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Chemistry

OXAZINE DYES AS SPOT TEST REAGENTS*

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The use of seven oxazine dyes, Capri Blue, Gallamine Blue, Celestine Blue, Solochrome Prune AS, Meldola's Blue, Cresyl Fast Violet Acetate, and Resazurin, as spot test reagents for the detection of Pd(II), Th(IV), Mo(VI), W(VI), Au(III), Fe(III), Fe(II), and $S_2O_3^{2-}$, is reported.

INTRODUCTION

GALLOCYANINE is the only oxazine dye that has been reported as a reagent for the spot test detection of lead (Pavelka, 1929) and zirconium (Pavelka, 1930). The present paper describes the use of seven oxazine dyes, Capri Blue (CB), Solochrome Prune AS (SPAS), Gallamine Blue (GB), Celestine Blue (CLB), Meldola's Blue (MB) (Colour Index Nos. 51015, 51040, 51045, 51050 and 51175 respectively), Cresyl Fast Violet Acetate (CFVA), and Resazurin (RSZ), as reagents for the spot test detection of Pd(II), Th(IV), Mo(VI), W(VI), Au(III), Fe(III), Fe(II) and $S_2O_3^{2-}$.

MATERIALS AND METHODS

The following solutions were prepared from analytical reagent grade chemicals using double distilled water and suitably diluted before use. 0.1 per cent palladium chloride (J & M) in 0.5 M HCl, 0.02 M thorium acetate (BDH) in water containing a little HCl, 0.1 M ammonium molybdate (BDH) in 0.5 M HCl, 0.1 per cent sodium tungstate (BDH) in water, 0.2 per cent gold chloride (J & M) in 0.25 M HCl, 0.05 M iron(II) ammonium sulphate (BDH) in 0.25 M H_2SO_4, 0.02M iron(III) ammonium sulphate (BDH) in 0.5 M H_2SO_4, and 0.1 per cent sodium thiosulphate (BDH) in water.

Solutions (0.1 per cent) of the dyes were prepared in doubly distilled water and suitably diluted. The dye samples employed were: CB, SPAS, MB and CFVA : Gurr; GB and CLB : Chroma; RSZ : Baird & Tatlock (London) Ltd.

Procedures

The following procedures are adapted for the detection of the different ions and the relevant identification and dilution limits are given in Table I.

(*a*) *Palladium (II)* : 2.5–2.6 ml of saturated solution of sodium hypophosphite is taken in a micro test-tube and treated with 0.1 ml of 0.01 per cent CB, MB, CFVA or RSZ or 0.15 ml of 0.01 per cent GB, CLB or SPAS, and 0.3 ml of palladium(II) chloride solution and the mixture is shaken well. In the presence of 0.3 μg of

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TABLE I

Identification and dilution limits

Ion detected	Dyes	Identification limit	Dilution limit
Pd(II)*	CB, MB, CFVA & RSZ	0.12 μg/3 ml	1:2.5 × 10^7
	GB, CLB & SPAS	0.18 μg/3 ml	1:1.7 × 10^7
Th(IV)[α]	GB & CLB	0.18 μg/1.5 ml	1:8.3 × 10^6
	SPAS	0.22 μg/1.5 ml	1:6.8 × 10^6
Mo(VI)—Procedure A[α]	GB, CLB & SPAS	0.25 μg/1.5 ml	1:6 × 10^6
Procedure B[β]	CB, GB, CLB, SPAS MB & RSZ	0.04 μg/0.3 ml	1:7.5 × 10^6
W(VI)[α]	GB, CLB & SPAS	0.10 μg/1.5 ml	1:1.5 × 10^7
Au(III)[α]	GB	0.18 μg/1.0 ml	1:5.5 × 10^6
	CLB	0.12 μg/1.0 ml	1:8.3 × 10^6
	SPAS	0.30 μg/1.0 ml	1:3.3 × 10^6
Fe(III)[α]	GB, CLB, & SPAS	0.12 μg/1.5 ml	1:1.25 × 10^7
Fe(II)[β]	CB	1.0 μg/2.5 ml	1:2.5 × 10^6
	GB & SPAS	0.20 μg/2.5 ml	1:1.25 × 10^7
	CLB	0.35 μg/2.5 ml	1:7.1 × 10^6
	MB	3.0 μg/2.5 ml	1:8.3 × 10^5
	RSZ	5.5 μg/2.5 ml	1:4.5 × 10^5
$S_2O_3^{2-}$[β]	CB	5.0 μg/3.0 ml	1:6.0 × 10^6
	GB, CLB, SPAS,MB & RSZ	8.0 μg/3.0 ml	1:3.75 × 10^5

*At 28 °C; [α]CB, MB, CFVA & RSZ are not suitable; [β]CFVA is not suitable.

palladium(II), the colour is discharged in about 30–60 sec at room temperature (28 °C) and about 5–8 sec at the temperature of boiling water bath (96 °C).

(*b*) *Thorium (IV)* : 2–3 drops of 0.008 M HCl is treated with one drop of 0.1 per cent GB, CLB, or SPAS, the mixture is diluted to 1.1 ml and treated with 0.4 ml of the test solution containing thorium. The pink colour of the mixture changes to blue immediately.

CB, MB, CFVA and RSZ are not suitable for this test.

(*c*) *Molybdenum (VI)* — (A) : 2–3 drops of 0.008 M HCl is taken in a micro test-tube and treated with one drop of 0.1 per cent GB, CLB or SPAS. To this mixture, 0.7–0.8 ml of water and 5–6 drops of the molybdate solution are added and the mixture is diluted to 1.5 ml. The pink colour of the mixture immediately changes to blue.

CB, MB, CFVA and RSZ are not suitable for this test.

(*c*) *Molybdenum (VI)* — (B) : 0.2 ml of a solution containing 50 mg of hydrazine sulphate is treated with one drop of 0.1 per cent solution of CB, GB, CLB, SPAS, MB, or RSZ followed by 2 drops of the molybdenum(VI) solution and the mixture is heated to boiling. The colour of the solution will be discharged in 2–3 min in all cases except RSZ, in which case, the colour changes from pink to light yellow.

CFVA is not useful in this test.

(*d*) *Tungsten(VI)* : 0.2–0.4 ml of 0.008 M HCl is treated with one drop of 0.1 per cent CLB or 2 drops of 0.1 per cent GB or SPAS. The mixture is diluted to 1.3 ml and treated with 0.2 ml of the tungsten(VI) solution. The colour immediately changes from pink to blue while using CLB and GB and from violet to blue while using SPAS.

The test does not respond with the remaining four dyes.

(*e*) *Gold(III)* : 0.15–0.50 ml of 0.008 M HCl is treated with 0.3 ml of 0.01 per cent GB or 0.2 ml of 0.01 per cent CLB or 0.15 ml of 0.01 per cent SPAS and the total volume is made upto 0.7–0.8 ml by adding water. When 0.2–0.3 ml of the gold(III) solution is added to the above mixture, the colour changes from pink to yellow.

The remaining four dyes are not suitable for this test.

(*f*) *Iron(III)* : 1–2 drops (0.20–0.25 ml while using SPAS) of 0.01 M HCl is treated with one drop of 0.01 per cent solution of GB, CLB or SPAS. To this mixture, one drop of the iron(III) solution is added and the mixture diluted to 1.5 ml with water. A colour change from pink to blue indicates the presence of iron(III).

(*g*) *Iron(II)* ; To 1.6–2.3 ml of syrupy phosphoric acid (85 per cent), 0.1 ml of 0.1 per cent GB, CLB, SPAS or MB or 0.05 ml of 0.1 per cent CB or RSZ and 0.1–0.8 ml of the iron(II) solution are added and the total volume is made upto 2.5 ml by adding phosphoric acid or water (as the case may be). The colours of the solutions are discharged in a short time. The times of discharge of the colours and the approximate acid concentrations for the test using the different dyes are mentioned in Table II.

CFVA is not useful in this test.

(*h*) *Thiosulphate* : 0.1 ml (0.05 ml with RSZ) of 0.01 per cent solution of CB, GB, CLB, SPAS or MB is taken in a micro test-tube and treated with sufficient 1:1 HCl, so as to give an overall acid concentration of 2.0–4.0 M when diluted to 3.0 ml, and sodium thiosulphate solution. The solution is boiled for 2–3 min and kept aside for 1 min, when the colour of the solution will be discharged.

Interferences : The interferences of various substances in the spot tests now reported have been studied and the results are incorporated in Table III.

TABLE II

Conditions for detection of iron (II)

Dye and initial colour of solution	$[H_3PO_4]$, M	Time of discharge of colour, sec
CB, green	8.3	150
GB, pink	11.4	20
CLB, pink	10.9	60
SPAS, pink	11.4	20
MB, pink	10.4	60
RSZ, pink	8.3	60

TABLE III

Interferences in the spot tests

Ion detected	Ions which interfere	Ions (in mg) which do not interfere
Pd(II)φ	Fe(II), Mo(VI), W(VI), Ce(IV), Cr(VI).	Pt(IV) : 0.5, Ir(III) : 0.5, Os(VIII) : 0.1, Au(III) : 0.1, Th(IV) : 0.05, Fe(III) : 0.01, U(VI) : 1.2.
Th(IV)	Zr(IV), Mo(VI), W(VI), Au(III), Fe(III).	Fe(II) : 0.15, U(VI) : 0.1, Pb(II) : 3.8, Zn(II) : 2.3.
Mo(VI)— Procedure A.	W(VI), Th(IV), Zr(IV), Fe(III), V(V), Au(III).	Fe(II) : 0.15, U(VI) : 0.1, Pb(II) : 3.8, Zn(II) : 1.1.
W(VI)	Mo(VI), Cr(VI), Th(IV), Zr(1V), Au(III), Fe(III), V(V).	Fe(II) : 0.15, U(VI) : 0.10, Pb(II) : 15.0, Zn(II) : 4.5
Au(III)	Ag(I), V(V), Cr(VI).	Pt(IV) : 1.0, Os(VIII) : 0.5, Th(IV) : 0.04, Mo(VI) : 0.2, W(VI) : 0.3, Hg(II) : 7.4, Pb(II) : 7.6, Zn(II) : 2.3
Fe(III)	Mo(VI), W(VI), V(V), Cr(VI), Th(IV), Au(III).	Fe(II) : 0.15, Co(II) : 0.4, Ni(II) : 1.0, Mn(II) : 6.4, U(VI) : 0.1.
Fe(II)	Mo(VI), Cr(VI), Ce(IV), V(V).	Fe(III) : 1.2, Co(II) : 1.0, Ni(II) : 0.4, Mn(II) : 3.2, W(VI) : 11.0, Au(III) : 0.2, Th(IV) : 5.5.
$S_2O_3^{2-}$	Mo(VI), W(VI), Hg(II), I^-.	SO_4^{2-} : 18.3, $S_2O_8^{2-}$: 0.08, acetate : 16.6, phosphate : 5.4

φ at 28 °C.

RESULTS AND DISCUSSION

(*a*) *Detection of palladium(II)* : In his studies on the kinetics of reduction of inorganic substances by hypophosphorous acid, Mitchell (1923) has postulated that hypophosphorous acid exists in two forms, an active form and an inactive form :

$$\underset{\text{Inactive}}{H_2PO(OH)} \rightleftharpoons \underset{\text{Active}}{HP(OH)_2} \xrightarrow{(+O)} H_3PO_3$$

and according to Paal and Friederici (1932), the active form of hypophosphite reduces palladium salts to elemental palladium and at the same time, the hypophosphite, in contact with finely divided metallic palladium, undergoes decomposition as follows

$$NaH_2PO_2 + 2\,H_2O \rightarrow NaH_2PO_4 + 2\,H_2$$

Since hydrogen behaves as though it were nascent (atomic) when it is taken up by palladium or other platinum group metals, in the spot test now reported, the oxazine dyes are reduced to the corresponding leuco bases by the nascent hydrogen thus liberated. The increase in the speeds of discharge of the colours of the dyes at higher temperatures may be attributed to an increased rate of production of hydrogen. In this connection, it may be noted that Rao and Dutt (1970), while working with some triphenylmethane dyes, have expressed a similar view.

(*b*) *Detection of thorium(IV)* : Separate experiments have shown that the dyes GB, CLB and SPAS form blue complexes with thorium(IV). Therefore, the principle underlying the spot test detection of thorium(IV) is 'complex formation'.

(*c*) *Detection of molybdenum(VI)* — The authors have observed that molybdenum(VI) forms blue complexes with GB, CLB and SPAS and hence the feasibility of the spot test as per Molybdenum(VI) — (A) is due to 'complex formation'.

The mechanism involved in procedure pertaining to Molybdenum (VI)—(B) may be the same as that postulated by Lang (1948), namely, the reduction of molybdenum(VI) to molybdenum(V) by hydrazine sulphate and subsequent reduction of the oxazine dyes to the leuco forms by the molybdenum(V), under the conditions obtaining in this procedure.

(*d*) *Detection of tungsten(VI) and iron(III)* : Separate experiments of the authors have shown that the dyes GB, CLB and SPAS form blue coloured complexes with tungsten(VI) and iron(III). Therefore the principle underlying the spot tests is complex formation.

(*e*) *Detection of gold(III)* : Gold(III) oxidises the dyes GB, CLB and SPAS at low acidities and hence the mechanism involved in the detection of gold(III) is oxidation of the dyes.

(*f*) *Detection of iron(II)* : According to Rao and Sagi (1962), iron(II) in high phosphoric acid medium behaves as a powerful reductant. Since the phosphoric acid concentration is in the range of 8.3–11.4 M in the spot test now reported, the mechanism involves reduction of the dyes to the leuco forms, by the iron(II).

(*g*) *Detection of thiosulphate* : Since the colours of the dyes are discharged in the spot test for thiosulphate, the spot test detection of thiosulphate can be explained on the basis of reduction of the dyes to the corresponding leuco forms.

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