

Fig. 2. Temperature-programmed gas chromatogram of a mixture of tetramethylene sulphide, tetramethylene sulphoxide and tetramethylene sulphone. TMS (0.6488 g); TMSO (0.6552 g); TMSO₂ (0.7613 g); and DPM (0.9779 g)

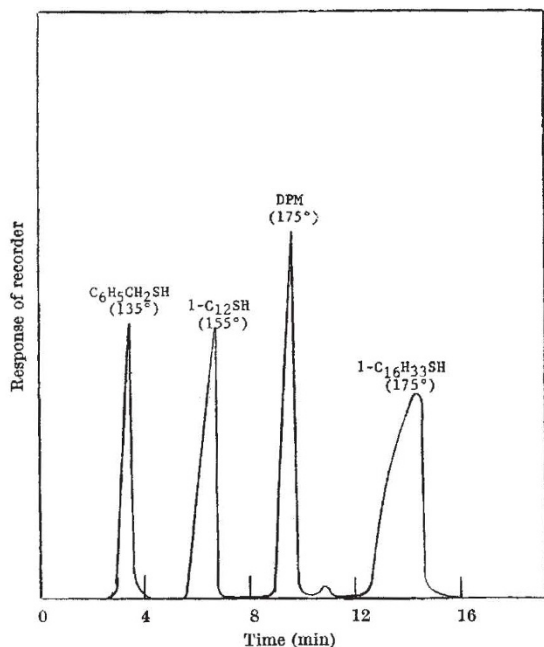


Fig. 3. Temperature-programmed gas chromatogram of a mixture of thiols. $\text{C}_6\text{H}_5\text{CH}_2\text{SH}$ (0.9246 g); $1\text{-C}_{12}\text{H}_{25}\text{SH}$ (1.2096 g); $1\text{-C}_{16}\text{H}_{33}\text{SH}$ (1.6174 g); and DPM (0.9991 g)

technique is more accurate and much simpler to perform than potentiometric and spectrophotometric methods. Further, the method also allows one to work with much smaller quantities of each component.

We have also found that this technique can be used for the separation and identification of thiols and disulphides. Some of our results on a mixture of thiols are shown in

Table 1. RESPONSE FACTORS BETWEEN DIPHENYLMETHANE AND SOME SULPHUR DERIVATIVES

Compound	CH_3SCH_3	$\text{CH}_3\text{-S(=O)-CH}_3$	$\text{CH}_3\text{SO}_2\text{CH}_3$			
K^*	2.65	2.13	1.50	1.61	1.59	1.05

* Where $K = W_{\text{compound}} \times \text{area standard} / W_{\text{standard}} \times A_{\text{compound}}$.

Fig. 3. A 6- μl . sample of a mixture of α -toluenethiol, 1-dodecanethiol, 1-hexadecanethiol and diphenylmethane was injected into the unit at 135°. A constant attenuation of 128 was utilized. After α -toluenethiol had been eluted, the remaining portion of the mixture was temperature-programmed at 13°/min up to 175°. Complete separation of the mixture required about 15 min. For disulphides in the C₄ to C₁₂ region good separation usually requires temperatures of 175°–225°. From this brief description, it can be seen that this method of analysis has a fair degree of versatility.

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Fluorine-19 Nuclear Magnetic Resonance of Pentafluorophenyl Derivatives of Thallium and Mercury

WE have prepared the recently reported compounds, *bis*(pentafluorophenyl)mercury and *bis*(pentafluorophenyl)thallium bromide, in order to compare their fluorine-19 resonance spectra with the spectra previously reported for other pentafluorophenyl compounds¹, and with the proton resonance investigations on phenyl derivatives of thallium².

Bis(pentafluorophenyl)mercury was prepared by the reaction of pentafluorophenylmagnesium bromide with mercuric chloride and identified by its melting point and infra-red spectrum. *Bis*(pentafluorophenyl)thallium bromide was prepared in a similar fashion from thallic chloride (calculated from $(\text{C}_6\text{F}_5)_2\text{TlBr}$, C = 23.3 per cent, H = 0.0 per cent, molecular weight, M , = 618; found, C = 23.3 per cent, H = 0.0 per cent, M (osometry in benzene) = 1,098) (ref. 3). Interestingly, this air-stable white solid (melting point 217°–219°, with decomposition) exists mainly as the dimer in benzene, presumably via thallium-bromine bridging.

The fluorine-19 shift parameters (± 0.5 p.p.m.) relative to CCl_3F as internal standard are:

$(\text{C}_6\text{F}_5)_2\text{TlBr}$	119.3 (<i>ortho</i>)	158.2 (<i>para</i>)	167.0 (<i>meta</i>)
$(\text{C}_6\text{F}_5)_2\text{Hg}$	119.7 (<i>ortho</i>)	150.6 (<i>para</i>)	159.0 (<i>meta</i>)

The shifts for the *ortho* fluorine atoms are consistent with the suggestion of a dominant paramagnetic term which is larger for these heavy atoms than it is for lighter atoms in the Main Groups of the Periodic Table. In this respect mercury and thallium resemble lead¹.

The spin-spin coupling constants, $J_{\text{Tl-F}}$, between the thallium-205 nucleus and the fluorine-19 nuclei have also been measured for *bis*(pentafluorophenyl)thallium bromide. They are, in c/s (± 5 c/s): 799 (*ortho*), 343 (*meta*) and 99 (*para*). In phenyl thallium compounds the *ortho*, *meta* and *para* couplings, $J_{\text{Tl-H}}$, are in constant proportion, respectively, to the *ortho*, *meta* and *para* couplings $J_{\text{H-H}}$ (ref. 2). No such simple relation between $J_{\text{Tl-F}}$ and $J_{\text{F-F}}$ couplings exists in the pentafluorophenyl compounds.

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