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Electrothermal atomic absorption spectrometer with spiral tungsten filaments as platform for determination of antimony

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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 best results were achieved by using spiral tungsten filaments-ETAAS. The new method approved by using certified standard IAEA. Certified standard reference materials were analyzed for the assessment of accuracy of proposed method. Calibration plots for Antimony in both methods were achieved. The calibration plot was liner from 20 to 120 ppb for the spiral tungsten filaments-ETAAS. Correlation coefficients found were at least 0.998 for direct calibration and the recovery was 102%.

Keywords: Graphite furnace atomic absorption spectrometry; Antimony 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 [1,3].

The issues regarding antimony have been extensively studied due to high toxicity of this element. The concentration of antimony in earth's crust varies between 0.2 and 0.5 μg g− 1 in general. The oxidation states of Sb is mostly found in two oxidation states (III and V)in environmental samples. These two forms exhibit pronounced differences in their analytical behavior, toxicity and mobility[4], inorganic compounds of antimony are more toxic than its organic forms; toxicity of Sb (III) has been shown to be 10 times higher than that of Sb (V).

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 [4,5,8]. 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 [9,12]. Their used has been extended to use as combination for vaporizer samples into inductively coupled plasma [13,18]. The tungsten devices used in atomic spectrometry as atomizers or vaporizers are summarized in recent review[19].

Tungsten coil have been used as atomizers in portable, battery powered atomic absorption spectrometers [20]. The low cost and low power requirements of these devices make them ideal candidates for field application [21]. 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 [22].

Among the techniques for determination of antimony, flame atomic absorption spectrometry (FAAS) and hydride generation atomic absorption spectrometry (HGAAS) require only a simple flame AAS instrument and some attachments; therefore these techniques in principle provide the most economical alternatives. Hydride generation (HG) is one of the most popular and powerful techniques of vapor generation for chemical analysis [23], although in principle HG is a sample introduction technique and thus can be coupled to any atomic detector including atomic fluorescence spectrometry (AFS), inductively coupled plasma optical emission spectrometry (ICPOES) and inductively coupled plasma mass spectrometry (ICPMS), HGAAS is the most often used one due to its simplicity and low cost. Some recent applications for determination of antimony include diverse techniques such as, electrothermal atomic absorption spectrometry (ETAAS)[24], ICPMS[25] and instrumental neutron activation analysis (INAA) [26] and stripping voltammetry [27]. Chemical pre-concentration on a micro column 28 and cloud point pre-concentration [29,30] are few recent examples. A recent approach for sensitivity enhancement is trapping, applications in literature are the use of hydride generation and integrated atom trap[31].

The main problem in the determination of antimony 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[32].

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 does not need to realignment the optical path for the hallow cathode Lampe. The new mounting used for the determination of trace Sb 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 Sb can be successfully performed . Finally aim of our work was to develop direct, quick and accurate method for determination of Sb 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.

Antimony hollow cathode lamps were used as the spectral radiation sources. The wavelengths, spectral widths and current were set to 217.6 nm, 0.2 nm for cadmium and 7.0 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 igneous rock JGB certified standard IAEA with 0.11 ug Sb per gram of the certified standerd. 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 20 to 160 ppb of Sb. The calibration curves were liner between 20-100 ppb 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 igneous rock JGB-1 certified standard IAEA sample preparation was carried out by weight accurately 2.00 gram of the sample in PTFE beaker. The sample was digested by adding 20 ml of concentrate hydrofluoric acid and 2 ml of concentrate $HClO_4$. The sample heated using hot plate to nearly dry. After digestion the sample was re-dissolve by concentrate hydrochloric acid and transferred into 10 ml volumetric flask and the volume make up to 10 ml by dionized water. 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 condition for the determination of Antimony in the of igneous rock JGB-1 certified standard IAEA .

2.4.Developed method and optimization

The illustrated the laboratory set up for the mounted of spiral tungsten filaments into the graphite furnace explained elsewhere [3] and showed the concave valley between the two spiral tungsten filaments that can support the aliquot sample easily and steady. A 10 µl 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.

RESULTS AND DISCUSSION

3.1. Antimony behavior without/with spiral tungsten filaments ETAAS.

With respect to the small concentration of antimony in set up the instrument conditions, the aqueous solution of antimony 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 1800 to 2000 ^{O}C / 3 sec, respectively for all the experiments. The temperature curves for ashing recorded by varying ashing temperature between 200 ^{O}C to 700 ^{O}C each step 100 ^{O}C, while keeping atomization temperature on 1400 ^{O}C. Then the temperature curve for atomization were recorded by varying the atomization temperature between 700 to 1800 ^{O}C, while fixed the ashing temperature on 300 ^{O}C. Figure 1 presented the ashing and atomization curves for the conventional ETAAS.

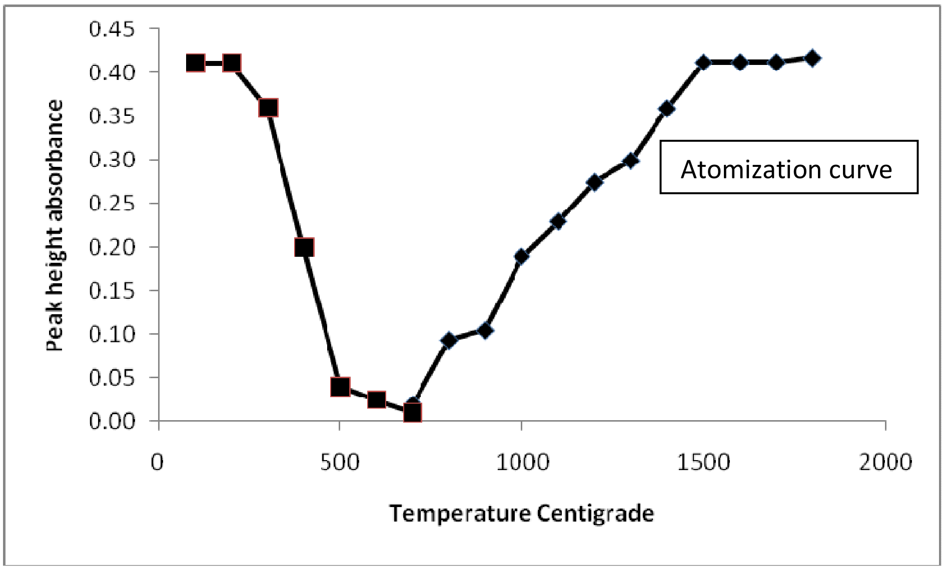

Fig. 1. Ashing and atomization temperature curves for 100 ppb Sb in aqueous solution without spiral tungsten filaments ETAAS

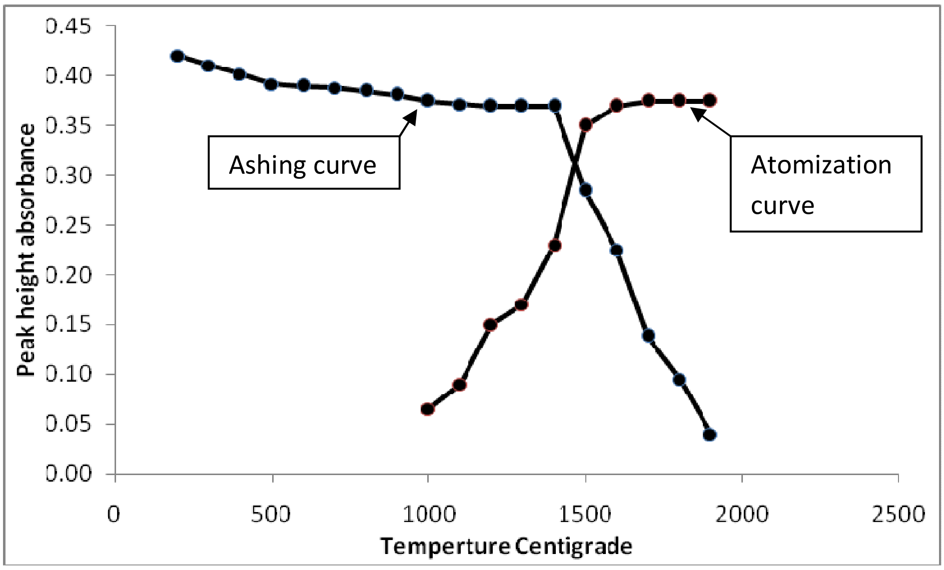

Fig. 2. Ashing and atomization temperature curves for 100 ppb Sb in aqueous solution with spiral tungsten filaments ETAAS

Figure (2) showed the ashing and atomization curve for 100 ppb of antimony with spiral tungsten filament ETAAS implemented in the same manner as above. Figure (1) &(2) showed the absorbance signal of Sb without/ with spiral tungsten filaments which indicated that the ashing temperature with spiral tungsten increased from 300^{O}C to 1300^{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 1300 ^{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.

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

It was noted that the absorbance signal for Sb sensitive to the acid type and concentration. Hydrochloric acid and nitric are among the most acids used in digestion of the samples. Figure (3) 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 Sb absorbance signal as well as the signal with HCL give much lower absorbance signal for Sb. The behavior of Sb with spiral tungsten filaments ETAAS but the signals was similar as shown in figure (3)& (4). It was found that the Sb signals are a steady level between 0.05 to 0.7 M for the HNO_3 and HCL. The use of HNO_3 was found to be less effective in lowering the absorbance signal with spiral tungsten filaments technique as it demonstrated in figure (3) and (4). To get similarity in our study a morality of 0.05 of both acid were take as working concentration for further study.

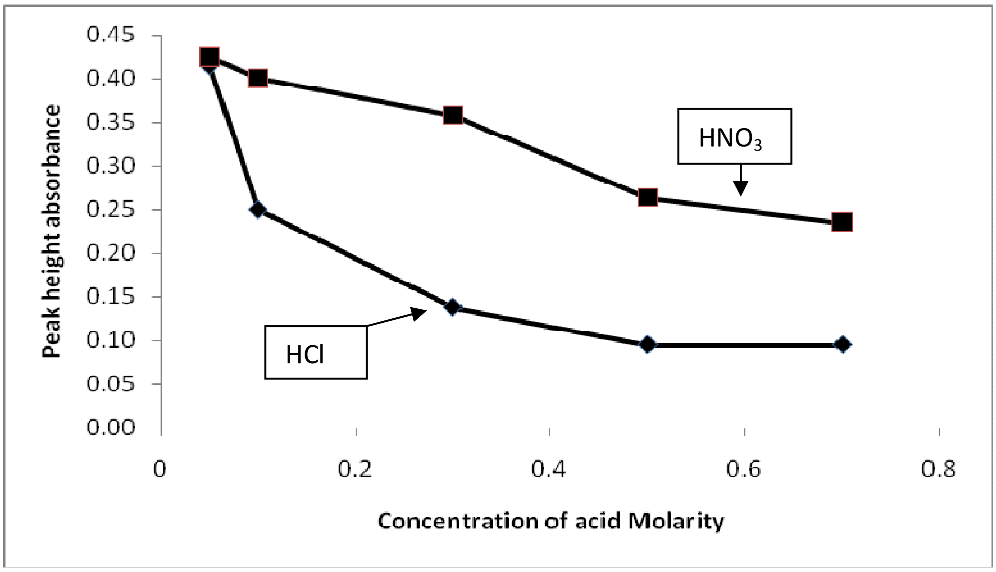

Fig. 3. Effect of different concentration of nitric acid and hydrochloric acid on the 100 ppb Sb absorbance signal without spiral tungsten filaments ETAAS

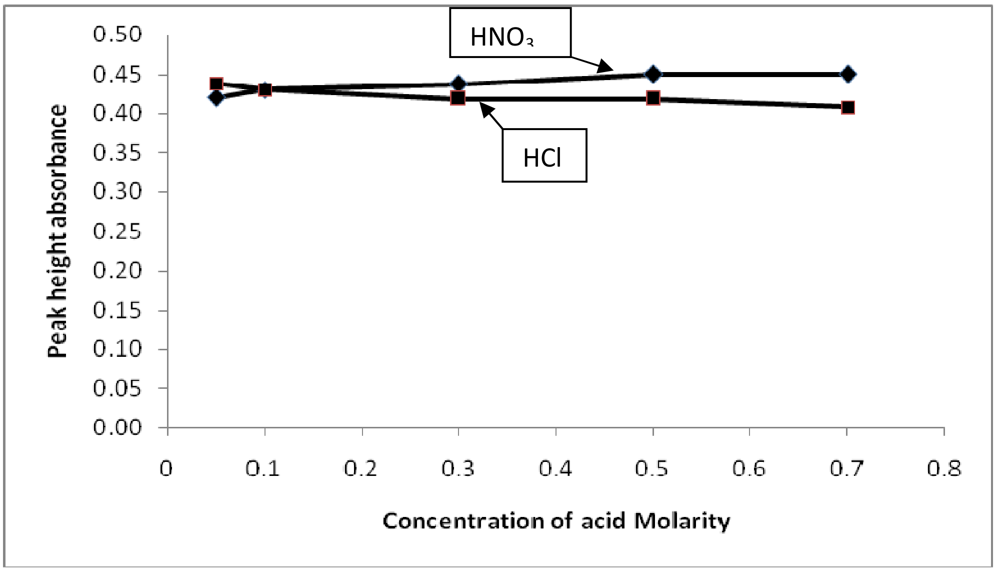

Fig. 4. Effect of different concentration of nitric acid and hydrochloric acid on the 100 ppb Sb absorbance signal with spiral tungsten filaments ETAAS

3.3. Ashing and atomization temperature curves for 100 ppb Sb in HCL and HNO3 without/with spiral tungsten filaments acid type ETAAS.

Figures (5)&(6) showed the ashing and atomization curves for the 100 ppb Sb 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 Sb with spiral tungsten filaments give higher responses than the conventional ETAAS which improved in sensitivity. The ashing temperature in HCl increased for 100 ^{O}C to 1200^{O}C without /with STF respectively. Under ashing study for Sb in the 0.05 M HNO3 the ashing temperature increases form 400 ^{O}C to 1400 ^{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 800 and 2000 ^{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 100 ppb Sb thought the study.

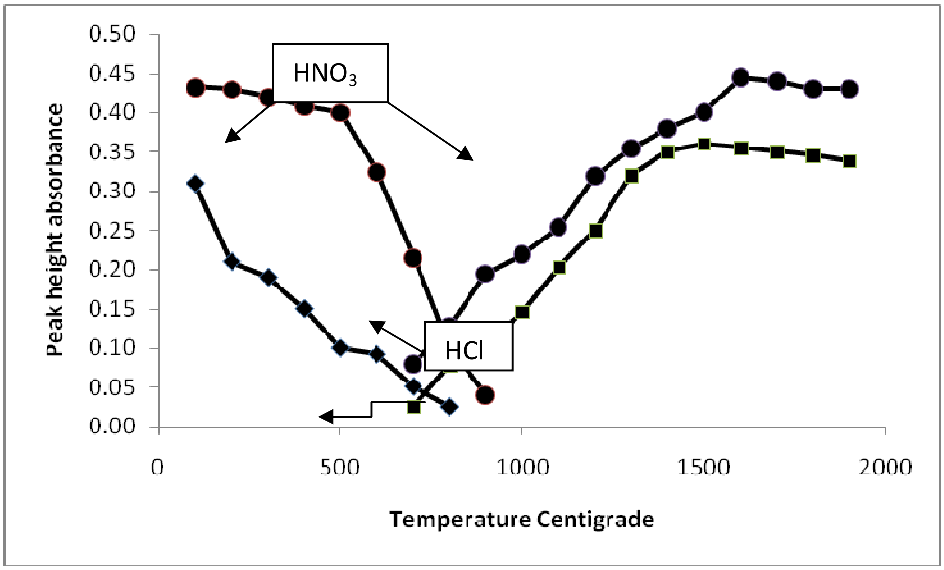

Fig. 5. Ashing and atomization temperature curves for 100 ppb Sb in 0.05 M nitric and hydrochloric acid without spiral tungsten filaments ETAAS

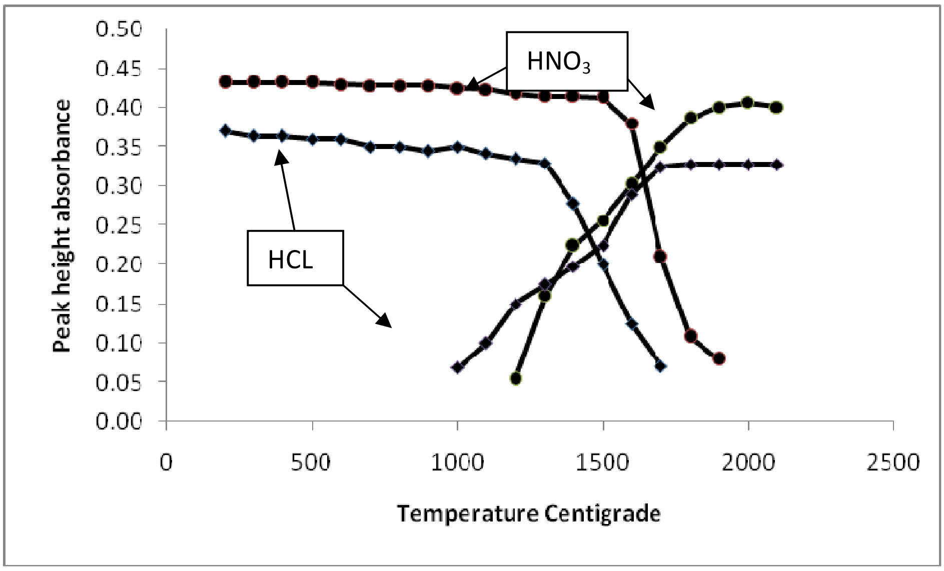

Fig. 6. Ashing and atomization temperature curves for 100 ppb Sb in 0.05 M nitric and hydrochloric acid with spiral tungsten filaments ETAAS

Table 1. Optimum conditions heating programs for 100 ppb Antimony without/with spiral tungsten filaments ETAAS and in different acid media

Atomization surface conditions	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 (µl)	10	10	10	10	10	10
Wavelength (nm)	217.6	217.6	217.6	217.6	217.6	217.6
Slit band width (mA)	0.2	0.2	0.2	0.2	0.2	0.2
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	180/20	1300/20	400/20	100/20	1400/20	1200/20
Atomization step: ^{O}C/sec	1600/4	1800/4	1700/4	1600/4	1900/4	1900/4
Cleaning step: ^{O}C/sec	1900/4	2000/4	2000/4	2000/4	2200/4	2200/4

3.5. Calibration plots for Antimony without/with spiral tungsten filaments ETAAS

Calibration plots without and with using spiral tungsten filament were constructed. The linear portion of calibration without spiral included Sb concentrations of 20-120 ppb using peak height values. In this linear range, linearity equation was found as y=0.004x+0.058 and correlation coefficient (R^2) was found as 0.998; y is absorbance value and x is concentration in ppb. In the spiral tungsten studies, linear range included Sb concentrations of 0.10–120 ppb; best line equation was found to be y=0.003x +0.093 and correlation coefficient (R^2) was found as 0.997; y is absorbance for peak height measurement and x is concentration in ppb.

3.6. Method validation and sample analysis

The precision of the methods were examined by five replicate measurements of 100 ppb Sb in aqueous sample. The relative standard deviation found out was 3.88 % for the direct calibration and 2.13 % for the standard addition methods. The accuracy of the proposed method was checked by analyzing the igneous rock JGB-1 IAEA certificated reference material with heating cycling program Drying: 150 ^{O}C/30 sec ramp, ashing: 1300 ^{O}C/20 sec , atomization: 1800 ^{O}C/3 sec and cleaning: 2000 ^{O}C/4 sec and the results were in excellent accordance with both certificated and informed values (recovery better than 100 %).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 Sb in the certificated standard. The accuracy were 104.54% and 102.27% 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 antimony in aqueous solution as well as in the igneous rock JGB-1 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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