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THIN-LAYER CHROMATOGRAPHY OF ORGANIC SULPHUR COM-POUNDS BY THE MIXED FLUORESCENT MATERIAL METHOD

I. DETECTION OF VARIOUS CLASSES OF COMPOUNDS*

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SUMMARY

Organic sulphur compounds were detected on silica gel layers containing a mixed fluorescent material. Disulphides, thioureas, isothioureas, thioamides, thio-lactones, thioesters, thiurams, dithiocarbamates, xanthates, S-sulphonic acids, thio-cyanates, isothiocyanates and organothiophosphorus compounds were detected as coloured spots in amounts of 10^{-8} – 10^{-11} mole according to their ultraviolet absorption spectra and molar absorption coefficients. Thiols, sulphides, sulphonic acids, sulphinic acids, sulphates, sulphamates, sulphones and sulphoxides did not give any coloured spots in amounts of 10^{-7} mole. When the sulphur was replaced with oxygen, the positive compounds above were no longer detected even in amounts of 10^{-7} mole.

INTRODUCTION

Organic sulphur compounds have been detected on chromatograms mainly by using various spray reagents of relatively low specificity. The spraying method often requires troublesome procedures and lacks reproducibility, whereas the qualitative analysis of ultraviolet (UV)-absorbing compounds by the mixed fluorescent material method, recently developed by Tamura¹, requires no complicated procedures and is non-destructive unless the compounds are sensitive to UV light. Some classes of organic sulphur compounds, such as disulphides, thiurams, thioureas and xanthates, may absorb UV light at wavelengths above 250 nm, and the mixed fluorescent material method may therefore provide a unique analytical method for these compounds, especially disulphides, whose detection on chromatograms in an intact form, *i.e.*, without reduction to thiols or oxidation of the disulphide bonds, has not been reported.

This paper describes the *in situ* non-destructive detection of organic sulphur compounds on silica gel lavers containing a mixed fluorescent material.

* Presented at the 94th Annual Meeting of the Pharmaceutical Society of Japan, Sendai, April 1974.

EXPERIMENTAL

Reagents and solvents

L-Glutathione (oxidized). S-carbamyl-L-cysteine. S-acetylglutathione, DL-homocysteine hydrochloride, 1-thioglucopyranose pentaacetate and D-glucose-6-sulphate potassium salt were purchased from Seikagaku Kogyo Co., Tokyo, Japan, and diquinolyl-8,8'-disulphide and 2,2'-dihydroxy-6,6'-dinaphthyl disulphide from Wako. Osaka, Japan. 2-Naphthyl disulphide was obtained from Eastman-Kodak. Rochester, N.Y., U.S.A., and D(--)-biotin from E. Merck, Darmstadt, G.F.R. Uridine-4-disulphide and D-pantoyltaurine calcium salt were purchased from Sigma, St. Louis. Mo., U.S.A. Pantethine, D-pantethine 4',4''-diphosphate and di-D-pantothenoyl-L-cystine were provided by Daiichi Seiyaku Co., Tokyo, Japan. Fenthion (Baytex), ethion, disyston and mesurol were kindly provided by Nihon Tokushu Noyaku Seizo Co., Tokyo, Japan. Pantetheine-S-sulphonic acid and 4'-phosphopantetheine-S-sulphonie acid were prepared in this laboratory. All other reagents and solvents were purchased from Tokyo Kasei Kogyo Co., Tokyo, or Kanto Chemical Co., Tokyo, Japan.

Apparatus

A Pan UV lamp (Type PUV-1A, Tokyo Kogaku Kikai, Tokyo, Japan) was used, which provides continuous UV radiation at 250–400 nm through an available surface area (7.5 4.5 cm) of luminescence.

Thin-layer chromatographic plates

Thin-layer chromatography (TLC) was performed with commercially available chromatographic plates (Wakogel FM plate, 10 5 cm; Wako). The layer (250 μ m thickness) on the plates contained, in addition to silica gel and starch, three inorganic fluorescent additives, Sr₂P₂O₇/Sn (λ_{max} , 260 nm, blue fluorescence), Zn₂SiO₁ Mn (λ_{max} , 280 nm, green fluorescence) and YVO₁/Eu (λ_{max} , 330 nm, red fluorescence), in a ratio of 20:5:1.

Solvent systems

The two solvent systems used were (A) methanol-dioxane (1:1) and (B) *n*-propanol-28% ammonia (7:3). Most of the test compounds were developed with the neutral solvent system A with R_F values of above 0.5. Xanthates were developed with the alkaline solvent system B in order to prevent their decomposition.

Chromatographic procedure

Stock solutions of test compounds of concentration 0.1 M were prepared with appropriate solvents (water, methanol, ethanol, ethyl acetate, acetone, carbon disulphide, chloroform, benzene, 0.2 N hydrochloric acid, 0.2 N sodium hydroxide solution, 5% ammonia solution and their mixtures) and were diluted as required with the same solvents. A volume of 1 μ l of a stock solution or its dilution was applied with a micro-pipette ("Microcaps", Drummond, Broomall, Pa., U.S.A.) on to 0.8 cm of the lower edge of a TLC plate. After air-drying, the plate was developed for a distance of 8.5–9 cm in a small chromatographic chamber (ambient temperature *ca*.

25°). The developed plate was dried with a stream of air using a hair-dryer and was viewed from the back under UV light from the Pan UV lamp in the dark².

The compounds that gave no coloured spots in amounts of $1 \cdot 10^{-7}$ mole were designated as negative compounds.

RESULTS.

The colours and the limits of detection of various classes of organic sulphur compounds on Wakogel FM plates are summarized in Table I, together with λ_{max} , and log ϵ values taken from the literature. In general, disulphides, thioureas, isothioureas, thiocarboxylic acid derivatives (thiol acids, thioamides, thiolactones and thioesters), thiocarbamic acid derivatives (thiuram compounds and dithiocarbamates), xanthates. S-sulphonic acids, organothiophosphorus compounds, thiocyanates and isothiocyanates were detected as coloured spots in amounts of less than $1 \cdot 10^{-7}$ mole. On the other hand, thiols, sulphides, sulphonic acids, sulphinic acids, sulphates, sulphamates, sulphones and sulphoxides did not give any coloured spots at this level.

As expected, the positive compounds in Table I were exclusively those with λ_{max} , values above 250 nm and the sensitivities of detection depended mainly upon their log ϵ values. The colours of the positive compounds on the TLC plates under UV light differed according to their UV spectra. The characteristic colours of the sulphur-containing functional groups were altered by the presence of a linked aromatic ring, while an additive colour was developed by the presence of a separated aromatic ring. A representative example is aromatic disulphides: diphenyl disulphide and 2-naphthyl disulphide were visible as violet spots, benzyl disulphide gave red spots. In general, the linkage effect in aromatic disulphides contributed to the increase in sensitivity by a factor of approximately 10–100. In fact, the limits of detection of dialkyl disulphides and polar aliphatic disulphides were 10⁻⁸–10⁻⁹ mole, whereas those of aromatic disulphides, except benzyl disulphide, were 10⁻¹⁰–11⁻¹¹ mole.

When the sulphur was replaced with oxygen, the above compounds were no longer detected, even in amounts of $1 \cdot 10^{-2}$ mole. In view of the UV spectra and the log ϵ values given in Table II, these results are reasonable: no large absorption above 250 nm was observed.

DISCUSSION

The qualitative analysis of UV-absorbing substances has previously been performed on thin layers with fluorescent additives, the most popular being silica gel F_{251} and $HF_{251-366}$ (Merck). On these layers, however, all types of UV-absorbing substances are rendered visible as dark, uncoloured spots, while on layers containing the mixed fluorescent material used in the present work, different colours occur according to the wavelength of the UV light absorbed by the substances. Thus various organic sulphur compounds have been detected with a clear distinction of colour. For example, although disulphides, thiocyanates, isothiocyanates, thiolactones, thioureas, isothioureas and S-sulphonic acids generally showed a red colour on Wakogel FM plates, the colours of dithiocarbamates and thiuram compounds were reddish violet and that of alkylxanthates was bluish green. The presence of substituted groups that exert electromeric effects on the -SS- bond of disulphides gave rise to clear differences of

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LIMITS OF DETECTION OF VARIOUS CLASSES OF ORGANIC SULPHUR COMPOUNDS ON THIN LAYERS CONTAINING MIXED FLUORESCENT MATERIAL

Compound	Calaur*	Limit of detection** (mole)	<i>д.</i> тах. (109. г.) (1111)	Solvent	Reference
L-Cysteine DL-Homoeysteine	None None	10-7 10-7	230 (3.30)	Water (pH 8.32)	
Glutathione	None	2-01	No maxima 220-320	0.03 N HCI	4
Dithiothreitol n-Decyl mercaptan	arioN	10-7 10-7			
<i>ii</i> -Dodecyl mercuptan	None	-10-1			
<i>n</i> -1 ciraacey1 mercaptan <i>n</i> -Hexadeey1 mercaptan	None	01		•	
Thiophenol	Reddish violet	1.10-"	236 (3.93), 272 (2.81), 280 (2.84)	Isooctane	4
(A) Dialky1 disulphides					
Dimethyl disulphide	Red	<u>4-01</u>	203 (3,27), 254.5 (2.53)	Ethanol	4
Diethyl disulphide	Red	· 10- 1	202 (3,32), 251.5 (2.62)	Ethanol	4
Di-u-propyl disulphide	Red	1-10-1	250 (2.7)	Ethanol	5.
Di-n-butyl disulphide	Red	1 · 10- *	204 (3.32), 251.5 (2.60)	Ethanol	4
Di-isobutyl disulphide	Red	1.10-*			
Distance build disciplined	Red	*-01·1	254 (2,7)	Isooctane	~
Di-tervamyl disultation	Reddish violet	n- 10- 8			
Di-isoamy1 disulphide	Red	7.10-"	252 (2.6)	Isooctane	٣.
Di-terr,-heayt disulphide	Red	7.10-4			
Di- <i>n</i> -hept yl disulphide	Reddish pink	3.10-"			
Di- <i>tert</i> -octyl disulphide	Reddish pink	3.10-*			
Di-tertdodecyl disulphide Di-terttetradecyl disulphide	Reddish pink Reddish nink	3.10-4			
(B) Paler aliphatic disulphides					
Dithiodiacetic acid	Red		None above 250		9
at the substant of the set of the	Red	5.10-*			
	Compound 1-Cysteine 11-Homocysteine Glutathione Dithiothreitol 1-Dodeyl mercaptan 1-Dodeyl mercaptan 1-Dodeyl mercaptan 1-Hexadecyl mercaptan 1-Hexadecyl mercaptan 1-Hexadecyl mercaptan 1-Hexadecyl mercaptan 1-Hexadecyl mercaptan 1-Hexadecyl mercaptan 1-Hexadecyl mercaptan 1-Hexadecyl disulphide 1-n-propyl disulphide 1-n-propyl disulphide 1-n-terthexyl disulphide 1-n-terthexyl disulphide 1-n-terthexyl disulphide 1-n-tertdodecyl disulphide 1-n-tertdod	acid wide	<i>Calcure</i> Nome Nome Nome Nome Nome Nome Nome Nome	ColourLimit of (mate)Nome $Limit of$ (mate)Nome 10^{-7} (mate)Nome 10^{-7} (mate)Nome 10^{-7} (10^{-7} Nome 10^{-7} (10^{-7} Red $1 \cdot 10^{-7}$ (10^{-8} Red $1 \cdot 10^{-7}$ (10^{-8} Red $1 \cdot 10^{-7}$ (10^{-8} Red $1 \cdot 10^{-8}$ (10^{-8} Red $2 \cdot 10^{-9}$ Red $2 \cdot 10^{-9}$	CollentLanit of detrection λ_{max} . (log r) detrectionName 10^{-7} 230 (3.30)Nome 10^{-7} No maxima 220-320Nome 10^{-7} 203 (3.23), 272 (2.81),Nome 10^{-7} 203 (3.27), 254.5 (2.62)Nome 10^{-7} 203 (3.32), 251.5 (2.60)Red 10^{-7} 203 (3.32), 251.5 (2.60)Red 10^{-7} 203 (3.32), 251.5 (2.60)Red 10^{-7} 204 (3.32), 251.5 (2.60)Red 10^{-7} 250 (2.7)Red 10^{-7} 250 (2.7)Red 10^{-9} 250 (2.6)Red 10^{-9} 250 (2.6)Red 10^{-9} 250 (2.6)Red 10^{-9} 252 (2.6)Red 10^{-9} 252 (2.6)Red 10^{-9} 210^{-9} Red 10^{-9} 252 (2.6)Red 10^{-9} 252 (2.6)Red 10^{-9} 252 (2.6)Red 210^{-9} 252 (2.6)Red 10^{-9} 252 (2.6)Red 10^{-9} 252 (2.6)Red 10^{-9} 210^{-9} Red<

5 - 7	4	~ ~	44	4	
Water Methanol	0.1 N NaOH	Isooctane	Ethanol Ethanol	Ethanol	
243 (2.73) 333 (2.18)	249 (2.53)	238 (4.2), 270 (3.6), 300 (3.1) 221 (4.3)	24() (4.37), 351 (3.89) 315 (4.33)	248 (4.19), 332 (4.03), 410 (3.96)	
3.10 ^{- 4} 3.10 ^{- 4} 5.10 ^{- 6}		5 · 10 ⁻¹⁰ 2 · 10 ⁻¹⁰ 5 · 10 ⁻¹⁰	7.5 · [0 ⁻¹¹ 1 · [0 ⁻¹⁰ 5 ·]0 ⁻¹¹ 5 · [0 ⁻¹¹ 2 · [0 ⁻¹⁰	6-10 ⁻¹¹ 2.5-10 ⁻¹¹ 5-10 ⁻¹¹	1 · 10-10 1 · 10-10 1 · 10-10
Red Grey Red Reddish violet	Red Reddish orange Red Red Red Red Red Red	Violet Red Violet Violet brown	Reddish violet Brown Bluish green Bluish green Black	Violet black Black Reddish violet	Reddish violet Dark grey Bluish green Reddish violet
<i>h.///-</i> Dithiodipropionic acid Lipoic acid Cystamine Formannidine disulphide:2HCI	<i>J</i> -Atelnine L-Cystine Homocystine D-Pantethine 4, 4"-diphosphate D-Pantethine 4, 4"-diphosphate Di-D-pantethenoy]-1cystine Morpholine N, N'-disulphide (C) Aramatic disabilities	Diphenyl disulphide Benzyl disulphide 2-Naphthyl disulphide Diquinolyl-8,8,-disulphide	 disulphide disulphide a.aDinitrophenyl disulphide p.pDinitrophenyl disulphide 5.5 -Dithiobis (2-nitrobenzoic acid) 2.2 -Dithiodianiline 	2,2"-Dithiodibenzanilide Bis(2,4-dinitrophenyl) disulphide Thiamine disulphide Bis(2,4,5,rrichlorophide	disulphide 2,2'-Dibenzothiazolyl disulphide Uridine-4-disulphide UD) Polysulphides and athers Bis(2,4,5-trichlorophenyl) trisulphide

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(Continued on p. 200)

Chastification Contound Contour Limit of contention Zam, Ling r J Softent Sulfylur Sulfylur Dark grey 2-10 ^{-m} 200 (3,85), 236 (4,28), Eihmuol Narthinne hydride Dark grey 5-10 ^{-m} 3-00 (3,85), 336 (4,28), Eihmuol Narthinne hydride Dark grey 5-10 ^{-m} 3-00 (3,85), 335 (1,38), Eihmuol Okash and hydride Nome 10 ⁻² 210 (3,09), 229 (2,16) Eihmuol Narky sulfhide Nome 10 ⁻² 210 (3,09), 229 (2,16) Eihmuol Amy sulfhide Nome 10 ⁻² 210 (3,09), 229 (2,16) Eihmuol Narky sulfhide Nome 10 ⁻² 210 (3,09), 229 (2,16) Eihmuol Amy sulfhide Nome 10 ⁻² 210 (3,09), 229 (2,16) Eihmuol Narky sulfhide Nome 10 ⁻² 210 (3,09), 229 (2,16) Eihmuol Amy sulfhide Nome 10 ⁻² 210 (3,09), 229 (2,16) Marer Nome 10 ⁻² 210 (3,09), 229 (2,16) Narer Narer	TABLE 1 (continued)	()					
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1Methionine None 10 ⁻⁷ Featureless above 240 Dienkolic arcid None 10 ⁻⁷ Featureless above 240 Dienkolic arcid None 10 ⁻⁷ 10 ⁻⁷ Dienkolic arcid None 10 ⁻⁷ 8×10 ⁻¹⁰ Disturiar-butyttin Red 8×10 ⁻¹⁰ 8×10 ⁻¹⁰ Bisturiar-butyttin Red 6×10 ⁻⁸ 8×10 ⁻¹⁰ Bisturiar-butyttin Red 6×10 ⁻⁸ 3×10 ⁻¹⁰ Thiophene None 10 ⁻⁷ 231 (3.85) Thiophene None 10 ⁻⁷ 231 (3.85) Thiophene Red 10 ⁻⁷ 231 (3.85) Thiophene Red 10 ⁻⁷ 231 (3.85) Thiourea Red 10 ⁻⁷ 231 (3.85) R 1 1,3-Dimethythiourea Red 10 ⁻⁷ R 2 1,3-Dimethythiourea Red 1,10 ⁻⁹ N.N-Diarehythiourea Red 2,10 ⁻⁹ 208 (4,04), 275 (4,15) N.N-Distorrythiourea Red 2,5 10 ⁻⁹ 2,10 ⁻⁹ N.N-Dimethythiourea Red 2,5 10 ⁻⁹ 2,04,42,23 N.N-Diarehythiourea Red 2,5 10 ⁻⁹ 2,04,42,23 N.N-Dimethythiourea Red 2,10 ⁻⁹ 2,08 (4,04),275 (4,15)			None	10-7			
D:-LanthionineNone 10^{-7} Djenkolic acidNone 10^{-7} Djenkolic acidNone 10^{-7} Djenkolic acidNone 10^{-7} Djenkolic acidNone 10^{-7} MesurolRed $8 \cdot 10^{-10}$ Bistri- <i>n</i> -butytin sulphideRed $6 \cdot 10^{-8}$ BactracinBlue $3 \cdot 10^{-10}$ ThiopheneRed $6 \cdot 10^{-8}$ ThiopheneNone 10^{-7} $210 (3.04), 2.39 (1.73)$ ThiopheneRed 10^{-7} $231 (3.85)$ ThiopheneRed 10^{-7} $231 (3.85)$ ThiopheneRed 10^{-7} $231 (3.42)$ ThiopheneRed 10^{-7} $231 (3.64, 12)$ ThiouteaRed $1 \cdot 10^{-8}$ $235 (4.04)$ L.3-DinethythioureaRed $1 \cdot 10^{-8}$ $235 (4.04)$ L.3-DiethythioureaRed $1 \cdot 10^{-8}$ $235 (4.04)$ N.N'-DisopropythioureaRed $2.5 \cdot 10^{-9}$ $208 (4.04), 275 (4.15)$ N.N'-DisopropythioureaRed $2.5 \cdot 10^{-9}$ $1 \cdot 10^{-9}$ N.N'-DinethythioureaRed $2.5 \cdot 10^{-9}$ $1 \cdot 10^{-9}$		1Methionine	None	10-1	Featureless above 240	Water	- 1
Djenkolic acidNone 10^{-7} $10^{(1)}$ (AssurolNone 10^{-7} $10^{(1)}$ (AssurolNone 10^{-1} AssurolRed $8 \cdot 10^{-10}$ Bistri-n-burytin) sulphideRed $8 \cdot 10^{-10}$ Bistri-n-burytin) sulphideRed $8 \cdot 10^{-10}$ TriopheneBite $3 \cdot 10^{-10}$ ThiopheneNone 10^{-7} ThiopheneNone 10^{-7} ThiopheneNone 10^{-7} ThiopheneRed 10^{-7} ThioureaRed 10^{-7} ThioureaRed 10^{-7} ThioureaRed 10^{-7} ThioureaRed 10^{-7} Striphenyl-2-thioureaRed 10^{-7} N.N'-Di-utythioureaRed $1 \cdot 10^{-9}$ N.N'-Di-utythioureaRed $2 \cdot 10^{-9}$ N.N'-Di-utythioureaRed $2 \cdot 10^{-9}$ 1.1-Diphenyl-2-thioureaRed $2.5 \cdot 10^{-9}$ 1.1-Diphenyl-2-thioureaRed $2.5 \cdot 10^{-9}$ 1.1-Diphenyl-2-thioureaRed $2.5 \cdot 10^{-9}$		DiLanthionine	None	10-1			
13 (+) -Blotin None 10^{-1} Mesurol Red $8 \cdot 10^{-10}$ Bistri-n-burytin) sulphide Red $8 \cdot 10^{-10}$ Bistri-n-burytin) sulphide Red $6 \cdot 10^{-8}$ Bistri-n-burytin) sulphide Red $6 \cdot 10^{-8}$ Bistri-n-burytin Blue $3 \cdot 10^{-10}$ Thiophene None 10^{-7} 210 (3.04), 239 (1.73) Thiophene None 10^{-7} 231 (3.04), 239 (1.73) Thiophene None 10^{-7} 231 (3.04), 239 (1.73) Thiourea Red 10^{-7} 231 (3.04), 239 (1.73) R // 1, $3 - 10^{-10}$ 323 (4.42) 323 (4.42) R // 1, $3 - 10^{-10}$ 2.10^{-9} 235 (4.04) R // 1, $3 - 10^{-10}$ 2.10^{-9} 233 (4.13), 230 R // 1, $3 - 10^{-10}$ 2.10^{-10} $2.5 \cdot 10^{-9}$ N.N'-Di-nutythiourea Red $2.5 \cdot 10^{-9}$ 208 (4.04), 2.75 (4.15) N.N'-Di-nutythiourea Red 2.10^{-9} 208 (4.04), 2.75 (4.15) N.N'-Di-nutythiourea <t< td=""><td>-</td><td></td><td>None</td><td>-10-2</td><td></td><td></td><td></td></t<>	-		None	-10-2			
Red $8 \cdot 10^{-1}$ Bistrian-burytin) sulphide Red $6 \cdot 10^{-8}$ Bistrian-burytin) sulphide Red $6 \cdot 10^{-8}$ Triophene Red $6 \cdot 10^{-8}$ Thiophene Red 10^{-7} 210 (3.04), 239 (1.73) Thiophene Red 10^{-7} 231 (3.64 , 238) Thiourea Red 10^{-7} 231 (3.64 , 238) Thiourea Red 10^{-7} 233 (4.42) Thiourea Red 10^{-7} 233 (4.42) N.N'-Diethythiourea Red $1 \cdot 10^{-6}$ 235 (4.04) N.N'-Diethythiourea Red $1 \cdot 10^{-6}$ 238 (4.13), 230 N.N'-Diethythiourea Red $1 \cdot 10^{-6}$ 235 (4.04) N.N'-Diethythiourea Red $1 \cdot 10^{-6}$ 235 (4.13), 275 (4.15) N.N'-Diethythiourea Red $2 \cdot 10^{-9}$ 238 (4.13), 275 (4.15) N.N'-Diethythiourea Red $2 \cdot 10^{-9}$ 238 (4.04), 275 (4.15) N.N'-Diethythiourea Red $2 \cdot 10^{-9}$ 238 (4.04), 275 (4.15) N.N'-Diethythiourea		Distriction of the second seco	None	10-1			
Bactracin Blue $3 \cdot 10^{-10}$ Bactracin Blue $3 \cdot 10^{-10}$ Thiophene 10^{-7} $231 (3.04), 239 (1.73)$ Thiomen Red 10^{-7} $231 (3.04), 239 (1.73)$ Thiomen Red 10^{-7} $231 (3.85)$ Thiomen Red 10^{-7} $231 (3.85)$ Thiomen Red 10^{-7} $231 (4.42)$ Thiomen Red 10^{-7} $233 (4.42)$ RK') 1.3-Dimetrythiourea Red 10^{-9} I.3-Dimetrythiourea Red $1 \cdot 10^{-9}$ $238 (4.13), 280$ N.N'-Disopropythiourea Red $1 \cdot 10^{-9}$ $238 (4.13), 280$ N.N'-Disopropythiourea Red $2 \cdot 10^{-9}$ $238 (4.14), 275 (4.15)$ N.N'-Disopropythiourea Red $2 \cdot 10^{-9}$ $238 (4.04), 275 (4.15)$ N.N'-Disopropythiourea Red $2 \cdot 10^{-9}$ $238 (4.04), 275 (4.15)$ N.N'-Disopropythiourea Red $2 \cdot 10^{-9}$ $238 (4.04), 275 (4.15)$ N.N'-Diphenyl-2-thiourea Crevisitivitici $1 \cdot 10^{-10}$ $2.5 \cdot 10^{-9}$ 1.1-Diphenyl-		westreated Ristreate but of the carles bide	Dod	8-10-8			
TetrahydrothiopheneNone 10^{-7} 210 (3,04), 239 (1.73)ThiopheneThiophene 10^{-7} 231 (3,85)ThiazoleThiazole 323 (4,42)ThiazoleRed 10^{-7} 231 (3,85)ThiazoleRed 10^{-7} 233 (4,42)ThiazoleRed 10^{-7} 233 (4,42)ThioureaRed 10^{-7} 233 (4,13), 280R Y1.3-DinethylthioureaRed $1 \cdot 10^{-6}$ 235 (4,13), 280I.3-DiethylthioureaRed $1 \cdot 10^{-9}$ 238 (4,13), 280N.N'-DilethylthioureaRed $1 \cdot 10^{-9}$ 235 (4,13), 280N.N'-DilethylthioureaRed $2 \cdot 10^{-9}$ 235 (4,15)N.N'-DiletnylthioureaRed $2.5 \cdot 10^{-9}$ $2.5 \cdot 10^{-9}$ 1.3-Diphenyl-2-thioureaRed $2.5 \cdot 10^{-9}$ 2.10^{-9} 1.3-Diphenyl-2-thioureaGreyish violet $4 \cdot 10^{-10}$		Bactracin	Blue	1.10-10			
ThiopheneRed 10^{-7} 231 (3.85)ThiopheneThiazole $323 (4.42)$ $323 (4.42)$ ThioureaRed 10^{-7} $323 (4.42)$ ThioureaRed 10^{-7} $235 (4.04)$ ThioureaRed $1 \cdot 10^{-8}$ $235 (4.13), 280$ R NL.3-DiethylthioureaRed $1 \cdot 10^{-9}$ $238 (4.13), 280$ N.N'-DilisopropylthioureaRed $1 \cdot 10^{-9}$ $208 (4.04), 275 (4.15)$ N.N'-DilisopropylthioureaRed $2.5 \cdot 10^{-9}$ $2.6 \cdot 10^{-9}$ L.3-Diphenyl-2-thioureaGreyish violet $4 \cdot 10^{-10}$		Tetrahydrothiophene	None	<u>101</u>	210 (3.04), 239 (1.73)	Ethanol	Р
Thiazole*** Red 10 ⁻⁷ 323 (4,42) Thiourea Red 10 ⁻⁷ 323 (4,04) Thiourea Red 1,10 ⁻⁸ 235 (4,04) 1,3-Dimethylthiourea Red 1,10 ⁻⁸ 235 (4,04) 1,3-Dimethylthiourea Red 1,10 ⁻⁹ 238 (4,13), 280 1,3-Dimethylthiourea Red 1,10 ⁻⁹ 238 (4,13), 280 1,3-Dimethylthiourea Red 1,10 ⁻⁹ 238 (4,04), 275 (4,15) N.N'-Diisopropylthiourea Red 1,10 ⁻⁹ 208 (4,04), 275 (4,15) N.N'-Diisopropylthiourea Red 2,510 ⁻⁹ 208 (4,04), 275 (4,15) 1,1-Diphenyl-2-thiourea Red 2,510 ⁻⁹ 208 (4,04), 275 (4,15) 1,1-Diphenyl-2-thiourea Red 2,510 ⁻⁹ 208 (4,04), 275 (4,15) 1,1-Diphenyl-2-thiourea Red 2,510 ⁻⁹ 208 (4,04), 275 (4,15)		Thiophene	Red	10-1	231 (3.85)	Ethanol	┍╺┱
ThiazoleThiazoleRed 10^{-7} ThioureaRed 10^{-8} 235 (4.04)ThioureaRed $1 \cdot 10^{-8}$ 238 (4.13), 2801.3-DiethylthioureaRed $1 \cdot 10^{-9}$ 238 (4.13), 2801.3-DiethylthioureaRed $1 \cdot 10^{-9}$ 238 (4.13), 2801.3-DiethylthioureaRed $1 \cdot 10^{-9}$ 238 (4.13), 280N.N'-DiisopropylthioureaRed $2 \cdot 10^{-9}$ 208 (4.04), 275 (4.15)N.N'-DiisopropylthioureaRed $2.5 \cdot 10^{-9}$ $1 \cdot 10^{-9}$ 1.1-Diphenyl-2-thioureaRed $2.5 \cdot 10^{-9}$ $4 \cdot 10^{-10}$ 1.3-Diphenyl-2-thioureaGreyish violet $1 \cdot 10^{-10}$					323 (4,42)	Hexane	ŝ
ThioureaRed $1 \cdot 10^{-8}$ 235 (4.04)RR'11.3-DimethylthioureaRed $2 \cdot 10^{-9}$ 238 (4.13), 2801.3-DiethylthioureaRed $2 \cdot 10^{-9}$ 238 (4.13), 2801.3-DischylthioureaRed $1 \cdot 10^{-9}$ 238 (4.15)N.N'-DiisopropylthioureaRed $2 \cdot 10^{-9}$ 208 (4.04), 275 (4.15)N.N'-DiisopropylthioureaRed $2.5 \cdot 10^{-9}$ 2.10^{-9} 1.1-Diphenyl-2-thioureaRed $2.5 \cdot 10^{-9}$ $4 \cdot 10^{-10}$ 1.3-Diphenyl-2-thioureaGreyish violet $4 \cdot 10^{-10}$	-	Thiazole	Red	10-7			
1.3-DimethylthioureaRed $2 \cdot 10^{-9}$ $238 (4.13), 280$ 1.3-DiethylthioureaRed $1 \cdot 10^{-9}$ $238 (4.13), 280$ 1.3-DiethylthioureaRed $1 \cdot 10^{-9}$ $208 (4.04), 275 (4.15)$ N.N'-DiisopropylthioureaRed $2.5 \cdot 10^{-9}$ $208 (4.04), 275 (4.15)$ N.N'-DiisopropylthioureaRed $2.5 \cdot 10^{-9}$ $2.5 \cdot 10^{-9}$ N.N'-Dihenyl-2-thioureaRed $2.5 \cdot 10^{-9}$ 1.1 -Diphenyl-2-thioureaI.1-Diphenyl-2-thioureaGreyish violet 1.10^{-10}	(4) Thiourens	Thiourea	Red	1.10-*	235 (4.04)	Ethanol	ব
Red 1 · 10 ⁻⁰ Violet red 1 · 10 ⁻⁰ 208 (4.04), 275 (4.15) ntrea Red 2.5 · 10 ⁻⁰ irea Red 2.5 · 10 ⁻⁰ rea Greyish violet 4 · 10 ⁻¹⁰ rea Greyish violet 1 · 10 ⁻¹⁰	(RR'NCNRR')	1.3-Dimethylthiourea	Red	2-10-6	238 (4,13), 280	Ethanol	7
Nurea 2.5 · 10 ⁻¹ Nurea 2.5 · 10 ⁻¹ Red 2.5 · 10 ⁻¹ rea Greyish violet 4 · 10 ⁻¹⁰ rea Greyish violet	- . .	1. Acret vl. 2. thiourea	Violot rad	6-01·1	(31 F7 326 (F() F7 AUL	[24]1	
Red Greyish violet Greyish violet		N, N'-Diisopropylthiourea	Red	2.5.10-"			0
Greyish violet Greyish violet		N.NDi-u-butylthiourca	Red	2.5 . 10- "			
Greyish violet		1, 1-Diphenyl-2-thiouren	Greyish violet	4.10 ⁻¹⁰			
		1,3-Diphenyl-2-thiouren	Grevish violet	1.10-11			

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4 <u>0</u> % %		~ ~	ulter	2	(Continued on p. 202)
Water Ethunol pH 7.05 pH 12.0		Water Water	Phosphate buffer	Con unit	ت ن بالمراجعة مراجعة
2.35 (4.0) 2.35 (3.74), 285 (4.26) 2.20 (4.58) 2.38 (3.74)		245 (2,42) 262 (4,08)	232 (3.76)		
1 - 10-9 1 - 10-9 8 - 10- 10 1 - 10-9 1 - 10-9	2.10 ⁻⁰	1.10 ^{-*} 2.5.10 ⁻⁹ 1.10 ⁻⁹	3.10 ⁻⁹ 4.8.10 ⁻⁹	2.5 · 1() - 10 4 · 1() - 14	× - 0 - × - 0 - 1 - 1
Red Red Red Reddish violet Red	Red Red	Rod Rod Rod Bluish green	Red Red Red	Red Reddish violet	Red Reddish violet
Thiosemicarbazide•2HCl 4-Methylthiosemicarbazide N,N'-Dicyclohesylthiourea 2-Thiobarbituric acid Methylisothiourea sulphate	Ethylisothiourca·HBr //-Dimethylaminoethylisothiourca· 2HCl	 (.4) Thiol acids Thicacetic acid (B) Thiomutes Thiopropionumide Rubennic acid 	 (L) Inductiones Di-Homocysteine thiolactone hydrochloride N-Acetyl-Di-homocysteine thiolactone (D) Thiaesters S-Acetylglutathione 	Acetytthiocholine iodide 1-Thioglucopyranose pentaacetate	 (.4) Thiocarbamates S-Carbamyl-1cysteine (.B) Dithiocarbamates Sodium N.N-dimethyl- dithiocarbamate
(5) Isothiourcus	(R-S-C NH)	(6) Thiocarboxylic acid derivatives		(7) Thiocarbannic	acid derivatives

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	Reference	. • •							-		
	Refe	. .1			9	<u>`</u> m_`	-	01	<u></u>	ŝ	
							· 	ວແ			
	Salvent	Ethunol			Witter	Water	10% KOH	Cyclohexane		Ethanol	
			•		2)			.			
		257 (4,08), 290 (4,11)			226 (3.95), 301 (4.25)	0(1.7)	3 (4.2)	314 (2.82), 319 (2.83)) (2.7)	
	λ. _{wax} , (log r) (titt)	.08), 2	6 ()		.95), J	305 (4.2), 370 (1.7)	.9), 30	. 82), 3	240 (1.41,66)	275 (4.0), 340 (2.7)	
	l'max. ((nn)	257 (4	270 (4.0)		226 (3	305 (H	225 (3.9), 303 (4,2) 380 (1.7)	314 (2	240 (1	275 (4	
	Limit of derection** (mole)	2.10-4	4.10 ⁻¹⁰ 1.10 ⁻¹⁰ 2.10 ⁻¹⁰	3.10-10	4+10 ⁻¹⁰	4.10 ⁻¹⁰ 4.10 ⁻¹⁰ 4.10 ⁻¹⁰	#-01-t	×-01-5	5.10-4	2 · 10- # 1 · 10- #	د -01 د -01
		olet	olet olet	Ę	ទទ	555	55	-		olet olet town	
	Calaur	Reddish violet	Reddish violet Reddish violet Reddish violet	Brown Dark brown	Bluish green Bluish green	Bluish green Bluish green Bluish green	Bluish green Bluish green	Violet blue Red	Red	Greyish violet Red Reddish violet Reddish brown	Red Red
			le lide	phide							
			Tetramethylthiuram disulphide Tetraethylthiuram disulphide Tetra- <i>u</i> -butylthiuram disulphide Dipentamethylenethiuram	tetrasulphide Fetramet hylthiuram monosulphide	hate te	athafe nthate hate	thate hate	acid	-1		
		ethyl- ate	Tetramethythiuram disult Tetraethythiuram disulph Tetra-u-butythiuram disul Dipentamethylenethjuram	m man	nethyl samthate thyl samthate	 -propyl xanthate sopropyl xanthate -hutyl xanthate 	sobutyl xanthate -amyl xanthate	Carbon disulphide Pantetheine-S-sulphonic acid 4.Physobynomythono.s.	id niosulphate		
		dium N, N-dieth dithioeartamate Thinrans	hylthiu dthiura attylchi aethyle	lphide hylthiu	<i>ites</i> n meth n ethyl			lisulphi S-Sulp	s acid y Ithios	Jaytes)	seyanate yanate
-	Compound	Sodium N, N-diethyl- dithiocarbamate (C) Thinrana	stramet straet hy stra- <i>n</i> -h ipent an	tetrasu lphide etramet hylthiu	Potassium et al. (1-) <i>Xemthates</i> Tri reassium et Potassium et al.	Potassium 1 Potassium i Potassium 1	Potassium is Potassium //	Carbon disuphide	sulphonic acid Sodium ethylthic	Parathion Fenthion (Baytex) Ethion Disyston	Methyl thiocyanate ¹¹ Ethyl thiocyanate ¹¹¹
	(com	ž (j	2220	÷	() d () d ()	ਕ ਦ ਦ	ર્ગ તે તે	Paint C.	su Sodi		Meth
tinned)	• • •			<u>.</u>	lves			acids		Organothiophos- phorus compounds	les
l (com	ation			carbon	acid derivatives		· ·	S-Sulphonic RSSO.40		sanothi us com	ocyana CN)
TABLE I (continued)	Classification			(8) Thiocarbonic	acid			(9) S-Sulphonic acids		(10) Organothiophas- phorus compound	(11) Thiocyanates (RSCN)
E.	\sim			ت ب				ť			

Dioxane 10			Water 4			Water 5									Ethanol 4		Water 4	Dioxane 7					Cvelohexane 6				- - -	
245 (2.86)			Featureless 200-230			248 (3.9), 290 (2.8) V									262 (4.25) E	263 (4.2),			180				203 (3.4) C					ogel I [:] M plate, olatilities,
10 ⁻⁷ 10 ⁻⁷ 15.10 ⁻⁸				10-1		x		- - - - - - - - - - - - - - -		2~01						n 1.7.10-11				10-2		-		10-1			10-7	he compound on a Wake he owing to their high v
Methyl isothiocyanate" Red Ethyl isothiocyanate" Red Cyclohexyl isothiocyanate" Red	acid	dium salt	Cystele acta monohydrate None D1-Homocystele acid None		e calcium salt			Prevadecytsurphurfe acid sodium saft None D-Chucose-6-subhate rotassium saft None		inesulphinic acid			Cyclohexylsulphamic acid None	sodium salt		Sulphapyridine Brown	N-Ethylethanesulphonamide		114	Di-n-butyl sulphone None None	2	p.p.'-Sulphonyldianiline Purple	•	None None None None			truyt methanesulphonate None	 The colour was observed just after applying 1 · 10⁻⁷ mole of the compound on a Wakogel FM plate. Values after development. The limits of detection of these compounds are not reproducible owing to their high volatifities.
(12) Isothiocyanates (RNCS)	(13) Sulphonic acids (RSO ₃ H)						(14) Sulphates	(HI) DECIMIN	(15) Sulphimic acids	(RSO,H)	(16) Sulphamic acid	derivatives						(17) Subdahasi	(ISO.R')				(18) Sulphoxides		(19) Esters of in-	or game actus	compounds	The colour was observed Values after development.

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TABLE II LIMITS OF DETEC FLUORESCENT MA	TABLE JI LIMITS OF DETECTION OF NON-SULPHUR-CONTAINING ORGANIC COMPOUNDS ON THIN LAYERS CONTAINING MIXED FLUORESCENT MATERIAL	VTAINING ORGA	NIC COMPO	AVT NIHL NO SCIND	ERS CONTAINI	NG MIXED
Classification	Compound	Colaur	Limit of detection (mole)	<i>і.</i> тих. (log r.) (нн)	Solvent	Reference
(1) Alcohols (ROH)	Methano! Ethano! <i>n</i> -Butano! 1-Dodecanol 1-Octadecanol	None None None None	2 - 01 2 - 01 2 - 01 01	183.3 (2.18) 181 (2.51)	ano ano None	01
(2) Peroxides (ROOR')	- Methyl peroxide			22()	Hexane	13
(3) Ethers (ROR')	Dioxane Diethyf ether Difsaumyl ether Di-n-hexyl ether Di-n-decyl ether Di-n-docyl ether	None None None None None None		180 (3.8) 171 (3.60), 188 (3.30)	None None	4 <u>0</u>
(4) Ureas (RR'NCONRR')	Urea N.N'-Dicyclohexylurea Semicarbazide hydrochloride Barbiturie acid Barbital	Nume Nume Nume Red Red	10-7 10-7 5,10-1 6,10-9	No maxima 220-250 278 (- 0.7), 357 (- 1.1) 257.5 (4.33) 255 (2.9)	0,1 N NaOH Water 0,45 N NaOH	न २२ ल

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	Water							water	Fthanol	Water		Water			None	Methanol				Ethanol		•		Isooctane
219 (3.04)	262 (1.25)		215 (3.08)		208 (2.52)		2012	507	210 (1.70)	Featureless 200-230		220 (1.8)	175 (3.85)	•	162.1 (3.84), 197.4 (3.94) None	209 (1.63)				211 (1.76)		•		224,5 (1.68)
10-7 10-7	-10-2		∠ -01		2-10- <u>1</u>		10-7	10-1	10-2	10- 7		- 10- 2	~ 10-1	-10-2	∠-01∧	°-10-?	2-01 <	10-7		× 10-2	-10-1	10-2	1.1.1	01
None None	None		None		None		Nono	None	None	None		None	None	None	None	None	None	None		None	None	None	Name	None
O-Methylisourea sulphate Acetamidine hydrochloride	Guanidine hydrochtoride		Creatine		L-Arginine		(A) Carbayylic acids Acetic acid	<i>u</i> -Canrylic acid	Palmitic acid	L-Proline	(B) Acid amides	Acetamide	Propionamide	Formamide	N, N-Dimethylformamide (C) Lactones	?-Butyrolactone	D-()-Pantoyl factone	p-Glucuronolactone	(D) Esters	Ethyl acetate	2-Ethylbutyl acetate		Arothe analyzances	
(5) Isourca and amidinesNH₂	(R'-O-C	R NH); R	`u 'z	R' NH)		(6) Carboxylic acid	GUIVAINCS																	

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(Continued on p. 206)

Chool/finding Company Colume Limit of Law. (log r J. Solvent Represent (R.Y.NCOOR*) Unethance Nome (1)************************************	TABLE II (continued)			-			
 Mannonium carbanate None 10⁻⁷ · 220 Water None 10⁻⁷ Usethane None 10⁻⁷ · 220 Water None 10⁻⁷ Diethyl carbonate' None 10⁻⁷ Diethyl carbonate' None 10⁻⁷ Diethyl carbonate' None 10⁻⁷ Diethyl carbonate' None 10⁻⁷ Sphorts Trimethyl phosphite' None 10⁻⁷ Sichyl secsurate None 10⁻⁷ Scifyl secsurate None 10⁻⁷ Scifthysterone None 10⁻⁷ Scifthyste	Classification	Compound	Calow	Limit of detection (mate)	<i>Ž_{тик}, (log r)</i> (тп)	Solvent	Reference
Dimethyl earbonate* None 10 ⁻⁷ Diethyl earbonate* None 10 ⁻⁷ Sphorus Trinethyl phesphite* None 10 ⁻⁷ Trinethyl phesphite* None 10 ⁻⁷ 229 (1,74), 262.5 (0.97) Filhanol Trinethyl phesphite* None 10 ⁻⁷ 250 (1,6), 257 (2.80) Filyliscoyanate None 10 ⁻⁷ 250 (1,6), 257 (2.80) Eithanol * Eithyl phesphite* None 10 ⁻⁷ 250 (1,6), 257 (2.80) Eithanol * Eithyl scoyanate None 10 ⁻⁷ 250 (1,6), 257 (2.80) Eithanol * Eithyl scoyanate None 10 ⁻⁷ 250 (1,6), 257 (2.80) Eithanol * Filyliscoyanate None 10 ⁻⁷ 250 (1,6) 251 (2.30) Eithanol * Valetone None 10 ⁻⁷ 270 (1,25) Watter Cyclohexatrone None 10 ⁻⁷ 271 (1,41) Eithanol Disobutyl ketone None 10 ⁻⁷ 271 (1,41) Eithanol 2-Colabrobactan None 10 ⁻⁷ 271 (1,41) Eithanol	(7) Amie acids (RR'NCOOR")	Ammonium carbamate Urethane N-Methylurethane	None None None	10-1 10-7 10-7	. 22()	Water	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1
 sphorus Trimethyl phosphate[*] None 10⁻⁷ 229 (1.74), 262.5 (0.97) Ethanol Trimethyl phosphate[*] None 10⁻⁷ 256 (0.16) Ethanol Triethyl phosphate[*] Ruylisocyanate None 10⁻⁷ 260 (0.16) Ethanol Ethanol Ruylisocyanate None 10⁻⁷ 260 (1.16) Ethanol Ethanol Ruylisocyanate None 10⁻⁷ 260 (1.16) Ethanol Ruylisocyanate None 10⁻⁷ 260 (1.16) Ethanol Ruylisocyanate None 10⁻⁷ 270 (1.25) Water None 10⁻⁷ 285 (1.2) Ethanol Disobutyl ketone None 10⁻⁷ 271 (1.41) Ethanol Disobutyl ketone None 10⁻⁷ 271 (1.41) Ethanol Padecanone None 10⁻⁷ 271 (1.41) Ethanol Padecanone None 10⁻⁷ 291 (1.48) Ethanol Padecanone None 10⁻⁷ 291 (1.48) Ethanol Padecanone None 10⁻⁷ 195 (3.82) Water Pone 10⁻⁷ 195 (3.82) Water Pater Pone 10⁻⁷ 291 (1.91) Ethanol Pater Pater None 10⁻⁷ 291 (1.48) Ethanol Pater Pater None 10⁻⁷ 291 (1.48) Ethanol Pater Pat	(8) Carbonates (RO-C-OR)	Dimethyl carbonate Diethyl carbonate	•	7-01 10-7			
 Efflylisceyanate None (0⁻⁷ Plutylisceyanate None (10⁻⁷ Cyclohesylisceyanate None (10⁻⁷ 270 (1, 25) Water Acetone None (10⁻⁷ 270 (1, 25) Water None (10⁻⁷ 271 (1,41) Ethanol 2-Outanone None (10⁻⁷ 290 (1,48) Ethanol None (10⁻⁷ 290 (1,48) Ethanol Nater None (10⁻⁷ 290 (1,48) Ethanol (10⁻⁷ 290 (1,48) Ethanol (10⁻⁷ (10⁻⁷ (10⁻⁷ (10⁻⁷ (141) (141)	 Organophosphorus compounds 		N chine N chine N chine	-10-7 -01 -7-01	229 (1,74), 262.5 (0,97) 251 (2,76), 257 (2,80) 260 (0,16)	Ethanol Ethanol Ethanol	יט יט יע
AcctoneNone10 ⁻⁷ 270 (1,25)WaterMethyl ethyl ketoneNone10 ⁻⁷ 285 (1,2)EthanolCyclohexanoneNone10 ⁻⁷ 285 (1,2)EthanolCyclohexanoneNone10 ⁻⁷ 271 (1,41)EthanolDisobutyl ketoneNone10 ⁻⁷ 271 (1,41)Ethanol2-OctanoneNone10 ⁻⁷ 271 (1,41)Ethanol2-OctanoneNone10 ⁻⁷ 271 (1,41)Ethanol2-UndecanoneNone10 ⁻⁷ 290 (1,48)Ethanol2-UndecanoneNone10 ⁻⁷ 290 (1,48)Ethanol1CamphorNone10 ⁻⁷ 190 (3,85)Watern-ValerolactamNone10 ⁻⁷ 190 (3,85)Watern-CaprolactamNone10 ⁻⁷ 197 (3,99)Watern-CaprolactamNone10 ⁻⁷ 295 (1,11)Hexanen-CaprylaldehydeNone10 ⁻⁷ 295 (1,11)Decane	(f) Isocynnates (R NCO)	Ethylisocyanate <i>n</i> -Butylisocyanate Cyclohexylisocyanate	ano ano ano ano N	r=01 r=01			
Diffsobutyl ketoneNone10^-7271 (1,41)Ethanol2-OctamoneNone10^-7271 (1,41)Ethanol2-OutanoneNone10^-7290 (1,48)Ethanol2-UndecantoneNone10^-7290 (1,48)Ethanol3-DodecantoneNone10^-7290 (1,48)Ethanol3-DodecantoneNone10^-7190 (3,85)Water91CamplorNone10^-7197.5 (3,89)Watern-ValerolactamNone10^-7197.5 (3,89)Watern-CapronaldehydeNone10^-7295 (1,11)Hexanen-CapronaldehydeNone10^-7295 (1,11)Decanen-CaprinaldehydeNone10^-7295 (1,11)Decane	11) Ketones (RCOR')	Acetone [•] Methyl ethyl ketone Cyclohexanone	None None None	r-01	270 (1.25) 285 (1.2)	Water Ethanol	5 4
γ -ButyrolactamNone 10^{-7} 190 (3.85)Mater δ -ValerolactamNone 10^{-7} 197 (5.82)Water δ -ValerolactamNone 10^{-7} 197.5 (3.89)Water r -CapronaldehydeNone 10^{-7} 197.5 (3.89)Water n -CapronaldehydeNone 10^{-7} 295 (1.11)Hexane n -CaprinaldehydeNone 10^{-7} 295 (1.11)Hexane		Diisobutyl ketone 2-Octanone 2-Vonanone 2-Undecanone 3-Dodecanone 21-Camphor	ano ano ano ano ano ano ano X X X X A	01 01 07 01 01 01	271 (1,41) 200 (1,48)	Ethanol	
<i>u</i> -Capronaldehyde None [0 ⁻⁷ 295 (1.11) Hexane <i>u</i> -Caprinaldehyde None [0 ⁻⁷ 295 (1.11) Hexane <i>u</i> -Caprinaldehyde None [0 ⁻⁷ 222 (1.9), 293 (1.4) Decane	12) Lactams	;Butyrolactam b-Valerolactam r-Caprolactam	None None None	7-01 7-01 7-01	190 (3.82) 195 (3.82) 197,5 (3.89)	Eduanto Water Water Water	000
	(RCHO) Aldehydes (RCHO)	<i>n</i> -Capronaldehyde <i>n</i> -Caprylaldehyde <i>n</i> -Caprinaldehyde	Neme None None	10-7 10-7 10-7	295 (1.11) 222 (1.9), 293 (1.4)	Hexane Decane	v) 4

colour. As can be seen from the results on disulphides in Table I, such characteristic colours were useful for the identification of different compounds.

As shown in Table III, the response of the mixed fluorescent material method to organic sulphur compounds is different from that reported with other methods. The fact that most biologically active organic sulphur compounds, including sulphonamides and pesticides, were detected by the present method indicates a promising establishment of a screen test for them, based upon a unique principle.

There are no other non-destructive methods for the detection of disulphides on paper or thin-layer chromatograms. In most instances of assay of disulphides, the sodium nitroprusside procedure³¹ or the 5,5'-dithiobis(2-nitrobenzoic acid) (DTNB) method³² has been used after reduction of the disulphides with potassium cyanide or sodium borohydride. However, these methods are not specific for disulphides^{33,34}. On the other hand, the detection of disulphides by the mixed fluorescent material method involves no destructive procedure unless the compounds in question are sensitive to UV light. Moreover, the limits of detection of simple disulphides are in the range 10^{-8} – 10^{-9} mole, which indicates almost the same sensitivity as in conventional colorimetric methods^{31,32}. The present method is now conveniently utilized in our laboratory in checking the synthetic reactions of mixed disulphides and also in the detection of lipophilic disulphides which are not easily subjected to cyanolysis.

The organic sulphur compounds designated as positive (detectable in amounts of less than $1 \cdot 10^{-7}$ mole) can be classified into four groups, according to their chemical structures. The first group contains thioureas (>N-CS-N<), thiuram compounds (>N-CS-S_n-CS-N<), xanthates (-O-CS-S-) and dithiocarbamates (>N-CS-S-), which contain at least one chromophore C=S group. The compounds belonging to the second group are disulphides (-SS-) and S-sulphonic acids (-SSO₃H), and their UV absorption at about 250 nm can be attributed to the S==S bond. The third group consists of isothioureas (-S-C(=NH)NH₂), thiolactones (S-CO-) and thioesters (-S-CO-) which can be represented in the resonanced C==S form as follows:

$$-\ddot{S}-C-NH = -\ddot{S}-NH^-$$
; $-\ddot{S}-C- = -\ddot{S}=C-$
 NH_2 NH_2 O O^-

The fourth group consists of organothiophosphorus compounds (>P=S). The presence of two pairs of lone-pair electrons on the sulphur atom (divalent sulphur) and a group that resonates with them is considered to be neccessary for the detection of compounds by the present method. This assumption is supported by considering the negative compounds, which can be classified into compounds that contain no divalent sulphur (RSO_aH, RSO_aH, RSO_aH, RSO_aR' and RSOR') and compounds that contain a divalent sulphur atom but no resonating group (RSH and RSR').

Organic solvents that absorb UV light at 250–400 nm, e.g., ketones and aromatic compounds, may interfere in the detection, but then volatile solvents such as benzene, acetone and carbon disulphide can be used. Alcohols, ethers, esters and hydrocarbons can be used without difficulty. In the analysis of compounds that have large R_F values, the use of plates developed once with the same solvent in order to

BLE III

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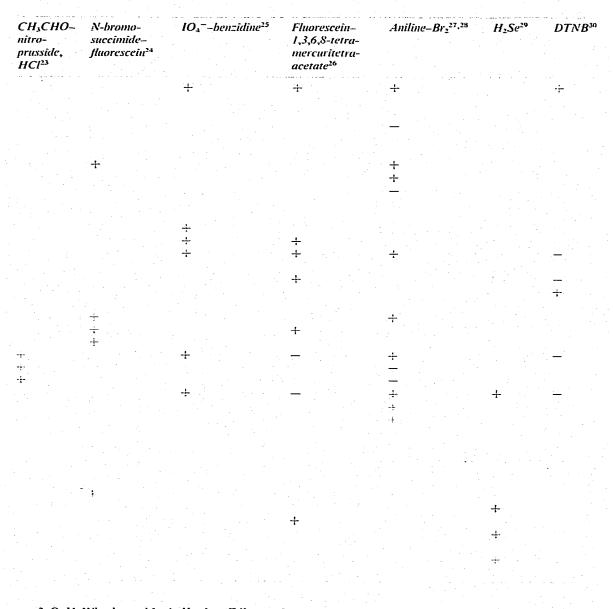
RIOUS METHODS FOR THE CHROMATOGRAPHIC DETECTION OF SULPHUR COMPOUNDS

remove traces of interfering substances in the adsorbent often increases the sensitivity. The use of the present method prior to the application of spray reagents would markedly increase the reliability of detection.

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