Mineral Composition and Germanium Contents in Some Phellinus Mushrooms in the Northeast of Thailand

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Abstract: Ash and mineral (Na₂O, K₂O, MgO, CaO, Al₂O₃, SiO₂, TiO₂, MnO, Fe₂O₃, and P₂O₅) content of 5 Phellinus mushrooms from the Northeast part of Thailand has been measured using X-Ray Fluorescence (XRF) spectrometry. A method for determination of trace levels of germanium by Graphite Furnace Atomic Absorption Spectrometry (GFAAS) with chemical matrix modifier and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was compared. The preparation of sample solutions for determination of trace levels of germanium by wet method and dry ashing method was studied. It was found that none of the cations interfered GFAAS by using palladium strontium and nickel as new matrix modifier and the linear correlation range was 0.0040-1.00 mg L⁻¹ and the detection limit was 0.0041 mg L⁻¹. The GF-AAS was applied to determine of trace levels of germanium in part per million (ppm) level in some Phellinus mushrooms with a recovery range of 75-95% which the results agree with the ICP-MS (81-111%). The ICP-MS was applied to determine of germanium in part per billion (ppb) levels in some Phellinus mushrooms with containing 0.32-1.56 ppm. The wet method for preparation sample solutions was not successful while dry ashing method was successful.

Key words: Phellinus mushrooms, germanium, aluminum oxide, graphite furnace atomic absorption spectrometry, palladium-strontium-nickel

INTRODUCTION

Mushrooms are considered as alternative food source to provide adequate nutrition to world’s increasing population. The consumption of mushroom will prevent increasing of serum cholesterol (Konuk et al., 2006). Especially, Phellinus mushroom has been used as a traditional medicine in oriental countries for the treatment of stomachaches, inflammation, arthritis of the knee, gastroenteric disorders, tumors and lymphatic disorders (Samchaid et al., 2009).

Germanium-containing dietary supplements were interested in remedies for certain diseases. Organo-germanium compounds especially carboxyethylgermanium sesquioxide or Ge-132 was considered to promote health and cure diseases. Organo-germanium compounds are described as antioxidants and inhibiting the progress of cancer and AIDS and destroying cancer cells (Krytak and Ritsema, 2004; McMahon et al., 2006). Small amounts of organo-germanium were found in some plant-based foods such as garlic, ginseng,

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comfrey, aloe and mushrooms. Therefore, germanium is an important element, the
determination of germanium in botanical samples is necessary. Several methods for
determination of germanium in trace levels have been developed such as atomic
absorption spectrometry (Yoshiki et al., 1980), hydride generation atomic absorption spectrometry
(Zaijun et al., 2007), inductively coupled plasma mass spectrometry (Krystek and Ritsema,
2004; Li et al., 1998; Shinohara et al., 1999), spectrophotometry and graphite furnace atomic
absorption spectrometry (McMahon et al., 2006; Studnicki, 1980; Dittrich et al., 1985;
Ueda and Kitadani, 1989; Hang and Chonghua, 1990; Tao and Fang, 1993; Matsusaki et al.,
1994; Xiao-Quan and Bai, 1995; Dong-Qun et al., 1995; Ni and He, 1995; Ni and Zang, 1995;
Zhang and Ni, 1996; Zhang et al., 1997; Peng et al., 1999; Yang and Zhang, 2002;
López-Garcia et al., 2005; Meeravali et al., 2007; Mizuno et al., 1988).

For the determination of germanium in trace levels, graphite furnace atomic absorption
spectrometry (GFAAS) or electrothermal atomic absorption spectrometry is a widely used
method due to its simplicity, low cost and decreasing from interferences, especially when palladium-
strontium is used as chemical modifier. The GFAAS can be applied to food,
botanical samples (Zhang et al., 1997, Yang and Zhang, 2002) and real food samples
(Zaijun et al., 2007). Many interferences such as Na⁺, K⁺, Ca²⁺, Mg²⁺, Cu²⁺, Co²⁺, PO₄³⁻, Cl⁻
and SO₄²⁻ disturb the signal in determination of germanium by GFAAS using tube wall
technique (Yang and Zhang, 2002). Many researchers try to overcome these interferences
by using matrix modifiers such as Ni, Ba (Dittrich et al., 1985), Pd, Pd-Mg (Hang and
Chonghua, 1990), Al-Co (Matsusaki et al., 1994) and Pd-Sr (Zhang and Ni, 1996), but it can
not overcome the sulfate ion in the case of amount sulfates. The GFAAS can be used to
determine Ge in more than 4.00 mg kg⁻¹ (ppm), whereas ICP-MS can be used in ng g⁻¹(ppb),
but ICP-MS has a high cost. Germanium in mushroom has in wide range 0.022-2000 mg kg⁻¹
(Mizuno et al., 1988), therefore the method was suitably selected.

Digestion of mushroom samples is an important consideration for determination of
germanium. In most cases, when using wet method (Zaijun et al., 2007), the germanium was
loosened and using dry ashing method (Mizuno et al., 1988) by hydrochloric acid with GFAS
was loosened too.

Currently Phellinus mushrooms is interested from several researchers (Kim et al., 2004;
Song et al., 2003, 2008; Li et al., 2008). This work aims to evaluate the chemical composition
of 5 Phellinus mushrooms in the Northeast of Thailand: Phellinus conchatus (Pers.) Quél.,
Phellinus rimosus (Berk.) Filat., Phellinus igniarius (L.) Quél., Phellinus gibbus (Schwein.)
Pat. and Phellinus nigrolimitatus (Remell) Bourdot and Galzin and to compare method
between GFAAS and ICP-MS for determination of germanium in some Phellinus mushrooms
and preparation of sample solutions between wet method and dry ashing method.

MATERIALS AND METHODS

Instrumentation
Wavelength Dispersive X-Ray Fluorescence Spectrometry (XRF)
A PANalytical XRF spectrometer Model Axios Advanced with an end-window Rh tube
was used for determination of chemical composition. Labor-Schoeps Automatic fusion unit
Model AAG-2 was used fused ash Phellinus mushroom.

Graphite Furnace Atomic Absorption Spectrometry (GFAAS)
Absorbance was achieved and monitored using a Varian Spectr AA Model 880Z and a
coated graphite partition tube with wall atomization and platform atomization. The source of
radiation used was a germanium hollow cathode lam.
The new chemical modifier (palladium, strontium and nickel solution) and other modifier 5 and 10 µL sample solutions were injected onto the graphite platform before each atomization cycle.

**Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)**

A Perkin-Elmer ELAN 5000 ICP-MS spectrometer equipped with an HGA-600MS electrothermal vaporizer was used for determination of germanium.

**Reagents**

The working solutions of germanium were prepared by serial dilution of a stock solution containing 1000 mg L\(^{-1}\) of germanium.

Palladium solution (2000 mg L\(^{-1}\)) was prepared by dissolving palladium (II) nitrate dihydrate 0.2504 g in deionized water and adjusted in 50 mL with deionized water.

Palladium-Strontium solution was prepared by dissolving strontium nitrate 0.1208 g in 50 mL 2000 mg L\(^{-1}\) palladium solution.

Aluminum-Cobalt solution was prepared by dissolving cobalt nitrate hexahydrate 0.0728 g in 50 mL 2 mol L\(^{-1}\) aluminum solution.

Nickel solution (5000 mg L\(^{-1}\)) was prepared by dissolving nickel (II) nitrate hexahydrate 0.2504 g in deionized water and adjusted in 50 mL with deionized water.

Five microliter of modifier solution and 10 µL of sample solution were used. 10 µL of interfere solution was used and solution of anion (sodium salt) and cation (nitrate salt) were prepared by dissolving the salts in deionized water.

**Sample Preparation**

*Phellinus* mushroom samples were cleaned from dirt and soil with brush, chopped up with a plastic knife, finely ground with agate mortar and dried at 65-70°C for 24 h.

**Dry Ashing**

The dry ashing method was modified from standard method (Curdová *et al.*, 1998). The dried *Phellinus* mushroom samples were ashing in 4 steps: 200°C for 1 h, 300°C for 1 h, 400°C for 1 hour and 450°C for 1 h and cooled down to room temperature.

**For XRF**

The ashing *Phellinus* mushroom sample, about 1.0 g each, was added with 66 % Li\(_2\)B\(_4\)O\(_7\) : 34 % Li\(_2\)B\(_4\)O\(_7\) flux (ratio 1 : 5) in platinum crucible (95 % Pt/5 % Au) and 0.05-0.10 g LiBr. Then, the mixed sample was fused at 1200°C for 5-10 min and the reference material was prepared from certified reference rocks in the same way.

**For GFAAS**

For the wet method, the dried mushroom, about 3 g, was spiked with the standard germanium 10 mg L\(^{-1}\) 1 mL and added with 10 mL concentrated HNO\(_3\) and 1 mL concentrated H\(_2\)SO\(_4\) in flask equipped with reflux overnight. Then the sample solution was heated about 80°C until the solution was completely digested. The solution was transferred in 50 mL volumetric flask and diluted to mask with deionized water. This solution was used to compare the preparation of sample solution.

**For ICP-MS and GFAAS**

For dry ashing method, the ashing *Phellinus* mushroom sample, about 0.2-0.4 g each, was put in 50 mL beaker and 10 mL of 5000 mg L\(^{-1}\) of Ni solution was added. For the
determination of the percent recovery, the standard germanium 10 mg L\(^{-1}\) mL was spiked in ashing mushroom. After 1 mL 1% HNO\(_3\) was added to dissolve, the solution was transferred in 50 mL volumetric flask and diluted to mask with 1% HNO\(_3\).

**RESULTS AND DISCUSSION**

This study used dry ashing method which gave the more concentrated solution and less-time consuming than the wet method. For example, dry ashing take 6-8 h and the ash can be dissolved in 5-10 min while wet method need overnight soaking of sample with nitric acid and sulfuric acid mixture and then needed refluxing for about 7 h. For mushroom with low ash content e.g., 4% ash, the use of 3 g ash in 50 mL is equivalent to digest 75 g of mushroom for wet method. The optimum condition of GFAAS furnace analysis conditions was showed in Table 1.

**X-Ray Fluorescence Spectrometry (XRF)**

Table 2 and 3 show the chemical composition of 5 *Phellinus* mushrooms in the Northeast of Thailand, it was found that the highest levels of SiO\(_2\), TiO\(_2\), K\(_2\)O, P\(_2\)O\(_5\), and ash were observed in *Phellinus conchatus* (Pers.) Quel. as 11.343, 0.037, 0.289, 0.083 and 17.45%, respectively. In *Phellinus igniarius* (L.) Quel. showed highest level of MgO, CaO and MnO as 0.328, 0.960 and 0.046%, respectively. The highest level of Al\(_2\)O\(_3\), and Fe\(_2\)O\(_3\) were 0.376 and 0.174%, respectively, in *Phellinus gilvis* (Schwein.) Pat. The highest Na\(_2\)O level was observed in *Phellinus rimosus* (Berk.) Pilát as 0.034%. The ash contents of each mushroom species varied as well as ash composition. The origin of these minerals are still under investigation such as silica, which may be from the defense system of biological species (32). If this is so, the medicinal properties of the mushroom may relate to silica content. Aluminium, which is not an essential in living system (33), worth maintaining. Our interest lies in the relationship of these mineral contents with germanium. Our hypothesis is germanium content may enter mushroom via the some mechanism as aluminium content due to similarity in atomic size as well as periodic table diagonal relationship. These results suggest that *Phellinus* mushrooms are very good mineral source (Table 2, 3). That is, besides being poor in lipid and very rich in protein, ash and fiber, the mushrooms examined could supply minerals.

**Pyrolysis and Atomization Temperature for Germanium in the Pd Modifier**

The main purpose of a modifier in GFAAS is to decrease the lost of germanium and to reduce the interference by the chemical matrix. The pyrolysis and atomization temperature

<table>
<thead>
<tr>
<th>Step</th>
<th>Temperature (°C)</th>
<th>Ramp time (sec)</th>
<th>Hold time (sec)</th>
<th>Inner gas (mL min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drying</td>
<td>120</td>
<td>5.0</td>
<td>30.0</td>
<td>300</td>
</tr>
<tr>
<td>Pyrolysis (ashing)</td>
<td>900</td>
<td>5.0</td>
<td>22.0</td>
<td>300</td>
</tr>
<tr>
<td>Atomization</td>
<td>2600</td>
<td>0.8</td>
<td>4.0</td>
<td>0</td>
</tr>
<tr>
<td>Tube clean</td>
<td>2600</td>
<td>0.0</td>
<td>2.0</td>
<td>300</td>
</tr>
</tbody>
</table>

**Table 2: The percent of the chemical composition in 5 *Phellinus* mushrooms from the Northeast of Thailand**

<table>
<thead>
<tr>
<th>Phellinus mushroom</th>
<th>Na(_2)O</th>
<th>K(_2)O</th>
<th>MgO</th>
<th>CaO</th>
<th>Al(_2)O</th>
<th>TiO(_2)</th>
<th>MnO</th>
<th>Fe(_2)O</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Phellinus conchatus</em> (Pers.) Quel.</td>
<td>0.001</td>
<td>0.289</td>
<td>0.265</td>
<td>0.702</td>
<td>0.227</td>
<td>0.637</td>
<td>0.005</td>
<td>0.105</td>
</tr>
<tr>
<td><em>Phellinus igniarius</em> (L.) Quel.</td>
<td>0.002</td>
<td>0.092</td>
<td>0.328</td>
<td>0.980</td>
<td>-</td>
<td>-</td>
<td>0.002</td>
<td>0.016</td>
</tr>
<tr>
<td><em>Phellinus gilvis</em> (Schwein.) Pat.</td>
<td>0.016</td>
<td>0.071</td>
<td>0.253</td>
<td>0.397</td>
<td>0.376</td>
<td>0.020</td>
<td>0.004</td>
<td>0.174</td>
</tr>
<tr>
<td><em>Phellinus nigrolineatus</em> (Ronell)</td>
<td>ND</td>
<td>0.139</td>
<td>0.176</td>
<td>0.788</td>
<td>0.201</td>
<td>0.025</td>
<td>0.005</td>
<td>0.082</td>
</tr>
</tbody>
</table>

ND: Not done
Table 3: The chemical composition in ash 5 Phellinus mushroom from the Northeast of Thailand

<table>
<thead>
<tr>
<th>Phellinus mushroom</th>
<th>% Ash</th>
<th>SiO₂</th>
<th>% P₂O₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phellinus conkanea (Pers.) Quel.</td>
<td>17.45</td>
<td>11.343</td>
<td>0.083</td>
</tr>
<tr>
<td>Phellinus rimosus (Berk.) Pihl.</td>
<td>5.00</td>
<td>1.346</td>
<td>0.046</td>
</tr>
<tr>
<td>Phellinus igniarius (L.) Quel.</td>
<td>16.53</td>
<td>0.263</td>
<td>0.043</td>
</tr>
<tr>
<td>Phellinus gilvus (Schwein.) Pat.</td>
<td>2.99</td>
<td>2.193</td>
<td>0.036</td>
</tr>
<tr>
<td>Phellinus nigrolineatus (Borner) Boudot and Galzin</td>
<td>12.98</td>
<td>7.577</td>
<td>0.070</td>
</tr>
</tbody>
</table>

Table 4: Comparison of peak area on different modifiers from sulfur interference

<table>
<thead>
<tr>
<th>Interferences (ppm)</th>
<th>Au+Co+Ni</th>
<th>Pd+Sr+Ni</th>
<th>Pd+Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₄²⁻, 0</td>
<td>0.2819</td>
<td>0.2308</td>
<td>0.2147</td>
</tr>
<tr>
<td>SO₄²⁻, 0.1</td>
<td>0.2676</td>
<td>0.2340</td>
<td>0.2075</td>
</tr>
<tr>
<td>SO₄²⁻, 1.0</td>
<td>0.2617</td>
<td>0.2462</td>
<td>0.2034</td>
</tr>
<tr>
<td>SO₄²⁻, 10.0</td>
<td>0.1699</td>
<td>0.2121</td>
<td>0.1694</td>
</tr>
<tr>
<td>SO₄²⁻, 20.0</td>
<td>-</td>
<td>0.1815</td>
<td>0.1381</td>
</tr>
<tr>
<td>SO₄²⁻, 40.0</td>
<td>-</td>
<td>0.1571</td>
<td>0.0810</td>
</tr>
</tbody>
</table>

Fig. 1: The pyrolysis and atomization temperature curves of 0.2 mg L⁻¹ germanium using 100 mg L⁻¹ Pd modifier in platform mode; the left the studied pyrolysis and the right the studied atomization curves of 0.2 mg L⁻¹ germanium using 100 mg L⁻¹ Pd modifier in platform mode are shown in Fig. 1 (When the pyrolysis was studied, the atomization was kept at 2600°C. In the case of the studied atomization, the pyrolysis was kept at 900°C). It was found that the pyrolysis temperature range is 700-1100°C and the maximum atomization is raised to 2600°C. Then, the pyrolysis temperature and atomization temperature was selected as 900 and 2600°C, respectively, for this research.

Comparison Between No Modifier and Modifier

The no modifier and difference modifiers using the pyrolysis temperature 900°C and atomization temperature 2600°C of 0.2 mg L⁻¹ germanium in platform mode are shown in Table 4 and Fig. 2a-e.

The results indicate that peak area was improved into isothermal temperature for all modifiers, but 0.02 mol L⁻¹ Al+0.01 mol L⁻¹ Co and 2000 mg L⁻¹ Pd+1000 mg L⁻¹ Sr modifiers had the high peak area and were improved successfully. Since Ge could form compound with the two set modifiers to give stable Ge-compound in pyrolysis step and was released slowly Ge atom in atomization step [11, 15, 21 and 22].

Modifiers for the Reduction of Interferences

The loss of germanium as volatile GeO and GeS during the pyrolysis and atomization steps results in a loss of analytical signal in the determination of germanium. To reduce this
Fig. 2: The comparison of peak area between no modifier and modifiers. (a) No modifier, (b) 100 mg L\(^{-1}\) Pd modifier, (c) 500 mg L\(^{-1}\) Pd modifier, (d) 0.02 mol L\(^{-1}\) Al + 0.01 mol L\(^{-1}\) Co and (e) 2000 mg L\(^{-1}\) Pd + 1000 mg L\(^{-1}\) Sr modifier

Effect of Aluminum-cobalt and Palladium-strontium were used to increase the analytical signal. Dittrich et al. (1985) has been reported the Ni\((\text{NO}_3)_2\) modifier increased the thermal stability of germanium by form as NiGeO\(_3\) in pyrolysis step. Therefore, the effect of interference such as Na\(^+\), K\(^+\), Mg\(^{2+}\), Ca\(^{2+}\), Cl\(^-\), PO\(_4^{3-}\) and SO\(_4^{2-}\) etc to analytical signal in determination of germanium was studied by addition of 1000 mg L\(^{-1}\) Ni in prepared sample solution with Aluminum-cobalt and Palladium-strontium as modifiers.

In this study, Aluminum-Cobalt plus Ni and Palladium-Strontium plus Ni mixed modifier was investigated to reduce interference on the peak area of germanium 0.2 mg L\(^{-1}\) and the results are shown in Fig. 3. The evaluation of optimum condition for Aluminum-Cobalt plus
Fig. 3: Comparison of mixed modifier on germanium 0.2 mg L$^{-1}$ in difference interferences

Ni and Palladium-Strontium plus Ni mixed modifier showed to reduce sulfate ions on the peak area of germanium 0.2 mg L$^{-1}$ and the results was shown in Table 5.

The results indicate that Aluminum-cobalt plus Ni mixed modifier can eliminate these ion except sulfate ion. Since, the reduction of sulfate ion is very important in determination of germanium by GFAAS. Whereas, Palladium-Strontium plus Ni mixed modifier can reduce interference from these ions. Then Palladium-Strontium plus Ni mixed modifier is good modifier with respect to Aluminum-cobalt plus Ni mixed modifier. Because Ni and Pd stabilize
Table 5: Comparison of peak area on difference modifiers from sulfate interference

<table>
<thead>
<tr>
<th>Interferences</th>
<th>AH-Co +Ni</th>
<th>Pd+Sr +Ni</th>
<th>Pd+Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₄²⁻, 0 ppm</td>
<td>0.2819</td>
<td>0.2308</td>
<td>0.2147</td>
</tr>
<tr>
<td>SO₄²⁻, 0.1 ppm</td>
<td>0.2676</td>
<td>0.2340</td>
<td>0.2075</td>
</tr>
<tr>
<td>SO₄²⁻, 1.0 ppm</td>
<td>0.2617</td>
<td>0.2462</td>
<td>0.2034</td>
</tr>
<tr>
<td>SO₄²⁻, 10.0 ppm</td>
<td>0.1699</td>
<td>0.2121</td>
<td>0.1694</td>
</tr>
<tr>
<td>SO₄²⁻, 20.0 ppm</td>
<td>-</td>
<td>0.1845</td>
<td>0.1381</td>
</tr>
<tr>
<td>SO₄²⁻, 40.0 ppm</td>
<td>-</td>
<td>0.1571</td>
<td>0.0810</td>
</tr>
</tbody>
</table>

Table 6: Recovery of germanium from various Phellinus mushrooms with Palladium-Strontium plus Ni as mixed modifier

<table>
<thead>
<tr>
<th>Phellinus mushroom</th>
<th>GF-AAS</th>
<th>ICP-MS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X</td>
<td>SD (n = 3)</td>
</tr>
<tr>
<td>Phellinus conchatus (Pers.) Quel.</td>
<td>91</td>
<td>4.6</td>
</tr>
<tr>
<td>Phellinus rimosus (Berk.) Pilat.</td>
<td>91</td>
<td>1.3</td>
</tr>
<tr>
<td>Phellinus igniarius (L.) Quel.</td>
<td>95</td>
<td>2.3</td>
</tr>
<tr>
<td>Phellinus gibvis (Schwein.) Pat.</td>
<td>75</td>
<td>1.8</td>
</tr>
<tr>
<td>Phellinus nigrolineatus (Romell)</td>
<td>86</td>
<td>3.5</td>
</tr>
</tbody>
</table>

GF-AAS: Graphite furnace atomic absorption, ICP-MS: Inductively coupled plasma mass spectroscopy

Table 7: Ash Phellinus mushroom Analysis by ICP-MS

<table>
<thead>
<tr>
<th>Ash Phellinus mushroom</th>
<th>Concentration of Ge (ng g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Phellinus conchatus (Pers.) Quel.</td>
<td>0.65</td>
</tr>
<tr>
<td>Phellinus rimosus (Berk.) Pilat.</td>
<td>1.56</td>
</tr>
<tr>
<td>Phellinus igniarius (L.) Quel.</td>
<td>0.32</td>
</tr>
<tr>
<td>Phellinus gibvis (Schwein.) Pat.</td>
<td>1.70</td>
</tr>
<tr>
<td>Phellinus nigrolineatus (Romell)</td>
<td>0.64</td>
</tr>
</tbody>
</table>

the Ge thermally and chemically in pyrolysis step owing to the formation of stable NiGeO₃ [11] and Pd-Ge [20], respectively. Strontium combined with sulphate ions to form SrSO₄ [21], but Aluminum combined with chloride ions and caused the spectral interference in Ge signal at 265.15 nm [15].

Analytical Merit

The absolute detection limit (3σ) of germanium based on the variability of the reagent blank which was carried out in the same way as the ashing method was found to be 0.0041 mg L⁻¹. The linearity of the method was assessed and the linear range was determined to be 0.0040- 0.5 mg L⁻¹, with an R² value of 0.9999.

Sample Analysis

The proposed method was applied to the determination of germanium in Phellinus mushrooms. For the wet method, the added germanium, for study recoveries, in the acid could not detect. For dry ashing method, the recoveries of spiked germanium in Phellinus mushrooms are in range of 75-95 % which agree with ICP-MS (81-111%) in Table 6.

When GF-AAS was applied to determination of germanium in real Phellinus mushrooms, the signal germanium was lower than detection limit (0.0041 mg L⁻¹). The ICP-MS was used to determine germanium in real Phellinus mushrooms, it was shown in Table 7. Comparison between ppm Ge and oxide of Al, Fe, Mg and Ca in ash Phellinus mushrooms were shown in Table 8.
Table 8: Comparison between ppm Ge by ICP-MS and oxide of Al, Fe, Mg and Ca by XRF in Ash of *Phellinus* mushroom

<table>
<thead>
<tr>
<th>Phellinus mushroom</th>
<th>Ge (ppm)</th>
<th>Al₂O₃ (%)</th>
<th>Fe₂O₃ (%)</th>
<th>MgO (%)</th>
<th>CaO (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phellinus conchatus (Pers.) Quel.</td>
<td>0.05</td>
<td>1.59</td>
<td>0.74</td>
<td>1.86</td>
<td>4.92</td>
</tr>
<tr>
<td>Phellinus rimousus (Berk.) Pilat</td>
<td>1.56</td>
<td>9.17</td>
<td>3.32</td>
<td>7.28</td>
<td>17.99</td>
</tr>
<tr>
<td>Phellinus igniarius (L.) Quel.</td>
<td>0.32</td>
<td>ND</td>
<td>0.38</td>
<td>13.13</td>
<td>38.40</td>
</tr>
<tr>
<td>Phellinus gilvus (Schwein.) Pat.</td>
<td>1.70</td>
<td>9.40</td>
<td>4.34</td>
<td>6.32</td>
<td>9.94</td>
</tr>
<tr>
<td>Phellinus nigrolineatus (Kornell)</td>
<td>0.64</td>
<td>2.01</td>
<td>0.82</td>
<td>1.76</td>
<td>7.88</td>
</tr>
</tbody>
</table>

The results show that ppm Ge was related to the oxide of Al and Fe especially ppm Ge and % Al₂O₃. Since Ge and Al was diagonal in periodic table and the properties were correspond, then amount of Al₂O₃ may be a useful indicator for amount of Ge in *Phellinus* mushroom. It has been reported of Ge content in food and fruits (Zajung *et al.*, 2001) but it has never been reported the amount of Ge in *Phellinus* mushroom before. This is the first reported of Ge and mineral content in *Phellinus* mushroom which could be supported the used this mushroom as medicinal mushroom.

CONCLUSION

Palladium and Strontium plus Nickel as mixed modifier can be used in determination of germanium by GF-AAS to reduce the matrix interference especially the serious interference of sulfate ion. The recoveries obtained by spiked germanium were found to be 75-95% for GF-AAS and 81-111% for ICP-MS. The GF-AAS was suitable for determination of germanium more than 4.0 ppm, whereas ICP-MS can use to determine Ge in ppb level. The preparation of sample solution for determination of germanium was suitable as the dry ashing method. The ppm Ge by ICP-MS and % Al₂O₃ by XRF in ash *Phellinus* mushrooms was closely relationship.

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