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# Synthesis, characterization and analytical properties of indane-1,2,3-trione monosemicarbazone: Spectrophotometric determination of copper(II) and palladium(II)

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### Abstract

Copper(II) and palladium(II) form 1 : 2 and 1 : 1 complexes with indane-1,2,3-trione monosemicarbazone (ITMS) respectively in sodium acetate-acetic acid buffer medium. Both complexes conform to Beer's law up to 3.49 ppm of copper [molar absorptivity ($\varepsilon$), $1.25 \times 10^4$ litre mol$^{-1}$ cm$^{-1}$ at 355 nm] and 7.66 ppm of palladium [$\varepsilon$, $7.21 \times 10^3$ litre mol$^{-1}$ cm$^{-1}$ at 360 nm]. The solid complexes of copper(II) and palladium(II) with ITMS are isolated and characterized and probable structures assigned. Tolerance limit for foreign ions are given and ITMS is used for the determination of copper in ferrous material.

Key words: Spectrophotometry, copper(II), palladium(II), indane-1,2,3-trione monosemicarbazone.

## 1. Introduction

Semicarbazones are infrequently utilized in the spectrophotometric determination of metal ions. A survey of literature[1,2] reveals that indanetrione derivatives of semicarbazide are not reported so far. Hence an attempt is made for the synthesis and characterization of indane-1,2,3-trione monosemicarbazone (ITMS). ITMS reacts with a few metal ions and is found to be particularly selective and sensitive reagent for the spectrophotometric determination of copper(II) and palladium(II).

## 2. Experimental

Beckman DU-2 spectrophotometer, Perkin Elmer 983 G Infrared spectrometer an ELICO pH-meter (Model LI-120) were used in the present study. IR spectra wer obtained by preparing KBr discs of the solid substances.

ITMS ($1 \times 10^{-2}$ M) reagent solution was prepared in dimethylformamide.

Copper(II) sulphate pentahydrate (AR, BDH) and palladium(II) chloride (AR) wer used for preparing stock solutions of copper(II) and palladium(II) respectively. Thes solutions were standardized[3].

Hydrochloric acid (1 M) + 1 M sodium acetate (pH 0.5–4.0) and 0.2 M sodium acetat +0.2 M acetic acid (pH 4.0–6.5) buffers were used in the pH metric study.

All reagents used were of analytical grade.

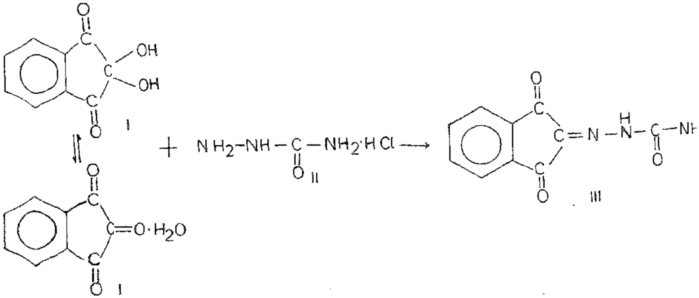
## 3. Synthesis, characterization and properties of ITMS

A mixture of 0.02 mole of ninhydrin (I) in ethyl alcohol and 0.02 mole of semicarbazid hydrochloride (II) in water was taken in a 250-ml round bottom flask and warmed on water bath for 30 min. Yellow coloured product was separated on cooling the reactio mixture in the flask. The product was recovered by vacuum filtration and recrystallize from absolute ethanol. m.p. 234–237°C. The infrared spectra was consistent with t structure (III) of ITMS.

The reagent has solubilities in dimethylformamide, methanol, ethanol, carbo tetrachloride, chloroform, benzene and n-amyl alcohol of 4.10, 0.25, 0.20, 0.11, 0.12, 0. and 0.10 g/l respectively. No visible colour reactions were observed for 25 cations teste except for copper(II), palladium(II), Au(III) [$\varepsilon = 1.98 \times 10^3$ at 335 nm in pH 2.0] an Os(VIII) [$\varepsilon = 2.1 \times 10^3$ at 340 nm in pH 5.0].

## 4. Analytical procedures

*Determination of copper:* Samples were prepared in 25-ml calibrated flasks by takin 10 ml of sodium acetate-acetic acid (pH 4.2) buffer solution, 0.32–3.49 ppm c copper(II), 2.5 ml of dimethylformamide and 2.0 ml of $1 \times 10^{-2}$ M ITMS solution Solutions were diluted to volume in 25-ml volumetric flask and absorbance was measure



at 355 nm against reagent blank prepared under identical conditions. Analytical graph was prepared similarly.

*Determination of palladium:* An aliquot of a solution containing 10 ml of sodium acetate-acetic acid (pH 5.0) buffer solution, palladium(II) [0.85–7.66 ppm], 2.5 ml of dimethylformamide and 2.5 ml of $1\times10^{-2}$ M ITMS solution, was diluted to 25 ml in calibrated flask and its absorbance measured at 360 nm against reagent blank prepared identically. A calibration graph was prepared accordingly.

*Simultaneous determination of copper and palladium:* Copper(II) [$3\times10^{-4}$ M, 1.0–4.0 ml] and palladium(II) [$2.5\times10^{-4}$ M 1.0–4.0 ml] solutions were added keeping the total volume constant at 5.0 ml in a set of 25-ml calibrated flasks, each containing 10 ml of buffer solutions of pH 4.5 and 2.5 ml of DMF. Reagent solution ($1\times10^{-2}$ M, 2.5 ml) was added to each flask and diluted to volume with water and absorbance [$A_{(Cu+Pd)}$] measured at 355 nm and 360 nm against reagent blank. In another set of 25-ml calibrated flasks identical solutions were prepared each containing 0.5 ml of thiocyanate ($2\times10^{-2}$ M) which masks palladium if it is added prior to the addition of ITMS solution. The absorbance [$A_{Cu}$] of these solutions was measured at 355 and 360 nm against a reagent blank. The values at 355 nm were referred to the analytical curve prepared in the copper determination. Palladium can be estimated using the difference in absorbance values at 360 nm for solutions containing with and without thiocyanate.

$$\text{Amount of copper (in ppm)} = A_{Cu}\times5.087 \qquad (1)$$

$$\text{Amount of palladium (in ppm)} = [A_{(Cu+Pd)}-A_{Cu}]\times14.76. \qquad (2).$$

## 5. Results and discussion

Various physico-chemical and analytical properties of copper and palladium complexes of ITMS are summarized in Table I. The colour formation reactions are instantaneous and complexes are stable for two days in the presence of 10% aqueous DMF. The order of addition of constituents [metal ion ($Cu^{2+}$ or $Pd^{2+}$), buffer and reagent] has no effect on the absorbance provided that DMF is added prior to the addition of ITMS solution.

*Synthesis and characterization of complexes*: Elemental and infrared spectral data[4-7] of ITMS and its copper and palladium complexes are given in Table II. Infrared data for $\nu C=N$ and $\nu NH_2$ suggest the participation of azomethine nitrogen atom[4] and terminal nitrogen' atom[5,6] in chelation.

*Effect of foreign ions*: Various ions werê examined for their effect on the determination of 3.17 ppm of copper(II) and 3.40 ppm of palladium(II). The tolerance limit was taken as the amount of foreign ion required to cause ±2% error in the absorbance. Of the 50 ions studied, only chromium(VI) interfers (may be because of its oxidizing property[8]) under chosen experimental conditions for copper and palladium determination. Larger amounts of iron(III) (235 ppm in Cu-system and 117 ppm in Pd-system) can be masked

**Table I**
**Physico-chemical and analytical characteristics of complexes**

| Characteristic | Cu-complex | Pd-complex |
|---|---|---|
| Colour | Yellow | Brownish red |
| $\lambda_{max}$(nm) | 355 | 360 |
| Mol of reagent required per mol of metal ion | 15 | 15 |
| Optimum pH range | 3.5–5.0 | 4.0–5.5 |
| Beer's law validity range (ppm) | 0.32–3.49 | 0.85–7.66 |
| Optimum concentration range as evaluated from Ringbom's plot (ppm) | 0.95–3.17 | 1.70–5.96 |
| Molar absorptivity (l mol$^{-1}$ cm$^{-1}$) | $1.25 \times 10^4$ | $7.21 \times 10^3$ |
| Composition (M:L) (Job's and Mole ratio methods) | 1:2 | 1:1 |
| Standard deviation* | 0.0089† | 0.0431‡ |

* For 10 replicate determination; † In the determination of 3.17 ppm of copper; ‡ In the determination of 3.40 ppm of palladium.

**Table II**
**Analytical and infrared spectral data of ITMS and its copper and palladium complexes**

| ITMS/Complex | Found (Calc.) % | | | Infrared spectral data ($\nu$; cm$^{-1}$) | | | Assignment |
|---|---|---|---|---|---|---|---|
| | M | C | H | ITMS | Cu-complex | Pd-complex | |
| $C_{10}H_7N_3O_3$ | — | 55.38 | 3.15 | 3393 | 3261 | 3251 | $\nu NH_2^{5,6}$ |
| | | (55.29) | (3.25) | 3326 | 3233 | 3231 | |
| | | | | 3259 | — | — | |
| $[Cu(C_{10}H_7N_3O_3)_2SO_4]$* | 10.50 | 40.51 | 2.15 | 1679 | 1650 | 1650 | $\nu C{=}N^4$ |
| | (10.69) | (40.42) | (2.37) | | | | |
| $[Pd(C_{10}H_7N_3O_3)Cl_2]$† | 26.91 | 30.97 | 1.75 | 1718 | 1719 | 1718 | $\nu$( C=O) |
| | (26.98) | (30.45) | (1.79) | | | | (Indane ring) |
| | | | | | 480 | 561 | $\nu M{-}N^7$ |
| | | | | | 441 | — | |
| | | | | | | 300 | $\nu M{-}Cl^7$ |

* and † pH at which isolated 4.2 and 5.0 respectively.

with 760 ppm of sodium fluoride. In the presence of 23 ppm of thiocyanate 5 ppm of palladium can be masked in copper determination. A 9-fold excess of platinum(IV) does not interfere in the presence of 280 ppm of oxalate in copper system. The tolerance limit for other associated ions are listed in Table III.

**Table III**
**Tolerance limit of foreign ions in the determination of 3.17 ppm of copper(II) and 3.40 ppm of palladium(II)**

| Ion added | Tolerance limit/ppm | | Ion added | Tolerance limit/ppm | |
|---|---|---|---|---|---|
| | Cu-system | Pd-system | | Cu-system | Pd-system |
| Fluoride | 1900 | 1900 | Fe(III) | 235* | 117* |
| Chloride | 709 | 638 | Co(II) | 59 | 7 |
| Bromide | 1120 | 869 | Ni(II) | 6 | 5 |
| Iodide | 1269 | 1086 | Cu(II) | — | 1.5† |
| Phosphate | 760 | 456 | Zn(II) | 78 | 130 |
| Sulphate | 106 | 15 | Sr(II) | 420 | 280 |
| Nitrate | 1240 | 1240 | Zr(IV) | 255 | 218 |
| Oxalate | 352 | 528 | Mo(VI) | 38 | 767 |
| Thiocyanate | 30 | — | Ru(III) | 8 | 10 |
| Thiosulphate | 8 | 77 | Rh(III) | 41 | 21 |
| Thiourea | 30 | 1 | Pd(II) | 1 | — |
| Tetraborate | 1411 | 1411 | Pd(II) | 5‡ | — |
| Citrate | 230 | 172 | Ag(I) | 17 | — |
| Tartrate | 726 | 1105 | Cd(II) | 135 | 90 |
| Chlorate | 167 | 167 | W(VI) | 29 | 37 |
| Bromate | 154 | 152 | Os(VIII) | 8 | 1 |
| Iodate | 210 | 280 | Ir(III) | 116 | 92 |
| Borate | 235 | 141 | Pt(IV) | 21 | 14 |
| V(V) | 1 | 8 | Au(III) | 3 | 2.3 |
| Cr(III) | 52 | 42 | Hg(II) | 54 | 8 |
| Cr(VI) | 0.2 | 0.2 | Pb(II) | 41 | 51 |
| Mn(II) | 66 | 484 | Pt(IV) | 31§ | — |

* In the presence of 760 ppm of sodium fluoride; † In the presence of 60 ppm of thiosulphate; ‡ In the presence of 23 ppm of thiocyanate; § In the presence of 280 ppm of oxalate.

## 6. Simultaneous determination of copper and palladium

Thiocyanate, which interferes seriously in the determination of palladium(II), is highly useful as a masking agent for masking palladium(II) in the determination of copper(II) using ITMS. Results obtained for the simultaneous determination of copper(II) and palladium(II) using thiocyanate as masking agent are presented in Table IV.

*Determination of copper in ferrous material*: Ferrous material sample solution was prepared by following the procedure given in literature[9]. A sample containing 0.5 g of ferrous material was dissolved in 25 ml of 1:1 hydrochloric acid and 2.5 ml of nitric acid. The solution was evaporated to dryness with several successive additions of hydrochloric acid. The residue was taken in water, neutralised with ammonium hydroxide, filtered and diluted to 100 ml in a volumetric flask.

Table IV
**Simultaneous determination of copper and palladium in a mixture**

| Sample no. | Amount of metal ion added/ppm | | Amount of metal ion found/ppm | | Error % | |
|---|---|---|---|---|---|---|
| | Copper | Palladium | Copper | Palladium | Copper | Palladium |
| 1. | 3.048 | 1.064 | 3.033 | 1.042 | −0.50 | −2.07 |
| 2. | 2.286 | 2.128 | 2.316 | 2.085 | +1.31 | +2.05 |
| 3. | 1.524 | 3.192 | 1.508 | 3.235 | −1.05 | −1.34 |
| 4. | 0.762 | 4.256 | 0.767 | 4.256 | +0.65 | — |

Table V
**Analysis of ferrous material**

| Ferrous material | Volume (ml) | Amount of copper (ppm) | | Error % |
|---|---|---|---|---|
| | | Taken | Found* | |
| Alloy cast iron† | 1.0 | 1.27 | 1.24 | −2.36 |
| | 1.5 | 1.90 | 1.92 | +1.05 |
| | 2.0 | 2.54 | 2.50 | −1.57 |
| | 2.5 | 3.17 | 3.20 | +0.95 |

* Average of three determinations; † Composition: Mn 0.63%, Cr 0.52%, Mo 0.48%, Ni 2.38% and Cu 1.54%.

To 10 ml of buffer solution of pH 4.2, 2 ml of 1.0 M sodium fluoride, sample solution (in the optimum concentration range), 2.5 ml of DMF and 2.0 ml of $1 \times 10^{-2}$ M ITMS solution were added. The solution was diluted to volume (25 ml) and the absorbance was measured at 355 nm against a reagent blank. The results are presented in Table V.

## 7. Conclusions

From the above discussion, it can be concluded that ITMS is a potential reagent for the spectrophotometric determination of copper(II) and palladium(II). The reagent is very easy to synthesize and purify. The most favourable characteristic of ITMS is its high specificity towards copper(II) and palladium(II) as no other metal ion in the first and the second row transition series is found to give colour reaction with the reagent. The colour reactions with $Cu^{2+}$ and $Pd^{2+}$ are rapid and the absorbance of both the complexes adheres to Beer's law over a wide range of metal ion ($Pd^{2+}$ or $Cu^{2+}$) concentration. Moreover, the present methods are simple without a need for heating or extraction or any incubation period for full colour development.

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