

Polyphenolic Compounds as Spray Reagents in Inorganic Paper Chromatography

Part I

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Summary

A study of 10 members of *o*-hydroxybenzoyl and isopentenylated *o*-hydroxybenzoyl group of compounds, as spray reagents in inorganic paper chromatography, for the detection of metal ions, shows, that resacetophenone, phloracetophenone, gallacetophenone and 5-*C*-prenyl gallacetophenone can act as very useful and often universal reagents. Comparative sensitivity limits with respect to Ti(IV), V(V), Mn(II), Fe(II), Fe(III), Co(II), Ni(II), Cu(II), Ce(IV) and U(VI) have been determined for these four reagents.

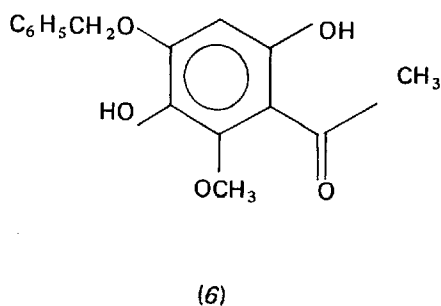
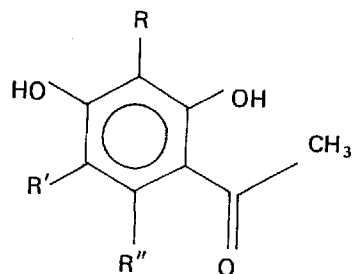
6 mol dm⁻³ HCl (1:1; V/V) was used as the solvent system for all investigations. Chromatograms were exposed to ammonia prior to spraying with a particular reagent. All reagents were used as 1 % solutions in 95 % ethanol. Whatman filter paper No. 3 was used in all investigations. Chromatograms were scanned in UV light using Hanovia UV lamps (England) and sensitivity limits were determined by the usual procedure in visible and UV light.

Introduction

The use of gallacetophenone as a spray reagent for the detection of metal ions in paper chromatography was reported by Dhar and Jain [1]. It has now been found that resacetophenone [2] (1), phloracetophenone [3] (2), 3-*C*-methylphloracetophenone [4] (3), gallacetophenone [5] (4), 2,4,5-trihydroxyacetophenone [6] (5), 2,5-dihydroxy-4-benzoyloxy-6-methoxyacetophenone [7] (6), 3-formylphloracetophenone [8] (7), 5-*C*-prenyl-2,3,4-trihydroxyacetophenone [9] (8), 5-*C*-prenyl-2,4-dihydroxyacetophenone [10] (9), and 3,5-di-*C*-prenyl-2,4-dihydroxyacetophenone [11] (10) also give vividly coloured spots on paper chromatograms with metal ions, especially 1, 2, 4 and 8. A comparison of the detectable ion concentration (μg) in respect of Ti(IV), V(V), Mn(II), Fe(II), Fe(III), Ni(II), Co(II), Cu(II), Ce(IV) and U(VI) by these four reagents shows that they can be usefully employed as sensitive and generally useful spray reagents.

Experimental

The metal ions were examined on paper chromatograms using the ascending technique. All were used in the form of A.R. or Pro-Analysis grade salts. The mixture *n*-butanol:



- (1) R = R' = R'' = H
(2) R = R' = H; R'' = OH
(3) R = CH₃; R' = H; R'' = OH
(4) R = OH; R' = R'' = H
(5) R = R'' = H; R' = OH
(7) R = -CHO; R' = H; R'' = OH
(8) R = OH; R'' = H; R' = Me₂C = CH - CH₂ - Or prenyl Unit
(9) R = R'' = H; R' = prenyl Unit.
(10) R = R' = prenyl Unit; R'' = H.

Results

The spot colours given by various ions with the reagents used are shown in Tables I and II. Table I corresponds to *o*-hydroxybenzoyl compounds and Table II to isopen-tenylated compounds (8), (9) and (10). Table III gives the relative quantities of ten ions (μg) detectable by (1), (2), (4) and (8).

Discussion of Results

Thirty three metals were examined with seven different *o*-hydroxybenzoyl compounds (1–7). The chromatograms were scanned in both visible and ultra-violet light, the results with gallacetophenone in visible light have already been reported [1]. The rest of the results show that resacetophenone (1) gives coloured spots with fourteen metals in visible light and fifteen metals are observed in ultra-violet light. The vividness of the colours is

observed in the case of Se(VI), V(IV), Mn(II), Fe(II), Fe(III), Cu(II), Ce(III), U(VI), and Pd(II) in both visible and UV light. Al(III) can be located only as a fluorescent white spot in UV light only.

Gallacetophenone can serve as a very useful and universal spray reagent as the number of metals indicated is large and spot colours are particularly vivid and intense. As many as twenty eight cations give coloured spots with the reagent in visible light [1] and a similar number in UV the colours being quite vivid, Ba(II), which does not give a coloured spot in visible light appears as a green spot in UV light.

Phloroacetophenone (4) is as widely applicable as gallacetophenone and spot colours with various ions in visible and UV light are quite vivid. As(III) and As(V) which do not give colours with resacetophenone and gallacetophenone show white spots with phloroacetophenone.

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

b = brown; bl = blue; blg = blue green; blgr = blue grey; c = chocolate; dg = dark green; dgr = dark grey; fbl = fluorescent blue; fy = fluorescent yellow; fw = fluorescent white; g = green; ggr = greenish grey; lb = light brown; lg = light green; lo = light orange; lgr = light grey; ly = light yellow; o = orange; oy = orange yellow; p = pink; v = violet; vg = violet green; vgr = violet grey; y = yellow; yg = yellow green; w = white.

S. No.	Metal Ion	Vis 1	UV 1	Vis 2	UV 2	Vis 3	UV 3	Vis 4	UV 4	Vis 5	UV 5	Vis 6	UV 6	Vis 7	UV 7
1.	Rb(I)	—	—	w	w	—	—	—	—	—	—	—	—	—	—
2.	Be(II)	—	bl	y	g	lb	w	y	yg	y	y	w	w	w	w
3.	Mg(II)	—	—	w	w	—	w	—	b	dg	w	w	—	—	—
4.	Ba(II)	—	—	y	fy	—	—	g	b	g	b	lg	—	—	—
5.	Al(III)	—	fw	w	w	—	w	g	g	yg	w	w	w	w	w
6.	Pb(II)	—	—	—	—	—	—	dg	—	—	—	fbl	—	—	—
7.	As(III)	—	—	w	w	—	—	dg	—	—	—	—	w	w	w
8.	As(V)	—	—	w	w	w	—	—	w	w	w	w	w	w	w
9.	Sb(III)	ly	—	w	w	—	w	—	—	w	w	w	w	w	w
10.	Bi(III)	—	—	y	ly	—	—	gy	y	fy	o	ly	w	w	w
11.	Se(VI)	o	yg	o	yg	lb	lg	dg	lb	lg	o	ly	w	w	w
12.	Te(VI)	—	—	w	—	w	w	—	—	—	—	—	—	—	w
13.	Ti(IV)	—	—	o	fy	ly	w	g	o	g	lb	y	—	fbl	—
14.	Zr(IV)	—	—	b	g	w	w	fy	y	fy	w	w	w	w	w
15.	V(IV)	g	g	g	g	lg	g	dg	b	g	b	g	lg	lg	lg
16.	V(V)	—	lgr	g	g	g	g	dg	b	g	g	g	lg	lg	lg
17.	Cr(III)	lg	lg	y	fy	—	—	lg	y	g	w	w	—	—	—
18.	Mn(II)	p	lb	p	lb	—	—	lb	—	—	—	—	—	—	—
19.	W(VI)	—	—	w	—	w	w	lgr	lb	—	y	—	—	—	—
20.	Fe(II)	C	dg	b	g	b	g	dgr	gr	g	b	g	b	g	g
21.	Fe(III)	C	dg	b	g	b	g	dgr	gr	g	b	g	b	g	g
22.	Co(II)	b	g	b	g	dp	g	—	b	g	p	gr	lb	y	y
23.	Ni(II)	b	g	p	fy	—	—	dg	b	dg	w	w	w	w	w
24.	Pt(IV)	ly	—	—	—	—	—	gy	—	—	—	—	—	—	—
25.	Cu(II)	lg	gr	b	dg	lg	lg	dg	b	g	y	y	—	—	—
26.	Au(III)	ly	vg	v	—	vgr	blg	ggr	blgr	blgr	blg	blgr	gr	gr	gr
27.	Zn(II)	—	—	b	g	b	—	dg	b	g	lb	lg	—	—	—
28.	Cd(II)	—	—	—	—	—	—	lg	—	—	—	—	—	—	—
29.	Ce(III)	b	gr	b	g	b	lg	dg	b	g	lb	w	—	—	—
30.	Ce(IV)	—	—	b	g	lb	y	dg	b	dg	b	w	w	w	w
31.	Th(IV)	—	—	b	yg	w	w	g	yb	g	w	w	w	w	w
32.	U(VI)	lo	yg	b	g	oy	fy	g	b	g	lb	w	y	y	y
33.	Pd(II)	gy	g	—	—	ly	lg	g	—	w	—	—	—	—	—

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

S. No.	Metal Ions	Vis	UV	Vis	UV	Vis	UV
		8	9	9	9	10	10
1.	Rb(I)	—	lg	—	—	—	—
2.	Be(II)	y	y	ly	—	ly	—
3.	Mg(II)	—	—	—	—	—	—
4.	Ba(II)	ly	lg	—	—	—	—
5.	Al(III)	y	g	y	y	ly	ly
6.	Pb(II)	—	—	—	—	—	—
7.	As(III)	y	dg	—	—	—	—
8.	As(V)	—	—	—	—	—	—
9.	Sb(III)	ly	ly	—	—	—	—
10.	Bi(III)	y	lg	—	—	—	—
11.	Se(VI)	b	lg	o	dg	o	g
12.	Te(VI)	—	—	—	—	—	—
13.	Zr(IV)	y	yg	ly	fy	—	—
14.	Ti(IV)	b	lg	lb	y	—	—
15.	V(IV)	dg	g	lg	yg	lb	g
16.	V(V)	dg	g	lg	g	lg	g
17.	Cr(III)	lg	lg	lg	lg	lg	g
18.	Mn(II)	—	—	—	—	b	db
19.	W(VI)	o	ly	—	—	—	—
20.	Fe(II)	dgr	g	C	g	C	g
21.	Fe(III)	dgr	g	C	g	C	g
22.	Co(II)	b	g	—	—	—	—
23.	Ni(II)	lg	lg	gy	y	gy	y
24.	Pt(IV)	lb	lg	lb	y	—	—
25.	Cu(II)	lb	lg	lg	yg	g	yg
26.	Au(III)	blv	g	bv	g	blv	vg
27.	Zn(II)	yg	g	—	—	lb	ly
28.	Cd(II)	—	—	—	—	—	—
29.	Ce(III)	b	dg	lb	y	lb	y
30.	Ce(IV)	db	dg	—	y	lb	—
31.	Th(IV)	oy	lg	lv	y	lb	—
32.	U(VI)	b	g	o	gy	lb	lg
33.	Pd(II)	gr	fg	db	g	grb	dg

3-Methylphloroacetophenone is a weaker reagent than those mentioned above giving weakly coloured spots with only twenty metal ions in visible and UV light. The other three reagents, viz, 2,4,5-trihydroxyacetophenone, 2,5-dihydroxy-4-benzyloxy-6-methoxyacetophenone and 3-formylphloroacetophenone are not as good as the above reagents.

Taken together resacetophenone, phloroacetophenone and gallacetophenone in this group of polyphenolics can be used as powerful spray reagents. Rb(I) which is not usually indicated by polyphenolic ligands gives white spots in visible and UV light with phloroacetophenone.

From the results it is obvious that 5-C-prenyl-2,3,4-trihydroxyacetophenone (8) is the most effective spray reagent of the compounds given in Tables I and II and with the exception of Mg(II), Pb(II), As(V), Te(VI), Cd(II) all other cations are indicated by this reagent.

Table III shows the comparative limits (μg) detectable by resacetophenone (1), phloroacetophenone (2), gallacetophenone (4) and 5-C-prenylgallacetophenone (8)

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

S. No.	Metal Ions	Reagent-1		Reagent-2		Reagent-4		Reagent-8	
		Vis	UV	Vis	UV	Vis	UV	Vis	UV
1.	Ti(IV)	4	2	40	10	2	1	10	9
2.	V(V)	6	5	4	2	2	1	3	2
3.	Mn(II)	7	7	8	8	2	1	9	8
4.	Fe(II)	0.4	0.2	0.4	0.4	0.2	0.8	0.8	0.6
5.	Fe(III)	3	2	0.8	0.6	0.3	0.2	0.3	0.2
6.	Ni(II)	0.6	0.4	0.4	0.2	0.2	0.1	0.4	0.2
7.	Cu(II)	4	1	6	4	2	0.9	4	2
8.	Ce(IV)	40	10	30	20	9	9	40	10
9.	U(VI)	6	4	10	8	5	4	4	4
10.	Co(II)	0.6	0.4	0.4	0.2	0.1	0.1	0.4	0.2

Metal ion concentrations in μg

in the case of Ti(IV), V(V), Mn(II), Fe(II) Fe(III), Co(II), Ni(II), Cu(II), Ce(IV) and U(VI). All four reagents, as is obvious, can be used for the detection of very small quantities of Fe(II), Fe(III), Ni(II), Co(II), Ti(IV), Cu(II), V(V), Mn(II) metal ions. A comparison of these limits with those for other known reagents [12] shows that in the UV the present reagents are quite sensitive for the detection of ions from 0.1 to 0.9 μg . Further, no other known single reagent can be used for the detection of such a large number of metal ions in semimicro and micro concentrations.

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