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Note

Persulphate ion as a reagent for the detection of aromatic amines and related compounds on thin-layer chromatography

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During the systematic study of the anilines[1], aromatic amines, phenols and other related compounds[2–5] by persulphate ion in the absence and in the presence of Ag^+ ion as a catalyst it was observed that these compounds either gave coloured solutions or precipitated oxidation. Hence it was thought possible that persulphate–silver nitrate mixture in aqueous media may be used as a spray reagent for the identification of aromatic amines and other related compounds by thin-layer chromatography (TLC). While Ekmann[6] developed the spots by diazotization (spray of 0.2 *M* $NaNO_2$ in 0.1 *N* hydrochloric acid followed by a spray of N-ethyl-1-naphthylamine hydrochloride in alcohol), Kitahara and Hiyama[7] used 1-naphthol-4-sulphonic acid, and Bertetti[8] used a $K_2Cr_2O_7$ solution acidified with sulfuric acid. In this paper we describe the results obtained by using an aqueous mixture of $K_2S_2O_8$ and $AgNO_3$ as a spray reagent for developing the spots separated by TLC.

EXPERIMENTAL

Materials

Analar-grade Fisher certified $K_2S_2O_8$ and $AgNO_3$ were used (Fisher Scientific, Pittburgh, Pa., U.S.A.). All the compounds studied were recrystallized from samples which were either C.P. or Analar of Fisher or Aldrich grade (Aldrich, Milwaukee, Wisc., U.S.A.). The solvents were checked for purity and distilled if necessary.

Spray reagent

A solution of $K_2S_2O_8$ (1.0% w/w) with traces of $AgNO_3$ (0.001 *M*) in distilled water was used.

Apparatus

TLC was used to separate amines and other related compounds by using a glass tank (28 × 26.5 × 9 cm). Silica gel GF (Analtech, Newark, Del., U.S.A.) plates were employed. Although no special temperature control was used, the laboratory temperature was maintained at 18 ± 0.5°.

Method

The solution of solid amines and other related compounds (0.05%) in an alcohol–water mixture (1:1) was spotted in the silica gel TLC plates, at equal distance, one inch above the edge of the plate, by the use of a fine capillary. The spots were allowed to be air dry. The organic phase solvent system butanol–acetic acid–water (50:10:40) was placed in the tank. The tank was covered and left for 2 h for equilibrium to reach between vapour and liquid phase. The plates were held in the tank and the spots were 2 cm above from the liquid surface. The chromatograms were developed until the solvent front had moved below 1 in. from the upper edge of the plate. The plates were removed from the tank and the solvent front was marked. The solvent was removed by evaporation by keeping it at room temperature for 1 h. The plates were further dried by blowing hot air for 5 min. The spot locations were determined by spraying the plates with the above spraying reagent. The coloured spots at once appeared except in cases of sulfapyridine, sulfanilic acid, N,N′-diphenylbenzidine, the spots appeared after keeping the plates at 45° in an oven for 5 min after spraying.

RESULTS AND DISCUSSION

Observations regarding the spot colour, sensitivity and the R_F values are given in Table I. In this process we successfully separated amines and other related compounds and obtained beautiful spots. It was observed that compounds containing a NH_2-group in *para*-position give sharp and bright spots at onze when sprayed with persulphate solution.

Ratney[9] used nitrogen dioxide as a reagent for the detection of various aromatic amines on thin-layer chromatograms and their sensitivities (smallest detectable

TABLE I

R_F VALUES AND COLOUR REACTIONS OF AMINES WITH A PERSULFATE–SILVER NITRATE MIXTURE

Compound	*Colour of the spots*	*R_F in butanol–acetic acid–water (50:10:40)*	*Smallest detectable amount (μg approx.)*
p-Aminophenol	Reddish brown	0.70	0.1
m-Aminophenol	Brown	0.78	0.3
p-Phenylenediamine	Bluish black	0.51	0.1
o-Phenylenediamine	Yellow	0.69	0.2
m-Phenylenediamine	Black	0.60	0.2
o-Tolidine	Dark yellow	0.77	0.1
3,5-Diaminobenzoic acid	Yellowish brown	0.68	0.2
3,4-Diaminobenzoic acid	Yellow	0.72	0.2
Diphenylamine	Black	0.92	0.2
Dimethoxybenzidine	Violet	0.73	0.1
N,N′-Diphenylbenzidine	Black (tailing)	0.96	0.3
Diaminobenzidine	Black	0.56	0.2
Benzidine	Yellowish black	0.74	0.3
4,4′-Diaminodiphenyl 3,3′-Diglycolic acid	Pink	0.76	0.3
Sulfapyridine	Light brown	0.81	[*]
Sulfanilic acid	Brown (tailing)	0.32	[*]

[*] Sensitivity not determined.

amount). The sensitivity varied from 0.1 to 11 μg. Although the present sensitivity results are similar to Ratney's, yet better sensitivity is obtained in the case of *o*-tolidine. However, we did not try all the amines listed in Ratney's study.

Very satisfactory results were obtained by using an aqueous solution of $K_2S_2O_8$ as a spraying reagent for the identification of aromatic amines separated by TLC using solvents like benzene–methanol[10] and benzene or chloroform[11]. However, chromatograms should be thoroughly dried. This spraying reagent could not be used where developing solvents contzin phenols.

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