

**Table 2** Force constant contributions from  $G^{-1} \lambda$  and intensities

Force Constant	Molecule	CH <sub>4</sub> F <sub>2</sub> Species	CD <sub>4</sub> F <sub>2</sub> Species	CT <sub>4</sub> F <sub>2</sub> Species
$F_{11}$	$G_{11}^{-1} \lambda_1$	5.373	5.559	6.466
	$F'_{11} (R)$	-0.01	-0.009	-
	$F'_{11} (IR)$	-0.004	-0.018	-0.139
$F_{22}$	$G_{22}^{-1} \lambda_2$	0.540	0.544	0.528
	$F'_{22} (R)$	0.191	0.078	-
	$F'_{22} (IR)$	0.072	0.063	0.188
$F_{12}$	$G_{12}^{-1} \lambda_1$	-0.099	0.063	-0.277
	$F'_{12} (R)$	0.580	0.582	-
	$F'_{12} (IR)$	0.165	0.034	0.156

become very simple.

$$F_{11} = G_{11}^{-1} \lambda_1 + \frac{(\lambda_2 - \lambda_1)}{I_1^2} (G_{11}^{-1} I_1^2 - A_1^2),$$

$$F_{22} = G_{22}^{-1} \lambda_2 + \frac{(\lambda_1 - \lambda_2)}{I_1^2} A_2^2,$$

$$F_{12} = G_{12}^{-1} \lambda_1 + \frac{(\lambda_2 - \lambda_1)}{I_1^2} (G_{12}^{-1} I_1^2 - A_1 A_2).$$

$F$  elements evaluated are given in table 2.

There are two striking features. (i) The contribution of the first term is very large compared to the intensity term. Though we do not have the Raman intensity for CT<sub>4</sub> one can perhaps say it is of the same order of magnitude as CH<sub>4</sub> and CD<sub>4</sub>. It is really interesting to see that  $G_{11}^{-1} \lambda_1$ ,  $G_{22}^{-1} \lambda_2$  and  $G_{12}^{-1} \lambda_1$  are so different for CT<sub>4</sub> compared to CH<sub>4</sub> and CD<sub>4</sub>; one wonders whether  $F_{11}$ ,  $F_{22}$  and  $F_{12}$  are really the same for these molecules. Perhaps the  $A$  elements are also not the same for isotopic molecules, but the intensity contribution is so small that the small variations of  $A$  are not important. It is also not possible to explain the difference in the value of  $G_{11}^{-1} \lambda_1$  as due to error in the determination of anharmonicity correction. (ii) The other point of interest is that  $F_{11}$  is a function of  $A_1^2$ . The polarizability derivative of stretching,  $F_{22}$  the bending force constant is proportional to  $A_2^2$  the polarizability change due to bending and in the same token  $F_{12}$  is proportional to  $A_1 A_2$ .

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## ANISALDEHYDE-4-PHENYL-3-THIOSEMICARBAZONE AS A NEW ANALYTICAL REAGENT FOR THE EXTRACTION SPECTROPHOTOMETRIC DETERMINATION OF COPPER

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ONLY a few phenylthiosemicarbazones are synthesized and used as chromogenic reagents for the spectrophotometric determination of metal ions. The renewed interest in synthesizing phenylthiosemicarbazones<sup>1-7</sup> is due to their sensitive reactions with metal ions and (easy) extractability of metal-phenylthio-semicarbazone complexes into organic solvents. Hence we describe the synthesis of anisaldehyde-4-phenyl-3-thiosemicarbazone and its use as analytical reagent for the determination of copper. A survey of the literature for the spectrophotometric determination of copper showed that relatively few reagents show high sensitivity for the metal ion. In some of these methods, tolerance limit of associated ions is less<sup>9-11</sup> and some others involve heating of the reaction mixture<sup>12</sup>. The proposed method besides being sensitive, is simple, rapid, requires no heating and has the advantage of virtual freedom from interference from many associated foreign ions. The high tolerance limit of zinc makes the method useful for the determination of copper in brass. The method is also extended for the determination of copper in steel samples.

### Synthesis of reagent:

A solution prepared by dissolving 0.835 g of 4-phenyl-3-thiosemicarbazide in 2 ml of glacial acetic acid was added dropwise to a solution of anisaldehyde (0.68 g) in 50 ml methanol while stirring. A white product quickly separated and was recrystallized in methanol or carbon tetrachloride (m.p. 182-184°C, yield 75%). The reagent (0.285 g) was dissolved in 50 ml of DMF ( $2 \times 10^{-2}$  M). Solutions of lower concentrations were obtained by dilution with DMF. Stock solution of Cu(II) containing 6.35 mg/ml was prepared from copper sulphate pentahydrate (BDH AR) and standardized titrimetrically<sup>8</sup>.

All chemicals used were of BDH AR grade.

### Recommended procedure

To an aliquot containing 0.11 to 1.7  $\mu$ g/ml of copper in a 25 ml separating funnel, add 5 ml buffer (sodium

acetate-acetic acid) solution of pH 5 and 1 ml of  $1.5 \times 10^{-3}$  M reagent solution. Shake the aqueous phase for one min with 10 ml of isobutyl methyl ketone (IBMK). Allow the layers to separate and discard the aqueous phase. Dry the organic layer with anhydrous sodium sulphate and measure the absorbance of copper-APT complex at 365 nm against a reagent blank prepared identically. Prepare a calibration curve similarly.

#### Selection of extractant

The Cu-APT complex is extractable into organic solvents like chloroform, amyl alcohol, butanol, ethyl acetate, benzene and isobutyl methyl ketone. The Cu-APT complex showed maximum absorbance in isobutyl methyl ketone and hence this solvent was selected for the extraction-spectrophotometric studies.

#### Influence of pH, reagent concentration and order of addition of components

The optimum pH range for maximum and constant percentage of extraction of the complex is found to be 4.0-7.0. Hence sodium acetate-acetic acid buffer solution of pH 5 was selected for further studies. A five-fold excess of reagent is sufficient for getting maximum and constant absorbance. The order of addition of constituents of reaction mixture has no effect on the absorbance.

#### Equilibration time and stability of the complex

A single extraction for 60 sec with 10 ml of IBMK is adequate for the quantitative extraction and prolonged shaking has no adverse effect on the extraction. The Cu-APT complex is stable for about 2 hr.

#### Photometric characteristics

The Cu-APT complex shows maximum absorbance at 365 nm where the reagent blank shows comparably low absorbance. A good straight line calibration graph passing through the origin is obtained using the recommended procedure for the determination of copper. The system obeys Beer's law in copper concentration range  $0.11$  to  $1.55 \mu\text{g ml}^{-1}$ . The molar absorptivity and Sandell's sensitivity of the method are  $4.57 \times 10^4 \text{ litre mol}^{-1} \text{ cm}^{-1}$  and  $0.00139 \mu\text{g of Cu cm}^{-2}$  respectively. The optimum concentration range for the successful determination of copper evaluated from Ringbom plot is  $0.35$ - $1.30 \mu\text{g ml}^{-1}$ . The standard deviation for ten determinations of  $0.45 \mu\text{g ml}^{-1}$  of copper is 0.0028.

#### Effect of foreign ions

Varying amounts of foreign ions were added to a fixed amount of copper ( $1.27 \mu\text{g/ml}$ ) and the recommended procedure for the extraction and spectrophotometric determination was followed. An error of  $\pm 2\%$  in absorbance readings was considered tolerable. The following amounts ( $\mu\text{g}$ ) of foreign ions were

Table 1 Determination of copper in alloy steels

Steel Sample	Copper ( $\mu\text{g/ml}$ )						
	Taken	Found	Error %				
BCS 409	0.367	0.360	1.90				
	0.530	0.535	1.60				
	0.734	0.734	—				
BCS 406-1	0.447	0.445	0.45				
	0.671	0.678	0.90				
	0.890	0.870	2.00				
BCS 406	0.500	0.490	2.00				
	0.756	0.754	0.25				
	1.000	0.980	2.00				
Content in %							
	Mn	Cr	Mo	Ni	Cu	V	Co
BCS 409	0.48	1.22	0.77	3.14	0.23	0.280	—
BCS 406-1	0.61	2.10	1.00	1.52	0.28	0.017	0.006
BCS 406	0.53	2.12	1.03	1.69	0.32	0.084	0.047



Table 2 Comparison with other thiosemicarbazone reagents

Reagent	Molar absorptivity $l\ mol^{-1}\ cm^{-1}$
Thiophene-2-aldehyde thiosemicarbazone	3.90
6-Methyl-picolinaldehyde thiosemicarbazone	2.60
Picolinaldehyde thiosemicarbazone	2.20
2-(3'-Sulphobenzoyl)pyridine-4-phenyl-3-thiosemicarbazone	2.12
3,5-Dibromo salicylaldehyde-4-phenyl-3-thiosemicarbazone	2.00
Ferroun thiosemicarbazone	1.45
2,4-Dihydroxy acetophenone thiosemicarbazone	1.40
Quinoline-2-aldehyde thiosemicarbazone	1.33
1,2-Naphthoquinone-2-thiosemicarbazone-4-sulphonic acid	1.33
Biacetylmonoxime 4-phenyl-3-thiosemicarbazone	1.27
Phenanthraquinone monothiosemicarbazone	1.16
Bi-2-pyridyl ketone thiosemicarbazone	1.13
Biacetylmonoxime thiosemicarbazone	1.06
Salicylaldehyde thiosemicarbazone	1.00
Dipyridylglyoxal dithiosemicarbazone	0.95
Bipyridylglyoxal bis(4-phenyl-3-thiosemicarbazone)	0.92
2,2'-Dihydroxyacetophenone thiosemicarbazone	0.86
3-Hydroxy picolinaldehyde thiosemicarbazone	0.85
Acetophenone thiosemicarbazone	0.83
Glyoxal dithiosemicarbazone	0.67
p-Anisaldehyde thiosemicarbazone	0.61
Acenaphthoquinone thiosemicarbazone	0.58
1,2-Cyclohexanedione bithiosemicarbazone	0.57
Cyclohexanene thiosemicarbazone	0.13
Anisaldehyde 4-phenyl-3-thiosemicarbazone	4.57

found to give less than 2% error in the determination of 1.27  $\mu\text{g/ml}$  of copper(II).

Mo(VI), 10,000; Mn(II) 5000; Cr(III), Mg(II) 3900; Zn(II) 2500; Sn(II) 1900; Fe(III) 1500; Ce(IV), V(V) 700; Co(II), 60; Ag(I) 30; Hg(II) 20; chlorate 40000; fluoride 19000; citrate 10000; borate, bromate, nitrate 5000; tartrate, thiourea 3900; sulphate 3000, nitrite, phosphate, acetate, bromide, iodide 2500; persulphate 1500; thiosulphate, thiocyanate 30. The tolerance limit of Fe(III) and Ni(II) can be increased to 5600 to 1100 by the use of fluoride ( $1800\ \mu\text{g}\ \text{ml}^{-1}$ ) and citrate ( $950\ \mu\text{g}\ \text{ml}^{-1}$ ) respectively as masking agents.

#### Application to steel sample

In order to confirm the usefulness of the proposed extraction spectrophotometric method, it was applied to the determination of copper in steel samples of BCS 406-1; BCS 409; BCS 406 type (Ni and Fe masked with citrate and fluoride respectively). The results are summarized in table 1.

#### Comparison with other thiosemicarbazone reagents

The reagent APT is compared with some well-known thiosemicarbazones<sup>13</sup> (table 2). It was found that APT

is a highly sensitive reagent for copper(II).

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## SPECTROPHOTOMETRIC DETERMINATION OF NITRITE

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SPECTROPHOTOMETRIC methods for the estimation of nitrite based on diazocoupling reactions are well known. When these methods are applied for the determination of nitrogen dioxide in air after fixing in alkali, they suffer from the interference of sulphur dioxide. The interference was overcome by the addition of acetone<sup>1</sup>, by selective oxidation using hydrogen peroxide<sup>2</sup> or by coupling the diazotised amine in alkaline medium<sup>3</sup>. The present method is based on the diazotization of *p*-nitroaniline with nitrite and coupling the product with resorcinol in alkaline medium. The present method is also free from the interference of the most of the common ions associated with the determination of nitrogen dioxide in air after sampling in alkali or nitrite in water samples. Experimental variables have been investigated in detail and the optimum values obtained are incorporated in the working procedure.

The standard sodium nitrite solution had 10  $\mu\text{g}$   $\text{NO}_2^-$  per ml. *p*-nitroaniline (0.01%) in 0.05 N hydrochloric acid was prepared. The coupling agent was 0.1% solution of resorcinol in 2N sodium hydroxide. The trapping solution of sodium hydroxide (0.2 N) had 2 ml of *n*-butanol per litre. This was diluted twice with water for air sampling.

Aliquots containing 0–25  $\mu\text{g}$  of nitrite were transferred to six test tubes each containing 5 ml of 0.2 N sodium hydroxide and diluted to 10 ml. These solutions were transferred to six 25 ml volumetric flasks kept in ice bath (0–5°C) each containing 5 ml of

*p*-nitroaniline reagent. The solutions were mixed well and allowed to stand for 5 min. Five ml of coupling agent were added to all the flasks, mixed well, diluted to the mark and allowed to attain room temperature. Absorbance, measured at 555 nm using 10 mm cells, was plotted against the concentration of nitrite which was a straight line passing through the origin (figure 1a).

### Nitrogen dioxide in air

The samples of air containing  $\text{NO}_2$  are passed through 10 ml of the trapping solution at 400 ml/minute and the nitrogen dioxide is fixed as nitrite. The trapping solution containing not more than 25  $\mu\text{g}$  of nitrite is used to determine the concentration of the nitrite following the procedure described under the calibration graph.

### Nitrite in water sample

Ten ml of the water sample containing not more than 25  $\mu\text{g}$  of  $\text{NO}_2^-$  was transferred to a 25 ml beaker. Two ml of 0.05 M EDTA and 1 ml of 5% triethanolamine solution were added and mixed well. This solution was transferred to the 25 ml standard flask kept in ice bath containing 5 ml of *p*-nitroaniline reagent and the analysis was completed by following the procedure described under the calibration graph.

### Results and discussion

Initial studies were carried out with sodium nitrite solution in 10 ml of 0.1 N alkali to fix the optimum acidity for the diazotization. Maximum colour was obtained when the overall acidity for diazotization was at least 0.125 N with respect to HCl and further increase in acidity upto 0.275 N did not affect the absorbance. Variation of the concentration of amine

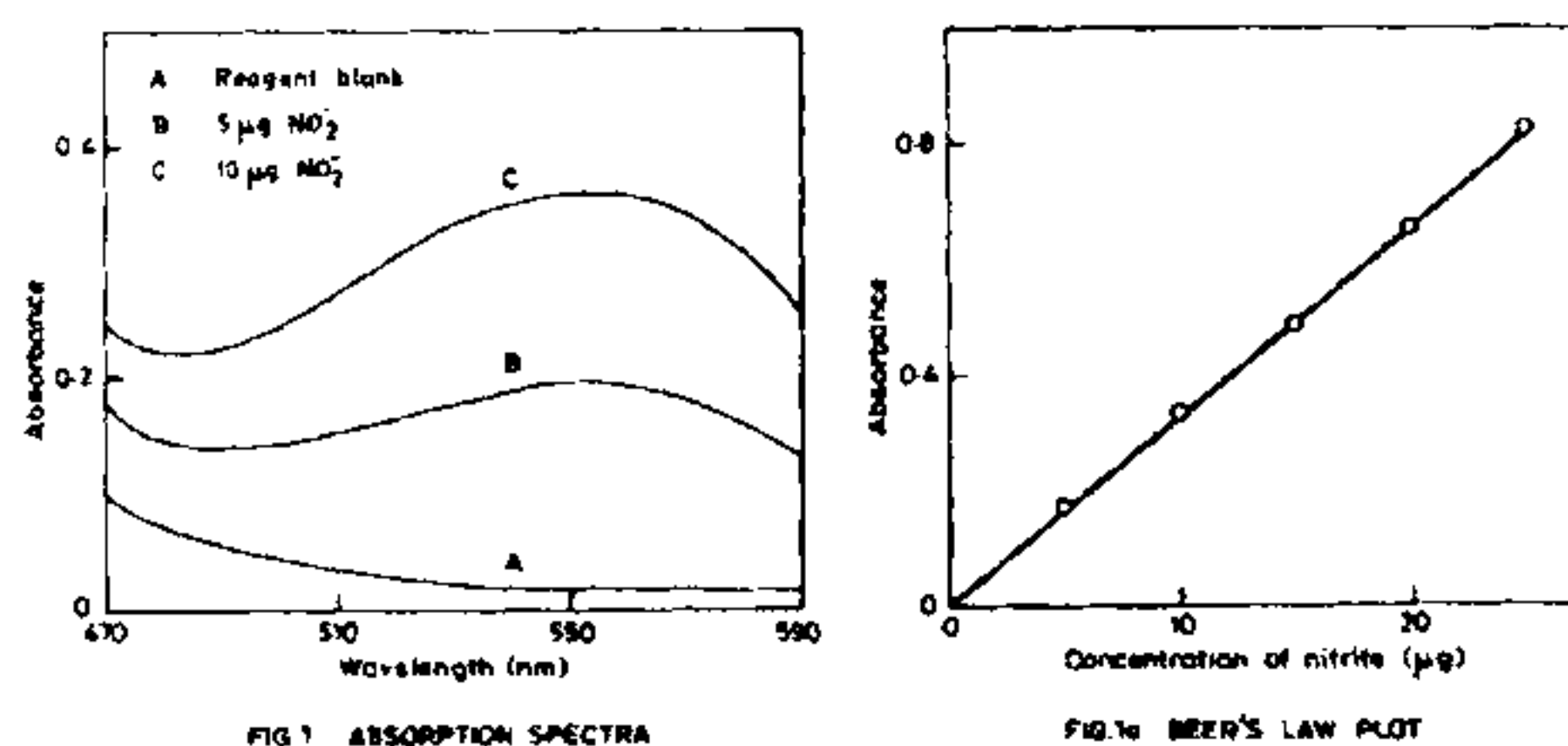


Figure 1. Absorption spectra, 1a. Beer's law plot.