

## Determination of Selenium and Tellurium by HG-AAS in Foods

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**Abstract :** A method has been investigated for the determination of selenium and tellurium in Ginseng, Ganoderma and Garlic using hydride generation atomic absorption spectrometry(HG-AAS). The concentration effects of hydrochloric acid and sodium tetrahydroborate on the hydride generation for the determination of selenium and tellurium were investigated. The method of sample decomposition was also investigated using various mineral acids, such as nitric, perchloric and sulfuric acid in the closed system, and foreign ion effects containing in the samples were studied. The calibration curves of selenium and tellurium were obtained in the range of 0~40 ppb.

The detection limits(S/N=2) of selenium and tellurium are 0.1 and 0.2 ppb. Analytical data of selenium and tellurium in Garlic, Ganoderma and Ginseng are 289, 296 and 198 ng/g for selenium and 146, 127 and 110 ng/g for tellurium, respectively.

**Keywords :** HG-AAS, Selenium, Tellurium, Ginseng, Ganoderma, Garlic

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### 1. Introduction

It is known that a trace of Se is a essential element of human and animal organism and has a demonstrated anticarcinogenic effects in numerous cases but a large present of Se in

the human body has toxicity like mercury and arsenic[1-3]. Nelson reported that Te has a remedy effect of tumor[4]. Thus there has been an increasingly interest in the determination of Se and Te.

Analytical methods of Se and Te currently in use depend, respectively, on neutron activation analysis[5], atomic absorption spectrometry[6] and spectrofluorimetry[7]. Since hydride generation atomic absorption spectrometry (HG-AAS) has been developed by Holak[8,9], many papers about this method were published [10-14]. HG-AAS is a sensitive determination method of Se and Te which has a analytical line in ultraviolet region. Se and Te are a volatile element. So it is important to dissolve the Se and Te sample. Selenomethionine does not decompose easily[15]. In order to determine the Se and Te in the organic sample, the sample should be decompose. A drying ash method is not a moderate method for decomposition of Se and Te sample because those elements are volatile. A wet digestion method[16] will be good. In this paper, we have been investigated the determination method of Se and Te in the foods, such as Ginseng, Galic and Ganoderma using HG-AAS and the decomposition of sample in close system, soxhlet.

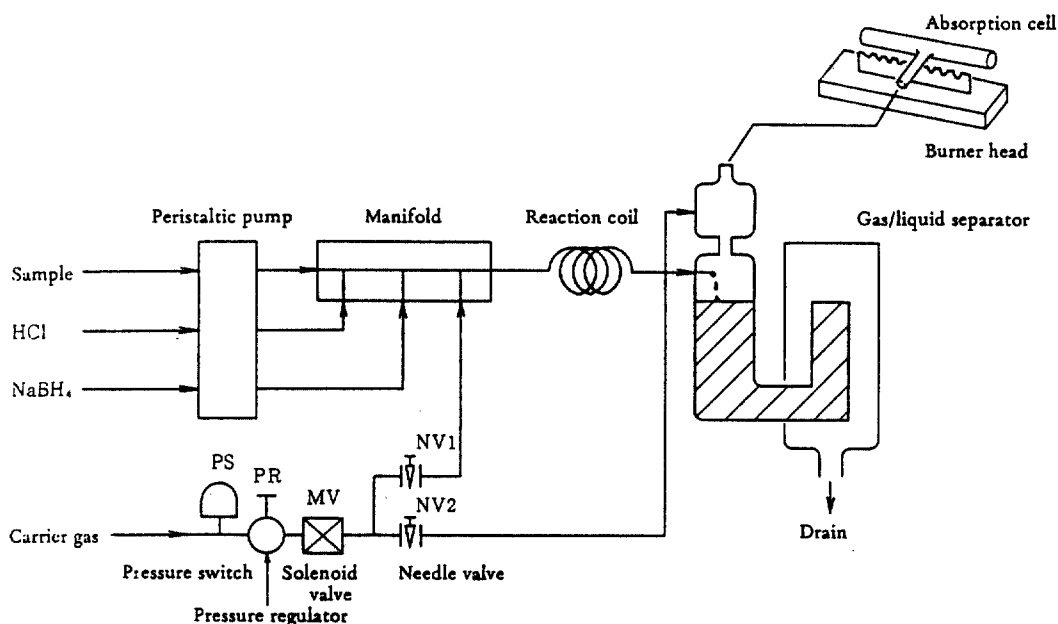
## 2. Experimental

**Apparatus and Reagent.** Atomic absorption spectrometry used is Shimadzu AA 670 and hydride vapor generator is Shimadzu HVG-1.

Deuterium lamp was used for the background correction. The continuous flow injection system used is *Fig. 1*.

The reagents used are analytical grade and water used the deionized water. Ginseng sample was a product of Kang Wha and Galic sample was a product of Jea Chon. Ganoderma sample was purchased in the market.  $\text{NaBH}_4$  solution was made by dissolving 2.5g  $\text{NaBH}_4$  in 500mL of 0.5% NaOH solution and kept at  $10^\circ\text{C}$ .

**Procedure.** In order to generate the metallic hydride vapor, the sample solution should be reacted with HCl and  $\text{NaBH}_4$  solution for 30~60sec. In the apparatus of *Fig. 1* sample solution or standard solution, 4M HCl and 0.7%  $\text{NaBH}_4$  solution were added to each bottle and



*Fig. 1* Continuous flow injection system.

the flow rate of argon carrier gas was adjusted at 70mL/min. The flow rate of sample, HCl and NaBH<sub>4</sub> solution were controlled at 7mL/min, 2.4mL/min and 2.4mL/min, respectively. The metallic hydride vapor generated was carried to the atomization cell by the carrier gas. The absorbance of Se and Te were measured at 196.0 nm and 214.3 nm.

**Sample decomposition.** Fig. 2 is the decomposition apparatus. 2.5g of the fine and dried sample was weighed and added in the sample flask and 50mL of 0.1M NaOH solution was added to the absorber in Fig. 2.

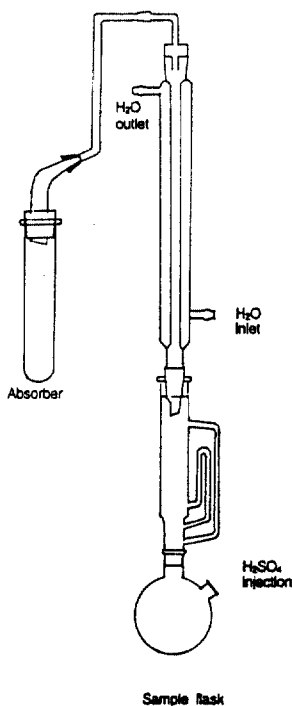


Fig. 2 Sample decomposition apparatus.

After water was passed through the cooling tube, 15mL of concentrated sulfuric acid was added and heated to 150°C for two hours. The absorber was removed to resist the back

current of 0.1M NaOH solution and the sample flask was cooled and added again 10mL 3:1 mixture solution of HNO<sub>3</sub> and HClO<sub>4</sub>. After combining the absorber, heated to oxidized the carbon produced. After oxidizing the carbon, 5mL of 1:1 HCl was added and heated to reduce the Se(IV) and Te(IV) to Se(VI) and Te(VI). The residue was diluted with water to mark 100mL. In order to correct the matrix effect, standard addition method was used.

### 3. Results and Discussion

**Concentration effect of HCl and NaBH<sub>4</sub> solution.** The optimum concentrations of HCl and NaBH<sub>4</sub> to generate the metallic hydride were investigated. The absorbance change of Se and Te standard sample were measured according to the concentration change of HCl and NaBH<sub>4</sub> solution at constant flow rate of sample (Fig. 3 and 4).

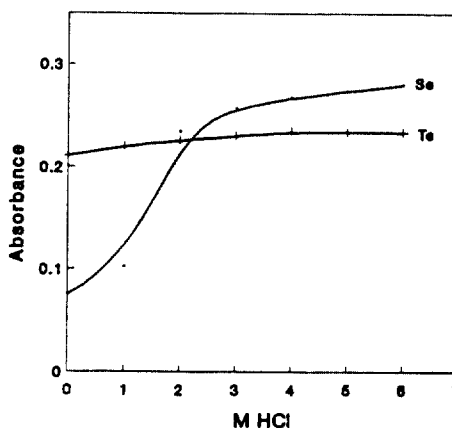


Fig. 3 Effects of HCl concentration on the Se and Te absorbance. Se: 20ng/ml ; Te: 20ng/ml

In those Figs, the absorbance of sample was increased with increase of HCl and NaBH<sub>4</sub> concentration until 4M for HCl and 0.7% for

$\text{NaBH}_4$ . So 4M HCl and 0.7%  $\text{NaBH}_4$  concentration were chosen for optimum HCl and  $\text{NaBH}_4$  concentration. Narsito[17] reported that the hydride generation was made through the competition reaction between the hydride formation reaction of metallic ion and  $\text{NaBH}_4$  and the decomposition reaction of  $\text{NaBH}_4$  in hydrogen ion.

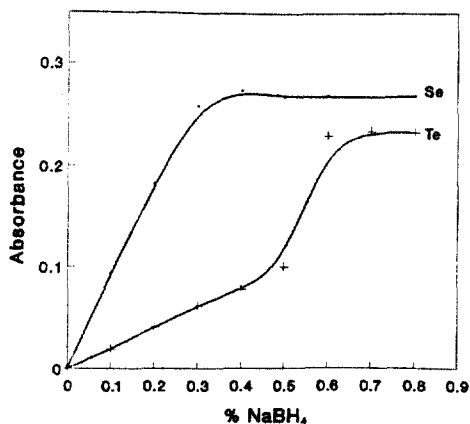


Fig. 4 Effects of  $\text{NaBH}_4$  concentration on the Se and Te absorbance. Se : 20ng/ml; Te : 20ng/ml

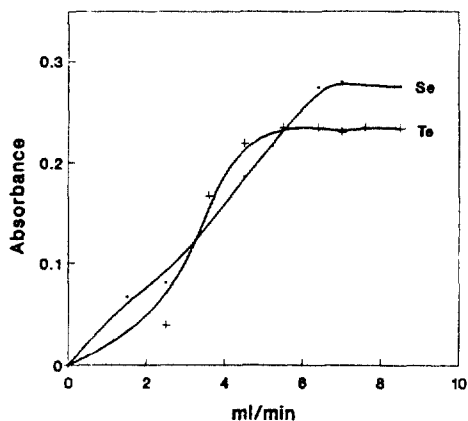


Fig. 5 Effects of sample flow rate on the absorbance. Se : 20ng/ml ; Te : 20ng/ml

**Flow rate effect of sample.** In order to study the optimum flow rate of sample, HCl

and  $\text{NaBH}_4$  solution, the absorbance change of Se and Te standard solution were measured according to the flow rate change of sample, HCl and  $\text{NaBH}_4$ . Fig. 5 is the result of the flow rate of sample. In this Fig, the absorbance was increased with the increase of sample flow rate until 7mL/min. Using the same method, we have found the optimum flow rate of HCl (2.4mL/min) and  $\text{NaBH}_4$  (2.4mL/min) solution.

**Acidity effect of sample solution.** The pH effect of sample solution were investigated.

The absorbance change of Se and Te standard solution were measured as a function of the pH change of sample solution. The result is Fig. 6. In acidic solution, the pH was controlled with HCl,  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  and in basic solution was controlled with NaOH solution. As can be seen Fig. 6, in the acidic

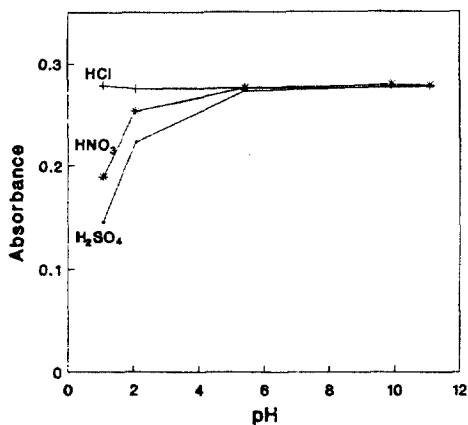


Fig. 6 Effects of sample pH on the absorbance. Se : 20ng/ml

pH solution of  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  the absorbance has a decrease tendency instead of the constant absorbance in the HCl and basic pH solution.

The reason of the absorbance decrease in  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  can be considered as the

resistance of reduction of Se(IV) and Te(IV) to Se(VI) and Te(VI) by the oxidizing acid. So it is found that the absorbance of Se and Te solution was not changed in the pH 1~10 range except the use of HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>.

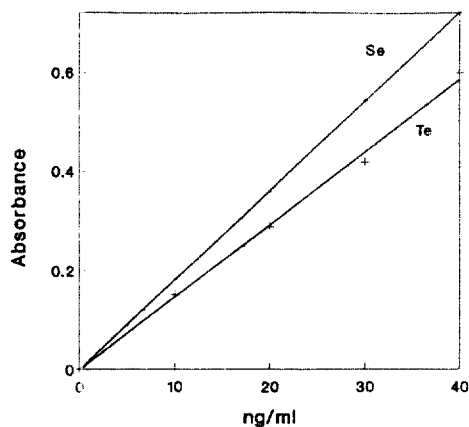


Fig. 7 Calibration curves of selenium and tellurium by HG-AAS.

**Calibration curve.** At the optimum conditions obtained above, the absorbance of Se and Te standard solution were measured as a function of those concentrations (Fig. 7). The relationship of the absorbance and the metallic ion concentration has a linearity in the range of 0~40 ppb and the detection limits ( $S/N=2$ ) of Se and Te are 0.1 ppb and 0.2 ppb, respectively.

**Influence of foreign ion.** The elements which have a similar analytical line to Se and Te can interfere the hydride generation of Se and Te. The analytical data of 20 ppb Se and Te containing 0.1~1000 ppm foreign ion solution were summarized in the Table 1. The transition elements, such as Cd(II), Fe(III), Fe(II) and Cu(II) interfered. The interference action of those ions was known as those ions were reduced to metal by NaBH<sub>4</sub> and the metal

accelerated the decomposition of the sample hydride or those ions were converted to metallic boride and the borides decomposed the sample hydride. The other ions, such as Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>, Eu<sup>3+</sup>, Y<sup>3+</sup>, and Sm<sup>3+</sup> did not interfere and S<sup>2-</sup> and SO<sub>3</sub><sup>2-</sup> which absorb the ultraviolet light gave a interference. When those ions present in the sample, background correction should be performed. Then the correction absorbance value was larger than the sample absorbance. So the correction was not precision.

**Volatile test of Se and Te.** The volatile test of Se and Te in the process of the sample decomposition was studied. Se and Te standard solution were added to the sample flask and treated as sample treatment process. After treatment, Se and Te in the sample flask and in the absorber were determined. The results were summarized in the Table 2. The total Se and Te were present in the sample flask.

So we think that Se and Te were not vaporized in the present decomposition process if the temperature of decomposition process maintained at 150°C. A food samples contain generally sulfur atom. If the sulfur atom is converted to S<sup>2-</sup> and SO<sub>3</sub><sup>2-</sup>, those ions will interfere the determination of Se and Te. So those ions should remove or convert to SO<sub>4</sub><sup>2-</sup>.

In order to convert S<sup>2-</sup> and SO<sub>3</sub><sup>2-</sup> to SO<sub>4</sub><sup>2-</sup>, S<sup>2-</sup> and SO<sub>3</sub><sup>2-</sup> solution were added to sample flask and treated it as the same process as a sample solution. The spectrum of the residue solution was measured in the ultraviolet region.

The spectra of S<sup>2-</sup> and SO<sub>3</sub><sup>2-</sup> was not appeared. This result can be considered as S<sup>2-</sup> and SO<sub>3</sub><sup>2-</sup> convert to SO<sub>4</sub><sup>2-</sup>.

#### Analytical data of Se and Te in a food.

Se and Te were determined by standard addition method. For example, 5, 10 and 20 ppb

**Table 1. Interferences of Foreign ions on the Determination of selenium and tellurium.**

Interfering Ion	Conc. (ppm)	Interference <sup>a</sup>		Interfering Ion	Conc. (ppm)	Interference <sup>a</sup>		
		Se	Te			Se	Te	
Sb(III)	0.1	-57	0	Te(IV)	0.1	+22		
	1	-100	-30		1	+55		
	10	-100	-68		10	+67		
As(III)	0.1	-9	0	Se(IV)	0.1		+4	
	1	-63	-4		1		+5	
	10	-100	-37		10		-48	
Cd(II)	1	0	0	Eu(III)	1	-4		
	10	0	-6		10	-6		
Ca(II)	1	0	0	Y(III)	1	0		
	10	0	0		10	0		
Co(II)	1	0	0	Sm(III)	1	0		
	10	0	0		10	0		
Cu(II)	1	-58	0	SO <sub>3</sub> <sup>2-</sup>	0.1	0	0	
	10	-100	-6		1	0	-18	
Fe(II)	0.1	-3	0	100	10	0	-27	
	1	-34	-6		100	-5	-37	
	10	-42	-10		ClO <sub>4</sub> <sup>-</sup>	1000	0	
Fe(III)	0.1	-25	0	NO <sub>3</sub> <sup>-</sup>	1000	0		
	1	-48	-12		1000	0		
	10	-74	-21			PO <sub>4</sub> <sup>3-</sup>	0	
Pb(II)	0.1	0	0	S <sup>2-</sup>	0.1	0		
	1	-3	-5		1	-3		
	10	-4	-12		10	-45		
Mg(II)	1	0	0	100	100	-90		
	10	0	0		SO <sub>4</sub> <sup>2-</sup>	1000	0	0
					S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	1000	0	0
				1000	0	0		
				CO <sub>3</sub> <sup>2-</sup>	1000	0	0	

$$^a \text{Interference effect} : \frac{\text{absorbance of 20 ng/ml of Te with Interfering ion}}{\text{absorbance of 20 ng/ml of Te without Interfering ion}} \times 100$$

Table 3. Analytical data of selenium and tellurium in foods.

Run No.	Garlic		Ginseng		Ganoderma	
	Se	Te	Se	Te	Se	Te
1	272	171	173	118	401	131
2	318	119	219	144	258	153
3	325	155	212	83	245	97
4	240	139	189	93	277	127
<b>Mean</b>	<b>289</b>	<b>146</b>	<b>198</b>	<b>110</b>	<b>296</b>	<b>127</b>
<b>R.S.D</b>	<b>13.9%</b>	<b>15.0%</b>	<b>10.7%</b>	<b>24.5%</b>	<b>24.2%</b>	<b>18.1%</b>

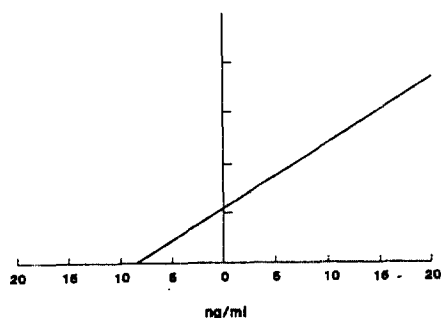


Fig. 8 Standard addition curve of Garlic sample.

### Conclusions

A method has been investigated for the determination of selenium and tellurium in Ginseng radix, Ganoderma lucidum and Garlic sample using hydride generation atomic absorption spectrometry (HG-AAS).

A soxhlet apparatus was used for the wet decomposition of sample using sulfuric acid, followed by a mixture acid of 3:1 nitric and perchloric acid and hydrochloric acid.

The analytical data of selenium and tellurium in Garlic, Ganoderma lucidum and Ginseng radix are 289, 296 and 198 ppb for selenium and 146, 127 and 110 ppb, for tellurium, respectively.

The detection limit of selenium and tellurium are 0.1ng/ml and 0.2ng/ml, respectively.

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