

# Graphite-Furnace Atomic Absorption Spectrometry of Organomercury and Organoselenium in Extracts of Biological Samples with an Organopalladium Matrix Modifier

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The sensitivity of organomercury in organic solutions has been found to be enhanced by applying 15  $\mu\text{l}$  of an ethanol solution of  $\text{Pd}(\text{acac})_2$  (500  $\mu\text{gPd ml}^{-1}$ , acac is acetylacetonate) to a graphite-furnace, which is then heated to make a Pd coating on the furnace. After this treatment, an ethanol solution of the sample is injected to the furnace and measured. With this method, the detection limit of organomercury was found to be 0.25 ng. In a slightly different way, in which 2 ml of an ethanol solution of  $\text{PdCl}_2(\text{PhCN})_2$  (1000  $\mu\text{gPd ml}^{-1}$ ) was added as a matrix modifier to 3 ml of an ethanol solution of organoselenium, selenium was determined with a detection limit of 0.12 ng. These methods can be successfully applied to the determinations of organomercury and organoselenium in an extract solution of a dolphin liver.

**Keywords** Organomercury, organoselenium, matrix modifier, palladium, organic solvent

Mercury gives only very poor sensitivity in conventional graphite-furnace atomic absorption spectrometry, and is therefore usually measured by cold-vapor atomic absorption spectrometry (CVAAS) to achieve a high sensitivity for practical purposes.<sup>1-6</sup> The detection limit of CVAAS has been reported to be 50 pg or 1.0 ng l<sup>-1</sup> for environmental samples.<sup>4</sup> The use of matrix modifiers has remarkably enhanced the capability of conventional graphite-furnace atomic absorption spectrometry (GFAAS) for volatile elements in real samples. For instance,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,<sup>7</sup>  $\text{Na}_2\text{O}$ ,<sup>7</sup> sulfate salt,<sup>8</sup> and a combination of  $\text{HCl-H}_2\text{O}_2$ <sup>9</sup> have been reported as matrix modifiers for inorganic mercury measurements. Ni and Shan reported, after a comparative experiment regarding the effect of gold, platinum and palladium, that the ashing temperature of mercury can be raised to 500°C by the addition of 400 ng of palladium; a detection limit of 0.2 ng Hg was obtained.<sup>10</sup> Weltz *et al.* have reported on a different palladium modification method for mercury, in which a graphite furnace is first coated with palladium by applying a Pd solution to the furnace and heating it before a mercury solution is applied to the furnace.<sup>11</sup>

Similarly to the case of mercury, vaporization loss causes a low sensitivity in selenium determination. For selenium measurements, nickel, magnesium, and palladium, or their combinations<sup>12-19</sup> ( $\text{CdCl}_2\text{-PdCl}_2$ ,<sup>20</sup> and  $\text{HgCl}_2\text{-PdCl}_2$ <sup>21</sup>) have been reported as modifiers. A detection limit of 28 pg Se has been reported with nickel being used as the matrix modifier and with a polarized Zeeman correction.<sup>15</sup> Larsen and Ekelund reported that the relative standard deviation was improved to 4.2% by using  $\text{Mg}(\text{NO}_3)_2\text{-Pd}(\text{NO}_3)_2$  in the determination of Se in a cultivated yeast standard reference material.<sup>19</sup>

In the present study, organopalladium compounds were examined as possible matrix modifiers for organomercury and organoselenium in organic solvents. Such matrix modification in an organic solvent has not been attempted for organomercury and organoselenium compounds, and seems to be promising and indispensable for characterization and speciation studies of the two elements in biological samples.

## Experimental

### Apparatus and measurement

A Hitachi Z-9000 atomic absorption spectrometer with a Zeeman background correction was used. Pyrolyzed graphite tubes were used for the measurements. Mercury and selenium atomic lines of 253.6 and 196.0 nm were used, respectively, and 20  $\mu\text{l}$  of a solution was used for the measurements. The heating program for the two elements were as follows—Hg: dry, 50–120°C for 60 s, 150°C for 20 s; ash, 350°C for 20 s; atomization, 1000°C for 5 s; and cleaning at 1500°C for 5 s; Se: dry, 80–120°C for 30 s, 120–200°C for 20 s; ash, variable for 30 s; atomization, 2400°C for 7 s; and cleaning at 2650°C for 3 s.

For a mercury measurement, 15  $\mu\text{l}$  of a 500  $\mu\text{gPd ml}^{-1}$  ethanol solution of  $\text{Pd}(\text{acac})_2$  (acac is acetylacetonate) was injected three times to the graphite furnace before the heating cycle was started. The furnace was heated with the program described above to make a Pd coating on the furnace. After this procedure, 20  $\mu\text{l}$  of a sample solution was injected and then measured.

For a selenium measurement, 2.0 ml of a 1000  $\mu\text{gPd}$

ml<sup>-1</sup> ethanol solution of PdCl<sub>2</sub>(PhCN)<sub>2</sub> was mixed with 3.0 ml of a sample solution; 20 µl of the mixed solution was injected for the measurement.

#### Extraction of Se and Hg from a dolphin liver

Part of a frozen dolphin liver was cut into small pieces with a knife, and extracted with acetone and ethanol, as the procedure described in Fig. 1 shows. The acetone and ethanol solutions were subjected to Hg and Se analyses. The heating conditions of GFAAS were those described above, except that the ashing temperature for Se was 1400°C for 30 s.

#### Reagents

The standard solutions of organopalladium compounds PdCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>, Pd(acac)<sub>2</sub>, PdCl<sub>2</sub>(PhCN)<sub>2</sub> were prepared by first dissolving each reagent-grade compound in a small amount of acetone, which was then diluted to 1000 µgPd ml<sup>-1</sup> with ethanol. For organomercury and organoselenium standard solutions, methylmercury chloride and selenourea were dissolved, respectively in ethanol to 1000 µg ml<sup>-1</sup>, and were used as standard solutions.

## Results and Discussion

#### Dependence of the mercury sensitivity on the ashing temperature and chemical forms of palladium

Without a Pd modifier the ashing temperature for a mercury measurement can be raised only to around 100°C, because volatilization loss of mercury occurs very easily even at low temperatures. We have already reported that the addition of Pd(NO<sub>3</sub>)<sub>2</sub> to inorganic mercury in an aqueous solution enables an ashing temperature as high as 450°C without any appreciable volatilization loss.<sup>22</sup> No attempt has been reported for an organomercury determination with palladium addition in organic solvents. We have reported that organopalladium can be used effectively for organotin in organonic solvents, just as inorganic palladium is widely used as a matrix modifier in aqueous solutions for various inorganic elements.<sup>24-26</sup> Organomercury is more volatile than inorganic mercury; it is of interest to examine whether organopalladium acts effectively to organomercury in organic solvents similarly to organotin. Our experiment shows, as in Fig. 2, that by coating the graphite furnace with Pd, the ashing temperature can be raised to 350°C, whereas without a Pd treatment the sensitivity rapidly decreases with the ashing temperature being raised to higher than 150°C. The sensitivity decreased to half when the Hg and Pd solutions were mixed, and the mixture was applied to the furnace. Once the Pd treatment was applied to the furnace, the surface of the furnace became stable and durable for about 40 Hg measurements without any appreciable sensitivity loss. Figure 2 also shows that the chemical form of the Pd compound does not affect the sensitivity, which is distinctly different from an

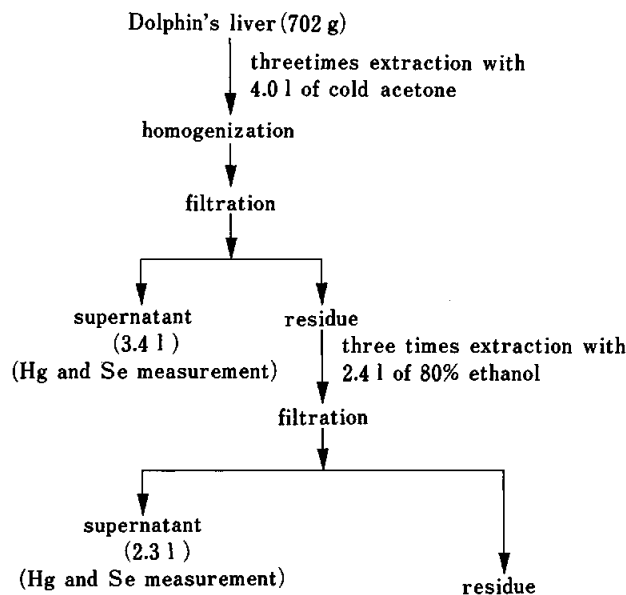


Fig. 1 Extraction procedure for the determination of Se and Hg in dolphin livers.

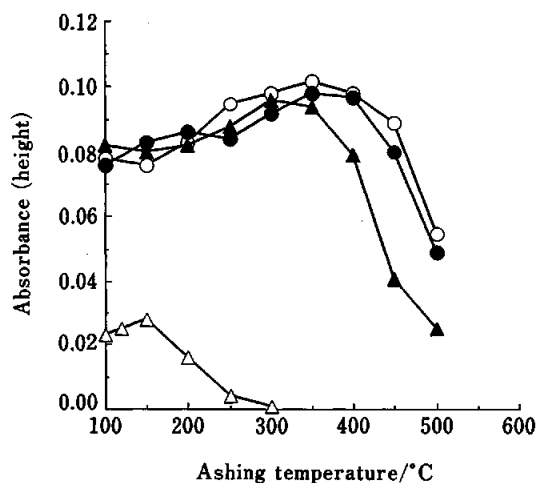


Fig. 2 Effect of the ashing temperature on the Hg sensitivity when several organopalladium compounds are added as matrix modifiers. ○ Pd(acac)<sub>2</sub>, Hg 1.0 µg ml<sup>-1</sup>; ● PdCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>, Hg 1.0 µg ml<sup>-1</sup>; ▲ PdCl<sub>2</sub>(PhCN)<sub>2</sub>, Hg 1.0 µg ml<sup>-1</sup>; △ without Pd, Hg 1.0 µg ml<sup>-1</sup>.

organotin measurement with organo Pd modifiers; in the latter case, Pd organic solutions are mixed before a measurement, and the mixed solution is applied to the measurement. The tin sensitivity and highest applicable ashing temperature differ significantly, depending on the palladium compound.<sup>24</sup> In the following analysis of extract solutions, Pd(acac)<sub>2</sub> was used. The best ashing temperature, enhancement ratio, and the detection limit are summarized in Table 1. The detection limit of the present study (3σ) is comparable to that of inorganic

Table 1 Enhancement ratios and detection limits of organomercury with several organopalladium matrix modifiers

Matrix modifier	Optimum ashing temp./°C	Enhancement ratio	Detection limit/ng
PdCl <sub>2</sub> (CH <sub>3</sub> CN) <sub>2</sub>	350	340	0.29
Pd(acac) <sub>2</sub>	350	340	0.25
PdCl <sub>2</sub> (PhCN) <sub>2</sub>	300	300	0.27
None	150	1.0	—

mercury in an aqueous solution with an inorganic Pd modifier.<sup>10</sup>

#### Dependence of the selenium sensitivity on the ashing temperature and chemical form of palladium

The effect of the ashing temperature on the selenium sensitivity is shown in Fig. 3 for several organopalladium modifiers. PdCl<sub>2</sub>(PhCN)<sub>2</sub> gave the highest possible ashing temperature of 1400°C with the highest sensitivity. Therefore, PdCl<sub>2</sub>(PhCN)<sub>2</sub> was used in the following experiment. With PdCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>, the Se sensitivity decreased and volatilization loss was observed above 700°C. The enhancement ratio and the detection limit are summarized in Table 2. Although each organopalladium compound exhibits different optimum conditions, but the enhancement ratios and detection limits are not very much different from each other. The detection limits (3σ) obtained in the present method are almost comparable to that of inorganic selenium in an aqueous solution with a HgCl<sub>2</sub>-PdCl<sub>2</sub> modifier.<sup>21</sup> Since

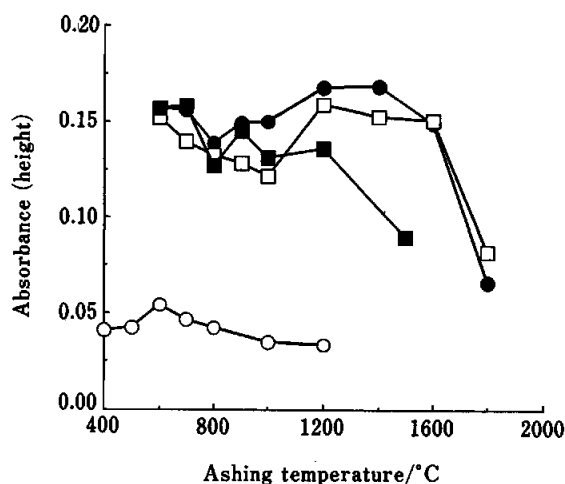


Fig. 3 Effect of the ashing temperature on the Se sensitivity when several organopalladium compounds are added as matrix modifiers. □ Pd(acac)<sub>2</sub>, 400 μgPd ml<sup>-1</sup>; ● PdCl<sub>2</sub>(PhCN)<sub>2</sub>, 200 μgPd ml<sup>-1</sup>; ■ PdCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>, 5.0 μgPd ml<sup>-1</sup>; ○ without Pd. A solution of 0.15 mgSe ml<sup>-1</sup> was used throughout the measurement. The above concentrations for the Pd compounds were optimized in a preliminary experiment.

PdCl<sub>2</sub>(PhCN)<sub>2</sub> allows the highest ashing temperature, the following Se determination was carried out with PdCl<sub>2</sub>(PhCN)<sub>2</sub>.

#### Analysis of mercury and selenium in the extract solutions of a dolphin liver

The above-described methods for organomercury and

Table 2 Enhancement ratios and detection limits of organoselenium with several organopalladium matrix modifiers

Matrix modifier	Optimum conc./μg ml <sup>-1</sup>	Optimum ashing temp./°C	Enhancement ratio	Detection limit/ng
PdCl <sub>2</sub> (PhCN) <sub>2</sub>	200	1400	2.8	0.12
Pd(acac) <sub>2</sub>	400	1200	3.0	0.14
PdCl <sub>2</sub> (CH <sub>3</sub> CN) <sub>2</sub>	5.0	700	2.8	0.08
None	0	600	1.0	—

Table 3 Determination of Hg and Se in acetone and ethanol extract solutions of a dolphin liver

Analyte	Added amount/μg ml <sup>-1</sup>	Acetone		Ethanol	
		Concentration <sup>a</sup> /μg ml <sup>-1</sup>	Recovery, %	Concentration <sup>a</sup> /μg ml <sup>-1</sup>	Recovery, %
Hg	0	0.68±0.08	—	2.06±0.14	—
	0.20	0.71±0.06	80.7	2.03±0.12	89.8
	0.40	0.89±0.03	82.4	2.26±0.15	91.9
	0.80	1.29±0.08	87.2	2.69±0.10	94.1
Se	0	0.23±0.02	—	0.89±0.07	—
	0.02	0.22±0.01	88.0	0.85±0.06	93.4
	0.05	0.26±0.05	92.8	0.84±0.04	89.4
	0.12	0.33±0.03	94.3	0.99±0.06	97.0

a.  $X \pm \sigma$  ( $\sigma$  was determined with five-time measurements).

Table 4 Analytical results ( $\mu\text{g ml}^{-1}$ ) of mercury and selenium in extract solutions of dolphin livers

Sample No.	Acetone <sup>a</sup>		Ethanol <sup>a</sup>	
	Hg	Se	Hg	Se
1	0.68±0.08	0.23±0.02	2.06±0.14	0.89±0.07
2	0.46±0.05	0.15±0.03	1.87±0.10	0.56±0.03
3	0.36±0.06	0.12±0.05	0.43±0.07	0.15±0.01
4	0.40±0.05	0.12±0.01	0.46±0.04	0.18±0.02
5	0.38±0.07	0.16±0.02	0.42±0.04	0.14±0.04

a.  $X \pm \sigma$  ( $\sigma$  was determined with five-time measurements).

organoselenium determinations were applied to the analysis of acetone and ethanol extract solutions of a dolphin liver. Table 3 shows the analytical results obtained with a standard addition method. The Hg recovery is better for ethanol solutions than acetone. The recovery of Hg is generally poorer than that of Se. Table 4 is the analytical results for the extract solutions of other dolphin livers. These results show that the present method is applicable to real samples.

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