Journal of Environmental Science and Engineering B 7 (2018) 209-214
doi:10.17265/2162-5263/2018.06.001

PUBLISHING

# Spectrophotometric Determination of Hydrogen Molecule in Drinking Water with *o*-Phenanthroline in the Presence of Colloidal Platinum

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**Abstract:** A simple rapid method for the determination of hydrogen molecule in water is developed. This method is based on the redox reaction of ferric ion and hydrogen molecule in the presence of colloidal platinum. The released ferrous ion was developed with *o*-phenanthroline and spectrophotometrically measured at 510 nm. The suitable pH condition of redox reaction of ferric ion and hydrogen molecule is pH 2. And 1 mol of molecular hydrogen reduced 2 mol of ferric ion. The molar coefficient for hydrogen molecule is $2.25 \times 10^4$ $L \cdot mol^{-1} \cdot cm^{-1}$. The stability of hydrogen water was also discussed.

**Key words:** Molecular hydrogen, colloidal platinum, ferroine, spectrophotometry.

## 1. Introduction

Hydrogen water was known to be most effective wet cleaning of silicone surfaces [1] and used for nutrient solution of Komatsuna plants [2]. On the other hand, many studies have been made for influence of health. Ohsawa, et al. [3] reported that hydrogen water can efficiently remove active oxygen, therefore, hydrogen water can be expected for treatment of cerebral infarction. Shimouchi, et al. [4, 5] reported when 7 adults took hydrogen water and 40% hydrogen has been consumed by acting with hydroxyl radicals. Although hydrogen water has attracted attention in these ways, there are surprisingly few methods for easily measuring the concentration of hydrogen.

There are some methods for determination of hydrogen molecule concentration by amperometry [6], gas chromatography [7], methylene blue drop test [8]. However, no study has been made concerning spectrophotometric determination of hydrogen molecule in water. So, authors try to consider determining method of hydrogen. By methylene blue drop test method, it counts droplet of methylene blue solution till the solution changes to blue color. Disappearing of the color of the solution did not occur in the absence of colloidal platinum. The colloidal platinum is served as catalyzer for blue color of methylene blue to colorless of leuco methylene blue. However, the colorless solution changed to blue color after standing with oxygen in air. Therefore, the method is difficult to apply for spectrophotometric determination of hydrogen molecule in water directly. However, the catalyzer of colloidal platinum is one good idea to make hydrogen as increment of reduction power. Hydrogen molecule oxidation reaction on platinum nanoparticles was also reported [9, 10]. The present paper used colloidal platinum as oxidative catalyzer of hydrogen molecule for reduction of ferric ion to ferrous ion. The produced ferrous ion was developed with *o*-phenanthrorine and the complex (ferroin) formed was determined spectrophotometrically.

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## 2. Experimental

### *2.1 Materials and Reagents*

Spectrophotometer measurements were made with a Shimazu UV-1800 spectrophotometer using 1 cm glass cells. A TOA HM-30V was used for pH measurement. MAGICPOT hydrogen generator CCMP was used for preparation of hydrogen water using drinking water (total hardness 50 mg/L). The average of concentration of hydrogen molecule in this water is near 0.5 mg/L. And the concentration was measured using dissolved hydrogen meter KM2100DH.

All reagents were of analytical grade and the solutions were prepared with deionized water from a ElGA PURELABOTION-S type.

Ferric solution: Weigh 0.362 g of ferric nitrate enneahydrate and add 2.5 mL of 1 mol/L hydrochloric acid and diluted with water to 250 mL.

$1 \times 10^{-3}$ mol/L of platinum nanoparticle dispersion solution was prepared with diluting with water using 10 mM of platinum nanoparticle dispersion from Renaissance Energy Research Ltd..

2% *o*-phenanthrorine solution: 2 g of *o*-phenannthroline dichloride monohydrate was dissolved in 100 mL of water.

pH 6.15 buffer solution: 10.2 g of 2-morpholinoethanesulfonic acid monohydrate was dissolved in water and the pH was adjusted with sodium hydroxide solution and make up 250 mL with water.

### *2.2 Standard Procedure*

Transfer 5 mL sample solution into volumetric flask. Add 0.5 ml of ferric solution, 0.15 mL of platinum nanoparticle dispersion solution, 0.5 mL of *o*-phenanthroline solution, 2 mL of buffer solution and diluted with water to 10 mL.

## 3. Results and Discussion

### *3.1 Influence of Colloidal Platinum*

Hydrogen gas was not able to reduce ferric ion to ferrous ion. The dissociative adsorption of a hydrogen molecule occurs at platinum colloids [11]. The surface provides reaction field, and it suggests that it promotes redox reaction of ferric ion and hydrogen molecule. Fig. 1 indicates the influence of colloidal platinum solution on reduction of ferric ion. If the colloidal platinum is not present, the absorbance of the solution is same of blank solution. Increment of colloidal platinum introduced increasing of absorbance and more than $1.2 \times 10^{-5}$ mol/L of colloidal platinum concentration indicates constant absorbance.

### *3.2 Effect of pH*

The optimum pH condition of redox reaction of hydrogen molecule and ferric ion was investigated. The result is shown in Fig. 2. From this result, it was shown the maximum pH was pH 2. And higher pH more than pH 2, the absorbance was decreased. The recommended pH condition for ferroin formation is beyond from pH 4 to 6 [12]. Therefore the pH 2 is only the condition of redox reaction of hydrogen and ferric ion.

### *3.3 Calibration Curve for Hydrogen Molecule in Water*

Linear calibration curve was obtained using a standard procedure (Fig. 3). Beer's law is obeyed in the range of 0 to $6.5 \times 10^{-6}$ mol/L. The molar coefficient for hydrogen molecule in water was $2.26 \times 10^{4}$ $L \cdot mol^{-1} \cdot cm^{-1}$ and exhibits an excellent linear correlation coefficient (0.9968). The molar coefficient is near twofold than ferroin, it means 1 mol of hydrogen molecule reduced 2 mol ferric ion. The detection limit of hydrogen in water is $6.96 \times 10^{-7}$ mol/L ($1.39 \times 10^{-3}$ ppm, $n = 16$).

### *3.4 Stabilization of Hydrogen Water*

Hydrogen gas is easily evaporated from the hydrogen water [13]. Stability of the hydrogen water on various temperature conditions was shown in Fig. 4. It indicates the stability of hydrogen water decreases depending on the temperature increased. The stability

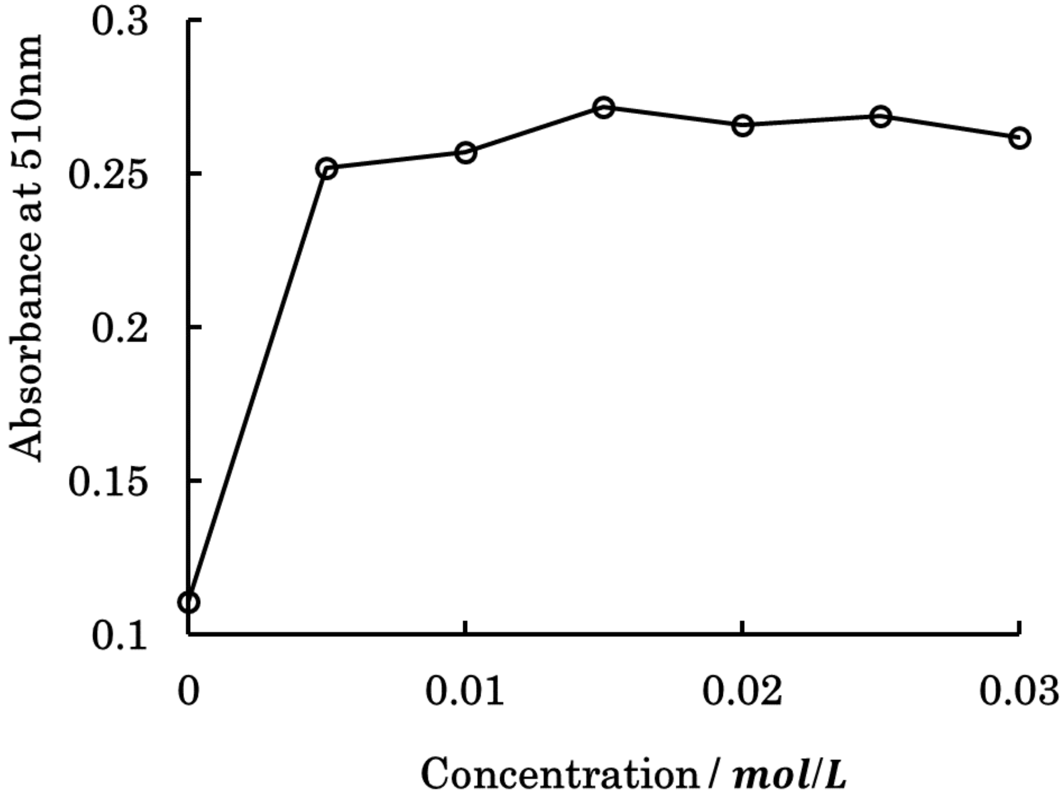


**Fig. 1 The influence of concentration of colloidal platinum on reduction of ferric ion.**

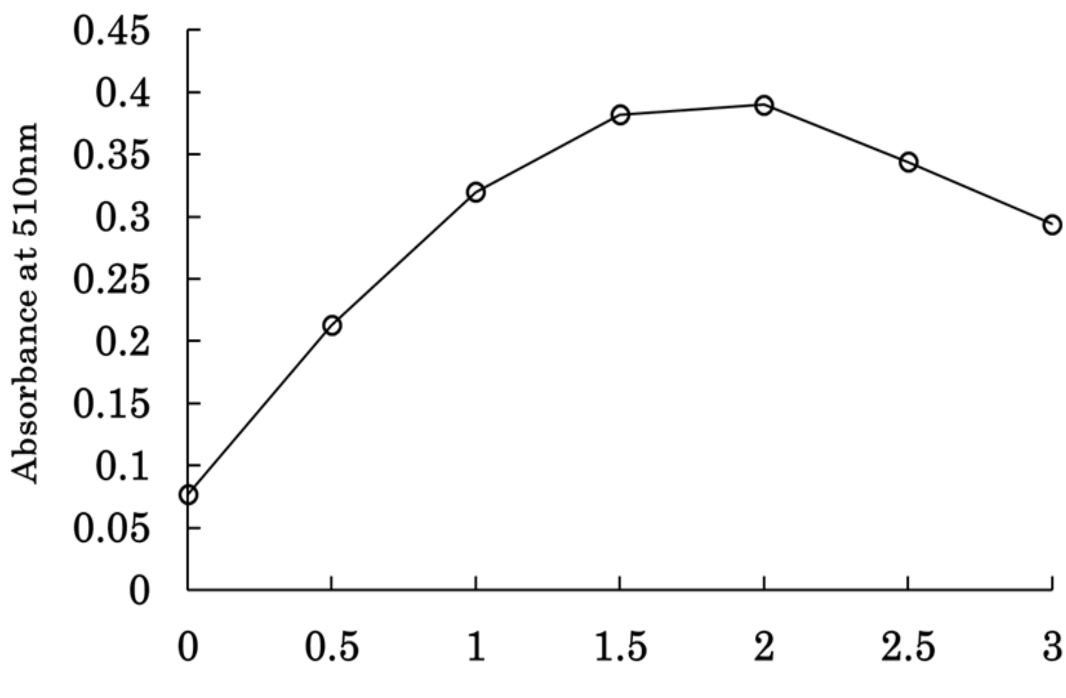


**Fig. 2 The optimum pH condition of redox reaction of hydrogen molecule and ferric ion.**

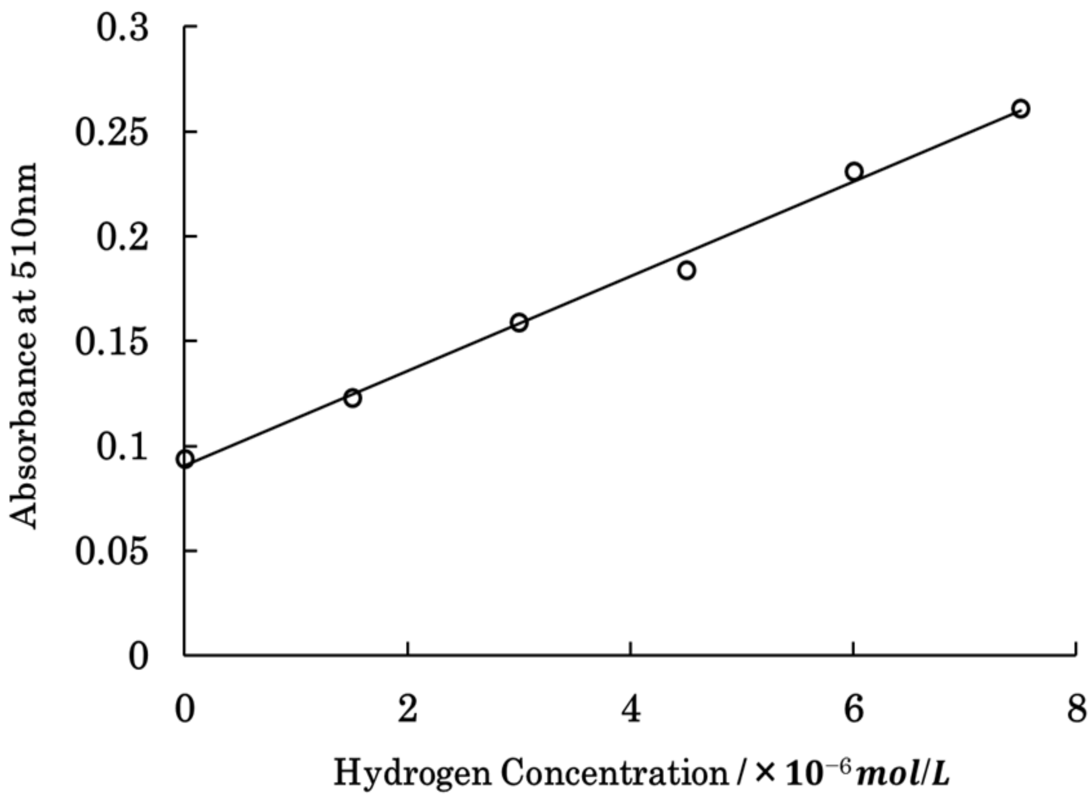


**Fig. 3 Calibration curve for hydrogen molecule in water.**

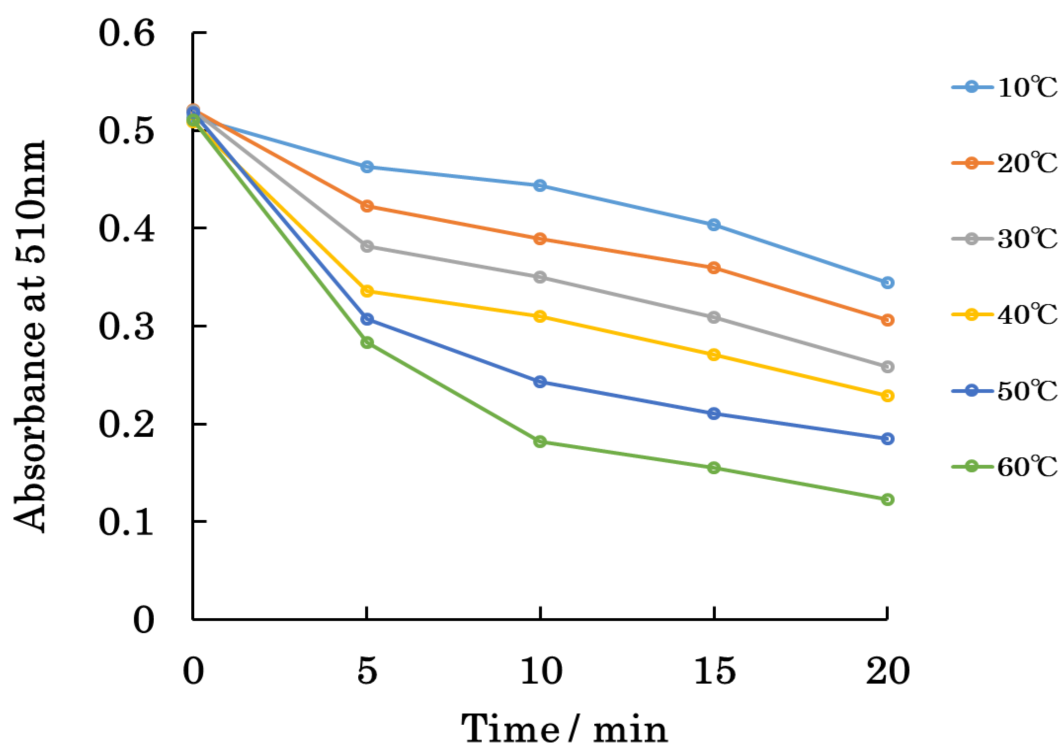


**Fig. 4 Stability of the hydrogen water on various temperature conditions.**

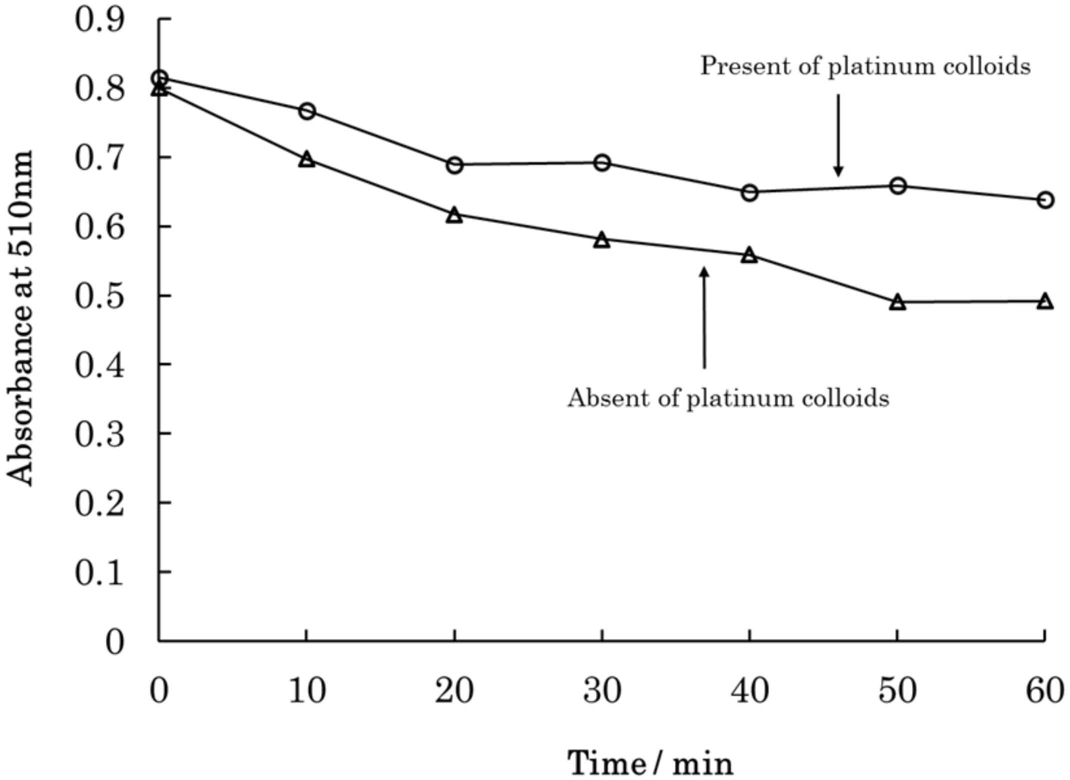


**Fig. 5 The stability of hydrogen water in the absence or present of platinum colloids.**

**Table 1 Effect of diverse ion (amount added, 10 ppm).**

| Ions | Added as | Absorbance | Relative error (%) | Ions | Added as | Absorbance | Relative error (%) |
|---|---|---|---|---|---|---|---|
| None | — | 0.327 | — | None | — | 0.302 | — |
| $Mg^{2+}$ | $MgSO_4 \cdot 7H_2O$ | 0.306 | -6.4 | $Cl^-$ | KCl | 0.290 | -4.0 |
| $Mn^{2+}$ | $MnSO_4 \cdot 5H_2O$ | 0.308 | -5.8 | $Br^-$ | KBr | 0.305 | +1.0 |
| $Ni^{2+}$ | $NiSO_4 \cdot 6H_2O$ | 0.320 | -2.1 | $I^-$ | KI | 0.628 | +108 |
| $Cu^{2+}$ | $CuSO_4 \cdot 5H_2O$ | 0.317 | -3.1 | $CH_3COO^-$ | $CH_3COOK$ | 0.274 | -9.3 |
| $Zn^{2+}$ | $ZnSO_4$ | 0.306 | -6.4 | $CrO_4^{2-}$ | $K_2CrO_4$ | 0.065 | -78.5 |
| | | | | $MnO_4^-$ | $KMnO_4$ | 0.071 | -76.5 |
| | | | | $CO_3^{2-}$ | $K_2CO_3$ | 0.268 | -11.3 |
| | | | | $NO_2^-$ | $KNO_2$ | 0.435 | +44.0 |
| | | | | $NO_3^-$ | $KNO_3$ | 0.264 | -12.6 |

of the hydrogen water was also tested using addition of platinum colloids (Fig. 5). The stability of hydrogen water increased by addition of platinum colloids. It means hydrogen molecule adsorbs on the surface of platinum.

### *3.5 Influence of Diverse Ions*

Influence of twenty amounts of various ions on the determination of molecular hydrogen was examined (Table 1). Oxidizing anions, such as dichromate, permanganate lead to negative errors. And iodide leads to positive error. These ions make redox reaction with ferrous or molecular hydrogen.

## 4. Conclusion

A simple rapid method for the determination of hydrogen molecule in water is developed. The suitable pH condition of redox reaction of ferric ion and hydrogen molecule is pH 2. And 1 mol of molecular hydrogen reduced 2 mol of ferric ion. The molar coefficient for hydrogen molecule is $2.25 \times 10^4$ $L \cdot mol^{-1} \cdot cm^{-1}$. Stability of hydrogen water was also discussed. The method influenced such as iodide, permanganate and chromate ions. The detection limit of hydrogen in water is $6.96 \times 10^{-7}$ mol/L ($1.39 \times 10^{-3}$ ppm, $n = 16$).

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