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Note

Thorium(IV) nitrate – a new chromogenic reagent for detection of phenols on thin-layer plates

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Besides iron(III) chloride, which is a very widely used chromogenic reagent, several other reagents have been developed[1–4] for the detection of phenolic compounds on thin-layer plates. These include titanium(IV) chloride in concentrated HCl (20%)[2], an aqueous solution of SeO_2 (3%)[3] and for aminophenols a solution of phenol in 20% Na_2CO_3 (1%)[3]. In the last case a process of overspraying with concentrated HCl was also adopted for immediate colour change. A specific reagent for the detection of *o*-dihydroxyl groups in phenolic compounds has also been reported[4,5]. This is Benedict's reagent, an acidic solution of sodium tungstate followed by addition of alkali and a solution of sodium cobaltinitrite.

Although iron(III) chloride is the most extensively used spray reagent, its colour range is not quite broad enough to identity a particular phenol. Titanium(IV) chloride, employed recently for phenolic compounds, has a similar drawback. In view of these considerations, thorium(IV) nitrate has been used for the detection of phenols and the results are reported in this paper along with a comparative study of titanium(IV) chloride and iron(III) chloride.

EXPERIMENTAL

Glass plates (20 × 5 × 0.3 cm) were coated with silica gel G (E. Merck) and then activated at 130°C for 30 min before use. 0.01 *M* Methanolic solutions of phenols were used as stock solutions. A Hamilton microsyringe was used for spotting the solutions. The plates were developed by spraying with (i) $Th(NO_3)_4 \cdot 6H_2O$ in methanol (4%), (ii) $TiCl_4$ in concentrated HCl (20%), (iii) methanolic $FeCl_3$ (2%), (iv) heating after spraying with these reagents at 120°C for 30 sec or 2 min and keeping the heated plate overnight.

RESULTS AND DISCUSSION

The phenols were chromatographed on silica-gel plates and then sprayed with a 4% methanolic solution of thorium(IV) nitrate. Table I records the colour produced on (i) spraying with thorium(IV) nitrate, (ii) heating the plates at 120°C for 30 sec or (iii) for 2 min, (iv) keeping the heated plates overnight. The limits of detection after development were 1–3 for all the compounds tested.

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TABLE I

COLOURS OF PHENOLS OBTAINED WITH THORIUM(IV) NITRATE ON THIN-LAYER PLATES

1 μl of a 0.01 *M* methanolic solution of each phenol was spotted unles indicated otherwise.

Compound	*Initial colour*	*After heating for 30 sec*	*After heating for 2 min*	*Colour with $FeCl_3$**	*Colour with $TiCl_4$*	*After heating for*	
						30 sec	*2 min*
Phenol**	–	–	Grey	Violet	Yellow	Yellow	Yellow
o-Cresol	–	Dull violet-grey	Violet	Brown	Brownish-violet	Brown	Brown
m-Cresol	Dull greyish brown	Dull violet-grey	Violet	Brown	Brown	Brown	Brown with yellow
p-Cresol	Buff	Faint violet	Light violet	Buff	Brown with yellow ring	Light brown	Muddy
o-Aminophenol	Greyish violet	Grey	Violet	Brown	Violet	Violet	Brownish violet
m-Aminophenol	Brownish grey	Faint violet-grey	Dark brown	Brown	Light violet	Light violet	Light brown
p-Aminophenol	Faint greyish violet	Violet	Violet	Reddish brown	–	–	–
p-Bromophenol	Light pink	Faint violet	Violet ring	–	Light yellow	Muddy	Muddy
p-Chlorophenol**	–	Yellow	Brown	–	Dark brown	Dark brown	Dark brown
2,4-Dichlorophenol	Faint fawn	Brown	Fawn	–	–	–	–
2,4,6-Tribromophenol	–	Fawn-red	Dirty grey	–	–	–	Yellow
p-Nitrophenol**	–	–	Yellow	Buff	–	Light yellow	Yellow
Catechol	Greyish green ring	Grey	Green	Violet-green	Brownish orange	Brownish orange	Brown
Resorcinol	Yellow	Yellow with violet ring	Dull brown	Violet	Light brown	Light brown	Light brown
Quinol	Light brown	Brown	Chocolate	–	Orange	Orange	Orange
Phloroglucinol**	–	–	Dull brown	Violet	Brown ring	Brown	Yellow with light brown ring
Pyrogallol	Green ring	–	Chocolate	Violet	Brown	Brown	Brown
α-Naphthol	Pinkish brown	Bluish grey	Violet with brown ring	Violet	Brown	Brown	Brown
β-Naphthol	Brown ring	Reddish brown ring	Red	Buff	–	–	–
Thymol**	–	–	Pink	–	–	–	–
2,4-Dimethylphenol	Yellow	Muddy	Brownish pink	Buff	Muddy	Muddy	Muddy

* Colour does not change on heating.

** 2 μl of the solution were used.

A comparative study with titanium(IV) chloride and iron(III) chloride was also undertaken. A distinctive feature of thorium, as a chromogenic reagent, is that it gives a colour with all the phenols. It also gives a wider range of colours compared to iron(III) chloride and titanium(IV) chloride for which the colour distinction is not quite as sharp, as is evident from the table. The range is so wide that one can even identify a particular phenol on the thin-layer plate. Compounds such as 2-methoxyethanol, chlorohexanol and keto–enol tautomers such as ethyl acetoacetate do not give any colour with thorium(IV) nitrate.

It was observed that addition of a methanol solution of thorium(IV) nitrate to some phenols gives a colour in some cases but no colours with a few others, even on heating (*e.g.*, thymol, pyrogallol, 3-aminophenol and 2,4,6-tribromophenol). On thin-layer plates coated with silica gel G a coloured spot was obtained with all the phenols (Table I). The rôle played by silica gel is not clear.

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