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# Determination of Trace Amounts of Gold(III) using Ethopropazine Hydrochloride and Isothipendyl Hydrochloride: A Spectrophotometric Study

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Two simple, sensitive and accurate spectrophotometric methods have been proposed for the determination of micro amounts of gold (III) using ethopropazine hydrochloride (EPH) and isothipendyl hydrochloride (IPH). The methods are based on the oxidation of phenothiazines by gold (III) to give red radical cations having maximum absorption at 513 and at 512 nm with molar absorptivities of  $2.0 \times 10^4$  and  $2.1 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$  for EPH and IPH respectively. Beer's law is valid over the concentration range 0.5-14.1  $\text{mg l}^{-1}$  for EPH and 0.5-14.5  $\text{mg l}^{-1}$  for IPH. The proposed methods have been successfully applied for the determination of gold (III) in synthetic mixtures.

## Introduction

The beauty and rarity of gold has led to its use in jewellery and in coinage and as a standard for monetary systems throughout the world. Since gold is such a soft metal, it is usually alloyed to give it more strength. Alloys of gold with the other elements of the copper group (IB) are most frequently used. Gold has been used in medicine for quite some time. Many spectrophotometric<sup>1-10</sup> methods have been reported for the determination of gold using reagents viz., 1-(2-pyridylazo)-2-naphthol<sup>1</sup>, malachite green<sup>2</sup>, copper complex of 4,7-dimethyl-2-thione-2-thiol-1,3,2-dioxaphosphorinane<sup>3</sup>, Nile blue B<sup>4</sup>, o-methoxy phenyl hydrazone-1,3,3-trimethyl-2-formilindoline perchloride<sup>5</sup>, Michler's thioketone<sup>6</sup>, 1-(2',4',6'-trichlorophenyl)-4,4,6-trimethyl-(1H,4H)-2-pyrimidinethiol in presence of tri-iso-octylamine<sup>7</sup>, trifluoroethylxanthate<sup>8</sup>, 8-methoxy-2-chloroquinoline-3-carbaldehyde thiosemicarbazone<sup>9</sup> and benzyldimethylphenyl ammonium chloride<sup>10</sup>. These methods require either extraction<sup>1-5,7,9</sup> or heating<sup>6</sup> or have less sensitivity<sup>7-9</sup> or suffer from interference by a large number of ions<sup>9-10</sup>. In continuation of our work on the utility of phenothiazines as analytical reagents for the spectrophotometric determination of some metal ions, viz., V (V)<sup>11-12</sup>, Cr (VI)<sup>13</sup>, Mo (VI)<sup>14</sup>, Pd (II)<sup>15</sup> and Se (IV)<sup>16</sup>, we are now reporting two simple, adequately sensitive, accurate, non-extractive spectrophotometric methods for the determination of gold (III) using EPH and IPH.

## Experimental

### Equipment and reagents

A Hitachi UV visible spectrophotometer model U-2001 with 1.0 cm quartz cells was used for the measurement of absorbances.

A gold (III) solution was prepared by dissolving the requisite amount of gold (III) chloride (John Matthey) in 1 M hydrochloric acid and diluting with distilled water. It was standardised gravimetrically<sup>17</sup>. A working solution of 100 mg l<sup>-1</sup> of gold (III) was prepared for the study. Two 0.2% solutions one of EPH and the other of IPH, were prepared separately in distilled water and stored in amber coloured bottles in a refrigerator. A 10 M phosphoric acid solution was prepared in distilled water. Solutions of diverse ions of suitable concentrations were prepared using AR grade reagents.

Synthetic mixtures were prepared by mixing solutions of gold (III) and other metal ions in suitable proportions as given in Table 1.

**Table 1.** Determination of gold (III) in synthetic mixtures

| Au (III) | Metal ions taken in mg l <sup>-1</sup> |         |         |         | Gold (III) found* in mg l <sup>-1</sup> |      | % RSD |      |
|----------|--|---------|---------|---------|---|------|-------|------|
|          | Cu (II)                                | Pt (II) | Pd (II) | Zn (II) | EPH                                     | IPH  | EPH   | IPH  |
| 2.00     | 0.15                                   | 0.050   | 0.050   | 0.050   | 1.98                                    | 1.98 | 0.94  | 1.04 |
| 4.00     | 0.30                                   | 0.100   | 0.100   | 0.100   | 4.04                                    | 4.00 | 0.86  | 0.78 |
| 6.00     | 0.45                                   | 0.150   | 0.150   | 0.150   | 5.97                                    | 5.99 | 1.09  | 0.91 |
| 8.00     | 0.60                                   | 0.200   | 0.200   | 0.200   | 8.06                                    | 8.03 | 0.84  | 1.01 |

\*Average of five determinations

## Procedure

### Preparation of the calibration graph

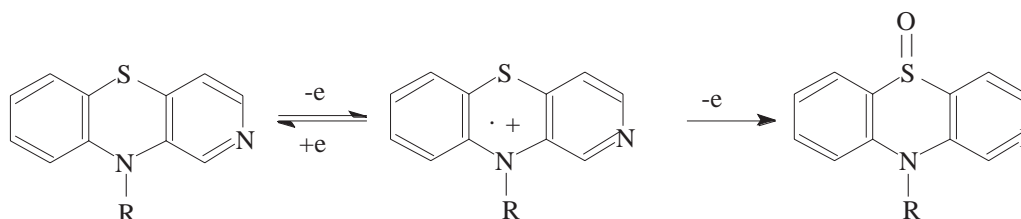
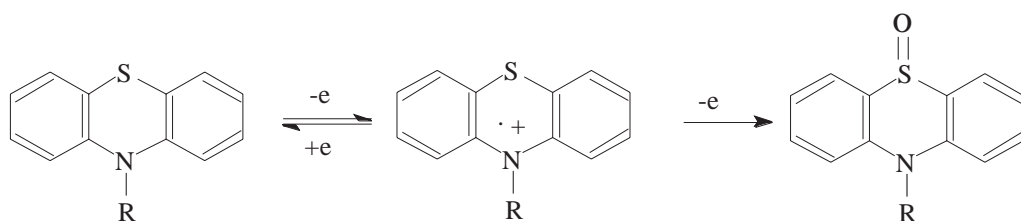
To a known volume of gold (III) solution were added 10 M phosphoric acid (4 ml for EPH or 2 ml for IPH) and EPH or IPH (1.0 ml). The contents were diluted to 10 ml with distilled water, mixed well and the absorbances were measured at 513 nm for EPH and at 512 nm for IPH. The amount of gold (III) in the sample solution was deduced from the calibration curve.

### Determination of gold (III) in synthetic mixtures

The proposed methods were successfully applied for the investigation of micro amounts of gold (III) in synthetic mixtures. The results presented in Table 1 are well supported by the statistical data.

## Results and Discussion

Investigations have shown that EPH or IPH reacts with gold (III) at room temperature in H<sub>2</sub>SO<sub>4</sub>, HCl, H<sub>3</sub>PO<sub>4</sub> and CH<sub>3</sub>COOH or in acidic buffers to give a red species that is believed to be a radical cation<sup>18</sup>, which is irreversibly oxidised to a colourless sulphoxide with the loss of one more electron as shown below:



The nature of the red species was confirmed by passing an aliquot of the solution through cation and anion exchange resins. Only the cation exchange resin retained the red species, supporting the cationic nature of the species.

### Effect of acids

The stability and sensitivity of the red radical cations depend on the nature and concentration of the acid medium. The red species were found to be unstable in HCl and H<sub>2</sub>SO<sub>4</sub> and did not give maximum colour intensity in CH<sub>3</sub>COOH. As HNO<sub>3</sub> oxidised the reagents to red species it was not used for the study. Maximum colour intensity and constant absorbances were observed in H<sub>3</sub>PO<sub>4</sub> medium in the concentration range of 3-5 M for EPH and 1-3 M for IPH. Hence, a 4 M and 2 M H<sub>3</sub>PO<sub>4</sub> were used for EPH and IPH respectively.

### Effect of reagent concentration

The effect of the reagent was studied by using 7 mg l<sup>-1</sup> gold (III) and by varying the concentration of the reagent. It was observed that 4.5– and 5.0– fold molar excesses of EPH and IPH were necessary for the complete development of the colour. However, 6.5– and 7– fold molar excess of EPH and IPH respectively were used for the study. The corresponding reagent blanks did not absorb at the respective  $\lambda_{max}$ .

### Sequence of addition of reagents

From experiments in which Au (III), H<sub>3</sub>PO<sub>4</sub>, EPH or IPH were added in all possible sequences, it was found that there was no appreciable change in the  $\lambda_{max}$ , colour intensity or stability of the coloured species.

### Effect of time and temperature

The formation of the coloured species was found to be instantaneous and the absorbances remained constant for more than 45 min over the temperature range of 10-60°C.

## Validity of Beer's law and sensitivity

Beer's law limits, molar absorptivity and Sandell's sensitivity values, regression equation and correlation coefficients for the Au (III)–EPH and Au (III)–IPH systems are given in Table 2. A linear relationship was found between absorbance at  $\lambda_{max}$  and the concentration of the coloured species in the concentration range of 0.5–14.1 mg l<sup>-1</sup> for EPH and 0.5–14.5 mg l<sup>-1</sup> for IPH. Regression analyses of Beer's law plots at their respective  $\lambda_{max}$  values revealed a good correlation. The graphs of absorbance versus concentration showed very low intercept values and are described by the regression equation  $Y = a + bX$  (where Y is the absorbance of a 1 cm layer, b is the slope, a is the intercept and X is the concentration of the metal ion solution in mg l<sup>-1</sup>) obtained by the least-squares method.

**Table 2.** Optical characteristics, precision and accuracy data.

| Parameter  | Value                 |                       |
|--|-----------------------|-----------------------|
|  | EPH                   | IPH                   |
| $\lambda_{max}$ (nm)                                       | 513                   | 512                   |
| Beer's law limits (mg l <sup>-1</sup> )                    | 0.5-14.1              | 0.5-14.5              |
| Molar absorptivity (l mol <sup>-1</sup> cm <sup>-1</sup> ) | 2.0 X 10 <sup>4</sup> | 2.1 X 10 <sup>4</sup> |
| Sandell's sensitivity (ng cm <sup>-2</sup> )               | 17.2                  | 15.3                  |
| Correlation coefficient (r)                                | 0.9990                | 0.9995                |
| Regression equation (Y) <sup>a</sup>                       |                       |                       |
| Slope, b   | 0.1105                | 0.091                 |
| Intercept, a   | 0.031                 | 0.0719                |
| Relative standard deviation (%) <sup>d</sup>               | 0.71                  | 0.94                  |
| % Range of error <sup>d</sup> (95 % confidence limit)      | 0.81                  | 0.76                  |

<sup>a</sup> $Y = a + bX$  where X is the concentration in mg l<sup>-1</sup> and Y is absorbance

<sup>d</sup>For six replicate analyses within Beer's law limits.

## Precision and accuracy

The precision and accuracy of the proposed methods were studied by analysing (5 replicates) 8 mg l<sup>-1</sup> of gold (III) and the RSD values were found to be less than 1.1 % .

## Effect of diverse ions

In order to assess the analytical potential of the proposed methods, the effects of some diverse ions which often accompany gold (III) were examined by carrying out the determination of 8 mg l<sup>-1</sup> of gold (III) in the presence of foreign ions. An ion was considered to interfere in the determination if the absorbances observed differed by more than  $\pm 2\%$  from that for gold (III) alone. The results presented in Table 3 indicate that many metal ions and anions do not interfere in the determination of gold. Hence gold minerals like porpezite containing trace amounts of Cu (II), Pb (II), Zn (II) and Pt (II) could be readily analysed. However, Ru (III), Rh (III), Pd (II) and Os (VIII) interfere seriously as they readily form coloured species with EPH and IPH. The tolerance limit of Os (VIII) and Rh (III) was enhanced by using 1000 mg l<sup>-1</sup> tartarate. Attempts to increase the tolerance limit of Pd (II) in the determination of Au (III) were not successful.

**Table 3.** Tolerance limits of diverse ions in the determination of 8 mg l<sup>-1</sup> of gold (III).

| Ion or species added | Tolerance limit (mg l <sup>-1</sup> ) |      | Ion or species added | Tolerance limit (mg l <sup>-1</sup> ) |      |
|----------------------|---------------------------------------|------|----------------------|---------------------------------------|------|
|                      | EPH                                   | IPH  |                      | EPH                                   | IPH  |
| Ni(II)               | 4000                                  | 4500 | Os (VIII)            | 1.0                                   | 1.0  |
| Cu(II)               | 2300                                  | 2500 | Os (VIII)*           | 2.5                                   | 2.5  |
| Co(II)               | 600                                   | 500  | Rh (III)             | 2.0                                   | 2.0  |
| Mn(II)               | 2000                                  | 1800 | Rh (III)*            | 8.0                                   | 9.0  |
| Cr(III)              | 200                                   | 200  | Zn (II)              | 1200                                  | 1000 |
| Hg(II)               | 1000                                  | 1200 | Acetate              | 4000                                  | 3800 |
| Fe(III)              | 650                                   | 700  | Tartarate            | 1000                                  | 1000 |
| Pd (II)              | 0.75                                  | 1.0  | Citrate              | 6000                                  | 5000 |
| Pt (II)              | 200                                   | 200  | Oxalate              | 1000                                  | 1000 |
| Ir (III)             | 10                                    | 8.0  | Nitrate              | 1500                                  | 1800 |
| Ru (III)             | 1.0                                   | 1.0  | Sulphate             | 2000                                  | 2200 |
| Pb (II)              | 800                                   | 1000 | Chloride             | 6000                                  | 6000 |
| Cd (II)              | 4200                                  | 4000 | Bromide              | 1100                                  | 1000 |

\* In presence of tartarate (1000 mg l<sup>-1</sup>)

## Conclusion

The proposed methods are simple and accurate and have advantages over the reported methods<sup>1-10</sup>, which suffer from interference by large number of ions or require either heating or extraction or are less sensitive.

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