

## Kinetic photometric determination of trace amounts of palladium (II) based on its catalytic effect on the reduction of safranin with hypophosphite

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A new kinetic method for the determination of trace amounts of palladium (II) based on its heterogeneous catalytic effect on the reduction reaction of safranin (SAF) by hypophosphite (HP) has been described. The reaction is monitored at 516 nm and the time elapsed,  $\Delta t$ , for the absorbance to decrease by 1.5 absorbance units from its initial value is recorded (variable time method). The influence of reaction variables such as safranin and hypophosphite concentrations, ionic strength, and pH have been examined. The range of linearity is 0.03-2.22 ppm palladium(II) at temperature of 25°C ( $n=7$ ,  $r=0.9998$ ). The detection limit is 0.02 ppm. The relative standard deviation of the developed method is 1.8% (for 10 replicate determinations of 1.11 ppm of Pd(II)). The effect of interferences from other metal ions and some anions is also studied. The procedure has been applied successfully to the determination of Pd(II) in real samples.

Palladium is one of the precious metals. Owing to its corrosion resistance nature and alloying ability, palladium is an important element in metallurgy. Its alloys are used in dental alloys and in jewelry manufacture. Moreover, palladium is used in the electronic industry<sup>1</sup>, as a component of three-way catalysts in automobile exhaust-gas catalysis<sup>2</sup>, and in the organic synthesis<sup>3,4</sup>.

Palladium can be determined by expensive instruments such as Neutron activation analysis (NAA) and inductively coupled plasma mass spectrometry (ICP-MS)<sup>5-7</sup>. However, even when sensitive techniques are employed as NAA and ICP-MS, it is necessary to separate the platinum group from matrix elements and concentrate them before analysis<sup>6</sup>, also it requires a long time for the analysis.

Simultaneous determination of platinum group metals (PGMs), can be carried out by the above two techniques, but in both cases, instruments of high sophistication are required. Among different analytical methods like HPLC<sup>8</sup>, FAAS<sup>9</sup>, NAA<sup>10</sup>, ICP-MS<sup>11</sup>, and spectrophotometry<sup>12-14</sup> the later is widely used method.

The determination of metal ions and inorganic oxoions by catalytic methods have also be reported<sup>15,16</sup>.

Some kinetic-spectrophotometric methods using conventional spectrophotometric methods for determination of some anions and cations<sup>17-20</sup> have been developed by us, but computer interfaced probe-typed photometer has some advantages such as, simplicity, speed, and possibility to acquire initial data which has high importance in initial rate kinetic methods. The work reported here is based on the Pd(0) catalysis of hypophosphite reduction of safranin. The catalyst is generated by reduction of palladium(II) by the hypophosphite, and in turn accelerates the reduction of dye, either via hydrogen formation or directly by hypophosphite adsorption. For all practical purpose, no reaction occurs in the absence of Pd(II).

## Experimental

All chemicals used were of the highest purity, and used without any further purification. Doubly distilled water was used throughout. Palladium chloride (1000 ppm, 0.1670g) was dissolved in 2.0 mL concentrated HCl (Merck, 37%), and the solution was transferred into a 100 mL standard flask, then diluted to volume with water to prepare Pd stock solution. Pd working solutions were prepared just before use, by transfer of the appropriate volume of Pd stock solution into a 50 mL volumetric flask. Safranin solution ( $2.0 \times 10^{-4}$  M) was prepared by dissolving 0.0351 g of safranin (Merck) and diluting to 500 mL in a calibrated volumetric flask. Hypophosphite (1.0 M) solution was prepared by dissolving 10.4090 g of potassium hypophosphite (Merck) in 100 mL water. Stock solutions of diverse ions (from Merck or Aldrich) for the interference studies were prepared by dissolving the calculated amount of each compound in order to give 9000 ppm solutions of each species. All reagents were placed in a 25°C water bath.

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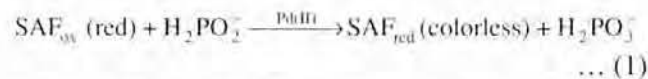
Absorption spectra were obtained with an ATiUnicam UV-vis model double-beam recording instrument. For other measurements at a single wavelength (516 nm) a Metrohm photometer model 662 was used. The photometer signals were processed using a low-noise amplifier (made in our laboratory) and analogue-to-digital converter (ADC, from Bit-Pardaz Co. Ltd., Iran) for direct transfer into personal computer. The Quick Basic software was designed to run on any computer capable of running Microsoft MS-DOS 6.2 or later version operating system. This system facilitates the data acquisition (20 data/second), and also facilitates for more sophisticated data processing, and display and archiving of results. All measurements were carried out in a Grant thermostat bath/circulator (Grant Instruments Ltd., Cambridge) also, during the all experiments, solutions were stirred with a magnetic stirrer (Zag-Chemie Co. Ltd., Iran). All pH measurements were carried out with a Metrohm pH-meter model 691.

#### Recommended procedure

In a 25 mL glass beaker, 3.0 mL of  $2.0 \times 10^{-4}$  M safranin, 7.0 mL of 1.0 M hypophosphite, 6.0 mL water and 2.0 mL of Pd(II) working solution were added. According to the experimental results, continuous stirring of the reaction mixture with a magnetic stirrer bar aids not only speed up the reaction significantly, but also gives reproducible results. The variable-time method was used for all measurements, time elapsed for the absorbance to decrease from its initial value to a reference point (5% of initial absorbance) was measured at 516 nm with a probe-type photometer.

#### Results and discussion

The reduction reaction of SAF with hypophosphite in the presence of Pd(II) is as follows:



In the absence of Pd(II) no reaction occurs, but addition of palladium(II) increases the rate of reaction remarkably. Initially, hypophosphite reduces Pd(II) to Pd(0). Oncoming in contact with finely divided Pd(0), HP decomposes producing hydrogen that reduces the safranin. It is well known that when hydrogen is adsorbed on Pd metals it becomes activated<sup>21,22</sup>. The absorbance signal of the dyestuff at 516 nm decreases by progress of reaction,

The influence of safranin concentration on the rate of reaction was investigated between  $5.5 \times 10^{-6}$ - $1.0 \times 10^{-4}$  M. The rate of reaction increased by increasing the amount of dye until a dye concentration of  $3.33 \times 10^{-5}$  M was reached. Further addition of dye reduces the rate of reaction. The optimum concentration of safranin was chosen as  $3.33 \times 10^{-5}$  M in final solution. The optimum condition of dye showed an absorbance of 1.790 at the beginning of the reaction.

At optimum concentration of dye the effect of HP concentration on the rate of catalyzed reaction was studied and optimum concentration of HP in the final solution obtained was 0.39 M.

The effect of ionic strength on the reaction rate of catalyzed reaction was also studied. The ionic strength of solution was varied from 0.0-0.5 M using KCl solution. The rate of reaction was found to remain constant at its maximum level when the KCl concentration is in the range  $0.0$ - $8.5 \times 10^{-2}$  M and decreases gradually with concentration greater than  $8.5 \times 10^{-2}$  M.

It was observed that pH of the reaction medium affects the rate of catalyzed reaction and the maximum rate was achieved over the pH range 2.6-4.3. The length of the induction time increases and the rate of reaction gradually decreases as the pH is increased above 4.3 or decreased below 2.6. The effect at low pH values may result from excessive protonation of the safranin. At high pH values, Pd(II) hydrolyzes and its catalytic activity decreases. Hence, subsequent studies were carried out at pH=4.3.

The influence of reaction temperature was studied in the range 15-60°C at optimum conditions. Significant increase in the rate of reaction was seen. For conveniences, temperature 25°C was selected for the further study.

Under optimum conditions described above, a linear calibration graph was obtained in the concentration range of 0.03-2.22 ppm with a correlation coefficient of 0.9998 and a regression equation of  $1/\Delta t = 0.007 + 4.450 \times 10^{-5} C$ , where  $t$  and  $C$  indicate the time elapsed (s) for the absorbance to decrease from its initial value to a reference point (5% of initial absorbance) and Pd(II) concentration (ppb), respectively. The detection limit is 0.02 ppm. The relative standard deviations of 10 replicate measurements is 1.8% for a 1.11 ppm Pd(II) solution. The method described provides a simple, fast and reliable means of determining trace amounts of palladium(II). The method should be applicable to the

Table 1—Tolerance limits of diverse ions on the determination of 1.11 ppm palladium(II) ions.

| Substance                                                                                                                                          | Tolerated ratio of foreign ion to palladium(II) ion |
|----------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------|
| Li <sup>+</sup> , K <sup>+</sup>                                                                                                                   | 2600                                                |
| Co <sup>2+</sup> , Sr <sup>2+</sup> , Mg <sup>2+</sup> , Ca <sup>2+</sup> , Ba <sup>2+</sup> , Be <sup>2+</sup> , Cs <sup>+</sup> , F <sup>-</sup> | 2000                                                |
| Ni <sup>2+</sup> , Cd <sup>2+</sup> , Na <sup>+</sup> , Cl <sup>-</sup>                                                                            | 1700                                                |
| NO <sub>3</sub>                                                                                                                                    | 1000                                                |
| Mn <sup>2+</sup> , Zn <sup>2+</sup> , SO <sub>4</sub> <sup>2-</sup> , PO <sub>4</sub> <sup>3-</sup>                                                | 700                                                 |
| Pb <sup>2+</sup>                                                                                                                                   | 400 <sup>A</sup>                                    |
| Fe <sup>3+</sup> , Mo(VI)                                                                                                                          | 200                                                 |
| Si(IV)                                                                                                                                             | 150                                                 |
| Al <sup>3+</sup>                                                                                                                                   | 100 <sup>B</sup>                                    |
| Cu <sup>2+</sup>                                                                                                                                   | 5 <sup>B</sup>                                      |
| Pt(IV)                                                                                                                                             | 3 <sup>B</sup>                                      |

A: excess precipitate, B: excess inhibit

Table 2—Comparison of accuracy of developed method and XRF method in the analysis of real samples.

| Sample No. | Present method (%)     | Average value (%) | RSD % | XRF    |
|------------|------------------------|-------------------|-------|--------|
| 1          | 0.027, 0.0268, 0.0262  | 0.0267            | 1.56  | 0.0270 |
| 2          | 0.0049, 0.0049, 0.0051 | 0.0049            | 2.3   | 0.0050 |

determination of Pd(II) in real samples, specially in Al-Si-Pd catalyst.

#### Interference study

The effect of various anions and cations on the determination of 1.11 ppm of Pd(II) were investigated and the results are summarized in Table 1. A tolerance limit was taken as the concentration of diverse ion causing less than 3% relative error. As can be seen, many anions and cations have no considerable effect on the determination of Pd(II).

#### Determination of palladium in real sample

The method was applied to the determination of palladium in silicon-aluminum catalysts. An accurately measured sample of Pd-containing catalysts dissolved in 10 mL aqua regia and evaporated to near dryness and another 10 mL aqua regia was added and the solution was evaporated to 2 mL, then diluted to 10 mL with doubly distilled water. After filtration, with filter paper Watman No.

42, 2 mL of the sample solution adjusted to pH 4.3, was transferred to glass beaker and determination carried out by the general procedure described above (Table 2). In order to validate the accuracy of the proposed method, the catalysts were also analyzed by XRF. As it is seen in Table 2, it is good agreement between proposed and XRF standard method.

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