Double Hydride Generation Gaseous Phase Enrichment with Flow Injection On-line Automatic Preparation for Ultratrace Amounts of Total Selenium Determination by Atomic Fluorescence Spectrometry

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Abstract: A double hydride generation technique was developed and successfully used for the determination of total ultratrace amounts of selenium by atomic fluorescence spectrometry (AFS). In this technique, the acid digested sample solution was used for the generation of selenium hydride first, after which, the SeH_2 formed was reacted with, and absorbed in, a small volume of alkaline solution ($0.5 \, mol \, L^{-1}$ $NaOH + 0.05 \, mol \, L^{-1}$ H_2O_2), in which automated organic selenium digestion by the flow injection technique was pursued. The alkaline solution with the selenium absorbed was mixed with the reductant and then acidified to achieve hydride generation for the second time. The concentration factor depends on the volume ratio of the sample and the alkaline solution. Selenium hydride was atomized in a quartz atomizer with a mini-hydrogen diffusion flame and detected by AFS. Under the conditions employed, a detection limit of $2-6 \, pg \, Se \, mL^{-1}$ and 2.8% relative standard deviation (RSD) (with

$1 \, \text{ng} \, \text{mL}^{-1}$ Se, n = 11), and 12% RSD (with $0.05 \, \text{ng} \, \text{mL}^{-1}$ Se, n = 7) were obtained by this enrichment technique and AFS detection.

INTRODUCTION

Selenium is an essential trace element that functions as a component of enzymes involved in antioxidant protection and thyroid hormone metabolism. It has also been reported that selenium helps the metabolism of vitamin E, ensures optimal liver function, and plays a protective role against several of the toxic effects of mercury either as the metallic ion or as methylmercury.[1−5] In addition, selenium is both essential and toxic to human health except for a relatively narrow concentration range (from $0.05 \, \mu\text{g} \, \text{g}^{-1}$ to $1.5 \, \mu\text{g} \, \text{g}^{-1}$).[6] Diseases associated with selenium intake deficiency, and excess, include heart failure and severe arthritis or hair loss, nail deformation, halitosis, and flu-like symptoms.[3] Reliable techniques for the determination of selenium are thus important in nutritional as well as toxicological studies. The concentrations of selenium found in natural water, which is one of the important dietary sources of this element, are too low to be determined directly; one or two enrichment and separation steps are often necessary prior to instrumental analysis.

The hydride generation (HG) technique has widely been used in atomic spectrometry because of its excellent detection limit and capability of separation of the analyte from the sample matrix. To improve sensitivity further, a preconcentration step following the HG process might be used. This could be a chemical reaction between the hydrides and a reagent in solution, such as, Ag-diethyldithiocarbamate for determination of As and Sb.[7] Also, an $HClO_4 - KMnO_4$ solution for selenium by Yamaya et al. has been described,[8] in which the selenium hydride was transformed to another compound. The enrichment could also be performed by a physical method, so that it does not undergo chemical change of the hydride. In this case, liquid nitrogen cold traps[9] have usually been used to collect hydrides. This procedure has been used in the generation of volatile species that need a longer reaction time, such as organometallic hydrides in speciation studies.[10] As a gaseous-phase enrichment method, the *in situ* preconcentration (trapping) technique, though applied widely and successfully in the field of hydride generation graphite furnace atomic absorption spectrometry (HG-GFAAS)[11] and which could increase the sensitivity further, has not received enough attention in the other detection methods so far.

In general, HG using sodium tetrahydroborate has normally been done under strongly acidic conditions ($1 - 10 \, \text{mol} \, \text{L}^{-1}$). The acidic conditions are

necessary in order to achieve both effective hydride formation and release of the gaseous hydrides from the solutions. In contrast, the reduction of the hydride-forming elements directly in neutral or alkaline solution has been said to be advantageous. The principles of hydride generation in alkaline solutions have been described in the literature.[12−16] The method is based on the fact that the tetrahydroborate ion is a strong reductant in alkaline solution. In addition, the alkaline solution could be an ideal absorbing medium for hydrides. In the past several years, a mixed solution of NaOH and H_2O_2 has been reported as the best absorbing solution and used by United States National Standard Methods for preconcentration and digestion for determination of volatile selenium species.[17]

In the current work, a double hydride generation gaseous concentration and automated sample organic selenium digestion by the flow injection technique was developed and successfully used for the first time for the preconcentration and determination of ultratrace amounts of total selenium in mineral water. In this method, the acid digested sample solution was used for the generation of selenium hydride at first, then the SeH_2 and possible volatile organic selenium species were purged into an enrichment cell, in which the volatile selenium species were digested and absorbed on-line in a small volume of alkaline solution ($2\,mL$ of $0.5\,mol\,L^{-1}$ $NaOH + 0.05\,mol\,L^{-1}$ H_2O_2) for enrichment. The concentration factor depended on the volume ratio of the sample and the alkaline solution. After that, the alkaline solution with the absorbed SeH_2 volatile selenium species was mixed with the reductant and then acidified to carry out a second hydride generation. The evolved selenium hydride was finally atomized in a quartz atomizer with a mini-hydrogen diffusion flame and detected by atomic fluorescence spectrometry (AFS).

EXPERIMENTAL

Apparatus

A double channel nondispersive atomic fluorescence spectrometer, model AFS-2201 (Beijing Vital Instruments Co., Ltd, Beijing, China) equipped with a selenium hollow cathode lamp specially designed for AFS measurements (Beijing Vacuum Electronics Research Institute, Beijing, China) were used throughout the work. For comparison experiments, an atomic absorption spectrometer (Perkin-Elmer Zeeman 3030), with a model HGA 500 graphite furnace (Perkin-Elmer, Germany) was used.

A laboratory-built double hydride generation gaseous phase enrichment system was used in this work. A schematic diagram of the system is shown in Fig. 1. The instrument consists of two peristaltic pumps, a switching valve, an absorbing cell, and a gas−liquid separator that separates the
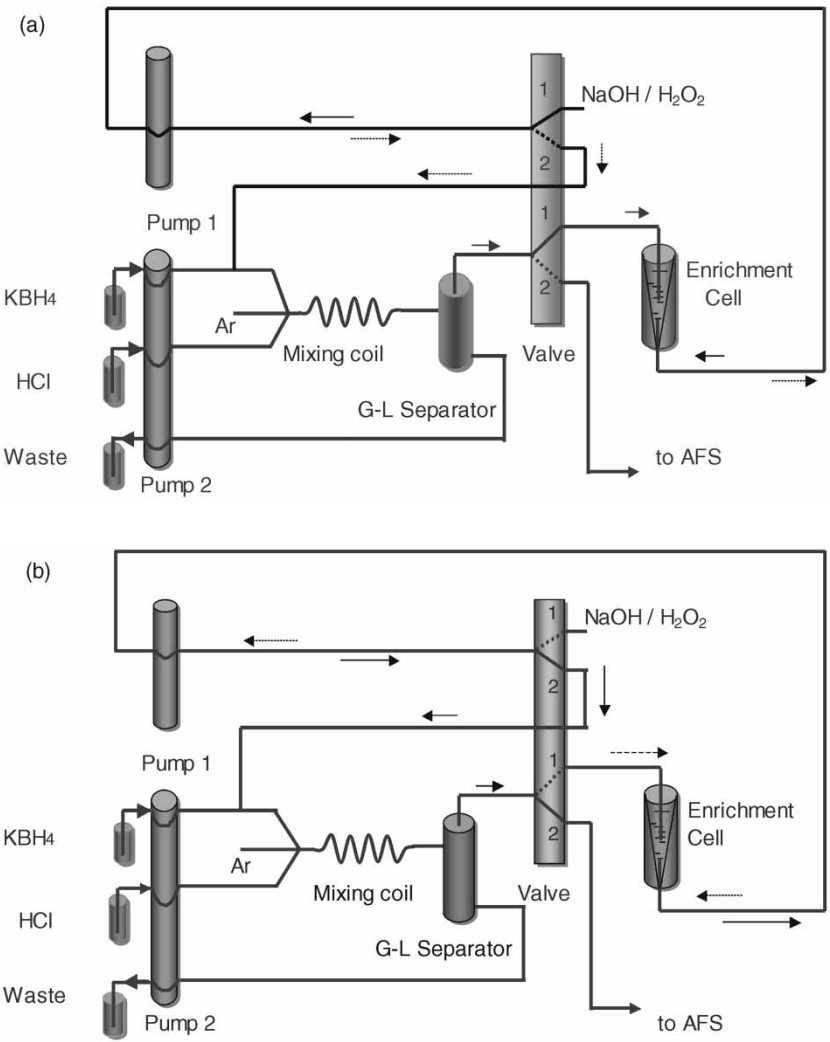
Figure 1. Schematic diagram of the double hydride generation gaseous phase enrichment system. (a) Valve position 1: enrichment stage. (b) Valve position 2: second-time hydride generation and AFS detection stage.

gaseous products from the solution and delivers them to an atom reservoir where subsequent determination can take place. Moisture and residue of solvents carried over from the separator was removed using an additional small gas–liquid separator (not shown in the figure). The working program used here is listed in Table 1.

Table 1. Working program for the double hydride generation gaseous phase enrichment system

Step	Time (s)	Flow rate (mL min^{-1})	Valve position	Function
1	10	$P_1 = 12$ $P_2 = 0$	1	The absorbing (alkaline) solution was propelled (pumped) into the enrichment (absorbing) cell.
2	300	$P_1 = 0$ $P_2 = 10$	1	The sampling tube was inserted into the sample solution, SeH$_2$ was generated by acid mode, absorbed, and enriched by alkaline solution.
3	5	$P_1 = 0$ $P_2 = 0$	2	Changeover of sampling tube into carrier solution.
4	15	$P_1 = 18$ $P_2 = 10$	2	The concentrated selenium alkaline solution was propelled with a high flow rate to mix with reductant first, then with acidic carrier solution, SeH$_2$ was generated second time by alkaline mode. AFS signal reading.
5	8	$P_1 = 12$ $P_2 = 0$	1	Clean the enrichment system.
6	15	$P_1 = 18$ $P_2 = 10$	2	Clean the double hydride generation system.
7	5	$P_1 = 0$ $P_2 = 0$	1	Return to step 1.

P_1, pump 1; P_2, pump 2.

Reagents

All reagents were of analytical reagent grade. Demineralized water was used throughout. Hydrochloric acid of $1 \, mol \, L^{-1}$, 1.0% m/v KBH$_4$ solution (Aldrich) in 0.5% (m/v) NaOH solution were used as carriers in the system. The Na$_2$SeO$_3$, Na$_2$SeO$_4$ (Aldrich, San Francisco, USA) stock solutions of $1 \, g \, L^{-1}$ were prepared in Milli-Q water. Working solutions were prepared daily by appropriate dilution in Milli-Q water. Argon was used to flush the hydrides formed to the detector.

Procedure

The manifold used for the double hydride generation of Se was designed. In the first step, the absorbing solution of $0.5 \, mol \, L^{-1}$ NaOH $+ 0.05 \, mol \, L^{-1}$ H$_2$O$_2$ was pumped by pump 1 through valve at position 1 to an enrichment

cell that was connected by polytetrafluoroethylene (PTFE) tubing to the gas–liquid separator. The acidic digested samples (sample digestion step 1) in the second step were propelled by pump 2 and mixed with the stream of $NaBH_4$ solution, and the SeH_2 formed was introduced into the gas–liquid separator where the hydride was flushed to the enrichment cell by a stream of argon and preconcentrated. In the third step, the absorbed alkaline solution was drawn out from the enrichment cell by reversing pump 1 and was mixed on-line with reductant first, and then with $1 \, mol \, L^{-1}$ HCl. The SeH_2 was formed again using the so-called "alkaline mode."[12–16] The hydride and the hydrogen formed were swept out of the gas–liquid separator by a stream of argon through valve position 2 into a hydrogen diffusion flame (the flame was maintained by the excess of hydrogen produced in the reaction between $NaBH_4$ and HCl). The hydride was atomized in the mini-flame, and the atoms were detected by atomic fluorescence spectrometry.

Determination of Selenium in Mineral Waters

For the determination of selenium, mineral waters and tap waters were pretreated with HCl plus Hbr. The method used was similar to the work by Brindle and Lugowska.[18] At sample digestion step 1, the 50 mL calibrated flasks containing 40 mL of pretreated water were covered loosely by plastic stoppers and immersed in the boiling water bath, along with calibration solutions containing Se for about 2 hr. This ensures the Se(VI) could be completely prereduced to Se(IV). After cooling down completely, the contents were then diluted to 50 mL and the determination of selenium was performed directly. Trace organic selenium, such as dimethylselenide and dimethyldiselenide, in water could be purged from mineral water samples by argon gas during the first hydride generation step. The samples are digested on-line by H_2O_2 and NaOH during the gas phase preconcentration procedure (sample digestion step 2) and hydrides generated at the same time as the inorganic selenium during the alkaline mode hydride generation.

Interference Studies

The proposed method for the preconcentration and determination of selenium described above was used for the study of interference effects of diverse elements on the enrichment. Solutions containing As, Sb, Bi, Te, Hg, Ge, Sn, Pb, Zn, Cd, and Se and other potential interference elements were prepared. Each of these solutions was subjected to the generation, preconcentration, and determination procedures. The resultant concentrations were compared with the values obtained by the standard solution that contained only Se to assess the extent of interference. As transition metals (such as

Cu^{2+}, Ni^{2+}, Co^{2+}) could not be preconcentrated during the gaseous phase enrichment procedure, the emphasis of this work was only on hydride-forming elements.

RESULTS AND DISCUSSION

NaOH and H_2O_2 Concentration

SeH_2 is relatively unstable and easily absorbed even by neutral solutions. This characteristic has been used for the collection of Se in the United States Standard Method.[17] As a suitable absorbing media for on-line automatic enrichment purposes, the absorbing solution should meet the following requirements: high absorption efficiency, high selectivity for SeH_2, and suitability for carrying out the second hydride generation in the same solution, so that it could be determined by AFS immediately. In this work, various concentrations of NaOH and H_2O_2 were tested on-line and compared with their performances for SeH_2 absorption and release by selenium hydride regeneration. The results indicated that the solution of $0.5\,mol\,L^{-1}$ NaOH was the best choice, because it could be used both for the trapping procedure and the second hydride generation (alkaline mode). About 98% of volatile selenium species was absorbed with satisfactory precision (RSD = 1.5%, n = 7, Se = $1\,ng\,mL^{-1}$). However, it was found that adding H_2O_2 to NaOH solutions gave positive effects in the recovery of selenium, as a result of improvement in the second hydride generation efficiency. The recovery of the determination increased with the concentration of H_2O_2 (from 0.005 to $0.05\,mol\,L^{-1}$) and kept constant when a higher H_2O_2 concentration was used. As a result, a concentration of $0.05\,mol\,L^{-1}$ was chosen as optimum, as described in the literature.[17]

Argon Flow Rate

Argon was used as carrier gas with two different purposes in the preconcentration and determination process. In the preconcentration process, the argon flow was used as a carrier gas to transport the hydrides and possible volatile selenium species from the gas–liquid separators to the enrichment cell. In the determination step, the argon flow was used to transfer hydride to the atom cell for detection after hydride generation by the alkaline mode in the fourth step (see Table 1).

In the enrichment step, argon flow rates should be kept as low as possible. A high flow rate could not ensure the complete digestion reaction between the volatile selenium species and the alkaline absorbing solution, and relatively poor precision was obtained (Table 2). A more serious carry-over problem

Table 2. Influence of the flow rate of the argon carrier gas on the precision of determination in the enrichment process[a]

Flow rate ($mL\,min^{-1}$)	Intensity of AFS signals (Arbitrary units, n = 11)	Reproducibility, RSD. (%)
0	0.625 ± 0.018	2.75
50	0.567 ± 0.010	1.83
100	0.580 ± 0.016	2.63
400	0.578 ± 0.018	3.08

AFS, atomic fluorescence spectrometry.
[a]Se = 1 $ng\,mL^{-1}$; enrichment time 2 min.
The precisions of measurements were evaluated by relative standard deviation (RSD) (with 1ng mL^{-1} Se, n = 11).

of the acid mist was also found when using a high argon flow rate. The acid mist consumed alkaline absorbing solution (it was often a small volume in order to get a high enrichment factor) and resulted in a reduction of the separation and enrichment effectiveness. So, a flow rate of argon was used as low as 50 $mL\,min^{-1}$ in this process. In the determination process (hydride generation by alkaline mode), with increased argon flow rate, the sensitivity of detection and sampling frequency were increased. However, the hydrogen flame was easily extinguished when the argon flow rate used was higher than 800 $mL\,min^{-1}$. As a result, a flow rate of 500 $mL\,min^{-1}$ was chosen as optimal during the determination.

Sample Flow Rate

As the overall flow rate of the double hydride generation system was increased, no significant effect on the sensitivity was observed. At a value above 7.5 $mL\,min^{-1}$, the hydrogen amount produced increased, and the total flow rate of the carrier gas could be high beyond the optimum range, thus causing a decrease in the enrichment efficiency. It was clear that the time used for the enrichment was decreased (consequently, the sampling frequency was increased) when high sampling flow rates were used. However, considering that the precision of the determination was the most important factor, we chose, as a compromise, a flow rate of 7.5 $mL\,min^{-1}$.

KBH$_4$ and HCl Concentrations

The KBH$_4$ concentration was studied in a range of 0.5–3.0% m/v (in 0.5% m/v NaOH solution). As the concentration used was lower than 1.5% m/v, it was

difficult to maintain a stable mini-hydrogen flame, as the H_2 produced was insufficient. Above 1.5% m/v of KBH_4, no significant improvement in the analytical signal was observed. Accordingly, 2.0% m/v was chosen as the optimal concentration. The concentration of HCl caused a minimal effect on the analytical signals in the range $0.5-4\,mol\,L^{-1}$. However, it was found that the carrier gas carried the HCl mist into the enrichment cell during the preconcentration process, which was becoming more serious with increasing HCl concentration. The acid mist consumed NaOH easily in the enrichment cell and resulted in decreased enrichment efficiency. So the HCl concentration should be kept at such a concentration to produce sufficient amounts of hydrogen for maintaining a stable mini-flame and to not produce too much acid mist. Finally, an acid concentration of $1\,mol\,L^{-1}$ was chosen.

Interference

It is well-known that a number of transition metals and many other hydride-forming elements could cause severe signal depression in the determination of selenium by the hydride generation technique. Without being preconcentrated in the gaseous phase, slight interferences from transition metals that existed in solutions could be expected in mineral water and tap water analysis, and no distinguishable depression in the fluorescence intensity of selenium signals was observed in the presence of $5\,mg\,L^{-1}$ of Ni^{2+}, Co^{2+}, or Cu^{2+}, respectively. Gas phase interference caused by hydride elements in the determination of selenium, which has been reported in the literature,[19,20] could become more serious after using any gaseous phase enrichment technique. So it was interesting to study the interferences from other hydride-forming elements in the double hydride generation technique. The results (Table 3) indicated that the proposed method showed excellent tolerance to different foreign species. In order to explain this phenomenon, a lamp of one or other of the hydride-forming elements was mounted on the second lamp rack of the instrument, and their signals were monitored simultaneously with that of selenium. By this approach, the behavior of other hydride-forming elements during this procedure was investigated. As seen from Fig. 2, it is interesting to note that the hydrides of some elements could not be generated in the media used in this study, and some of the hydrides could not be absorbed in the alkaline solution (see Fig. 2). Interferences from hydride (or volatile species) forming elements were eliminated easily using the high selectivity created by combining the acid mode of hydride generation with the alkaline mode of hydride generation.

Features of the Method

After the operating parameters had been optimized, the characteristics of the method were studied. The calibration curves of the two methods based on

Table 3. Effects of hydride (or volatile species) forming elements on the determination of selenium using double hydride generation gaseous phase enrichment AFS system[a]

Element	Concentration ($\mu g\,mL^{-1}$)	$[M]^{b}/[Se]$	Recovery (%) (n = 3, RSD = 10%)
As(III)	0.2	200	103
Sb(III)	0.1	100	99
Bi(III)	0.1	100	102
Hg(II)	0.04	40	100
Te(IV)	0.1	100	102
Ge(III)	0.1	100	103
Sn(IV)	0.1	100	99
Pb(II)	0.1	100	101
Cd(II)	0.1	100	98
In(III)	0.1	100	99
Tl(III)	0.1	100	102

[a]$Se = 1\,ng\,mL^{-1}$; enrichment time 2 min; sample volume 20 mL.
[b]Interferent concentration.
The precisions of measurements were evaluated by relative standard deviation (RSD, n = 3).
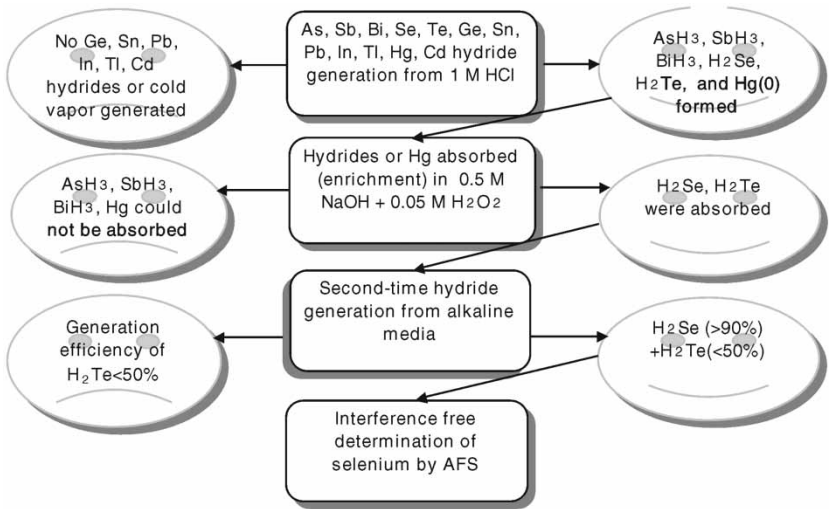
Figure 2. Elimination of interferences from hydride (or volatile species) forming elements on the determination of Se by double hydride generation gaseous phase enrichment techniques.

Table 4. Determination of selenium in mineral water[a]

| Sample | Se added ($ng\,mL^{-1}$) | This method | | HG-GFAAS method |
		Se found ($ng\,mL^{-1}$)	Recovery (%)	Se found ($ng\,mL^{-1}$)
Mineral water 1	0.00	0.08 ± 0.01		0.09 ± 0.01
	0.05 [Se(IV)]	0.14 ± 0.01	102 ± 8	0.14 ± 0.02
Mineral water 2	0.00	0.11 ± 0.01		0.11 ± 0.01
	0.05 [Se(IV)]	0.15 ± 0.01	98 ± 8	0.15 ± 0.01
Mineral water 3	0.00	0.28 ± 0.01		0.28 ± 0.01
	0.05 [Se(VI)]	0.33 ± 0.02	106 ± 6	0.33 ± 0.01
Tap water 1	0.00	0.03 ± 0.01		N.D.
	0.05 [Se(VI)]	0.08 ± 0.01	94 ± 12	0.06 ± 0.02

N.D., not detected.
[a]n = 3; enrichment time 5 min; sample volume 50 mL.

different enrichment times for a single selenium standard solution and different selenium concentrations of a standard series were set up. Both methods showed exceptionally good linearity with excellent coefficients of correlation. Under the recommended conditions, a detection limit of $2-6\,pg\,mL^{-1}$ Se was typically obtained, with a 3% RSD for $1.0\,ng\,mL^{-1}$ Se (n = 11), 5% RSD for $0.5\,ng\,mL^{-1}$ Se (n = 7), and 12% RSD for $0.05\,ng\,mL^{-1}$ Se (n = 7) by use of this enrichment technique and AFS detection.

The accuracy of the method was evaluated by recovery experiments, which were performed on mineral water and tap water samples spiked with $50\,ng\,L^{-1}$ Se (Na_2SeO_3), and from the results of determination of Se in the same samples by using *in situ* HG-GFAAS, which was reported by Sturgeon et al.[21] The results are listed in Table 4. The results obtained in recovery experiments indicated that the developed methods were reliable for the direct determination of Se in water at $ng\,L^{-1}$ levels; the precision of the results was satisfactory. Results obtained for total Se concentration by this method were also comparable to the values obtained by the other method. A similar result was obtained by spiking with $50\,ng\,L^{-1}$ Se(VI), (Na_2SeO_4).

CONCLUSIONS

For the first time, a double hydride generation gaseous phase concentration methodology with on-line automatic organic selenium digestion by the flow injection technique has been developed and successfully used for the preconcentration of ultratrace amounts of selenium in mineral water. Under the

recommended conditions, a detection limit of $2-6\,\mathrm{pg\,mL^{-1}}$ Se was typically obtained with a 3% RSD for $1.0\,\mathrm{ng\,mL^{-1}}$ Se (n = 11) using AFS detection. The interference from hydride-forming elements could be eliminated easily by using the selectivity of the acid and alkaline mode of hydride generation and the selective digestion and absorption of volatile selenium species with the alkaline solution. The methodology, which gives efficient enrichment of the analyte by gas-phase concentration technique, was rapid and simple. The method can be used for other hydride-forming elements if an adequate collection solution can be found.

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