Spectrophotometric determination of palladium by extraction of its chinoform complex with molten naphthalene

Masatada SATAKE*

(Received Jun. 15, 1977)

A new method is proposed for naphthalene extraction and spectrophotometric determination of palladium at the ppm level with chinoform. The method is based on the formation of a yellow complex which is extractable by molten naphthalene and on the dissolution of the extract in dioxane. The yellow solution follows Beer's law at 462 nm over the range of 7 to 140 μg of palladium per 10 ml of dioxane. The colour of the complex is stable for 80 min. The method is accurate and reproducible to within 1.3%, and it has more high sensitivity than chloroform method. The molar absorptivity is calculated to be $1.3 \times 10^3$ mol·l$^{-1}$·cm$^{-1}$, the sensitivity being 0.014 μg cm$^{-2}$ of palladium for the absorbance of 0.001. The other factors such as optimum wavelength, pH, amounts of reagent and naphthalene, digestion time, etc. are studied.

1 Introduction

In recent years, chinoform widely used for an intestinal sterilizer has been known to cause SMON DISEASE as a secondary effect. Chinoform (5-chloro-7-iodo-8-hydroxyquinoline), which is a derivative of oxine (8-hydroxyquinoline), forms water-insoluble complexes with various metal ions such as zinc, iron, magnesium, cobalt, nickel, copper, manganese, etc. existing in the interior of the human body, and these complexes are excreted out of the body in the form of urine and feces. Kidani and others$^{1)$-$2)$ have already reported that the mass spectrophotometric method gives a useful information about the fate of chinoform in the body of SMON PATIENTS by detecting metal linkages directly in the biological specimens, such as feces, urine, body fluid, blood, and tongue fur.

* Division of Applied Science
In this communication, a chinoform was chosen as a significant complexing reagent for the determination of trace palladium. This reagent reacts with palladium in acidic solution with the formation of a water-insoluble complex, which is quantitatively extracted into molten naphthalene at the temperature above 81°C. The extracted naphthalene mixture is dissolved in dioxane and the absorbance of the solution is measured at 462 nm. This method is about three times as sensitive as the chloroform method.

2 Experimental method

Apparatus and reagents

An Hitachi 200-20 spectrophotometer, with 10 mm glass cells, was used for the absorbance measurements.

All the pH measurements were done with a Toa Dempa pH meter, equipped with combined calomel and glass electrodes.

The chemicals used were either chemically pure or reagent-grade materials unless otherwise mentioned.

A stock solution of palladium was prepared by dissolving 10 ml of standard palladium solution (1000 ppm solution, Wako Pure Chemical Industries, LTD) to 1000 ml.

Chinoform solution, 0.1% was prepared by dissolving 0.1 g of chinoform in 100 ml of ethanol.

Buffer solutions of different pH were prepared by mixing 1M acetic acid and 1M ammonium acetate solution for pH 3-6, or 1M ammonia water and 1M ammonium acetate solution for pH 8-11.

Deionized water was used.

Procedure

To about 25 ml of each sample containing 1-13 ml of 1.0 x 10⁻⁴ M pd, in 80-ml tightly stoppered Erlenmeyer flask, is added 2.0 ml of the acetate buffer solution and 5.0 ml of 0.1% chinoform solution, and the solution is mixed well and heated on a water bath for about 60 min. After digestion, 2.0 g of naphthalene is added. Shake it vigorously till naphthalene solidifies forming fine crystalline deposit. After extraction, two phases is separated through a filter paper, and the surplus water attached to a filter paper is removed. Spread the crystals on a filter paper and allow to dry. Then dissolve them in dioxane and dilute to 10 ml. Measure the absorbance of the solution in 10 mm cell against the reagent blank. Calculate the amounts of palladium from a calibration curve.
3 Results and discussion

3.1 Absorption spectra

The absorption spectra of the dioxane solution of palladium-chinoform complex and reagent blank, extracted as above at pH 4.1, are shown in Fig. 1 against water. The curve of the complex shows an absorption maximum at 462 nm, and after that the absorbance sharply decreases and becomes insignificant beyond 520 nm. The reagent blank shows strong absorption below 375 nm. For absorbance measurements absorption maximum (462 nm) was chosen throughout subsequent study.

3.2 Effect of pH

The variation in the absorbance of the palladium complex with pH has been studied with different buffer solutions. The extraction curve in Fig. 2 shows that the extremely high absorbance is obtained in the pH range 2.8-4.9, and below and above this pH range the absorbance decreases sharply. From these experimental data, a pH range of 2.8 to 4.9 is suitable for the quantitative extraction. The pH measurements of the solution after extraction was made at room temperature. Therefore, pH 4.1 was chosen for the extraction of the complex throughout this experiments.

![Fig. 1 Absorption spectra of chinoform and palladium complex in naphthalene-dioxane solution](image1)

![Fig. 2 Effect of pH on absorbance](image2)

3.3 Effect of reagent concentration

Varying amounts of chinoform were added to the sample solution containing fixed palladium and reagent at pH 4.1 and the variation in the absorbance of the complex with reagent concentration was studied.
The result is shown in Fig. 3. From these experimental results, the absorbance increased with increasing amounts of reagent up to 2.0 ml of 0.1% solution. When more than 2.0 ml of this solution were used, the absorbances were reasonably constant. Therefore, 5.0 ml of the solution were sufficient throughout these experiments.

3.4 Effect of buffer solution

To the sample solution containing 53 μg of palladium and 5.0 ml of 0.1% chinoform solution were added varying amounts of the buffer solution (pH 4.1) and the effect of the buffer solution on the absorbance was investigated between 0.5 and 5.0 ml. The result is shown in Fig. 4. From these data, the absorbance was no change by addition of up to 5.0 ml of the buffer solution. Therefore, 2.0 ml of the buffer solution (pH 4.1) were used throughout these experiments.

3.5 Effect of digestion time

The effect of variation of digestion time on the absorbance was investigated and the results obtained is shown in Fig. 5. The reaction of palladium with chinoform to form a water-insoluble complex is practically slow even at high temperature and the digestion of long time is necessary. As shown in Fig. 5, the absorbance increases with increasing digestion time in the range of 5 to 50 min and becomes almost constant after about 50 min when the sample solution was heated on a water bath. On digesting the sample solution for an additional 60 min, a 15% increase in the absorbance was apparent. Therefore, 60 min of digestion time were used throughout these experiments.
3.6 Effect of naphthalene

The effect of the amounts of naphthalene on the extraction by molten naphthalene from the solution containing the palladium complex was investigated and some of the results obtained are shown in Fig. 6. As seen in Fig. 6, the absorbance is independent of the amounts of naphthalene in the range of 0.5 to 3.0 g. Therefore, 2.0 g of naphthalene were used throughout this experiments.

![Graph 1](image1)

**Fig. 5** Effect of digestion time on absorbance

- **PD**: 53 \( \mu g \)
- **0.1% CHINOFORM**: 5.0 ML
- **PH**: 4.1
- **WAVELENGTH**: 462 NM
- **NAPHTHALENE**: 2.0 g
- **STANDING TIME**: 15 MIN
- **SOLVENT**: DIOXANE
- **REFERENCE**: REAGENT BLANK

![Graph 2](image2)

**Fig. 6** Effect of naphthalene on absorbance

- **PD**: 53 \( \mu g \)
- **0.1% CHINOFORM**: 5.0 ML
- **PH**: 4.1
- **WAVELENGTH**: 462 NM
- **STANDING TIME**: 15 MIN
- **DIGESTION TIME**: 60 MIN
- **SOLVENT**: DIOXANE
- **REFERENCE**: REAGENT BLANK

3.7 Effect of standing time

The palladium complex was extracted into molten naphthalene according to the optimum conditions. The extract is dissolved in dioxane and the absorbance of the solution was measured after varying lengths of time from the dissolution of the mixture. The results obtained are shown in Fig. 7. From these experimental data, there was no change of the absorbance over a period of 80 min. Therefore, 15 min of standing time were taken for further study.

3.8 Calibration curve, molar absorptivity, sensitivity and precision

The calibration curves for the palladium determination were prepared by the optimum conditions. Beer's law was obeyed over the range of 7-140 \( \mu g \) of palladium in 10 ml of dioxane. The molar absorptivity was \( 7.8 \times 10^3 \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1} \) at 462 nm, and the sensitivity of the complex as expressed by Sandell's notation was 0.014 \( \mu g \) of palladium per cm². The results are shown in Fig. 8.

The precision of this method was estimated with 10 samples containing 53 \( \mu g \) of palladium. A mean absorbance at 462 nm was 0.391 with
a standard deviation of $5.49 \times 10^{-3}$, or a relative standard deviation of 1.40.

Fig. 7 Effect of standing time on absorbance
Pd: 53 $\mu$g; 0.1% chloroform: 5.0 mL; pH: 4.1; Wavelength: 462 nm; Digestion time: 60 min; Buffer solution: 2.0 mL
Reference: Reagent blank

3.9 Choice of solvent
After testing various organic solvents such as chloroform, benzene, dimethylformamide, dimethylsulfoxide, dioxane, chlorobenzene, acetonitrile, etc., dioxane was found to be the most suitable solvent of the complex. The sensitivity for the complex in dioxane was 2.5 times as high as that in chloroform, as well as chloroform extraction method.

The method was compared with the chloroform method. The results obtained are shown in Table 1.

Table 1 Comparison of this method with chloroform method

<table>
<thead>
<tr>
<th>Methods</th>
<th>Molar absorptivity (1·mol⁻¹·cm⁻¹)</th>
<th>Sensitivity (µg·cm⁻²)</th>
<th>Relative standard (%) deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene</td>
<td>$7.8 \times 10^{3}$</td>
<td>0.014</td>
<td>1.2</td>
</tr>
<tr>
<td>Chloroform</td>
<td>$3.1 \times 10^{3}$</td>
<td>0.035</td>
<td>0.8</td>
</tr>
</tbody>
</table>

References