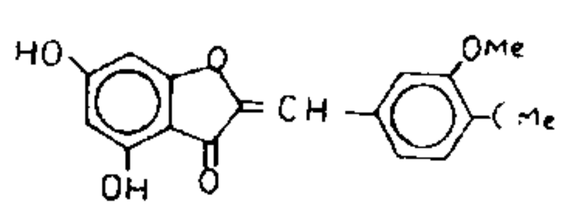
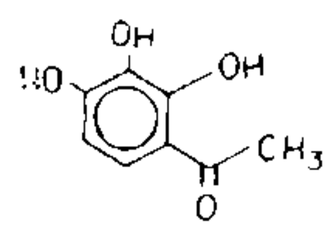
CHROMATOGRAPHIC SPRAYING REAGENTS FOR QUALITATIVE ANALYSIS OF INORGANIC CATIONS

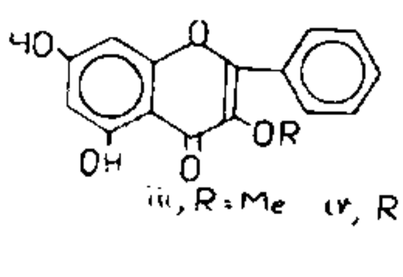
PAPER chromatography has been successfully employed in the past for qualitative analysis of inorganic cations[1]. Different spraying reagents are used for dfferent cations. In an attempt to discover spraying reagents which could give colours with a large number of inorganic cations, various organic chelating ligands were considered. 3-Phenyl-4, 5, 7-trihydroxy coumarin was used successfully by us recently as a chromatographic spraying reagent for Ti (IV), V (V), Mn (II), Fe (III), Cu (II), Mo (VI), Au (III), U (VI), Ce (III) cations[2]. Now six organic chelating ligands belonging to different groups of polyphenolics such as aurone, flavonol, xanthone and isoflavone have been explored. Some of the results are very useful ; they are described below :



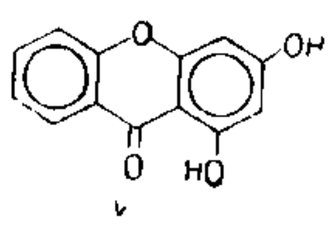
i

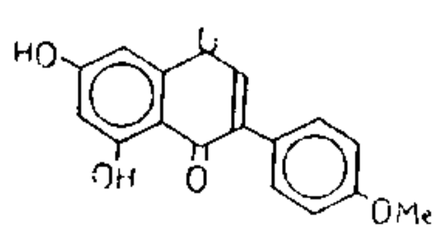


ii



iii, R = Me iv, R = H





Thirty-nine metallic cations which are usually analysed in the laboratory have been examined on paper chromatograms nsing *n*-butanol : 8 N HCl (1 : 1 v/v) as the solvent system. The chromatograms after exposure to ammonia have been sprayed separately with the following reagents in 1% alcoholic solutions : (1) 4, 6-dihydroxy-3′, 4′-dimethoxyaurone[3] (I) ; (2) gallacetophenone (II)[4]; (3) galangin-3 methylether (III)[5] ; (4) galangin (IV)[5] ; (5) 1, 3-dihydroxyxanthone (V)[6] and (6) biochanin-A (VI)[7]. The various colours given by the metal ions with the reagents are given in Table I.

A perusal of Table I shows that 4, 6-dihydroxy-3′, 4′-dimethoxyaurone and gallacetophenone can serve as very useful spraying reagents for a large number of cations. It may be mentioned that the colours of the spots are vivid with as many as twenty-seven cations in both cases, the intensity of the colour being more in the case of gallacetophenone than in the aurone. Further, with the exception of barium, thirty-five cations can be detected by spraying separately with these two reagents ; barium can be indicated by 1, 3-dihydroxyxanthone. The other reagents are also good but not so general.

Thirteen cations mostly of the transitional elements, namely, Be (II), Ti (IV), Zr (IV), Mn (II), Fe (II), Fe (III), Cu (II), Au (III), Ce (III), Th (IV) and U (VI) are indicated by all the six spraying reagents with nearly similar colour shades. Hence it suggests that these thirteen cations can be used for detecting chelation in organic compounds. So far, generally Fe (III) and sometime Ti (IV) ions are used.

TABLE I

S. No.	Metal ion	4, 6-Dihydroxy-3′, 4′-Dimethoxy aurone (I)	Gallaceto-phenone (II)	Galangin 3-Methyl-ether (III)	Galangin (IV)	1. 3-Dihydroxy Xanthone (V)	Biochanin-A (VI)
1	Li (I)	Faint yellow	Light brown	..	..	..	..
2	Na (I)	..	..	..	..	..	..
3	K (I)	..	..	..	..	..	..
4	Be (II)	Faint yellow	Greenish-yellow	Yellow	Light yellow	Yellow	Light yellow
5	Mg (II)	..	Light brown	..	..	..	..
6	Ca (II)	..	Light brown	..	..	..	..
7	Sr (II)	..	Light brown	..	..	..	..
8	Ba (II)	..	..	..	..	Yellow	..
9	Al (III)	Yellow	Yellow	Yellow	Brown	Yellow	Light yellow
10	Sn (II)	Orange-red	..	..	..	..	..
11	Pb (II)	Brown	..	..	Grey	..	..
12	As (V)	Orange	..	Faint yellow	..	..	..
13	Sb (III)	Orange-red	..	Faint yellow	..	..	..
14	Bi (III)	Yellow	Faint yellow	..	..	Light yellow	..
15	Se (IV)	..	..	..	..	..	..
16	Te (IV)	..	..	..	..	..	..
17	Ti (IV)	Orange-yellow	Brown	Yellow	Orange-yellow	Orange	Orange
18	Zr (IV)	Yellow-orange	Yellow	Yellow	Orange-yellow	Yellow	Light yellow
19	V (V)	Orange	Brownish-green	Yellow	Dirty green	Yellow	Light green

TABLE I (*Contd.*)

S. No.	Metal ion	4, 6-Dihydroxy-3', 4'-Dimethoxy aurone (I)	Gallaceto-phenone (II)	Galangin 3-Methyl-ether (III)	Galangin (IV)	1, 3-Dihydroxy Xanthone (V)	Biochanin-A (VI)
20	Cr (III)	Orange	Brown	Yellow-green	Grey	Light yellow	Grey
21	Mo (VI)	..	Light brown	..	..	..	..
22	W (VI)	..	Dark-brown	Light brown	Light brown	..	Light yellow
23	Mn (II)	Orange	Light brown	Yellow-brown	Brown	Brown	Brown
24	Fe (II)	Chocolate	Dark chocolate	Chocolate	Chocolate-brown	Chocolate	Chocolate brown
25	Fe (III)	Chocolate	Dark chocolate	Chocolate	Chocolate-brown	Chocolate	Chocolate-brown
26	Co (II)	Orange-yellow	Brown	Yellow	Orange-yellow	Yellow	Brown
27	Ni (II)	Orange	Brown	Yellow	..	Yellow	..
28	Pt (IV)	Light brown	Light brown	Light brown	Light brown	..	Light brown
29	Cu (II)	Orange	Brown	Yellow-green	Yellow green	Yellow-green	Green-yellow
30	Ag (I)	..	Grey	..	Grey	Light grey	Grey
31	Au (III)	Violet-grey	Violet-grey	Violet grey	Violet-grey	Violet-grey	Violet-grey
32	Zn (II)	Yellow	Brown	..	..	..	..
33	Cd (II)	Yellow	Brown	..	..	..	..
34	Hg (ous)	Orange	..	..	..	..	..
35	Ce (III)	Orange-brown	Brown	Brown	Brown	Light yellow	Brown
36	Th (IV)	Orange-yellow	Yellow	Yellow	Orange-yellow	Yellow	Light yellow
37	U (VI)	Orange-red	Orange	Orange	Orange	Orange	Orange
38	Pd (II)	Light orange	..	..	Brown	..	Brown
39	Hg (II)	Brown	Light brown	..	..	..	..

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PHASE STUDIES IN THE SYSTEM $FeZr_x\ Th_{(2-x)}O_5$

ZIRKELITE and thorianite, the naturally occurring minerals are often found together. Various workers[1-3] have analyzed the samples and also studied the X-ray diffraction patterns. They indexed these patterns on the basis of cubic symmetry. Bykova[2] and coworkers studied the X-ray pattern of zirkelite after roasting at 800° C for two hours and indexed the pattern on the basis of cubic symmetry. However they left the patterns unindexed which were roasted at 1100° C and commented that the patterns were complex but were characteristic of zirkelite. In order to investigate the structures of the zirkelite and thorianite, their structural correlation and the phases developed in the present system, we synthesized the minerals and studied their X-ray patterns. All the compositions were synthesized by mixing the appropriate quantities of the spectrochemically pure samples of ferrous oxalate, zirconium dioxide, and thorium dioxide; these samples were fired at 1000° C for 8 hours and at 1300° C for 4 hours and finally the samples were quenched to room temperature in air. The X-ray patterns were obtained by Philips diffractometer. These charts were used to calculate the lattice parameters and to study the developed phases. The results are given in Table I. On introduction of Th^{4} ions in the B-site replacing Zr^{4+} ions in zirkelite lattice, the lattice parameters increased

TABLE I

The system : Fe Zr_x $Th_{2(2-x)}$ O_5

S. No.	Composition	Molecular weight	Colour	Phases present
D_1	$Fe\ Zr_{1.6}\ Th_{0.4}\ O_5$	374·24	Brownish-red	Zirkelite a=6·29 Å
D_2	$Fe\ Zr_{1.2}\ Th_{0.8}\ O_5$	430·68	do.	do.
D_3	$Fe\ Zr_{0.8}\ Th_{1.2}\ O_5$	487·12	Faint brownish-red	Zirkelite + Thorianite a=6·33 Å
D_4	$Fe\ Zr_{0.4}\ Th_{1.6}\ O_5$	543·56	Pink	do.
D_5	$Fe\ Th_2\ O_5$	600·00	Pinkish-white	Thorianite a=6·37 Å