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Note

Application of the combined redox–complexation reaction to the detection of antipyrine and its derivatives in thin-layer chromatography

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The aim of this work was to obtain lower detection limits for phenylpyrazolone derivatives by using the following systems as detection agents: (I) Ce(IV), arsenazo III; (II) Fe(III), 1,10-phenanthroline or 2,2′-dipyridyl; (III) Cu(II), 2,2′-diquinolyl or disodium 2,2′-dicinchonate.

The reaction path is as follows:

$$nM^{(m+1)+} + R_R \overset{ne}{\rightleftarrows} nM^{m+} + R_0 \qquad (1)$$

$$M^{m+} + qL \rightleftarrows [M(L)_g]^{m+} \qquad (2)$$

where $M^{(m+1)+}$ and M^{m+} are the metal ion in oxidation states $(m + 1)+$ and $m+$, L is the complex ligand, q is the number of coordinated ligands, R_0 and R_R are the organic redox reagent in its oxidized and reduced forms, respectively, n is the number of exchanged electrons and $[M(L)]_q]^{m+}$ is the coloured complex.

This combined redox–complexation reaction has been applied previously in the absorption spectrophotometry of the antypyrine compounds[1,2].

EXPERIMENTAL AND RESULTS

Reagents and materials

Aqueous solutions of 1-phenyl-2,3-dimethylpyrazolone-5 (antipyrine), 1-phenyl-2,3-dimethyl-4-dimethylaminopyrazolone-5 (pyramidon), and sodium 1-phenyl-2,3-dimethyl-5-pyrazolone-4-methylaminomethanesulphonate (novalgin, dipyrone) were prepared at concentrations of 1, 0.5, 0.25, 0.01, 0.0025 and 0.0005 mg/cm^3.

A 0.05 *M* solution of 1,10-phenanthroline in 0.15 *N* sulphuric acid, a 0.05 *M* solution of 2,2′-dipyridyl in 0.2 *N* hydrochloric acid, a saturated ethanolic solution of 2,2′-diquinolyl, a 1% aqueous solution of disodium 2,2′-dicinchonate and a 0.05% aqueous solution of arsenazo III were prepared.

A Ce(IV) solution containing 1 mg/cm^3 of cerium, an Fe(III) solution containing 5 mg/cm^3 of iron and a Cu(II) solution containing 12.5 mg/cm^3 of copper were used.

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Other reagents and organic solvents were of analytical-reagent grade.

Glass thin-layer chromatographic (TLC) plates covered with silica gel 60 (without a fluorescent agent) were obtained from Merck (Darmstadt, G.F.R.).

Detection of antipyrine and its derivatives after chromatographic separation

Our aim was to obtain the best detection effects with the above group of compounds in terms of the highest colour contrast between the chromatographic spots and their background. The best results were obtained with the following concentrations of detection agents: (1) Ce(IV) solution, 1 mg/cm^3; arsenazo III solution, 0.05%; (2) Fe(III) solution, 1 mg/cm^3; 1,10-phenanthroline and 2,2′-dipyridyl solutions, 0.05 *M*; and (3) Cu(II) solution, 12.5 mg/cm^3; saturated ethanolic solution of 2,2′-diquinolyl and 1% solution of disodium 2,2′-dicinchonate.

It was established that drying of the chromatograms in a thermostatic chamber (80°C) after each spraying with a detection agent accelerated the colour reaction and increased the colour intensity of the spots.

Detection limits for antipyrine, pyramidone and novalgin

The efficiency of the applied systems as detection agents for antipyrine and its

TABLE I

"DETECTION INDICES" FOR ANTIPYRINE AND ITS DERIVATIVES

Detection agent	*Sample compound*	*(µg) Detection limit*	*Mean surface area of chromatographic spot (n = 6) (mm^2)*	*"Detection index"* (µg/mm^2)*
Fe(III)–1,10-phenanthroline	Antipyrine	–	–	–
	Pyramidone	0.025	3.7	0.007
	Novalgin	0.05	4.2	0.012
Fe(III)–2,2′-dipyridyl	Antipyrine	–	–	–
	Pyramidone	0.005	4.1	0.001
	Novalgin	0.05	4.0	0.012
Cu(II)–2,2-diquinolyl	Antipyrine	–	–	–
	Pyramidone	0.005	4.2	0.001
	Novalgin	0.005	4.0	0.001
Cu(II)–Na$_2$DC**	Antipyrine	–	–	–
	Pyramidone	0.05	3.9	0.013
	Novalgin	0.005	3.8	0.001
Ce(IV)–arsenazo III	Antipyrine	1.25	4.0	3.1
	Pyramidone	0.05	4.6	0.011
	Novalgin	0.05	4.1	0.012
Dragendorff reagent	Antipyrine	12.5	4.7	2.66
	Pyramidone	5.0	4.2	1.2
	Novalgin	50.0	4.0	12.5
UV light	Antipyrine	1.25	6.2	0.20
	Pyramidone	0.5	5.3	0.09
	Novalgin	5.0	5.8	0.86

* "Detection index" is the ratio of the smallest amount detected in micrograms with a given reagent to the area of the chromatographic spot[3].

** Na$_2$DC = disodium 2,2′-dicinchonate.

derivatives was established by comparing the detection limits with those obtained using Dragendorff's reagent and examination under UV light. Volumes of 5 μl of the sample solutions were applied to the TLC plates, which were placed in chromatographic chambers and developed by means of the ascending technique to a distance of 10 cm with chloroform–acetone (1:1) as the mobile phase[4]. After drying, the chromatograms were treated with the detection reagents. The results obtained are shown in Table I.

CONCLUSION

The detection agents examined produced high permanence and good colour contrast with antipyrine and its derivatives. The most efficient were Cu(II), 2,2′-diquinolyl; Fe(III), 2,2′-dipyridyl; and Cu(II), disodium 2,2-dicinchonate. "Detection indices" for all the pyrine derivatives examined obtained using Dragendorff's reagent were greater than 1.0 μg/mm^2. Application of UV light gave "detection indices" in the range 0.1–0.9 μg/mm^2. The use Cu(II)–2,2′-diquinolyl as the detection agent reduced the "detection indices" to 0.001 μg/mm^2.

Hence it can be concluded that the detection agents examined give significantly lower TLC detection limits for antipyrine and its derivatives.

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