

pressing between two sheets of absorbent paper and dried at room temperature for an hour. The solvent was prepared by mixing chloroform, water and liquid paraffin 25:25:1 and allowing it to stand for 12 h. The chromatograms were run by the descending technique for 7 h. The lower organic phase was placed in a dish on the floor of the tank. The sulphidimines were located by spraying with acidified potassium iodide (1% in 0.2 N hydrochloric acid) and heated at 80°.

TABLE I
CHROMATOGRAPHY ON PARAFFIN PAPER

<i>Sulphidimine</i>	<i>R_{methyl}</i>
Dimethyl sulphide	1
Methyl ethyl sulphide	0.72
Diethyl sulphide	0.51
Di- <i>n</i> -propyl sulphide	0.20
Ethyl isopropyl sulphide	0.31
Ethyl <i>n</i> -propyl sulphide	0.29
Tetrahydrothiophene	0.65

Results

Owing to slight variations in impregnation it was found advisable to use the technique of ASATOOR⁶ and express the rate of movement of each sulphidimine spot relative to that of the sulphidimine of dimethyl sulphide. The *R_{methyl}* values for the average of six experiments are set out in Table I.

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¹ D. LEAVER AND F. CHALLENGER, *J. Chem. Soc.*, (1957) 39.

² J. PETRANEK AND M. VECERA, *Chem. Listy*, 52 (1958) 1279.

³ F. CHALLENGER, *Aspects of the Organic Chemistry of Sulphur*, Butterworths, London, 1959, p. 18.

⁴ A. R. FOLKARD AND A. E. JOYCE, *J. Sci. Food. Agr.*, in the press.

⁵ D. S. TARBELL AND C. WEAVER, *J. Am. Chem. Soc.*, 63 (1941) 2939.

⁶ A. M. ASATOOR, *J. Chromatog.*, 4 (1960) 144.

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A new detection method for aromatic compounds

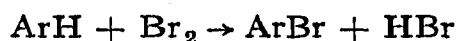
In paper chromatography, gaseous compounds are particularly suitable for spot indication as they will not distort the spot. In our institute we have employed iodine vapour as a developer¹.

Owing to its higher vapour pressure and reactivity bromine was also thought to be suitable. A number of organic compounds were exposed to the action of bromine vapour. It was found that, except for a few instances, the spots had only a very slight pale yellow hue, or were colourless, and that as soon as the paper strips were removed

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from the bromine atmosphere the spots tended to fade very rapidly. This would indicate that bromine is not as capable of forming adsorption compounds or, when it does form such compounds, they are weaker than those with iodine. This phenomenon may be explained by the atomic weight of bromine which is lower than that of iodine². On the other hand it is likely that bromine, which has a higher normal potential, will have a greater effect upon chromatographed compounds than iodine and will involve them in chemical reactions as well.

It was assumed that when the spots of chromatographed organic aromatic compounds are exposed to the action of bromine vapour, a substitution reaction will probably take place as follows:



If this reaction actually takes place, hydrogen bromide will be liberated and can be detected with an acid-base indicator.

This assumption has been confirmed by our preliminary experiments. When paper strips with the spots of various aromatic compounds were exposed to bromine vapour and subsequently sprayed with the solution of a suitable acid-base indicator after removal of excess bromine vapour by standing the papers in the air, the spots of a number of compounds showed up in a vivid red colour. Since HBr is a strong acid dimethyl yellow (4-dimethyl amino-azobenzol; colour change red to yellow, pH 2.9-4.0) proved more suitable for our purpose.

Procedure

After development and removal of the acid and basic solvents the papers are placed in a desiccator (apparatus shown in Fig. 1). About 10 to 15 ml of bromine are placed in the glass bottle and bromine vapour is pumped into the desiccator for 5-10 sec using a nitrogen cylinder at a pressure of 0.5 atm. After leaving the bromine for 1-2 min, the papers are aerated for 15-20 min in a fume chamber with a good draught; then they are sprayed with a 0.5 % alcoholic solution of dimethyl yellow. The spots of the reacting compounds will show up in red on a yellow background.

In the paper chromatographic separation of basic materials for drugs, the following developers have been employed: *n*-butanol-water-glacial acetic acid (4:5:1) and *n*-butanol saturated with 1.5 *N* ammonium hydroxide. Development of the chromatogram was by the procedure described in an earlier paper³; the only difference was a longer period of drying in order to remove completely the acetic acid and the ammonia.

Table I gives the sensitivity of some organic compounds employing the above reaction.

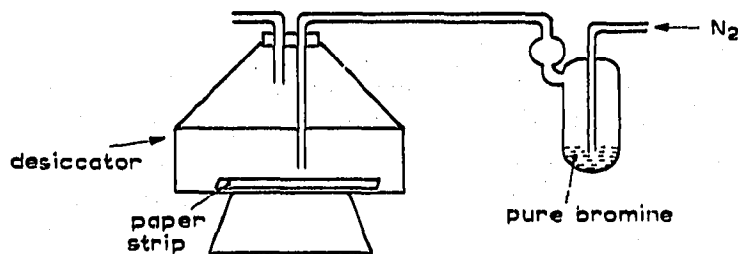


Fig. 1. Apparatus for detection of spots.

It should be noted, however, that some impurities in the paper migrate with the solvent front and are also coloured red in the process of development; consequently, they are apt to impair the reaction of compounds with R_F values close to 1.0. This

TABLE I

Denomination of substance	Quantity of substance applied μg	
	1	2
Acetanilide	10+ +	15+
Amidazophen	5+	10+
Atropine sulphate	50+	30 (yellow)
Azophen	5+ + +	5+ + +
Thiamine hydrochloride	20+	30+
Ethyl-morphine chloride	15+	15+
Phenacetin	30+ + +	15+ +
Phenolphthalein	15+ + +	10+ + +
Physostigmine salicylate	30+ +	30+
Hexamethylenetetramine	30 (yellow)	15 (yellow)
Potassium guaiacol-sulphonate	10+	10+ +
Codeine chloride	30+ +	30+ +
Caffeine	20+ +	20+ +
β-Naphthol	10+	10+ +
Methyl <i>p</i> -hydroxybenzoate	15+ + +	15+ + +
Ethyl <i>p</i> -aminobenzoate	10+	10+
Sodium [1-phenyl-2,3-dimethyl- pyrazolon-(5)-yl-(4)]-methyl- aminomethanesulphonate	10+ +	10+ +
Papaverine hydrochloride	30+ +	60+
Resorcinol	10+ + +	10+ + +
Salicylic acid	10+ +	10+ +
Strychnine nitrate	30+	30
Sulphanilamide	15+ + +	15+ + +
Amethocaine hydrochloride	30+ +	15+ + +

Mixtures: 1 = Butanol-glacial acetic acid-water (4:1:5).

2 = Butanol saturated with 1.5 *N* ammonia.

+ = definitely noticeable; ++ = strong; +++ = very strong.

effect can be eliminated by washing the paper with distilled water prior to chromatography.

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