Determination of Antimonite (Sb(III)) and Antimonate (Sb(V)) Species using Hydride Generator-Quartz Flame Atomic Absorption Spectrophotometry (HG-QFAAS) Techniques

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Abstract

The determination of antimonite (Sb(III)) and antimonate (Sb(V)) species using HG - QFAAS have been done. To increase the sensitivity of the measurements, a gas-liquid reactor - separator integrated into the HG-QFAAS system has been successfully prepared. In fact, this gas-liquid reactor-separator is able to increase the sensitivity of determination of Sb ions in solution. The optimum conditions of parameters measurement in the determination of Sb ion species with HG method are influenced by the type of acids, the acid concentrations, and the reductant concentrations have been determined, and can increase the measurement of analytical performance simultaneously.The result obtained showed that the antimony species provide a good measurement signal. The optimization results showed that the highest absorbance value can be obtained by using 5 M HCl and 1%$NaBH_4$.The analytical performance obtained is very good, which is shown by repeatability level has been shown by it's coefficient of variance was 2,33% for the Sb(III) standard concentration 6 µg.L^{-1} and 4,40 % for the Sb(V) standard concentration 150 µg.L^{-1},linearity of the calibration curve are 2 - 10 µg.L^{-1} for Sb(III) and 50 - 250 µg.L^{-1} for Sb(V), detection limit of 0,26 µg.$L^{-1}$for the Sb(III)and 8,42 µg.L^{-1} for the Sb(V).

Keywords: *Antimony species, hydride generation, antimonite (Sb(III)), antimonate (Sb(V)), HG-QFAAS.*

1. Introduction

Antimony in nature is usually found in the form of stibnite ore (Sb_2S_3) and valentinite (Sb_2O_3). Antimony is used as a catalyst in the production of chlorofluorocarbons (CFCs) and is applied to the paint industry, batteries, rubber, drugs, bullets, pipes, and lighters. Very pure antimony is used to make semiconductor devices such as diodes and infrared detectors, while antimony compounds in stibnite form are used in the cosmetics industry. Antimony and its compounds can be released into the environment in the form of dust, volcanic eruptions, sea water, forest fires, and biogenic sources (Atlanta.G.A., 2010).

Antimony found in nature in several chemical forms as antimonite (Sb(III)) and antimonate (Sb(V)), and Sb were combined with organic compounds and inorganic or colloid (Andreae, 1983). Antimonite (Sb(III)) and antimonate (Sb(V)) is the Sb species normally present in the environment and can be obtained on the plants from soil containing Sb that causes health effects in humans (Wilson, SC., 2010).The antimony toxicity depends on the chemical form that is obtained, in which the element antimony is more toxic than salt and compounds of antimony in the trivalent form is generally more toxic than the pentavalent form (Ida De Gregori, et al., 2007). The allowed maximum content of Sb in drinking water is allowed in China is 5 µg/L, while the WHO establish Sb level in safe drinking water is 20 µg/L (Wang X., 2012). The toxicity and Sb different species migration in the environment that affect the health of the community. To evaluate the toxicity and biogeochemistrySb in the required environmental speciation analysis (Zheng J.,2000).Speciation of antimony and its compound include the determination of antimonite (Sb(III)) and antimonate (Sb(V)) and antimony organic compounds. The speciation has been done by gas chromatography, liquid chromatography and capillary electrophoresis method (B. Michalke, 1999).

Determination by HG-AAS is a sensitive analytical method for the elements As, Bi, Ge, Pb, Sb, Sn, and Te. Because of low interference, more selective, and more sensitive,Hydride Generation (HG) combined with AAS detection has been selected for the determination of elements in the form of hydrides (Kumar, A.R.., 2005).
Several methods of analysis speciation of antimony compounds using various detection techniques have been done before, among others, the analysis of the speciation of Sb(III) and Sb(V) compounds by HG-ICP-OES method (Cabral, et al., 2008), detection of methylantimony compounds by QFAAS (Craig, et al., 1999), analysis of antimony speciation by HG-AFS method (Long deng, et al., 2001).HG-QFAAS detection techniques for antimonite (Sb(III)) and antimonate (Sb(V)) determination has been described in this paper. Theoptimization has been studied include the type and concentrations of acid, and concentrations of reductor ($NaBH_4$).

2. Materials and Methods

The instruments used in this study are: Hydride Generator (HG) and Quartz Flame Atomic Absorption Spectrophotometer (QFAAS) double beam-Avanta GBC®6506.
All chemicals and reagents used in this study are: Potassium antimonyl tartrate trihydrate (Sigma-Aldrich), Potassium hexahydroxoantimonate (V) (Sigma-Aldrich), HCl 37% p.a (Merck), HNO_3 65% (Merck), H_2SO_4 98% (Merck), NaOH, $NaBH_4$p.a (Merck), and aquadest.

Experimental Procedure

2.1Measurement of Sb(III) and Sb(V) ions with HG-QFAAS

The determination of Sb(III) and Sb(V) ions is performed to obtain the optimum HG-QFAAS measurement conditions by varying the various parameters that affect the measurement results such as the concentration and type of acid. In this case the types of acids studied were HCl, HNO_3, and H_2SO_4. Also studied the concentration of HCl and $NaBH_4$.

2.2 Types and Concentrations of Acid

In optimizing the type of acid and concentration, the concentration of $NaBH_4$ is fixed. Concentrations of acidic solutions were made to remain 5 M. The types of acids studied were HCl, HNO_3, and H_2SO_4. From the experiments that have been done, will get the type of acid that provides optimal response. This selected acid was used in subsequent studies by varying the concentration. The acid concentration was varied at concentrations of 1, 2, 3, 4, and 5 M.

2.3 $NaBH_4$ Concentration

After obtaining the optimum type and concentration of acid then varied $NaBH_4$ concentration with both parameters above made fixed. Variation of $NaBH_4$ concentration was 0.1; 0.5; 1; 1.5 and 2.0%.

2.4 Analytical Performance Determination of HG-QFAAS

Various measurements include measurement repeatability, linear range (calibration curve), and measurement detection limits using the optimum conditions obtained. Repeatability is determined by measuring the absorbance of standard solutions of Sb 50 and 100 mg/L repeatedly with the same measurement conditions under the optimum conditions as above. Resonance is represented by% CV (coefficient of variance).Measurements to find the measured linear range of measurements were made by varying the concentrations of standard ion solutions of Sb(III) and Sb(V) ions, where the standard injection volume parameters, concentrations and types of acids, $NaBH_4$ concentrations as well as acid and $NaBH_4$ flow rates were fixed. The concentration variations of Sb(III)are 2, 4, 6, 8, and 10 µg/L and Sb(V) used are 50, 100, 150, 200, and 250 µg/L. From this experiment we will get the equation of regression line for the measurement of Sb(III) and Sb(V) with the concentration of standard series solution. The detection limit is determined by measuring the smallest absorbance pricing that can still be determined and differentiated from the signal given by the blank with multiple measurements. The detection limit is expressed as a standard signal comparison (S) against the blank signal (N) or S / N = 3.

3. Results and Discussion

3.1 Determination Sb Ions with AAS Method

Sb(III) and Sb(V) metal ions can be determined by measuring directly with AAS. In this study, the calibration curves Sb(III) and Sb(V)using water solvent can be seen in Figure 1 and Figure 2.

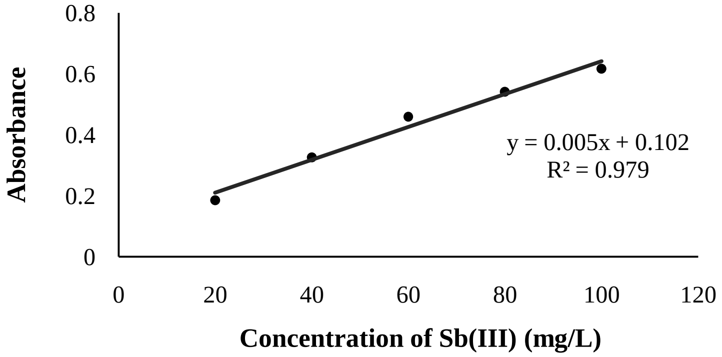

Figure 1: Calibration curve ofSb(III) using water solventwith AAS method

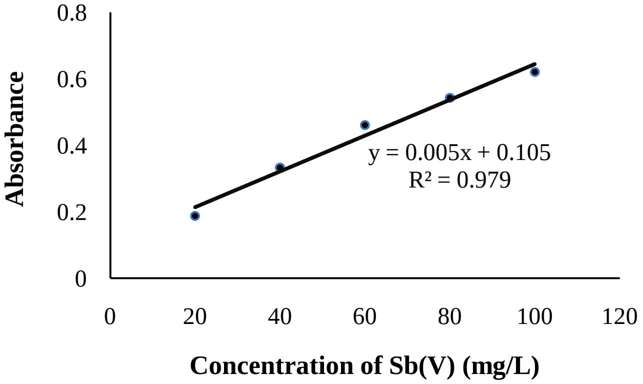

Figure 2: Calibration curve of Sb(V) using water solvent with AAS method

From the result of measurement of calibration curve in Figure 1. and Figure 2. obtained linear range of concentration Sb(III) and Sb(V) are 20 - 100 mg/L, obtained regression equations are :y = 0,0054 x + 0,1024 and y = 0,0054 x + 0.1056 with correlation coefficient (R^2) for Sb(III) = 0.9792 and correlation coefficient (R^2)for Sb(V)= 0.9792. The calibration curves Sb(III) and Sb(V) usingHClsolvent can be seen in Figure 3. and Figure 4.

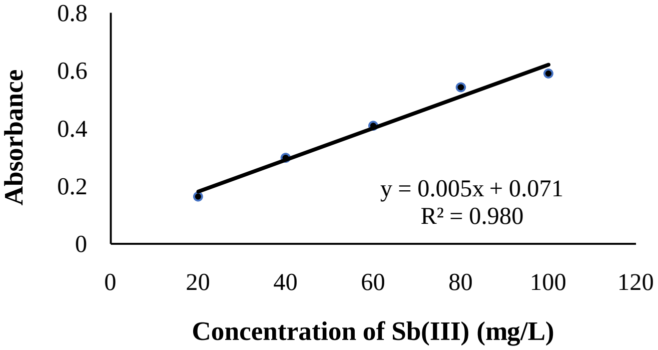

Figure 3: Calibration curve of Sb(III) using HCl solvent with AAS method

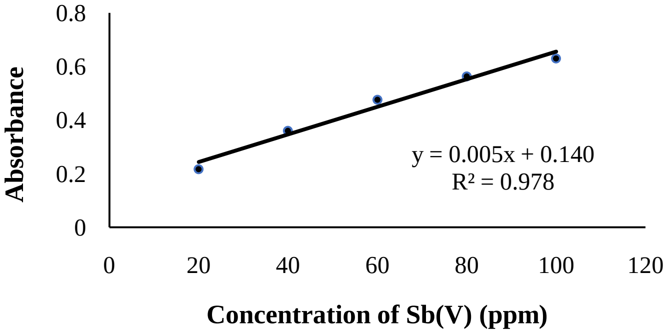

Figure 4: Calibration curve of Sb(V) using HCl solvent with AAS method

From the result of measurement of calibration curve in Figure 3. and Figure 4. obtained linear range of concentration Sb(III) and Sb(V) are 20 - 100 mg/L, obtained regression equations are : y = 0,0055 x + 0,0071 and y = 0,0051 x + 0.1405 with correlation coefficient (R^2) for Sb(III) = 0.9809and correlation coefficient (R^2)for Sb(V) = 0.9784.

From the result of measurement of calibration curve of Sb(III) and Sb(V) ions with AAS directly obtained a small absorption when compared with measurement of Sb calibration curve with HG-QFAAS technique (in Fig. 8 and Fig. 9) the obtained absorption is bigger thus affecting the detection limit and measurement sensitivity.

3.2Optimization Type of Acid with HG-QFAAS Techniques

Sb(III) and Sb(V) ion measurements can be determined by hydride generation(HG) method to increase the detection limit and measurement sensitivity. In this method the Sb ion is first derivatized into a hydride form and subsequently atomized in quartz cells in AAS. The HG-QFAAS techniques in this study is used for the determination of antimony species (Sb(III) and Sb(V)).

The result obtained showed that the antimony species provide a good measurement signal. Measurements were made by varying the three types of acids are HCl, H_2SO_4, and HNO_3 with the same concentration of 5 M to obtain the most optimization type of acid in the hydride formation process. The formed hydride by using HCl, H_2SO_4, and HNO_3 which produces the highest absorbance value can be obtained by using HCl. It can be seen in Figure 5.

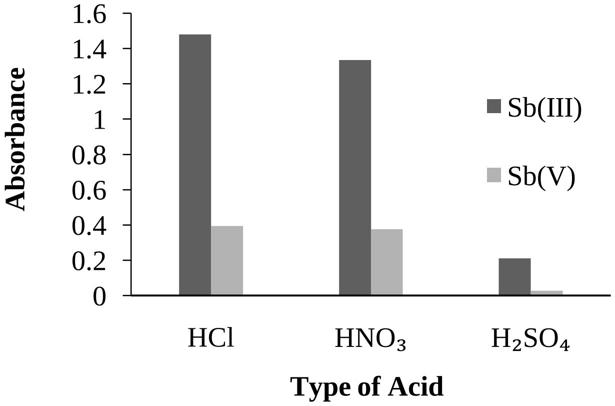

Figure 5: Influence type of acid on the absorption Sb(III) and Sb(V) using HG-QFAAS techniques

According to Figure 5. can be seen that the absorbance of Sb(III) obtained is higher than the absorbance of Sb(V), this is due to the reaction of the formation of hydride Sb(III) to SbH_3 required only 1 reaction stage while the hydride Sb(V) to SbH_3 required 2 stages of reaction so less efficient.

3.3 Optimization of HCl Concentrations with HG-QFAAS Techniques

Based on various of HCl concentration which result the highest absorbance value can be obtained by using 5 M HCl, it can be seen in Figure 6.

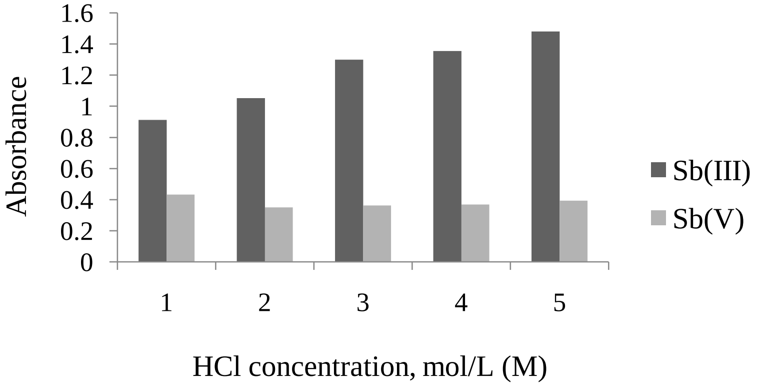

Figure 6:The influence of HCl concentration on the absorption Sb(III) and Sb(V) using HG-QFAAS techniques

From Figure 6. shows that concentrations of HCl below 5 M the formation reaction hydride of Sb is not all Sb ions form SbH_3. In this research, the most optimum absorbance values are obtained at 5 M HCl concentration. This shows that the greater the concentration of HCl, the greater of the absorbance.

3.4Influence of $NaBH_4$ Concentration

Various concentrations of reductor ($NaBH_4$) performed to obtain optimization absorbance value Sb(III) and Sb(V) can be seen in Figure 7.To reduce Sb ions to SbH_3, $NaBH_4$ is used as reductant. This reduction reaction in an acidic condition when the Sb solution has been mixed with the reductant. To determine the effect of $NaBH_4$ concentration, the variation of $NaBH_4$ concentration 0,1% - 2% using the optimum acid and concentration of 5 M HCl can be seen in Figure 7.

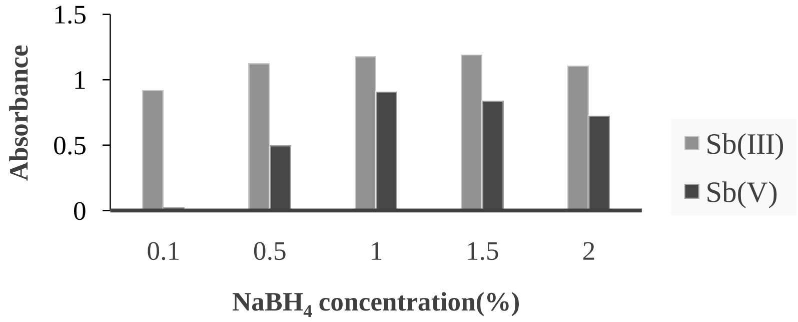

Figure 7: The influence of $NaBH_4$ concentration (%) on the absorption Sb(III) and Sb(V) using HG-QFAAS techniques

From the Figure7. can be seen that the highest absorption Sb(III) and Sb(V) using 1% of $NaBH_4$. This is supported by a calibration curve for Sb(III) and Sb(V) in Figure 7. From Figure 7 can be seen that the optimized absorbance of Sb(III) and Sb(V) were 1% $NaBH_4$ concentration. This is due to the concentration of $NaBH_4$ below 1% absorbance is not maximized.

At higher concentrations of $NaBH_4$ does not increase significantly in absorbance values, but tends to decrease. Because of the higher concentration of $NaBH_4$make the reaction is too fast, so there is a certain amount of water vapor that enters the quartz cell in the AAS can interfere its atomization process. The amount of H_2 is produced more so that dilution can occur in the gas-liquid separator. So for the next use of $NaBH_4$ solution with concentration of 1% as reductant.

3.5Analytical Performance of HG-QFAAS

Based on the optimum conditions obtained on the determination of Sb(III) and Sb(V) by HG-QFAAS technique can be seen in Table 1. Furthermore, it can be determined analytical performance that is determination of repeatability, linearity, and detection limits of measurements.

Table 1: Condition of the optimum parameters of Sb ions measured by HG-QFAAS technique

Parameter measurement	Measurement results
The size of the gas-liquid separator reactor	9,0 x 3,0 cm
Type of acid	HCl
Concentration of acid	5 M
Concentration of $NaBH_4$	1% (NaOH 1%, b/v)

3.5.1 Determination of repeatibility

Repeatability measurements can be determined by the relative standard deviation. The smaller the standard deviation relative is indicated by the better repeatability measurements. Repeatability indicated by % CV (coefficient of variance). From the results obtained repeatability (% CV for Sb(III) = 2,33%; Sb(V) = 4,4%). % CV relatively small shows that this measurement method having high precision and can be used for micro analysis.

3.5.2 Linearity of measurement

Linearity measurements can be shown on a calibration curve Sb(III) and Sb(V) obtained from the regression linear curve that is the correlation coefficient (R^2) which is close to the value 1. Figure 6 shows the area of the linear range of concentration Sb(III) are2 -10 µg.L^{-1} obtained regression equation : y = 0.0625 x + 0.073 with a correlation coefficient (R^2) = 0.9936. While the linear range of concentration Sb(V)are 50-250 µg.L^{-1} obtained regression equation : y = 0.0034 x + 0.0027 with correlation coefficients (R^2) = 0.9942.The measurement calibration curve Sb(III) and Sb(V) can be seen in Figure 8 and Figure 9.

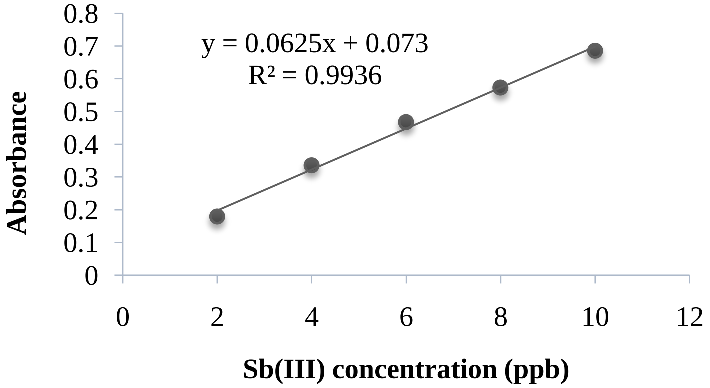

Figure 8: The calibration curve of determination of Sb(III)by HG-QFAAS techniques

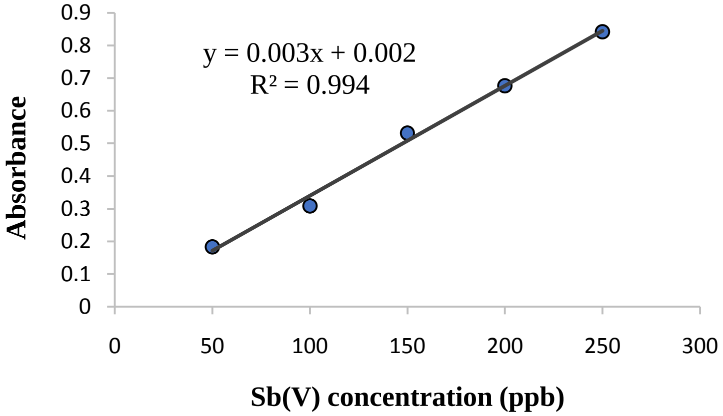

Figure 9: The calibration curve of determination of Sb(V) by HG-QFAAS techniques

From figure 8 and figure 9 it can be seen the linear regression for Sb(III) and Sb(V) obtained are y = 0.0625 x + 0.073 and y = 0.0034 x + 0.0027 which shows the linearity of the measurements.

3.5.3 Detection Limit of Measurement

Detection limits are determined by the smallest absorbance measurements that can still be determined and distinguished from the signals provided by the blank with multiple measurements. This detection limit shows the smallest concentration of analyte that can still be detected. From the experimental results, the detection limit for the determination of Sb(III) with the HG-QFAAS techniques is 0.26 µg.L^{-1}. While the detection limit for determination of Sb(V) by HG-QFAAS techniques is 8.42 µg.L^{-1}.The detection limit indicates the smallest amount of analyte concentration that can be detected. From the results obtained the detection limit for the determination of Sb(III) and Sb(V) with HG-QFAAS techniques were 0.26 µg.L^{-1} and 8.42 µg.L^{-1} respectively.

4. Conclusion

The optimization results for the determination of Sb(III) and Sb(V) with HG-QFAAS techniques showed that the highest absorbance value can be obtained by using 5 M HCl and 1% of $NaBH_4$. A good analytical performance has been obtained as indicated by repeatability (% CV for Sb(III) = 2.33%; Sb(V) = 4.4%), the linearity of the calibration curve (2-10 µg.L^{-1} for Sb(III) and 50-250 µg.L^{-1} for Sb(V)) and limit of detection for Sb(III) and Sb(V) are 0.26 µg.L^{-1} and 8.42 µg.L^{-1} respectively.

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