

## Separation of Co(II), Ni(II), Cu(II) and Pd(II) with 4-benzoyl-3-methyl-1-phenylpyrazol-5-one using tetradecyldimethylbenzylammonium chloride-naphthalene as an adsorbent

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A method has been established for the determination of Co(II), Ni(II), Cu(II) and Pd(II) after preconcentration with 4-benzoyl-3-methyl-1-phenylpyrazol-5-one (BMPP) supported on tetradecyldimethylbenzyl ammonium chloride (TDBA)-microcrystalline naphthalene using a simple funnel-tipped glass tube. The metals form a water insoluble metal-BMPP complex with  $\lambda_{\max}$  at 360 nm for Co(II), 480 nm for Ni(II), 430 nm for Cu(II) and 380 nm for Pd(II)-complexes. The molar absorptivities and Sandell's sensitivities for all these complexes are found to be in the range  $1.09 \times 10^4$ - $1.87 \times 10^4$   $l \text{ mol}^{-1} \text{ cm}^{-1}$  and 0.0046-0.0058  $\mu\text{g cm}^{-2}$  respectively. The proposed method has been tested for the determination of nickel(II) and copper(II) in standard alloys and vehicle exhaust particulates.

Pyrazolones have been reported to be potential extractants<sup>1,2</sup> and powerful drugs<sup>3</sup>. Their varied chemical and physical properties such as high extractive efficiency, quantitative extraction at low pH, high selectivity and ease of stripping have led to their application in a number of industrial processes<sup>4</sup>. For trace analysis, the transition metals, i.e., Co(II), Ni(II), Cu(II) and Pd(II) often require concentration prior to their determination. In the present note, an efficient method for separation of these metals is reported using 4-benzoyl-3-methyl-1-phenylpyrazol-5-one (BMPP) as a reagent and microcrystalline naphthalene-TDBA as an adsorbent. The method has been used for the determination of Ni(II) in alloy and Cu(II) in vehicle exhaust particulate sample.

### Experimental

All the chemicals used were of AR and GR grades of BDH or E Merck. BMPP was prepared by the literature method<sup>4</sup>. The compound was recrystallized from *n*-hexane and used as a 0.5%

solution in a mixture of water and dioxane. Britton-Robinson buffers in the pH range 3.0-11.0 were prepared from AR grade chemicals.

A Shimadzu UV-visible spectrophotometer (UV-160A) with 10 mm matched quartz cells were used for absorption spectra. A funnel-tipped glass tube (i.d., 50 × 6 mm) was used as a column. The column was plugged with coarse polypropylene fibers and packed with TDBA-naphthalene adsorbent to a height of 1-1.5 cm.

### Preparation of TDBA-naphthalene adsorbent

A solution of naphthalene was prepared by dissolving 20 g of naphthalene in 40 ml of acetone at 35°C. The solution was transferred to a 150 ml RB flask and to it a solution of TDBA (1.5 g) in 500 ml water was added slowly. The naphthalene coprecipitated with TDBA was stirred and allowed to stand for 2 hrs. The slurry was washed twice with water and stored in a brown bottle.

### General procedure

An aliquot of solution containing Co(II) (5-70  $\mu\text{g}$ ), Ni(II) (4-80  $\mu\text{g}$ ), Cu(II) (5-105  $\mu\text{g}$ ) or Pd(II) (6-84  $\mu\text{g}$ ) was taken in a 50 ml beaker. To it were added 0.6 ml of 0.5% BMPP and 0.5 ml of buffer solution (pH 4.5). The solution was diluted with 30 ml of distilled water and passed through a column packed with the TDBA-naphthalene adsorbent at a flow rate of 2 ml/min. The column was washed with small amounts of water and aspirated for a few minutes while pushing with a flat glass rod. The metal complex along with naphthalene was stripped with 10 ml of DMF, and the absorbance was measured against the reagent blank at  $\lambda_{\max}$  360 nm for Co(II), 480 nm for Ni(II), 430 nm for Cu(II) and 380 nm for Pd(II). The molar absorptivities and Sandell's sensitivities of these complexes were found to be in the ranges  $1.09$ - $1.87 \times 10^4$   $l \text{ mol}^{-1} \text{ cm}^{-1}$  and 0.0046-0.0058  $\mu\text{g cm}^{-2}$  respectively.

### Results and discussion

The cobalt(II), nickel(II), copper(II) and palladium(II)-BMPP complexes were quantitatively adsorbed on the TDBA-microcrystalline naphthalene adsorbent. Absorbance remains constant in the pH range 3.0-7.0. Therefore, all the experiments were carried out at pH 4.5. The addition of 0.5-3.0 ml of the acetate buffer did not affect the ret-

Table 1 — Determination of Cu(II) and Ni(II) in alloy, and vehicle exhaust particulates

Sample	Composition	Metal ions	
		Cert. value	Found <sup>a</sup>
NKK 920 Aluminium alloy	Sn : 0.20, V : 0.05, Si : 0.78, Mg : 0.46, Zn : 0.80, Mn : 0.20, Sn : 0.20, Bi : 0.06, Pb : 0.10, Ti : 0.15, Cr : 0.27, Fe : 0.72 <sup>d</sup> Ca : 0.03, Ga : 0.05 Cu : 0.71, Ni : 0.29 (in %)	Cu <sup>b</sup> : 0.71 (%) Ni <sup>c</sup> : 0.29 (%)	Cu : 0.72 ± 0.02 (%) Ni : 0.27 ± 0.03 (%)
NIES, No 8 <sup>†</sup> Vehicle exhaust particulates	K : 0.115 ± 0.008, Ca : 0.530 ± 0.020, Zn : 0.104 ± 0.005, Mg : 0.101 ± 0.005, Al : 0.330 ± 0.020, Na : 0.192 ± 0.008, Sr : 89.0 ± 3.0, Cu : 67.0 Ni : 18.5, Cd : 1.1 ± 0.1 Pb : 219 ± 9.0, As : 2.6 ± 0.2 Cr : 25.5 ± 1.5, V : 17.0 ± 2.0 Sb : 6.0 ± 0.4, P : (510), Cs : (0.24), Rb : (4.6) Sc : (0.55), La : (1.2) Br : (56.0), Ag : (0.2) Se : (1.3), Mo : (6.4) Ce : (3.1), Th : (0.35) Sm : (0.20), Eu : (0.05) Lu : (0.02), (in µg/g)	Cu <sup>b</sup> : 67.0 (µg/g) Ni <sup>c</sup> : 18.5 (µg/g)	Cu <sup>b</sup> : 67.25 ± 1.2 (µg/g) Ni <sup>b</sup> : 18.4 ± 0.5 (µg/g)

<sup>a</sup>Average of five replicate determinations

<sup>b</sup>Copper masked by 5 ml of 5% KI solution in the determination of Ni(II)

<sup>c</sup>Nickel masked by 5 ml of 5% EDTA solution for the determination of copper

<sup>d</sup>Iron(III) masked by 2 mg of Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>

<sup>†</sup>NIES No. 8 supplied by Iron and Steel Institute of Japan, Tokyo, Japan

ention but the use of 0.5 ml buffer is recommended. The flow rate was varied from 1-30 ml/min and the optimum flow rate was found to be 2 ml/min.

The retention on this adsorbent remained constant when the volume of the aqueous phase did not exceed 160 ml. For convenience, in all the subsequent experiments, 30 ml of the aqueous solution was used. To study the effect of concentration of reagent, 0.1-2.0 ml of 0.5% BMPP solution were tested. Although retention remained constant when 0.2 ml of this reagent was used, a volume of 0.6 ml was used for further studies. The solid mass material is insoluble in common organic solvents such as toluene, xylene, nitrobenzene, methylisobutylketone, but soluble in methyl alcohol, ethyl alcohol, butyl alcohol, iso-amyl alcohol, 1,4-dioxane, acetonitrile, DMSO and DMF.

In DMF absorbance was maximum, therefore, DMF was found to be the most suitable solvent.

Under the optimum conditions described above, calibration curves were plotted over the concentration range 0.5-7.0 ppm for Co(II), 0.4-8.0 ppm for Ni(II), 0.5-10.5 ppm for Cu(II) and 0.6-8.4 ppm for Pd(II), for 10 ml of the final solution. The molar absorptivities and Sandell's sensitivities of these complexes are found to be in the range  $1.09-1.87 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$  and  $0.0046-0.0058 \text{ µg cm}^{-2}$  respectively. Seven replicate determinations of 3.0 ppm of Co(II), 2.4 ppm of Ni(II), 4.2 ppm of Cu(II) and 3.9 ppm of Pd(II) gave mean absorbance of 0.724, 0.518, 0.622 and 0.685 respectively, with relative standard deviation of 0.70, 0.35, 0.65 and 1.00%, respectively.

#### Effect of diverse ion

The interference of foreign ions in the estima-

tion of 30  $\mu\text{g}$  of Co(II), 24  $\mu\text{g}$  of Ni(II), 42  $\mu\text{g}$  of Cu(II) and 39  $\mu\text{g}$  of Pd(II) was studied under optimum conditions. The following (amount shown in parentheses) did not interfere; sodium acetate (80 mg),  $\text{NH}_4\text{Cl}$ ,  $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$  (10 mg),  $\text{KH}_2\text{PO}_4$  (5 mg), ammonium citrate, potassium tartrate,  $\text{Na}_2\text{C}_2\text{O}_4$  (3 mg each),  $\text{KNO}_3$ ,  $\text{NaCl}$ ,  $\text{NH}_4\text{F}$ ,  $\text{Na}_2\text{S}_2\text{O}_3$  (2 mg each), EDTA (10  $\mu\text{g}$ ). Among the cations examined,  $\text{Ca}^{2+}$ ,  $\text{W}^{6+}$ ,  $\text{Mg}^{2+}$  (2 mg each),  $\text{Cr}^{3+}$ ,  $\text{Ag}^+$  (150  $\mu\text{g}$ ),  $\text{Pb}^{2+}$ ,  $\text{Au}^{3+}$ ,  $\text{Pt}^{4+}$  (500  $\mu\text{g}$  each),  $\text{Zn}^{2+}$ ,  $\text{Hg}^{2+}$  (200  $\mu\text{g}$  each),  $\text{Al}^{3+}$ ,  $\text{Bi}^{3+}$  (100  $\mu\text{g}$  each) did not interfere.  $\text{Fe}^{3+}$  interfered in all the determinations and was masked with 2 mg of  $\text{Na}_2\text{C}_2\text{O}_4$ . The interference due to  $\text{Pd}^{2+}$  in the determination of copper(II) and cobalt(II) could be eliminated by adding 5 ml of 5% NaCN at pH 2.0. While interference of  $\text{Ni}^{2+}$  in the determination of copper(II) was masked with 5 ml of 5% of EDTA, that of  $\text{Cu}^{2+}$  in the determination of nickel(II) was eliminated by masking with 5 ml of 5% KI solution.

The developed method has been tested for the standard alloy sample. The alloy sample (10 mg) was dissolved completely in 5 ml of conc  $\text{HNO}_3$  by heating on a water bath.  $\text{H}_2\text{O}_2$  (0.5 ml, 30% v/v) was added. The solution was evaporated to near dryness to remove excess acid and dissolved in minimum amount of distilled water and filtered. The volume was made up to 100 ml with distilled water. Samples of vehicle exhaust particulate (1 g) was dissolved in 18 ml of conc  $\text{HNO}_3$ , 18 ml of conc  $\text{HClO}_4$  and 2 ml of conc HF in a 100 ml teflon beaker. The mixture was evaporated to a small volume, filtered through a filter paper and the volume was made up to 50 ml with distilled water. The studied metal ions were determined by the recommended procedure. The results obtained (Table 1) are in agreement with the certified values.

A simple and rapid method has been reported for the separation of Co(II), Ni(II), Cu(II) and Pd(II) after preconcentration with 4-benzoyl-3-methyl-1-phenylpyrazol-5-one (BMPP) supported on quaternary ammonium salt-microcrystalline naphthalene in a column. The present method is more sensitive than the method using 2,2'-biquinoline<sup>5</sup> (Sandell's sensitivity,  $S=0.010$ ), 3',5'-dimethyl-2'-hydroxyazobenzene-4-sulphonic acid<sup>6</sup> ( $S=0.0130$ ), 1-phenyl-4,4,6-trimethyl (1H, 4H) pyrimidine-2-thiol<sup>7</sup> ( $S=0.0081$ ) for copper(II); 8-hydroxyquinoline<sup>8</sup> ( $S=0.008$ ), 2-methyloxime<sup>9</sup> ( $S=0.012$ ), dimethylglyoxime<sup>10</sup> ( $S=0.020$ ), nixoime<sup>11</sup> ( $S=0.016$ ), tetrahydrofurfurylxanthate<sup>12</sup> ( $S=0.018$ ), phenanthraquinoxime<sup>13</sup> ( $S=0.076$ ) for nickel(II). Although the present method is less

sensitive than earlier reported methods using 4-(2-quinolazo)phenol<sup>14</sup> ( $S=0.0012$ ), 1-(2'-amino-3'-hydroxypyridyl-4'-azo)benzene-4-sulphonic acid<sup>15</sup> ( $S=0.0022$ ), 9,10-phenanthroquinonemonoxime<sup>16</sup> ( $S=0.001$ ) for copper(II) and morpholine-4-carbodithiamate<sup>17</sup> ( $S=0.004$ ) for nickel(II), the present method is simple and trace amounts of copper(II) and nickel(II) can be preconcentrated from large volumes of aqueous solution. Although the solvent extraction is a simple and efficient separation procedure, it is difficult to extract some metals in the presence of surfactants because of emulsion formation in the two phases on shaking. In such cases, large amount of salting-out agent must be added for proper phase separation of the complex. The proposed method is simple and requires only small volumes of organic solvents and reagents. Regeneration of the adsorbents is not required as in the case of ion-exchange procedure using Chelex-100 on activated carbon. The sensitivity of the method may be improved by using other optical analytical techniques such as flameless atomic absorption spectrophotometry or HPLC.

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