Polyphenolic Compounds as Spray Reagents in Inorganic Paper Chromatography – Part II

M. L. Dhar* / K. Pandita

Department of Chemistry, University of Jammu, Jammu-180001, India

A. C. Jain

Department of Chemistry, H.P. University, Simla-171005, India

Key Words

New Reagents For Metal Detection

Summary

A study of 9 compounds belonging to 4 different groups of polyphenols: 3-phenyl-4-hydroxycoumarins, aurones, xanthones and desoxybenzoins shows that 5 of them: 3-phenyl-4,5,7-trihydroxycoumarin, 4,5,7-trihydroxy-3-(p-methoxyphenyl)coumarin, 4,5,7-trihydroxy-3-(3′,4′-methylenedioxyphenyl)coumarin, 4,6-dihydroxyaurone and 4,6-dihydroxy-3′,4′-dimethoxyaurone act as sensitive and widely applicable chromatographic spray reagents for the detection of metal ions in paper chromatography. The sensitivity limits determined for these 5 reagents establish that they are even better reagents than the ones commonly used for this purpose. The 2 aurone derivatives are better than the 3 coumarin ones.

Introduction

Dhar and Jain [1, 2] have earlier reported a brief and limited study of the successful use of the polyphenols: 3-phenyl-4,5,7-trihydroxycoumarin [1] and 4,6-dihydroxy-3′,4′-dimethoxyaurone [2] as spray reagents for the detection of metal ions. Similarly, a detailed study of ten other polyphenolic compounds belonging to the group of o-hydroxybenzoyl and isopentenylated o-hydroxybenzoyl compounds has shown them to be sensitive and useful spray reagents [3].

A more systematic study of 9 other polyphenolic chelating compounds for similar purposes has been carried out. The compounds are:

a) 3-Phenyl-4-hydroxycoumarin Derivatives

3-phenyl-4,5,7-trihydroxycoumarin [4] (1), 4,5,7-trihydroxy-3-(p-methoxyphenyl)coumarin [4] (2) and 4,5,7-trihydroxy-3-(3′,4′-methylenedioxyphenyl)coumarin [4] (3)

b) Aurones

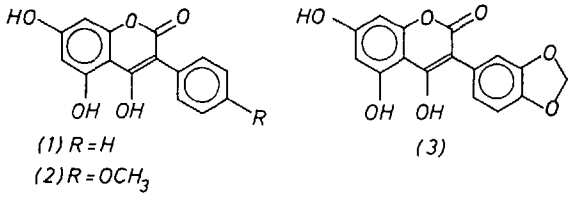
4,6-dihydroxyaurone [5] (4) and 4,6-dihydroxy-3′,4′-dimethoxyaurone [5] (5)

c) Xanthones

1-hydroxyxanthone [6] (6)

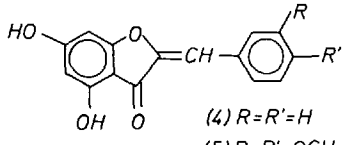
d) Desoxybenzoins

2,4-dihydroxyphenylbenzylketone [7] (7), 2,4-dihydroxy-2′,4′-dimethoxyphenylbenzylketone [8] (8) and 2-hydroxy-4-prenyloxyphenylbenzylketone [8] (9)

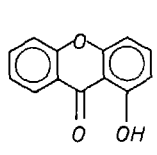


(1) R = H
(2) R = OCH_3

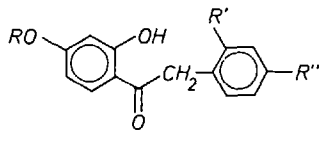
(3)



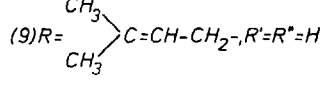
(4) R = R′ = H
(5) R = R′ = OCH_3



(6)



(7) R = R′ = R″ = H
(8) R = H, R′ = R″ = OCH_3



(9) R = CH_3, CH_3 > C=CH-CH_2-, R′ = R″ = H

* Author to whom correspondence should be sent.

0009-5893/79/05 299-03 $ 02.00/0

Table I. Colour reactions of metal ions in visible and UV light

S.No.	Metal Ion	Vis	UV	Vis	UV	Vis	UV	Vis	UV	Vis	UV	Vis	UV	Vis	UV	Vis	UV	R_f*
		(1)		(2)		(3)		(4)		(5)		(6)		(7)		(8)		(9)		
1.	Li(I)	–	–	–	–	–	–	ly	fw	fy	fw	–	–	–	fy	–	–	–	–	–
2.	Na(I)	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
3.	K(I)	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
4.	Rb(I)	–	fbl	–	–	–	fbl	–	–	–	–	–	–	–	–	–	–	–	–	–
5.	Be(II)	–	fbl	lb	fp	yg	fbl	gy	db	fty	b	dy	oy	ib	fw	ly	fw	fty	blw	0.81
6.	Mg(II)	–	fbl	–	–	–	–	dy	y	–	y	–	–	ftp	–	–	–	–	lgr	0.47
7.	Ba(II)	–	fbl	–	–	gbl	blgr	oy	v	–	yb	ly	–	lp	lv	–	lgr	y	lgr	0.82
8.	Al(III)	–	fbl	–	blp	–	fbl	ly	dy	y	yb	y	rv	lp	fw	ly	fw	ly	fy	0.65
9.	Pb(II)	–	fbl	–	w	–	lgr	ob	b	b	rv	–	vbl	–	fw	–	–	–	–	0.67
10.	As(III)	–	fbl	–	lg	lv	lgr	–	–	–	–	–	–	–	–	–	–	–	–	0.69
11.	As(V)	–	fbl	–	fbl	–	–	–	–	o	v	–	–	–	–	–	–	–	–	–
12.	Sb(III)	–	fbl	–	fbl	lv	gr	oy	lv	or	b	–	–	–	–	–	–	–	–	0.66
13.	Bi(III)	–	fbl	lb	lbl	ftv	lgr	lgr	gr	y	y	–	–	–	–	–	lgr	ftb	lgr	0.72
14.	Se(IV)	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
15.	Se(VI)	b	g	o	y	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
16.	Te(IV)	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
17.	Te(VI)	–	fbl	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
18.	Ti(IV)	y	dg	o	yg	dy	ygr	ly	lgr	oy	dgr	ly	–	y	ygr	ly	yg	y	ygr	0.68
19.	Zr(IV)	–	–	lb	fbl	lv	lgr	y	or	oy	or	y	or	p	v	ly	fy	–	lgr	0.47
20.	V(IV)	dgr	dgr	cgr	dg	grg	vgr	–	–	–	–	–	–	–	–	–	–	–	–	0.60
21.	V(V)	gr	dgr	cgr	dg	dgr	vgr	fty	lgr	o	gr	ly	vbl	lgr	lbl	lgr	vgr	lgr	lgr	0.72
22.	Cr(III)	–	–	bl	–	–	dgr	ygr	gr	o	v	fty	–	vgr	dv	lv	lgr	–	gr	0.62
23.	W(VI)	ly	lbl	ly	lp	–	dgr	–	–	–	–	–	–	–	–	–	–	–	–	0.69
24.	Fe(II)	c	dv	dgr	g	c	dv	c	dv	c	dv	c	dv	db	dv	db	dv	b	db	0.75
25.	Fe(III)	c	dv	dgr	g	c	dv	c	dv	c	dv	c	dv	db	dv	db	dv	b	db	0.76
26.	Ni(II)	–	fbl	–	–	lv	lgr	dy	vbl	o	v	ly	v	lgr	lv	lgr	–	lgr	lgr	0.67
27.	Pt(IV)	lb	fbl	lb	yg	–	–	–	–	lb	–	–	–	–	–	–	–	–	–	–
28.	Cu(II)	dg	dg	lb	lp	drg	dv	or	dbl	o	vbl	oy	db	ygr	dv	gr	gr	gr	lgr	0.75
29.	Au(III)	vgr	vbl	vgr	g	–	–	–	–	vgr	–	–	–	–	–	–	–	–	–	–
30.	Zn(II)	–	fbl	–	fbl	p	fw	dy	rb	y	dy	ly	–	lp	fw	–	–	–	fbl	0.90
31.	Cd(II)	–	fbl	–	–	–	fw	y	ry	y	yb	–	–	lp	lv	–	–	–	fbl	0.91
32.	Ce(III)	db	db	cb	g	lgr	lbl	lo	ygr	ob	v	ly	–	lv	ygr	lb	lgr	gy	gr	0.51
33.	Ce(IV)	cb	gr	b	g	lgr	gr	–	–	–	–	–	–	–	–	–	–	–	–	0.52
34.	Th(IV)	lb	lbl	lb	lbl	v	vgr	oy	dv	oy	dv	y	or	dp	yb	ly	oy	ly	lbl	0.52
35.	U(VI)	lo	dg	b	dg	do	vgr	o	lb	or	b	lo	dv	o	vgr	y	ygr	oy	lbl	0.70
36.	Pd(II)	lb	lg	lb	g	–	–	–	–	lo	–	–	–	–	–	–	–	–	–	–
37.	Co(II)	–	–	–	–	dgr	dv	oy	vbl	oy	b	y	vbl	gr	vgr	ygr	gr	lo	dgr	0.67
38.	Mn(II)	yg	v	–	–	yg	dv	oy	b	o	v	ly	–	gy	ftv	lb	lgr	–	–	0.63
39.	Ca(II)	–	–	–	–	–	–	ly	yg	–	y	–	–	p	–	–	–	–	lgr	0.55
40.	Sn(II)	–	–	–	–	–	–	y	lgr	or	db	–	–	ftp	lv	–	vgr	–	–	0.61
41.	Mo(VI)	yg	gr	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0.85
42.	Sr(II)	–	–	–	–	–	–	ly	y	–	y	–	–	lp	–	–	–	lb	–	0.50
43.	La(III)	–	–	–	–	–	–	–	–	–	–	–	–	lp	ygr	ly	w	fty	ly	0.51
44.	Ag(I)	–	–	–	–	–	–	–	–	–	–	–	–	lp	–	–	–	–	–	0.78
45.	Hg(I)	–	–	–	–	–	–	fty	lgr	o	b	–	dv	ftp	vgr	–	–	–	–	0.92
46.	Hg(II)	–	–	–	–	–	–	y	or	b	b	–	dv	ftp	vgr	–	vgr	–	–	0.91

* A dash under R_f means no measurement.

fbl = fluorescent blue, b = brown, y = yellow, dgr = dark grey, gr = grey, g = green, dg = dark green, lb = light brown, o = orange, cgr = chocolate grey, fp = fluorescent pink, blp = blue pink, w = white, lg = light green, lbl = light blue, yg = yellow green, gbl = green blue, lv = light violet, ftv = faint violet, dy = dark yellow, grg = grey green, blgr = blue grey, lgr = light grey, ygr = yellow grey, vgr = violet grey, ly = light yellow, c = chocolate, db = dark brown, cb = chocolate brown, lo = light orange, dv = dark violet, vbl = violet blue, v = violet, bl = blue, lp = light pink, drg = dirty green, p = pink, do = dark orange, fw = fluorescent white, gy = green yellow, oy = orange yellow, ob = orange brown, fy = fluorescent yellow, fty = faint yellow, or = orange red, yb = yellow brown, rv = red violet, ftp = faint pink, lp = light pink, ftb = faint brown, blw = blue white, dbl = dark blue, rb = red brown, ry = red yellow and dp = dark pink.

Experimental

The metal ion solutions were prepared in deionized water and were either in the form of chlorides or nitrates. They were in all cases of AnalaR or Proanalysis grade. The reagents (1–9) were prepared in accordance with known procedures [4–8], and samples purified by repeated crystallisation until they gave single spots in TLC. 1% solutions of the reagents in ethanol (95%) were used for spraying the chromatograms. Whatman 3 MM filter paper was used. The solvent system was n-butanol: 6 mol dm^{-3} HCl (1:1, v/v) and ascending chromatography at room temperature was used with spots of single metal ions. The chromatograms were run until the solvent front moved 25–30 cm. They were then dried and exposed to ammonia prior to spraying. The sensitivity limits were determined by the usual procedure.

Results and Discussion

The colour reactions given by the various metal ions with the 9 spray reagents (1–9) are given in Table I and II.

Table I and II show that coumarin derivatives (1–3) are useful spray reagents. The order of usefulness being (1) > (3) > (2). The colour reactions with the 2 aurone derivatives (4–5) are particularly intense both with transition and non-transition metal ions. 1-hydroxyxanthone (6) is not as good as the aurones or coumarins. The 3 desoxybenzoins (7–9) could be considered to lie between the aurones, coumarins and the xanthone derivatives.

The sensitivity limits (Table II) with respect to the reagents (1), (2) and (3) for 9 metal ions: Ti(IV), V(V), Mn(II), Fe(II), Fe(III), Cu(II), Mo(VI), Ce(III) and U(VI) and of the two aurone derivatives (4) and (5) for 16 metal ions: Al(III), Ti(IV), V(V), Mn(II), Fe(II), Fe(III), Co(II), Ni(II), Cu(II), As(III), Cd(II), Sn(II), Sb(III), Ce(III), Bi(III) and U(VI) are listed.

Table II. Sensitivity (μg) of metal ions with various spray reagents

S.No.	Metal Ions	Vis	UV	Vis	UV	Vis	UV	Vis	UV	Vis	UV
		(1)		(2)		(3)		(4)		(5)	
1.	Al(III)	–	–	–	–	–	–	5	1	6	1
2.	Ti(IV)	0.9	0.6	–	–	1	0.5	4	1	4	1
3.	V(V)	7	5	7	4	5	3	7	4	7	3
4.	Mn(II)	4	2	–	–	3	2	1	0.6	2	0.6
5.	Fe(II)	0.5	0.2	2	1	0.1	0.1	0.4	0.1	0.6	0.1
6.	Fe(III)	0.6	0.4	4	1	0.2	0.1	0.5	0.1	0.5	0.1
7.	Co(II)	–	–	–	–	–	–	1	0.8	6	1
8.	Ni(II)	–	–	–	–	–	–	4	0.9	4	1
9.	Cu(II)	10	8	6	5	3	2	4	0.9	1	0.8
10.	As(III)	–	–	–	–	–	–	6	2	10	3
11.	Mo(VI)	30	20	–	–	–	–	–	–	–	–
12.	Cd(II)	–	–	–	–	–	–	6	3	8	5
13.	Sn(II)	–	–	–	–	–	–	4	2	6	3
14.	Sb(III)	–	–	–	–	–	–	3	2	6	2
15.	Ce(III)	10	9	9	8	9	9	9	6	10	8
16.	Bi(III)	–	–	–	–	–	–	10	4	10	4
17.	U(VI)	4	1	20	10	15	8	6	4	3	1

The polyphenolic compounds (1–9), in general, can be used as wide range and sensitive reagents for the detection of metal ions. Using combinations of these and appropriate solvent systems it should be possible to separate and differentiate metal ions in large numbers on single chromatograms. Of the 5 reagents whose sensitivity has been determined, it is obvious that the aurone derivatives are the most sensitive followed by the coumarin compounds. These reagents are better than the reagents commonly employed [9]. They are even better than o-vanillin oxime [10] and β-resorcylaldehyde [11]. The xanthones and desoxybenzoins on the other hand have relatively limited application.

The nature and composition of the chelates formed by 3-phenyl-4,5,7-trihydroxycoumarin, 4,6-dihydroxyaurone and 4,6-dihydroxy-3′,4′-dimethoxyaurone with various metal ions have already been determined [12–16]. Work on similar investigations for the other reagents and also their use as spectrophotometric and gravimetric reagents for estimation of metals has been investigated [16] and further and detailed work is in progress.

References

[1] *M. L. Dhar* and *A. C. Jain*, Curr. Sci. 41, 177 (1972).

[2] *M. L. Dhar* and *A. C. Jain*, Curr. Sci. 41, 563 (1972).

[3] *M. L. Dhar, A. C. Jain* and *Ravinder Raina*, Chromatographia 6, 344 (1978).

[4] *A. H. Gilbert, A. McGookin* and *A. Robertson*, J. Chem. Soc. 3740 (1957).

[5] a) *D. M. Fitzgerald, J. F. O. Sullivan, E. M. Philbin* and *T. S. Wheeler*, J. Chem. Soc. 860 (1955).
b) *A. C. Jain* and *V. K. Rohatgi*, Ind. J. Chem. 7, 6 (1969).
c) *F. E. King, J. J. King* and *D. W. Rustidge*, J. Chem. Soc. 1119 (1962).

[6] *Pankajamani, Seshadri*, J. Sci. Ind. Research 13B, 369 (1954).

[7] *Finzi*, Monatsh 26, 1219 (1905).

[8] *S. M. Jain, Ph. D. Thesis*, University of Jammu (1972).

[9] *F. Feigl*, Spot Tests, Vol. 1, Elsevier Amsterdam, 1954, p. 451.

[10] *M. L. Dhar, S. M. Jain* and *Ravinder Raina*, J. Chromatography, 488–490 (1976).

[11] *M. L. Dhar* and *Kuldeep Pandita*, Paper presented at the Annual Convention of Chemists, India (1977).

[12] *M. L. Dhar* and *A. C. Jain*, Curr. Sci. 41, 809 (1972).

[13] *M. L. Dhar* and *A. C. Jain*, Curr. Sci. 43, 714 (1974).

[14] *M. L. Dhar* and *A. C. Jain*, Curr. Sci. 43, 409 (1974).

[15] *M. L. Dhar* and *A. C. Jain*, J. Ind. Chem. Soc., LIV, 636–637 (1977).

[16] *M. L. Dhar* and *A. C. Jain*, unpublished work.

Received: April 11, 1978
Revised Manuscript Received: May 31, 1978
Accepted: Oct. 19, 1978
C