



Determination and interference studies of bismuth by tungsten trap hydride generation atomic absorption spectrometry[☆]

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ABSTRACT

The determination of bismuth requires sufficiently sensitive procedures for detection at the $\mu\text{g L}^{-1}$ level or lower. W-coil was used for on-line trapping of volatile bismuth species using HGAAS (hydride generation atomic absorption spectrometry); atom trapping using a W-coil consists of three steps. Initially BiH_3 gas is formed by hydride generation procedure. The analyte species in vapor form are transported through the W-coil trap held at 289°C where trapping takes place. Following the preconcentration step, the W-coil is heated to 1348°C ; analyte species are released and transported to flame-heated quartz atom cell where the atomic signal is formed. In our study, interferences have been investigated in detail during Bi determination by hydride generation, both with and without trap in the same HGAAS system. Interferent/analyte (mass/mass) ratio was kept at 1, 10 and 100. Experiments were designed for carrier solutions having 1.0 M HNO_3 . Interferents such as Fe, Mn, Zn, Ni, Cu, As, Se, Cd, Pb, Au, Na, Mg, Ca, chloride, sulfate and phosphate were examined. The calibration plot for an 8.0 mL sampling volume was linear between $0.10 \mu\text{g L}^{-1}$ and $10.0 \mu\text{g L}^{-1}$ of Bi. The detection limit (3 s/m) was 25 ng L^{-1} . The enhancement factor for the characteristic concentration (C_0) was found to be 21 when compared with the regular system without trap, by using peak height values. The validation of the procedure was performed by the analysis of the certified water reference material and the result was found to be in good agreement with the certified values at the 95% confidence level.

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1. Introduction

It is known that bismuth (Bi) has been used for different medical purposes. For instance, some of its compounds have been added to pharmaceutical samples for the treatment of gastritis and peptic ulcer [1]. It was also reported that though Bi is not essential element for human being, nearly 5–20 μg of this element is taken with food in general population [2]. Indeed, due to its potential for inducing metallothionein expression, this element has some effect on reducing tissue toxicity after cisplatin cancer therapy [3].

For the determination of Bi in different matrices, many analytical techniques have been applied. For example, atomic absorption

spectrometry (AAS), electro thermal atomic absorption spectrometry (ETAAS), inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) in different matrices [4–6]. Even though AAS has been presented in many analytical laboratories, sensitivity of this technique is not enough for the trace level. Thus, ETAAS has been largely used for trace levels. However, elimination of matrix causing interferences to improve the lifetime of graphite tubes is the requirement [4]. Although ICP-MS has very low detection limits, this instrument is not commonly used for Bi determination due to its high cost. Hydride generation atomic absorption spectrometry (HGAAS) is undoubtedly one of the most sensitive and convenient analytical techniques for the determination of bismuth because of its appropriate sensitivity. Therefore, this technique is ideally suited for the trace and ultratrace analysis of Bi. In addition, in the literature, the detection limits for Bi have varied from one technique to other. For instance, the detection limit was found as 0.02 ng mL^{-1} determination of Bi in tap water and biological samples such as urine and hair by ETAAS after preconcentration by the

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cloud point extraction technique [7]. By using ICPOES system with a continuous-flow hydride generation technique (HG-ICP) detection limit was found to be 0.7 ng mL^{-1} [8]. Although it is expected that ICP-MS has very low detection limit, this value was found to be 9.7 ng mL^{-1} for Bi in serum and urine by direct injection nebulization inductively coupled plasma mass spectrometry [9].

In order to improve sensitivity in Bi determination, different sorts of traps have been applied. W-coil was used for on-line trapping of volatile bismuth species using HGAAS; a limit of detection of 2.7 ng L^{-1} was obtained [10]. Quartz was also used as an atom trap with a detection limit of 3.9 ng L^{-1} [11].

In the analytical chemistry, elimination of any possible interferences during measurement step is very crucial in order to obtain accurate results. Although Dedina and Tsalev have explained the basic mechanism of interferences, number of studies in this field is not high [12]. Recently, interference effects of some elements were studied for hydride generation system [13,14]. According to Dedina and Tsalev, interferences can be categorized not only as spectral and non-spectral interferences but also as liquid phase and gas phase interferences occurring during either in transportation or in the atomizer. It is expected that most of the liquid phase interferences can be eliminated using W-coil trap HGAAS system due to elimination of these type interferences prior to atom cell. In the literature, there have been so many studies related with the effects of different kinds of interferences on Bi determination using hydride generation technique.

The objective of the present study was not only to find and develop a sensitive method but also decide whether the tungsten trap has any advantages for the elimination of different interferences on Bi signal or not. Interferences have been investigated in detail during Bi determination by hydride generation in both with and without W-coil trap in the same HGAAS system.

2. Experimental

2.1. Instrumentation

An ATI Unicam 929 atomic absorption spectrometer equipped with a deuterium background correction system was used. A Philips data coded hollow cathode lamp was operated at 12.0 mA; the analytical line at 223.1 nm was used in the measurements with 0.5 nm as the spectral bandwidth. Quartz T-tube atomizer (QTA) heated by a stoichiometric air/acetylene flame was used as atomizer. QTA consisted of a horizontal arm with dimensions of 140 mm in length, 15 mm in od and 12.8 mm in id; inlet arm was 90 mm in length, 7 mm in od and 4.5 mm in id. Another smaller quartz tube was inserted and fixed in the inlet arm with dimensions of 4.0 mm in od and 2.0 mm in id; it extended between the open end of the inlet arm and a point that was 5.0 mm away from the W-coil; analyte vapor was transported through this inner tube. Hydride generation for both conventional and trap systems was carried out in continuous-flow (CF) mode using a Gilson Minipuls 3 (Villers le Bell, France) 4-channel peristaltic pump. Tygon peristaltic pump tubing of 0.8 mm id (Ismatec, Germany) was used for pumping the analyte and reductant solutions that are mixed in a 3-way PTFE connector (Cole Parmer Instrument Co., USA). For the separation of Bi hydride from the liquid phase, a laboratory-made cylindrical gas-liquid separator (GLS) was employed. Tygon tubing of length of 4.0 cm and 6.0 mm id (Masterflex, Cole Parmer Instrument Co.) was used between the GLS and the inlet arm of the silica T-tube atomizer. The composition of the gas mixture was the same for both conventional HGAAS and collection stage on W-coil trap. A mixture of H_2 and Ar was used in both conventional HGAAS and W-coil trap studies. The flow rates of these gases were measured by two separate flow meters (Cole Parmer Instrument Co., USA).

The W-coil used for trapping was obtained from a 15 V, 150 W projector bulb (Halogen Photo optic Lamp Xenophot, Osram, Germany) and placed in the inlet arm of a silica T-tube, 5.0 cm away from the connection point to the horizontal arm. The experimental set-up for hydride generation and trap was reported previously [15] except for the fact that the way W-coil was inserted into the inlet arm. In this study, a laboratory-made quartz female joint was attached to the inlet arm. The W-coil with its socket base was fixed inside the male portion of the glass joint; in order to assure immobilization of the set-up, ordinary silicone type glue was used. This configuration allows a very rapid and convenient change of W-coil trap when needed. The W-coil was positioned so that its longer axis was perpendicular to the gas flow that is reaching to it through the smaller quartz tube in the inlet arm. The coil temperature was manually controlled by a variable potential power supply (Variac) and a 750 W transformer connected to mains electricity (220 V ac) through a power switch. The input voltage of the variable potential power supply was 220 V. The temperature measurements were carried out with a Ni-Cr thermocouple.

2.2. Reagents

All reagents used throughout the study were at least analytical reagent grade. The standard solutions of Bi were prepared by making necessary dilutions from 1000 mg L^{-1} Bi (Aldrich) of stock standard solution. In order to obtain the optimum acidification of reagents, appropriate amount of analytical grade 65% (w/w) HNO_3 (Merck) was used. Reductant solutions were prepared daily from the powder sodium tetrahydroborate (III) (Merck, min. Purity 98%). For the stabilization of the NaBH_4 solution, NaOH (Carlo Erba, Milano, Italy) was used. Dilutions were made using $18 \text{ M}\Omega \text{ cm}$ deionised water obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA).

2.3. Procedure

The experiments were carried out in continuous-flow (CF) mode in both the conventional HGAAS and the W-coil trap-HGAAS studies. The HNO_3 and NaBH_4 concentrations were optimized in conventional HGAAS studies by using a 20.0 ng mL^{-1} of Bi solution containing 1.0 mol L^{-1} HNO_3 . Blank was 1.0 mol L^{-1} HNO_3 solution. The reductant and analyte solutions were pumped at the flow rates of 8.0 mL min^{-1} which were optimised by both reductant and analyte solutions. The optimizations were made in several cycles until the results obtained did not differ from the last optimized value. During any optimization as the value of the parameter in question was varied, all the other parameters were in their optimized values. The generated Bi hydride was separated from the liquid phase by the GLS and was transferred to QTA through a Tygon tubing using a carrier gas mixture composed of H_2 and Ar at flow rates of 37.5 mL min^{-1} and 75 mL min^{-1} , respectively.

In trap experiments, initially the carrier gas mixture was sent through the system. Then, the trap was brought to its optimum collection temperature and the pumps were activated to start the flow of carrier and reductant solutions. The transferred bismuth hydride was trapped on the W-coil atom trap placed in the inlet arm of quartz T-tube explained in Section 2.1. At the end of the collection period, the power to heat the trap was discontinued and the pumps were deactivated. Under optimum gas flow, the trap temperature was brought to the optimum value for volatilization and the residence time of the 0.1 ng L^{-1} for Bi on the light path is very short and transient signal is obtained in less than 1.0 s shown in Fig. 1.

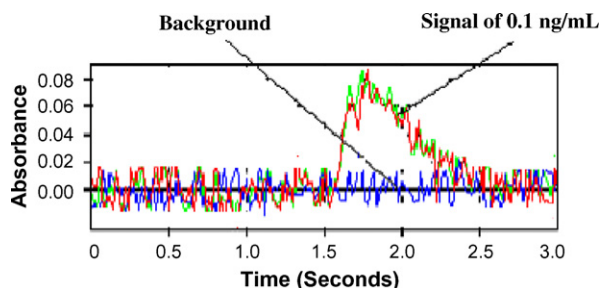


Fig. 1. The analytical signal obtained by the W-trap HGAAS method for 0.1 ng mL⁻¹ Bi.

3. Results

3.1. W-coil system

For the Bi determination, resistively heated W-coil was used as a trap medium in this study. Each coil can be used for at least 100 firings under optimum parameters. H₂ flow in the system directly affects the firing amount. If W-coil trap is not changed, sensitivity of system is around 25% decreased because of oxidation of W-coil. If the flow rate of the H₂ is lower than 37.5 mL min⁻¹ in collection and revolatilization step, the lifetime of W-coil becomes shorter. The presence of H₂ gas is necessary for both affecting a more efficient revolatilization and protecting the W-coil against oxidation. The coil should be heated as fast as possible at the revolatilization stage to obtain relatively sharp signals. For this purpose, a power switch was connected in front of the variable potential power supply and then the switch was turned on to assure the highest heating rate. Although the chemical nature of the revolatilized analyte species is not known, heating of quartz T-tube atomizer was necessary.

3.2. Optimization of system

The optimization of the experimental parameters was carried out using both CF-HGAAS and W-coil trap HGAAS. In the optimization studies, one parameter was varied while the others were kept constant. Optimization cycles were repeated until stable and repeatable signal was obtained. Optimizations of reaction and stripping coil lengths, concentrations of carrier and reductant solutions were common in both CF-HGAAS and W-coil trap HGAAS systems. The optimum HNO₃ and NaBH₄ concentrations were determined in no-trap studies in CF mode by using 20.0 ng mL⁻¹ Bi as a standard solution.

3.2.1. Optimization of lengths of reaction and stripping coils

Reaction coil consists of the tubing between the merging point of sample and reductant solutions and the point where Ar and H₂ are introduced as the purge gases; as the continuation of the flow system, stripping coil is the tubing between the Ar/H₂ introduction point and the GLS. In the optimization study, length of reaction coil was varied between 5 cm and 30 cm while length of stripping coil was changed between 2 cm and 30 cm. The optimum lengths for reaction coil and stripping coils were found to be 10 cm and 4 cm, respectively. The analyte signal decreased with the values both lower and higher than the optimum values.

3.2.2. Optimization of concentration of reductant solution

For the production of Bi hydride species, NaBH₄ was used as a reductant solution. The effect of NaBH₄ concentration on BiH₃ production was investigated by using continuous flow. In order to find the optimum NaBH₄ concentration in the reductant solution, concentration was varied between 0.1% and 1.2% (w/v); 0.5% (w/v) NaBH₄ was found as the optimum reductant solution using

the changes in the peak height of the analytical signal with respect to reductant concentration for no-trap studies. In this optimization, it was observed that the signal increased up to a concentration of 0.5% (w/v) and decreased for higher values. The decrease can be explained by the dilution effect, since more H₂ was generated at higher concentrations of reductant.

In addition, NaOH was used for the stabilization of NaBH₄. Concentration of NaOH was varied between 0.1% and 0.5% (w/v). Concentration of NaOH was optimized in no-trap studies and then checked also in W-trap HGAAS system. It was found that concentration of NaOH has a significant effect on the analytical signal of bismuth. The highest signal for bismuth was obtained using the reductant solution containing 0.2% (w/v) of NaOH while the other parameters were kept at their optimum found values.

3.2.3. Optimization of concentration of carrier solution

In this study, HNO₃ was used as carrier solution. In order to find the optimum HNO₃ concentration, HNO₃ concentration in the analyte solution was varied between 0.5 mol L⁻¹ and 3.0 mol L⁻¹. The optimum value for HNO₃ was found as 1.0 mol L⁻¹, somewhat in the middle of the plateau. Higher and lower values resulted in a gradual decrease in the peak height of the analytical signal. When the concentration of HNO₃ in either solution exceeds 1.0 mol L⁻¹, decreases in signals were investigated. The effect of sample acidity was also checked in W-coil trap HGAAS system and found to be as same as in no-trap system.

3.2.4. Optimization of flow rates and composition of gases in the collection and revolatilization stages

In the hydride generation system, different carrier gases introduced before the stripping coil are used to separate the volatile species from the liquid phase and furthermore transport these species from GLS to externally heated quartz T-tube atomizer. In this study, a mixture of Ar and H₂ was applied not only in the collection but also in the revolatilization steps. In general, the flow rate of H₂ was kept constant at an optimized value where the oxidation of the W-coil trap was minimized or eliminated. Here, H₂ was used not only to prevent oxidation of the W-coil by creating a reducing environment around the W-coil but also to improve the revolatilization efficiency of Bi species from the W-coil trap. If flow rate of H₂ higher than optimized value, excess H₂ causes temperature decrease around the coil that affects sensitivity.

In the optimum collection and revolatilization steps, Ar flow rates were determined in CF mode in both without and with trap studies. Ar and H₂ flow rate were kept constant at 75 mL min⁻¹ and 37.5 mL min⁻¹ for both steps; and found that lower H₂ flow rates caused oxidation of the W-coil, which resulted in relatively higher background absorption.

The flow rate of Ar was varied between 50 mL min⁻¹ and 400 mL min⁻¹ during the optimization. The optimum value was found to be 75 mL min⁻¹; signal decreased for lower and higher values. Also the flow rate of H₂ was varied between 10 mL min⁻¹ and 150 mL min⁻¹ during the optimization. The optimum value was found to be 37.5 mL min⁻¹; signal decreased for lower and higher values.

3.2.5. Optimization of flow rates of carrier and reductant solution

The efficiency of the production of Bi hydride species is directly related with the flow rates of carrier and reductant solutions. In this study, the flow rate of HNO₃ that was used as the carrier solution was varied between 1.0 mL min⁻¹ and 10.0 mL min⁻¹ and the optimum value was found to be 8.0 mL min⁻¹. The signal increased as the flow rate was increased until the value of 8.0 mL min⁻¹ is reached and stayed constant afterwards. The flow rate of NaBH₄ solution was varied between 1.0 mL min⁻¹ and 10.0 mL min⁻¹; the optimum result was found as 8.0 mL min⁻¹. For the higher and

lower flow rates of NaBH₄, the peak height of Bi signal sharply decreased.

Optimization of concentrations and flow rates for HNO₃ and reductant solutions were carried out by keeping all parameters constant while only the test parameter was varied.

In this study, also the suction rate of the waste rate optimization was carried. The suction rate of the waste affected the Bi signal. If the suction rate of the waste was increased, Bi signal was decreased. In this study, suction rate of the waste was selected as 6 mL min⁻¹. As an example, if suction rate of the waste is selected 15 mL min⁻¹ instead of 6 mL min⁻¹, signal intensity is decreased around 28%. Therefore, the waste rate must be minimum. If the suction rate is very low, waste could have gone to the atomizer. To the best of our knowledge, waste rate optimization is the first study in the literature.

3.2.6. Optimization of collection and revolatilization trap temperatures

In order to obtain a high trapping efficiency, W-coil atom trap temperature should be carefully optimized. In this study, collection trap temperature was varied from 100 °C to 540 °C. The trapping efficiency of W-coil increases sharply as the temperature increases up to approximately 289 °C. Increasing the trapping temperature resulted in a decrease in the analytical signal due to the partial release of the trapped Bi species and lowered trapping efficiency. Hence, 289 °C was found as the optimum trap temperature for efficient preconcentration of Bi species on W-coil trap. Revolatilization trap temperature was varied from 750 °C to 1500 °C while the collection temperature was kept constant at its optimized value. The optimum temperature for revolatilization was 1348 °C at which the highest signal was obtained. There is no need for waiting to cool the W-coil atom trap after revolatilization step or heat for the activation of W-coil before each collection cycle because the trap cools down very rapidly in only few seconds due to the continued gas flow. In order to protect the W-coil trap, hydrogen flow should be on throughout the experiment.

3.3. Analytical figures of merit

3.3.1. Calibration plots and linearity

Calibration plots with and without using W-coil trap were constructed. The linear portion of calibration without trap included Bi concentrations of 2.0–100 ng mL⁻¹ using peak height values. In this linear range, linearity equation was found as $y = 0.0105x + 0.0263$ and correlation coefficient (R^2) was found as 0.9977; y is absorbance value for CF mode and x is concentration in ng mL⁻¹. In the W-coil trap studies, linear range included Bi concentrations of 0.1–10.0 ng mL⁻¹; best line equation was found to be $y = 0.2603x + 0.0376$ and correlation coefficient (R^2) was found as 0.9997; y is absorbance for peak height measurement and x is concentration in ng mL⁻¹. When the slope of calibration curve in trap studies is divided to that of the without trap studies, preconcentration factor was found to be 24.8.

3.3.2. LOD, LOQ and C₀

Three and ten times the standard deviation of blank values were used in the LOD and LOQ calculations, respectively. In W-coil trap studies, 1.0 min collection period was applied for the LOD and LOQ calculations. LOD values in W-coil trap and no-trap study are 25 ng L⁻¹ and 470 ng L⁻¹, respectively. The enhancement factor in the limit of detection found to be 19 when compared to conventional CF-HGAAS. In calculations of characteristic concentration, C₀, for W-coil trap and no-trap studies, 15.9 ng L⁻¹ of Bi and 336 ng L⁻¹ Bi were used, respectively. Peak height values were used in all calculations. Analytical figures of merit mentioned above are shown

Table 1

Analytical figure of merit and enhancement factors for Bi calculated by using peak height of analytical signal without trap and with trap medium.

	With trap	Without trap
LOD (ng L ⁻¹)	25	470
C ₀ (ng L ⁻¹)	15.9	336
% RSD	5.2	9.21

in Table 1. Using C₀ values, an enhancement factor of 21 is found for the present conditions.

The accuracy of the method was tested using the certified reference material (CRM) Trace metals in Drinking Water (Cat. No. CRM-TMDW Lot # 818921) supplied by High Purity Standards (Charleston, SC, USA) and containing 10 ng mL⁻¹ Bi. Analysis of CRM was carried out by diluting 1.0 mL of the CRM to 100 mL with 1.0 mol L⁻¹ HCl, resulting in a solution of 0.100 ng mL⁻¹ Bi. The result ($n = 3$ for each analysis) was 10.2 ± 1.3 ng mL⁻¹ Bi and the result is in good agreement with the certified value.

3.4. Interference studies

Two classes of interferences are observed in AAS that is spectral and non-spectral. Spectral interferences are owing to radiation absorbed by species rather than free atoms of the analyte. Non-spectral interferences are due to influence of sample constituents on the analyte signal. Owing to the separation of analyte from the matrix, spectral interferences in hydride generation AAS are much less serious than for liquid sampling AAS. Line interferences do not occur at all; nonselective background absorption can be observed when a significant amount of species transported to the atomizer from a hydride generator. This may typically happen in the presence of an excess of other hydride forming elements in sample matrix or in the case of hydride generation from non-aqueous media [12].

Recently, interference effects of some elements were studied for hydride generation system. In our study, interferences have been investigated in detail during Bi determination by hydride generation, both with and without trap in the same HGAAS system. It is known that since W-coil trap system is capable of having better sensitivity and diluted interferences are less effective. Interferent/analyte (mass/mass) ratio was kept at 1, 10 and 100. Experiments were designed for carrier solutions having 1.0 M HNO₃. Interferents such as Fe, Mn, Zn, Ni, Cu, As, Se, Cd, Pb, Au, Na, Mg, Ca, chloride, sulfate and phosphate were examined in this study.

In the preliminary of the interference studies, a concentration level was used to be the same for both systems that are with and without trap, thus 20 ng mL⁻¹ was chosen for analyte concentrations. And also in trap studies, collection time was selected as 6 s to reach same absorbance value with no-trap studies. Interferent/analyte (mass/mass) ratio was kept as 1, 10 and 100, respectively. Experiments were designed for carrier solutions having 1.0 M HNO₃. In this circumstance, Mn and Cu which are called as transition elements, As, Cd and Pb which are called as hydride forming elements and Au show severe interferences in both cases. Besides this study, Bi concentration was changed as 0.4 ng mL⁻¹ and collection time was selected as 300 s in order to keep total amount of Bi constant with 20 ng mL⁻¹ Bi where collection time was selected as 6 s in trap studies. When this solution was used, interference effects of Mn, Cu, As, Cd, Pb and Au were obviously decreased by using W-coil trap study as shown in Figs. 3, 5 and 7, respectively. This shows that if the analyte solution is diluted, interference effects of these elements on Bi signal are decreased.

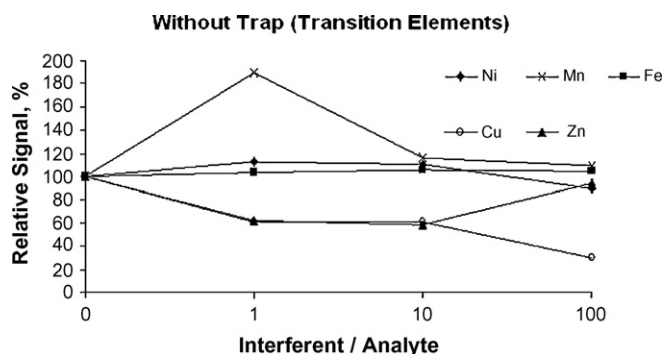


Fig. 2. Relative signal of Bi in different transition metals medium by without trap studies.

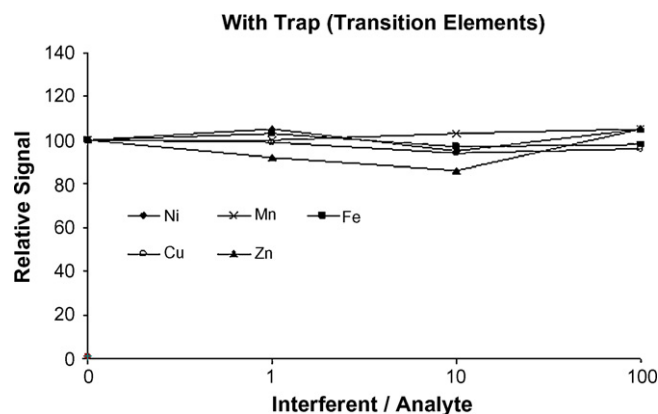


Fig. 3. Relative signal of Bi in different transition metals medium by trap studies (Bi concentration: 0.4 ng mL⁻¹ and collection time: 300 s).

4. Discussion

Optimization of the systems was carried out by keeping all parameters constant while only the test parameter was varied. The analyte signal decreased with the values both lower and higher than the optimum values.

The analytical signal obtained by W-coil trap HGAAS under optimum conditions was very sharp. The residence time of the 0.1 ng mL⁻¹ for Bi on the light path is very short and transient signal is obtained 0.1 ng mL⁻¹ for Bi in less than 1.0 s shown in Fig. 1. The shape and base width of the analytical signal depend on the heating rate of the coil and also the carrier gas flow rates. If higher collection temperatures were used, the quartz around W-coil trap reaches to temperatures at which volatile Bi species are partially trapped on this surface. At the releasing stage, these trapped species revolatilized gradually as quartz surrounding the W-coil trap is being heated relatively slow compared to the W-coil trap. Under these conditions, a tailing is observed in the analytical signal. In addition, since there is a temperature gradient between the trap and the atomizer due to the heating effect of flame, some of the volatile Bi species are trapped on the inner surface of quartz inlet arm between trap and the atomizer. Regardless of the collection temperature, if a higher releasing temperature, which is sufficient for revolatilization of Bi species trapped on quartz surface, the analytical signal tails due to gradually revolatilization of Bi species from quartz surface between trap and the atomizer. Deviations from the optimized collection and release cycles may cause degraded repeatability due to undesired trapping and releasing effects. Under optimum conditions, where optimum collection and revolatilization temperatures were not exceeded, only a single sharp peak created by volatile Bi trapped on W-coil trap is achieved. The precision of the measurements based on the peak height of the analytical signal has an RSD of 5.2%, which is obtained by replicate measurements of reagent blanks for a collection volume of 8.0 mL corresponding to 1.0 min collection.

Effects of some transition elements on Bi determination using both without trap and W-coil trap studies can be seen in Figs. 2 and 3, respectively. As seen, Mn and Cu show severe interference in without trap experiment. It is well known that Cu is an interferent in HGAAS determination of Bi. During the determination of Bi in geological reference samples, the Cu/Bi mass ratio was only 3 and no interference was observed. Elsewhere, a signal reduction of 77% and 100% signal reductions was reported for Cu/Bi mass ratio values of 20 and 200, respectively [10]. Trap system has lower interference effect in cases Fe and Zn. In these interference studies, the concentration of the Bi analyte was selected as 20.0 ng mL⁻¹ in without trap experiments and in with trap experiment Bi concentration was selected as 0.4 ng mL⁻¹, collection time was 300 s. When 0.4 ng mL⁻¹ was used, interference effects of Mn, Fe, Cu, Zn and Ni were obviously decreased using W-trap studies as seen in

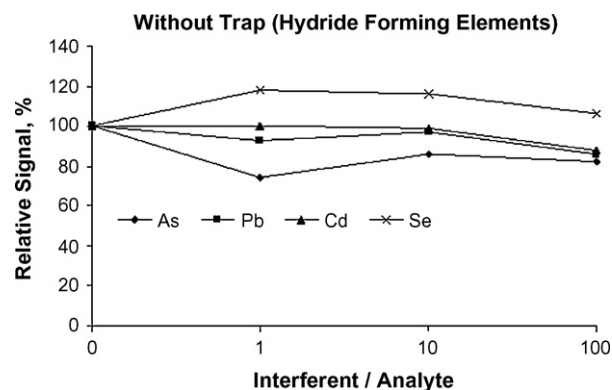


Fig. 4. Relative signal of Bi in hydride forming elements medium by without trap studies.

Fig. 3. This shows that if the analyte solution is diluted, interference effect of the elements on Bi signal is decreased.

Effects of some hydride forming elements on Bi determination using both without trap and W-coil trap studies shown in Figs. 4 and 5, respectively. Hydride forming elements may be in gas phase interferents and liquid phase interferents. In the liquid phase interferences, due to compound and matrix interferences, signal may be decreased. If these types of interferences occurred, using trap, these effects could not be eliminated because interfering effects of liquid phase interferents are finished before the trap medium. So, trap is not a way to minimize effects of liquid phase interferents. On the other hand, when 0.4 ng mL⁻¹ Bi concentration

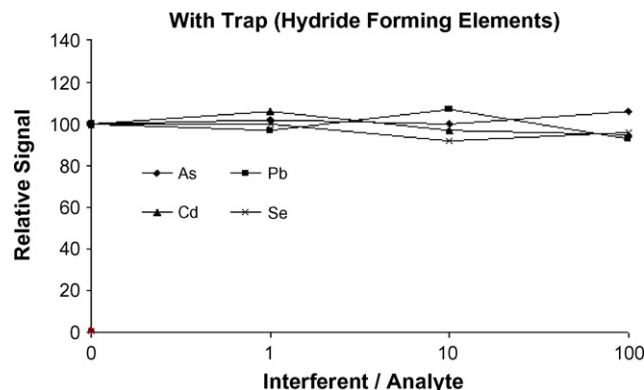


Fig. 5. Relative signal of Bi in hydride forming elements medium by trap studies (Bi concentration: 0.4 ng mL⁻¹ and collection time: 300 s).

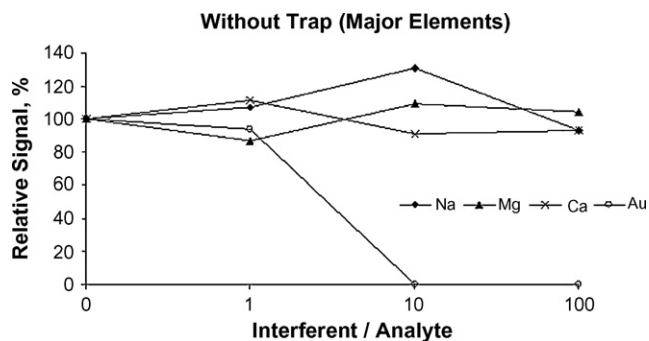


Fig. 6. Relative signal of Bi in major elements medium by without trap studies.

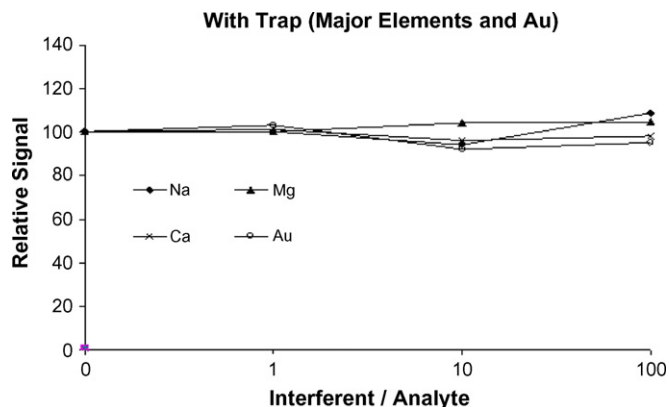


Fig. 7. Relative signal of Bi in major elements medium by trap studies (Bi concentration: 0.4 ng mL^{-1} and collection time: 300 s).

was used, interference effect of As was reduced owing to dilution effect as shown in Fig. 5.

Figs. 6 and 7 show the effect of major elements on Bi determination using both without trap and W-coil trap studies. It can be seen from Fig. 6, Au shows very high interferent effect on Bi signal especially interferent/analyte concentration is 10 and 100 in without trap study. On the other hand, when the Bi concentration was changed from 20 ng mL^{-1} to 0.4 ng mL^{-1} in trap study, interference effect of the Au on Bi signal was reduced using W-coil trap due to dilution effect as shown in Fig. 7.

And also, the interference effect of the some anions on the Bi signal in both without trap and W-coil trap were studied. By using W-coil trap, interference effect of the PO_4^{3-} , SO_4^{2-} and Cl^- was reduced. Therefore interference effect of these anions is in gas phase.

Besides, for the decreasing of the interference effect of the some elements on the Bi signal, analyte concentration was diluted but total amount of the analyte was not changed. By doing this, interference effect of the elements on the Bi signal was decreased very well. This shows that trap has two advantages regarding interferences: dilution + trap itself.

5. Conclusion

A simple flame AAS instrument, a peristaltic pump and a simple flow system are needed to obtain sensitivity at ng L^{-1} Bi concentration level. All experimental parameters that influence the collection/volatilization efficiency were optimized in order to have the best sensitivity in W-coil trap HGAAS system.

Interferences have been investigated in detail during Bi determination by hydride generation in both with and without W-coil trap in the same HGAAS system. Experiments were designed for carrier solutions having 1.0 M HNO_3 . Interferents such as Fe(III), Mn(II), Zn(II), Ni(II), Cu(II), As(III), Se(IV), Cd(II), Pb(II), Au(III), Na(I), Mg(II), Ca(II), chloride, sulfate and phosphate were examined in this study. In the case of W-coil trap, interference effects from chloride, sulfate and phosphate ions are significantly reduced as compared with the no-trap system. Cd, Pb and Mg have effects within $\pm 10\%$ in without trap study. On the other hand, when W-coil trap is used, the interference effect of these analyte is decreased. Mn, Zn, Se, As, Na and Cu show severe interference effect on Bi signal in without trap study. Trap system has lower interference effect in cases of these elements. Another important point is that in no-trap study, Au shows severe interference effect on Bi signal especially interferent/analyte concentration is 10 and 100. When the W-coil trap is used, the interference effect of Au was decreased severely. In this study, also optimization of waste suction rate was carried. The calibration plot for an 8.0 mL sampling volume was linear between $0.10 \mu\text{g L}^{-1}$ and $10.0 \mu\text{g L}^{-1}$ Bi. The detection limit (3 s) was 25 ng L^{-1} . The enhancement factor for the characteristic concentration (C_0) was found to be 21 when compared with the regular system without trap, by using peak height values.

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