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## Note

# Paper electrophoretic characterization of thiols, sulphides and disulphides as sulphonium salts

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The problem of the identification and determination of thiols, sulphides and disulphides in different materials is often encountered and many methods involving paper, thin-layer, gas and high-performance liquid chromatography and electrophoresis have been suggested[1–5].

The approach described in this paper is based on the alkylation of a mixture of the above compounds with methyl fluorosulphonate ("magic methyl") to form dimethylalkylsulphonium salts of thiols and disulphides, and monomethylsulphonium salts of sulphides. The products obtained can be readily resolved and identified by high-voltage paper electrophoresis. Leaver and Challanger[6] and Kronrăd and Pănek[7] used an S-methylation reaction for the identification of sulphides, involving the reaction of sulphides with methyl iodide or sulphate, followed by separation by paper chromatography.

The proposed method allows to better variations in the migration distances of the separated compounds and the time of separation is shorter. Additionally, "magic methyl" reacts with the investigated compounds very rapidly, and does not give other by-products from exchange reactions of adjacent alkyl groups. Such exchange reactions may occur when methyl iodide is used as the methylating agent[8].

## EXPERIMENTAL

### Chemicals

Methyl fluorosulphonate ("magic methyl"), purity 97%, was obtained from EGA-Chemie and nitromethane from POCh (Glíwice, Poland).

All thiols were of analytical-reagent grade from Fluka (Buchs, Switzerland), E. Merck (Darmstadt, F.R.G.) or Aldrich Europe (Beerse, Belgium). Symmetrical sulphides were of analytical-reagent grade from Fluka or E. Merck. Unsymmetrical sulphides were synthesized in this laboratory from the corresponding thiols and alkyl halides according to the literature[9]. Diamyl and dioctyl disulphides were synthesized in this laboratory by oxidation of the corresponding thiols using iodine according to the literature[10]. All other disulphides were of analytical-reagent grade from Fluka, E. Merck or Aldrich Europe.

### *Solutions*

The pH 1.7 buffer solution was an aqueous solution of 0.05 mole/dm$^3$ orthophosphoric acid, 0.1 mole/dm$^3$ orthoboric acid and 10% (v/v) ethylene glycol.

Dragendorff's reagent was prepared by mixing 5 cm$^3$ of solution A and 5 cm$^3$ solution B adding 20 cm$^3$ of glacial acid, followed by dilution with water to 100 cm$^3$. Solution A was 0.85 g of bismuth subnitrate dissolved in a mixture of 40 cm$^3$ of water and 20 cm$^3$ of glacial acetic acid and solution B was 8 g of potassium iodide dissolved in 20 cm$^3$ of water.

### *Sample derivatization procedure*

To 0.1 cm$^3$ of a nitromethane solution containing about 2 mg of the sample compound, 0.05 cm$^3$ of methyl fluorosulphonate was added. After 10 min the sample was ready for electrophoretic separation.

### *Electrophoresis*

Paper electrophoresis was conducted in an apparatus for high-voltage electrophoresis (Type AEA; WSR, Olsztyn, Poland), using Whatman No. 1 chromatography paper in 8 × 37 cm strips. Sample were applied to the paper by means of a syringe as 1–3-$\mu$l spots. The separation was conducted at 2000 V for 45 min. The paper was spraying with Dragendorff's reagent, which rendered the compounds visible as compact pink spots on a pale yellow background.

## RESULTS AND DISCUSSION

The mobilities of sulphonium derivatives were calculated relative to that of the trimethylsulphonium cation and are given as average values of five measurements, which did not vary by more than about ±0.02. Table I gives the relative mobilities of dimethylalkyl(aryl)sulphonium cations which were obtained from thiols.

Tables II and III give the relative mobilities of sulphonium cations obtained from sulphides and disulphides.

The electrophoretic separation of thiols, sulphides and disulphides can be used

TABLE I

MOBILITIES OF THIOLS AS DIMETHYLALKYL(ARYL)SULPHONIUM SALTS RELATIVE TO $S(CH_3)_3^+$

| *No.* | *Parent thiol* | *Relative mobilitie* | *No.* | *Parent thiol* | *Relative mobility* |
|---|---|---|---|---|---|
| 1 | Methyl | 1.00 | 10 | *n*-Hexyl | 0.61 |
| 2 | Ethyl | 0.90 | 11 | *n*-Heptyl | 0.56 |
| 3 | *n*-Propyl | 0.78 | 12 | *n*-Octyl | 0.52 |
| 4 | Isopropyl | 0.79 | 13 | *n*-Nonyl | 0.45 |
| 5 | *n*-Butyl | 0.68 | 14 | *n*-Dodecyl | 0.30 |
| 6 | Isobutyl | 0.69 | 15 | *n*-Hexadecyl | 0.06 |
| 7 | *tert.*-Butyl | 0.70 | 16 | Benzyl | 0.59 |
| 8 | *n*-Pentyl | 0.64 | 17 | Phenyl | 0.71 |
| 9 | Isopentyl | 0.65 | 18 | Naphthyl | 0.44 |

TABLE II

MOBILITIES OF SULPHIDES AS METHYLDIALKYL(ARYL)SULPHONIUM SALTS RELATIVE TO $S(CH_3)_3^+$

| *No.* | *Sulphide* | | *Relative mobility* |
|---|---|---|---|
| | *$R_1$* | *$R_2$* | |
| 1 | $CH_3$ | $CH_3$ | 1.00 |
| 2 | $CH_3$ | $C_2H_5$ | 0.87 |
| 3 | $CH_3$ | $C_3H_7$ | 0.75 |
| 4 | $CH_3$ | $C_4H_9$ | 0.70 |
| 5 | $CH_3$ | $C_5H_{11}$ | 0.62 |
| 6 | $C_2H_5$ | $C_2H_5$ | 0.77 |
| 7 | $C_2H_5$ | $C_3H_7$ | 0.73 |
| 8 | $CH_2=CHCH_2$ | $CH_2=CHCH_2$ | 0.68 |
| 9 | $C_3H_7$ | $C_3H_7$ | 0.63 |
| 10 | $C_3H_7$ | $C_4H_9$ | 0.55 |
| 11 | $C_4H_9$ | $C_4H_9$ | 0.50 |
| 12 | $C_4H_9$ | $C_6H_5CH_2$ | 0.46 |
| 13 | $C_6H_5$ | $C_6H_5$ | 0.51 |
| 14 | $C_6H_5CH_2$ | $C_6H_5CH_2$ | 0.40 |

for the identification of these compounds in non-aqueous solvents. This method is very simple and sensitive.

As shown in Table I, using this method we can separate aliphatic thiols containing 1–16 carbons in the molecule. The method is not satisfactory for the separation of isomeric thiols (see Table I, Nos. 3, 4 and 5, 6, 7 and 8, 9).

Disulphides react with methyl fluorosulphonate as follows:

$$RSSR + R'X \rightarrow \underset{\text{I}}{RR'\overset{+}{S}\text{–}SR\ X^-} \rightarrow \underset{\text{II}}{R_2'R\overset{+}{S}\ X^-}$$

except for dimethyl and diethyl disulphide, which give derivative I[11]. The electrophoretic method is suitable for the identification of symmetrical and unsymmetrical

TABLE III

MOBILITIES OF DISULPHIDES AS DIMETHYLALKYL(ARYL)SULPHONIUM SALTS RELATIVE TO $S(CH_3)_3^+$

| *No.* | *Disulphide* | | *Relative mobility* |
|---|---|---|---|
| | *$R_1$* | *$R_2$* | |
| 1 | $CH_3$ | $CH_3$ | 0.97 |
| 2 | $C_4H_9$ | $C_4H_9$ | 0.68 |
| 3 | $C_5H_{11}$ | $C_5H_{11}$ | 0.63 |
| 4 | $C_8H_{17}$ | $C_8H_{17}$ | 0.51 |
| 5 | $C_6H_5$ | $C_6H_5$ | 0.68 |
| 6 | $C_6H_5CH_2$ | $C_6H_5CH_2$ | 0.60 |

disulphides, and for mixtures of unsymmetrical disulphides the analysis gives information about the alkyl groups.

The relative mobilities of the investigated sulphonium salts were confirmed from the mobilities calculated for pure sulphonium salts obtained and identified previously[12].

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