Interferences study for Selenium determination using of on Liquid Nitrogen Trap Hydride generation atomic absorption Spectrometry

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Abstract:

A method has been developd determine selenium by hydride generation atomic absorption using nitrogen trapping technique. A series of experiments was performed to obtain the optimum condition. The results show that this method has the advantage of being sensitive, accurate, rapid and simple. Transition metal and other hydride forming elements interferences on the determination of selenium was studied. A substantial increase in the range of interference – free determination of selenium can be achieved by increasing the hydrochloride acid concentration .

Keywords: HGAAS, Interferences, selenium, D.L, linear range

Introduction

Selenium is an essential trace element [1,2] . Selenium is not only a nutritional anticancer element but also a strong antioxidant [3,4] . It can suppress the effect of chemical carcinogenic substances . Selenium plays a part in the study of tumours , cancer cardiology , liver diseases [5] , and has received great attention in the medical field [6] .

Many investigation have reported the determination of selenium using fluorimetry , polarography [7,8] , neutron activation , graphite furnace atomic absorption spectrometry [9] and hydride generation atomic absorption spectrometry.

Hydride generation atomic absorption spectrometry is a sensitive and accurate method . It is well known however , a number of transition metals can cause sever signal depression in the hydride generation technique , and selenium is one of the elements that is most affected by these interferences . The cold trap absorption generation technique combined with atomic absorption spectrometry offers the

advantage of high sensitivity , together with reduction of matrix interference .

The adaptation of a preconcentration step to the hydride generation (HG) process has been extensively developed . Preconcentration is still used nowadays to improve sensitivity , pre concentration can be performed at low temperature (mainly using liquid nitrogen) . Very useful information about hydride generation and preconcentration in a cold trap is provided by Dedina [10,11] .

Materials and Methods

Reagents

All chemicals used of analytical reagent grade. "Aristar" acids were used in all cases. Deionized water was used for preparing all solutions.

Glasses were used for preparing standards were usually soaked over night 50% nitric acid , washed and rainsed with distilled water .

The 3% W/V sodium borohydride reductant solution was in 1% W/V NaOH solution was filtered before used on the day of preparation . 1000 μg ml^{-1} selenium (IV) stock standard solution , was prepared from SeO_2 .

The transition metal solution for the interferences test were prepared from cobalt chloride ($CoCl_2$) , copper chloride ($CuCl_2.2H_2O$) and nickel chloride ($NiCl_2.6H_2O$) . All these salts were of analytical reagent grade of high purity.

Apparatus

A perkin Elmer model 360 atomic absorption spectrometry equipped with an electrodeless discharge lamp for selenium were used . A spectral band pass of 0.2 nm was selected to isolate the 196.0 nm line . The atomization is achieved in an air – hydrogen flame using quartz cuvette burner . The system was modified in such away that the selenium hydride formed was swept by the stream of helium carrier gas to the cold trap.

Hydride Generation System

Design of reaction Vessel / Collection of the hydride

The reaction Vessel was made from pyrex glass. The head was blown from 29/42 ground glassjoint, with a 6mm outer diameter tubing for the helium gas inlet and outlet. The reaction cell have aside-arm (6mm o.d. , 2.3 cm long) that ends just below the liquid surface. The helium inlet and tubing was connected to a double obique valve in order to allow the helium flow to by pass the vessel and pass directly through the trap at the heating stage.

Cold trap / Column

The cold trap consist of a 6.0 mm of pyrex U-tube the total length of the U-tube being about 30 cm . The first 8 cm in the

limb of the U-tube adjacent to the reaction vessel, is left unfilled, the rest is packed with a chromatographic packing (15% OV-3 on chromosorb w.Aw-DMCS 60/80 mesh, 5655 p) . About 1m of nichrome wire is wound around the outside of the trap / column and connected to avariable transformer, this permits the trap to beheated at a controlled rate after the removed of the liquid nitrogen bath.

Quarts Cuvtte Burner

The quartez cuvette flame system consists of a quartz glass tube 9 mm inner diameter and 8 cm long, which was mounted in the optical beam of the atomic absorpition spectrometer by a brass bracket. The carrier gas from the trap / column was mixed with air, and the mixture entered the burner cuvette at the centre from the front, hydrogen was introduced from the opposite side of the cuvette.

Result and Discussion

Previous test

Previously studies carried out on the determination of selenium using continuous hydride generation with out preconcentration step. The results obtained with the detection limit = 1.7 ng and the sensitivity of 0.8 ng selenium. As a consequence considered the generation and trapping conditions improve the sensitivity and detection limit.

Analytical Conditions

A large number of operational parameters were involved in this study, an aqueous standard selenium (IV) solution was used during the optimization .

Hydrochloric Acid Concentration

The effect of hydrochloric acid concentration is shown in Fig. 1. The maximum absorbance value was reached on addition of hydrochloric acid up to 0.5 M, after 0.5M concentration the absorbance was stable. It was found that 0.5M hydrochloric acid concentration obtained optimum sensitivity. An acid concentration below 0.5 M gave lower sensitivity and poor reproducibility owing to the incomplete and variable rate of reduction by sodium borohydride.

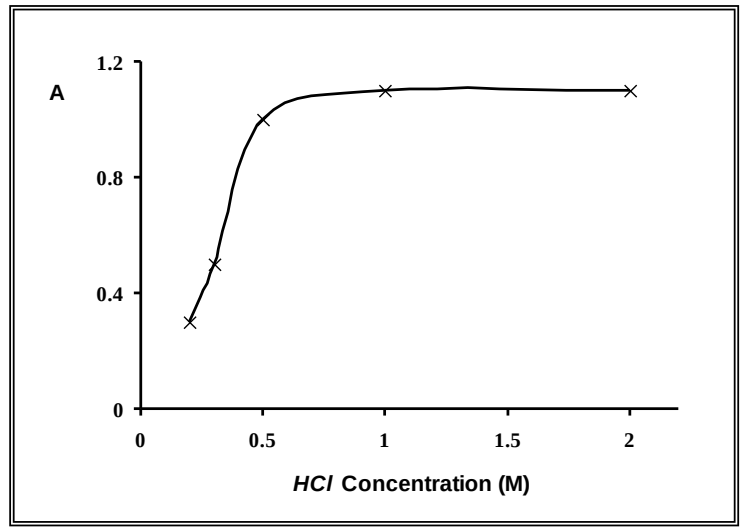

Fig. 1. Relationship between concentrations of hydrochloric acid and absorbance values.

Volume of Sodium Borohydride Solution

The concentration of borohydride reagent was chosen as 3% (w/v) to provide a convenient volume for injection into the reaction solution. The maximum absorbance was found at 2ml of sodium porohydride . The choice of this volume was considered to be a reasonable compromise between sensitivity and economic use of the reagent . Fig. 2.

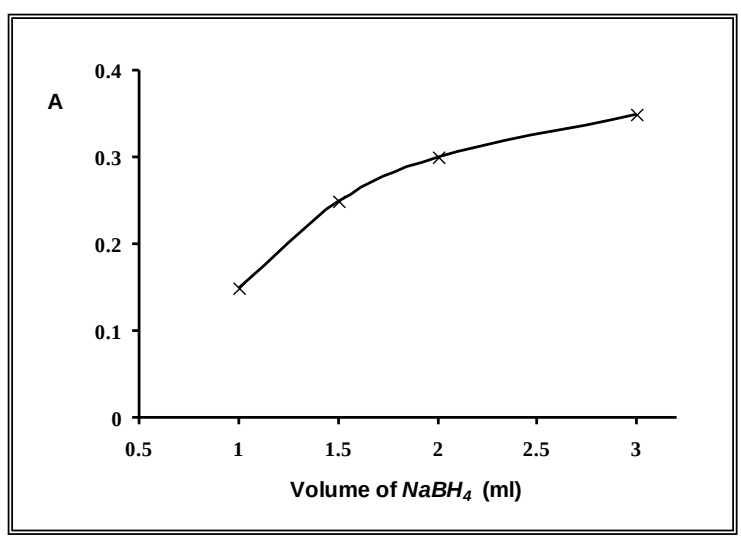

Fig. 2. Choise of amount of sodium borohydride (3% w/v).

Injection Time

The optimum injection time was selected as one minute for aqueous selenium solution. A time of less than one minute is not recommended due to the vigorous reaction which takes place in the reaction cell.

Carrier Gas

Helium was preferred as carrier gas over nitrogen, since it does not condense in the liquid nitrogen cooled trape and a back pressure was observed with nitrogen and argon. The flow of helium was adjusted from 100 ml min^{-1} to 400 ml min^{-1}. A flow of 300 ml min^{-1} was chosen since it gives maximum stable absorbance signal.

Analytical Characteristics

Under the optimum condition found , the analytical characteristics were calculated , the sensitivity defined as the amount of element required to give 1% absorption , detection limit (the concentration corresponding to a signal of twice the standard deviation of the blank signal) , reproducibility (expressed as a Relative standard deviation) and the linear range were calculated . The experimental results are shown in Table 1.

Table (1)
Analytical characteristics

Sensivity	0.2 ng selenium
D.L	0.37 ng
RSD	1.5 %
Linear range	0-200 ng selinum

Interference Analysis

A number of transition metals can cause sever signal depression in selenium hydride generation technique. A pure selenium standard (50 ng) was placed in the reaction cell of the hydride system, and different interfering metal ions concentration of Cu (II) , Co (II) and Ni (II) were added separately . Fig. 3 and Fig. 4 show that the presence of Ni and Co interference had only slightly effect on the selenium signel when present at low concentration .

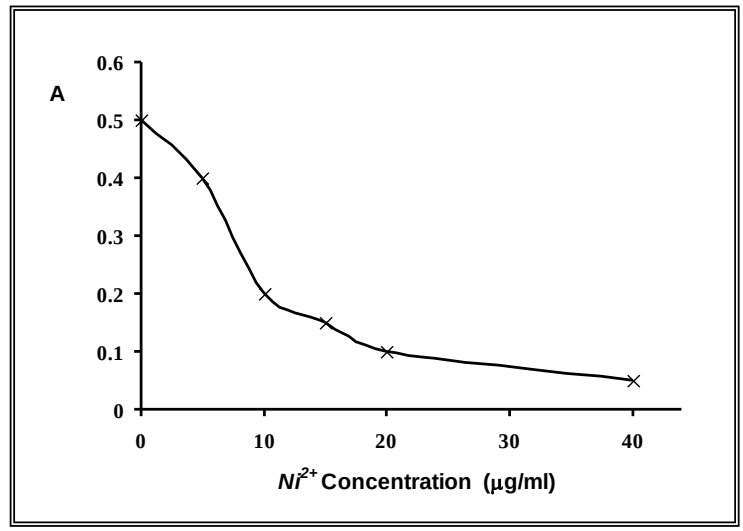

Fig. 3. Influence of nickel on the determination of selenium in 0.5M hydrochloric acid

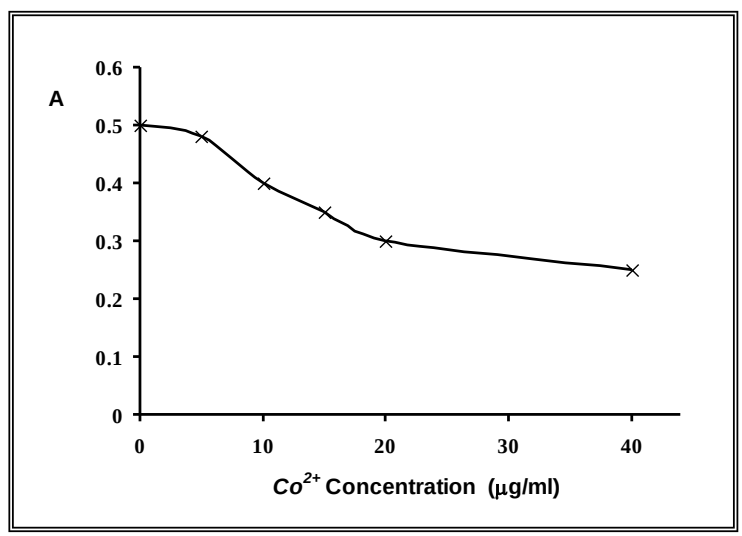

Fig. 4. Influence of cobalt on the determination of selenium in 0.5M hydrochloric acid

The presence of copper (II) cause serious interference, even at 0.5µg ml^{-1} as shown in Fig. 5 .

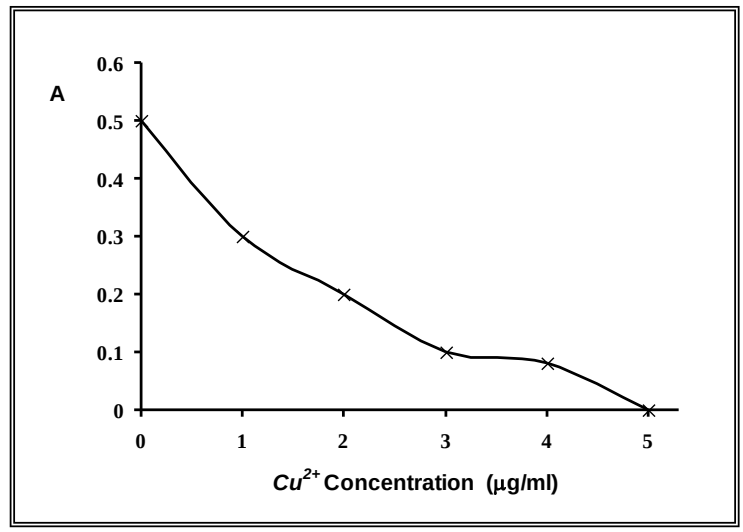

Fig. 5. Influence of copper on the determination of selenium in 0.5M hydrochloric acid

Hydrochloric Acid Effect

The effect of hydrochloric acid concentration on the determination of selenium in the presence of copper , nickel and cobalt were studied . The relation ship between hydrochloric acid concentration and the observed interference from Ni and Cu on selenium was investigated with solution containing 50 ng selenium and 5µg ml^{-1} Cu and 25µg ml^{-1} Ni . Fig. 6 illustrates the effect off hydrochloric acid concentration on the interference of solution containing Cu (II) . It may be noted that the interference of 5µg ml^{-1} Cu on the signal response of 50 ng selenium is virtually eliminated with acid concentration reaching 50% V/V . Fig. 6 shows that the presence of high nickel concentration required an increase in the acid concentration to 50% V/V . The effect of acid on cobalt was not investigated as cobalt did not interfere severely at low concentration levels.

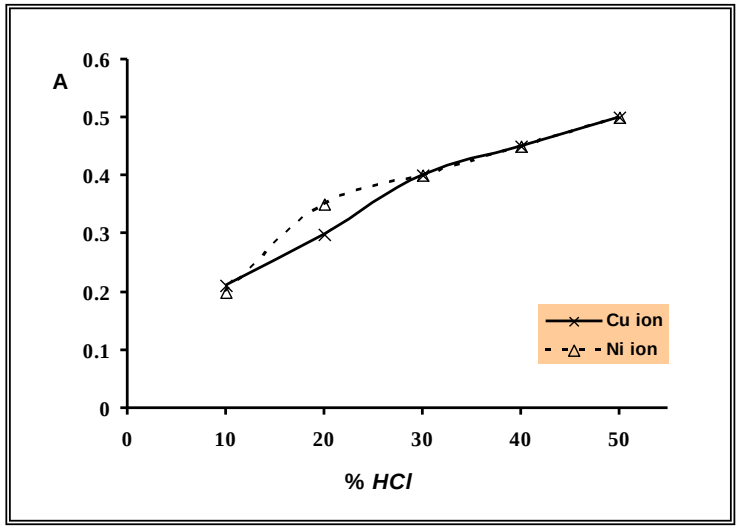

Fig. 6. Effect of HCl on the nickel and copper interferences

Interferences of Various Cations

The following concentration of cations were investigated : 0-1000 µg ml^{-1} Na^{+} and K^{+} . The results showed that there were no interferences of Na^{+} and K^{+} on selenium signal . The concentration of other cations tested included Mg^{2+} (0-100 µg ml^{-1}) , Ca^{2+} (0-200 µg ml^{-1}) . No chemical interferences were observed from the above cations .

Interferences of other Hydride Forming Elements

On the new system had been prepared for the determination of Se , other hydride forming elements , such as Ge , Te , Bi were tested .

Germanium and Tellurium

A complete study using different Ge and Te hydride generation condition from acid media was made . Several tests were made modifying the concentration of HCl (0.5 – 6M) and $NaBH_4$(2.6%) and no signal was found in any case for germanium and tellurium .

Bismuth

It was not possible to determine bismuth using the liquid nitrogen trap because its hydride is very unstable and the preconcentration is not effective [15] .The bismuth hydride signal was obtained just before the liquid nitrogen trap ; The signal disappeared after trapping in the liquid nitrogen trap .

Applications

The method is used to determine serum selenium concentration in normal people (n=5). The average concentration of serum selenium in normal people is 95.5 mgL^{-1} . No matrix interferences was found by standard addition method and the evaluation of selenium concentration can be carried out directly against a calibration curve established with aqueous standard solution.

Conclusion

It has been shown that the investigated metals Cu and Ni start to effect the determination of selenium only at high concentration . The sever interferences reported in the literature are caused by the reaction of gaseous hydrogen selenide with the metallic species that are precipitated in a finely dispersed from by the tetrahydroborate . The most obvious means of increasing the range of interference free determination of selenium is therefore , to prevent reduction and precipitation of the transition metal ions . One way that has been found effective is to increase the acid concentration on the solution for measurement .

A concentration of HCl of 50% v/v appears to be a favourable environment for the determination of selenium in the presence of various interferents .

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