High concentrations of As and Se in mining wastes covering a large area in the mine operating countries present a threat to public health, environment and ecological diversity in different countries. Therefore, a rapid, cost-effective, affordable and routine analysis is needed to monitor the preliminary contamination levels in these countries. In order to achieve this goal, this study has optimised the flame atomic absorption spectrometry (FAAS) to determine the high concentrations of As and Se using standard samples. The best result of the calibration curve fit ($R^2 = 0.959$) was found for the standard As concentrations of 0, 5.61, 11.22, 16.83 and 22.45 mg/L; and indicated the very strong linearity of calibration. This procedure allowed a rapid determination of As from minimum 4.462 mg/L to higher concentrations without sample pretreatment. Besides As, this method successfully measured Se concentrations from minimum 1.0 mg/L to higher concentrations. The results showed that FAAS can measure lower concentrations of Se than As. Therefore, this method can be widely applied in different countries for determination of As and Se in environmental samples with high concentrations for the rapid, cost-effective and routine analysis, who can not afford the expensive methods such as ICP-MS, ICP-AES, ICP-OES etc. The study finally suggests the implications of the findings to chemical education. [AJCE, 2(3), July 2012]
INTRODUCTION

Due to the high toxicity and carcinogenic activity, arsenic (As) has achieved great notoriety (1) and public health concern. Although selenium (Se) is an essential micronutrient for humans, animals and some plants (2), its safety margin between its nutrient and toxic doses is very narrow; and levels as low as 0.01 mg/L can cause deformation and death of wildfowl. Recommended guideline limits of As are 0.01 mg/L for drinking water, and 50 mg/kg for agricultural soil (3). Extremely high concentrations of As, occasionally Se, up to some hundreds or thousands of mg/kg are found in As-rich sulfidic mining waste derived from As, antimony, gold, tin, tungsten, mercury, base metals, uranium, coal, sulphur and other mining activities, as for example, abandoned Machavie Gold Mine near Potchefstroom, South Africa (4), although its crustal average is only 2 mg/kg (3). And subsequently, it is released from the solids through the various processes of dissolution, redox reactions, and adsorption–desorption, because all of which control its behaviour in the environment (5). Therefore, it is very important to find out a rapid, low cost and appropriate method for routine analysis of As and Se concentration in order to monitor the preliminary contamination levels in mining affected areas.

A large number of analytical techniques are being used to quantify the concentrations of trace metals in different environmental samples. For example, inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectrometry (ICP-AES) or inductively coupled plasma optical emission spectrometry (ICP-OES), flame atomic absorption spectrometry, hydride generation and graphite furnace- atomic absorption spectrometry are widely used for analysis of As, Se and other metals in different types of samples (6). Atomic absorption spectrometry (AAS) is an easily affordable, sensitive, well established and well-known technique for the determination of As, Sb, Se and many other elements using either flame
or hydride generation (HG) or electrothermal atomization (7). The AAS method using flame is rapid, precise and applicable to about 67 elements. However, the sensitivity of this technique is lower with limits of detection (LOD) in the range of mg/L and needs higher amount of samples when compared to hydride generation or electrothermal AAS. Graphite furnace or electrothermal methods of analysis on the other hand are slower and less precise; however, these are more sensitive and need much smaller samples. In AAS, the flame atomiser and furnaces (electrothermal atomiser) that generate a temperature in the range of 1500 to 3000°C are the most common methods of atomisation. Graphite furnace AAS and HGAAS have been widely used for determination of As and Se in different environmental samples including water, soil, sediment, plant, fish, petroleum products, wine, beer, mining wastes, and any other types of inorganic, organometallic and biological samples, because both of these methods are the most sensitive techniques with LOD in the range from μg/L to ng/L (8).

GFAAS offers high selectivity, simplicity, low tolerance to complex matrices, and relatively high cost of equipment for routine analysis (9). By contrast, FAAS offers simplicity, and relatively low cost of equipment for routine analysis (10). Direct analytical techniques are preferred for routine analysis over those that require significant sample preparation; and FAAS is offering the possibility for direct analysis. However, both GFAAS and HGAAS need complex sample preparation, and matrix modification is usually necessary in GFAAS to remove matrix effects (11) for determination of the accurate elemental concentrations in the samples. For the past decade, many studies have been performed in order to understand the behaviour of As, Sb, Bi, Pb, Ag, Cd, Cr, Hg, and Ni in presence of different matrices and modifiers as well (12-14). However, even after several years of development, GFAAS or ETAAS has not been widely applied for the direct determination of above metals and metalloids in different environmental
samples. In the recent years, the interference problems in ETAAS have been reduced by improving the background correction techniques. However, there are still interferences in the determination of As by ETAAS (15).

HGAAS presents very low LOD for these elements in many kinds of matrices, including environmental and biological samples (16). An important advantage is related to the analyte separation from the matrix components, offering considerable suppression of matrix effects. However, this technique is prone to some drawbacks that could occur in the process of generation and release of the hydride, during the transport up to the atomization cell, and in the gas phase during the atomization step (16).

Given the above complexity of sample preparation, removal of interferences, cost and time of measurement, therefore, it is important to develop a suitable and affordable proper method of low cost for fast, accurate and routine analysis of a large number of environmental and mining samples in different countries. In order to determine As in complex residues from gold mining, Pantuzzo et al. (17) optimised the PerkinElmer (Norwalk, Connecticut, USA) model A300 FAAS equipped with a deuterium background correction and a specific As electrodeless discharge lamp. Flame AAS can directly measure the high concentrations of As and Se in microwave assisted acid digest samples, clear solutions, without any further modification. Therefore, the aim of this study was to evaluate the adequacy and appropriateness of FAAS for As and Se analysis in standard samples with very high concentrations. For this optimisation study, TG 990 FAAS equipped with a deuterium background and hollow cathode lamp (HCL) was used.
MATERIALS AND METHODS

Preparation of As and Se standard solution

The standard stock solutions for As(V) (231 mg/L) were prepared in 100 mL calibrated flask by dissolving Na$_2$HAsO$_4$·7H$_2$O in acidic high purity deionized water (0.1% nitric acid). Standard solutions of As(V) were prepared by stepwise dilution of a 231 mg/L standard solution just before use. Diluted working solutions were prepared daily by serial dilutions of this stock solution. Three different As concentration ranges of working standard solutions used in this study were (1) 0, 1.15, 2.31, 4.62 and 9.24 mg/L, (2) 0, 0.558, 2.231, 4.462 and 11.154 mg/L, and (3) 0, 5.61, 11.22, 16.83 and 22.45 mg/L. The standard stock solutions of Se(VI) (100 mg/L) were prepared in 100 mL calibrated flask by dissolving Na$_2$SeO$_4$ in acidic high purity deionized water (0.1% nitric acid). Diluted concentrations of Se(VI) were prepared daily by dilutions of this stock solution just before use. The Se concentrations of working standard solution were 0, 1.04, 3.14, 5.24, 10.48 and 20.97 mg/L.

Instrument and operating conditions for As and Se

Arsenic and Se were measured by FAAS. The operating conditions for As and Se measurement are described in Table 1. The burner parameters and the burner position were optimized daily to have the As and Se HCL radiation at target point.

RESULTS

Measurement of As

The analysis of As standard samples demonstrated that the solutions of concentrations like 4.62 and 9.24 mg/L produced the positive signals with the absorbance of 0.037 and 0.061,
respectively, whereas the As concentrations of 1.15, and 2.31 mg/L did not show any positive signal. The statistical analysis of the results found for all five As concentrations of 0, 1.15, 2.31, 4.62 and 9.24 mg/L presented the calibration curve fit of $R^2 = 0.85$ indicating the poor linearity of calibration. The second set of standard As solutions, as for example, 0, 0.558, 2.23, 4.46 and 11.154 mg/L demonstrated the calibration curve fit of $R^2 = 0.903$ indicating the good linear relationship. The standard As solutions of 0.558, and 2.231 mg/L did not produce any positive signal; however, As concentrations of 4.462 and 11.154 mg/L did strongly. Arsenic standard solutions with concentrations more than 4.462 mg/L produced always good signal, accurate and re-producible results. The calibration curve fit was $R^2 = 0.959$ for the standard As solutions of 0, 5.61, 11.22, 16.83 and 22.45 mg/L indicating the very strong linearity. The As standard solutions of 5.61, 11.22, 16.83 and 22.45 mg/L produced positive signal. Some standard samples of As concentration less than 5.61 mg/L did not produce positive signal indicating that the results of As concentrations less than 5.61 are not accurate and re-producible, but As concentrations more than 5.61 mg/L produced positive signal, and re-producible results.

**Measurement of Se**

For the Se standard solutions of 0, 1.04, 3.14, 5.24, 10.48 and 20.97 mg/L, the calibration curve fit was $R^2 = 0.999$, that indicated the very strong linearity. The Se standard solutions of concentrations such as 1.04, 3.14, 5.24, 10.48 and 20.97 mg/L produced good positive signal. Some standard samples of Se concentration less than 1.0 mg/L produced negative signal indicating that the Se concentrations less than 1.0 mg/L can not be measured by FAAS. However, Se concentrations more than 1.0 mg/L produced positive signal, and re-producible results.
DISCUSSIONS

Although we know that the environmental samples contain high levels of As and Se, but it is essential to determine their concentrations before we perform the remediation activities and waste treatment. Therefore, this method will be beneficial to determine their concentrations in the environmental samples and mining wastes before we perform the remediation activities. The objective and purpose of this study was to develop the analytical method by the optimization of flame atomic absorption spectrometry and determine the high concentrations of arsenic and selenium in the standard samples. Therefore, we did not use this optimized method to the real samples. If this method is used to determine more than 22.45 mg/L As and 20.97 mg/L Se, as for example 100 mg/L or 1000 g/L, then the sample solutions should be diluted according to the operating ranges.

IMPLICATION FOR CHEMISTRY EDUCATION

The finding of this study has practical implications for undergraduate and postgraduate degree, because atomic absorption spectroscopy is a compulsory course in the undergraduate and postgraduate education of Chemistry in general and Analytical Chemistry in particular. Flame atomic absorption spectroscopy is a common course for the laboratory of instrumental analytical chemistry in the university. For Chemistry Education major students in my University, teaching and science come together in a fluid way, with excellence in both areas. Many universities’ chemistry programs encourage the students to be active in research starting in the freshman year. Atomic absorption spectrometry is used in the representative research works of Analytical Chemistry in the university. As a Chemistry teacher in a university, we can use the findings of this study in teaching-learning program, because our optimized method is a rapid, cost-effective,
affordable and routine analysis technique to analyse arsenic and selenium in the environmental samples, food, soil and water. I recommend the chemistry curriculum developers (in a university or others) to incorporate this method in the teaching and instrumental analytical chemistry.

CONCLUSIONS

This procedure allows a rapid determination of As and Se from minimum 4.462 mg/L and 1.0 mg/L, respectively, to higher concentrations without sample pre-treatment and stabilization of the analyte for a sufficiently long period of time between sample preparation and the analysis, minimizing errors due to analyte losses. The results showed that FAAS is more sensitive for Se and can measure lower concentrations of Se than those of As. It is worth mentioning that the use of FAAS for determination of As and Se in the environmental samples, mining wastes, mining contaminated water and soils from different African countries (South Africa, Ghana, Zambia, Zimbabwe, Botswana, Democratic Republic of Congo, etc.) and other countries of the world will greatly reduce the cost and time for routine analyses.

REFERENCES

Table 1. Operational conditions employed in the determination of As and Se by FAAS

<table>
<thead>
<tr>
<th>Parameter</th>
<th>As</th>
<th>Se</th>
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<tbody>
<tr>
<td>Wavelength (nm)</td>
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<td>196.1</td>
</tr>
<tr>
<td>Spectral bandwidth (nm)</td>
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<td>1.0</td>
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<tr>
<td>Lamp</td>
<td>As HCL</td>
<td>Se HCL</td>
</tr>
<tr>
<td>Lamp current</td>
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<td>10 mA</td>
</tr>
<tr>
<td>Oxidant (air) L/min</td>
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</tr>
<tr>
<td>Fuel (acetylene L/min)</td>
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<td>2.2</td>
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<tr>
<td>Signal processing</td>
<td>Peak area (absorbance)</td>
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</tr>
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<td>Replicate</td>
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<td>Background correction mode</td>
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