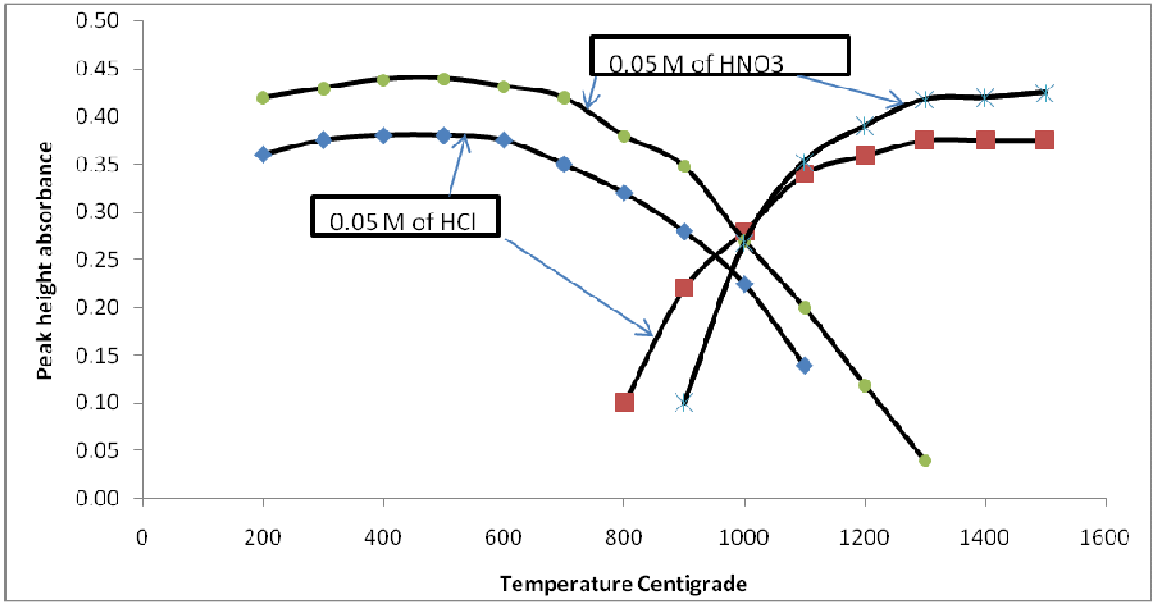

Fig. 8. Ashing and atomization temperature curves for 10 ppb Cd in 0.05 M nitric and hydrochloric acid with spiral tungsten filaments ETAAS.

Table 1. Optimum conditions heating programs for 10 ppb Cadmium without/with spiral tungsten filaments ETAAS and in different acid media.

Atomization surface / Condition	Graphite furnace without spiral	Graphite furnace with spiral	Interferences			
			Without spiral		With spiral	
			HNO_3 0.05M	HCl 0.05M	HNO_3 0.05M	HCl 0.05M
Sample aliquot (ul)	10	10	10	10	10	10
Wavelength (nm)	228.8	228.8	228.8	228.8	228.8	228.8
Slit band width (mA)	4.0	4.0	4.0	4.0	4.0	4.0
Back ground corrector	ON	ON	ON	ON	ON	ON
Drying step: ^{O}C/sec, ramp	150/30	150/30	150/30	150/30	150/30	150/30
Ashing step: ^{O}C/sec	200/20	700/20	400/20	100/20	700/20	700/20
Atomization step: ^{O}C/sec	1200/3	1100/3	1200/3	1200/3	1200/3	1200/3
Cleaning step: ^{O}C/sec	1400/3	1300/3	1400/3	1400/3	1400/3	1400/3

3.4. Calibration plots for Cd without/with spiral tungsten filaments ETAAS

Figure 9 and 10 showed the calibration plot for the cadmium in aqueous solution of nitric acid. The calibration ranges of 3 ppb-11 ppb and 1 ppb-13 ppb for Cd without/ with STF respectively. Correlation coefficient founded 0.999 for the both methods, three replicates were used for measurements. It was found that linearity for Cd without / with STF deteriorated above 11 and 13 respectively. Calibration was performed with the standard calibration technique using aqueous standard.

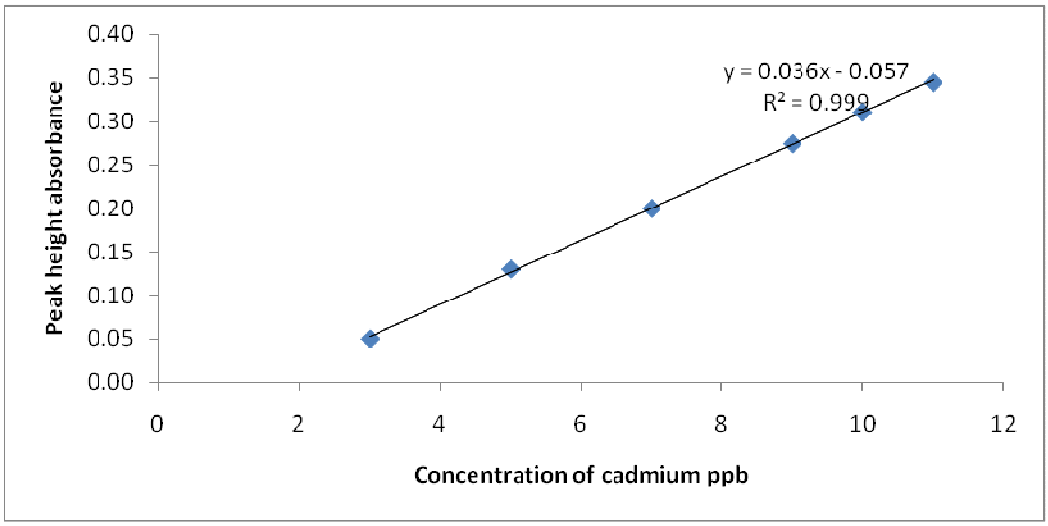

Fig. 9. Calibration plot of cadmium without spiral tungsten filaments ETAAS

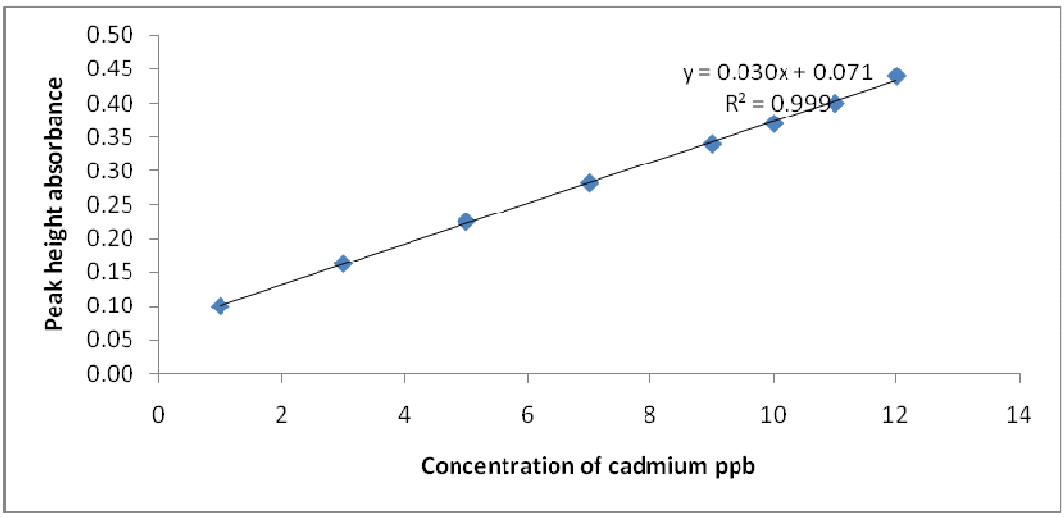

Fig.10. Calibration plot of cadmium with spiral tungsten filements ETAAS

3.5. Method validation and sample analysis

The precision of the methods were examined by five replicate measurements of 10 ppb Cd in aqueous sample. The relative standard deviation found out was 3.20 % for the direct calibration and 3.35 % for the standard addition methods. The accuracy of the proposed method was checked by analyzing the No. 1577 Bovine liver IAEA certificated reference material with heating cycling program Drying: 150 ^{O}C/20 sec ramp, ashing: 700 ^{O}C/20 sec , atomization: 1100 ^{O}C/3 sec and cleaning: 2200 ^{O}C/3 sec and the results were in excellent accordance with both certificated and informed values (recovery better than 99 %).Standard addition were applied for the two samples direct calibration using the previous program , It was noted that there is not slope differences are shown for direct method and for the standards addition method for the determination of the Cd in the certificated standard. The accuracy were 99.63% and 99.26% for the direct calibration and the standard addition methods respectively. . Taking into account the sample dilution during the preparation step.

CONCLUSION

The new construction of the two spiral tungsten filaments provides a simple way for the determination of cadmium in aqueous solution as well as in the No. 1577 bovine liver IAEA certified reference standard material with a simplicity, low cost, optimize a fast and reliable, excellent accuracy and precision. They were in good agreement

with the results obtain by direct ETAAS calibration measurements and the standard addition method and they were in the same slope. Simple apparatus and minimum of chemical materials are the main advantages of proposed technique. Additional studies are in progress on evaluating the performance of spiral tungsten filaments technique for the determination of another volatile elements. The proposed method is suitable for routine metals monitoring in samples. It can be observed that spiral tungsten filaments give privilege to the volatile element to heat indirectly by the wall of the furnace as in the L' Vov platform without losing in the interest elements and volatile the materials which is ceasing the interferences. Our recommendation is the use of spiral tungsten filaments as a platform for atomization for the volatile compound. The next project will continue to cover the anther volatile element.

An increase in the life time of the tube due to the injection of the sample not injected on the wall of the graphite furnace. The device would not required to re-change the level of the graphite furnace because the diameter of the filament is to marrow that not disturbed the path line. The results encouraging the author to extend this study and technique for study father elements.

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