stand that there is theoretical justification for this (Littlewood, A. B., private communication). When considering other carrier gases the importance of $H$ (equation 1) cannot be ignored as it can with hydrogen and helium. This greatly complicates the mathematics, and systems worth studying would be helium in hydrogen and water vapour in both, where $k_1$ and $k_2$ are nearly equal but $H$ can be ignored.

A final point not mentioned by Ray is that the temperature of the wire rises when the working substances he uses are eluted in helium, but falls when they are eluted in argon. This has been missed by Schmauch and Dinerstein, who give responses only for substances which cause a rise in the temperatures of the wire with nitrogen. The results are not, therefore, comparable. In any event, the point is a simple one. Helium is obviously much more easily detected by katharometer in nitrogen or argon than in hydrogen.

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## Use of Katharometers in Gas Chromatography

In a recent communication[1], Ray attacks the tenet that "the use of hydrogen or helium as the carrier gas in gas chromatography gives the highest sensitivity with a thermal conductivity detector". He derives an equation describing katharometer behaviour from which he infers that the carrier gas with the lowest thermal conductivity will give the highest sensitivity. He concludes that nitrogen, argon, or carbon dioxide will provide greater sensitivity than hydrogen or helium. We wish to point out that the conclusion drawn from this equation does not follow generally, although it may be valid in certain instances. Furthermore, a basic assumption in Ray's derivation is contrary to the usual operating procedure for katharometers.

His equation, $dt/dx = -a(k_1 - k_2)/k_1^2$, states that the sensitivity of the detector, $dt/dx$, is proportional to the difference between the thermal conductivity of the carrier gas, $k_1$, and the vapour, $k_2$, and inversely proportional to the square of the thermal conductivity of the carrier gas. As Ray implies, this function has an arbitrarily large negative value as $k_1$ approaches zero. He fails to note that it also exhibits a maximum when the thermal conductivity of the carrier gas is twice that of the vapour being analysed.

We have computed values (Table 1) of katharometer sensitivity using this equation and the values of thermal conductivity for various carrier gases and organic vapours given in the International Critical Tables[2] for 0° C. It will be seen that argon provides high sensitivity for methane, low sensitivity for ethylene and again high sensitivity for benzene. This is because in the first instance the thermal conductivity of argon is approximately one-half that of the methane; in the second instance, the thermal conductivities of carrier and vapour are nearly identical, and in the third instance the thermal conductivity of argon is almost exactly twice that of benzene. Thus, the response of the katharometer may be either positive or negative depending on whether the organic vapour being detected has a smaller or larger thermal conductivity than the carrier, and also varies greatly in absolute value. In contrast, helium, the thermal conductivity of which is high relative to organic vapour, gives a nearly constant sensitivity, which permits quantitative estimation of the concentration of each component in a complex mixture.

Table 1. Thermal Detector Sensitivities Relative to Methane in Helium

| | Argon ($k$ = 1·58) | Nitrogen ($k$ = 2·28) | Helium ($k$ = 13·9) |
|---|---|---|---|
| Methane ($k$ = 2·94) | −9·82 | −2·11 | 1·00 |
| Ethane ($k$ = 1·80) | −1·58 | 1·61 | 1·11 |
| Ethylene ($k$ = 1·64) | −0·44 | 2·11 | 1·12 |
| *m*-Pentane ($k$ = 1·16) | 2·98 | 3·86 | 1·16 |
| Benzene ($k$ = 0·825) | 5·44 | 4·91 | 1·19 |

Table 2. Constant Hot-Wire Temperature

| | Argon | Nitrogen | Helium |
|---|---|---|---|
| Methane | −1·09 | −0·35 | 1·00 |
| Ethane | −0·18 | +0·27 | 1·10 |
| Ethylene | −0·05 | 0·35 | 1·12 |
| *m*-Pentane | 0·34 | 0·62 | 1·15 |
| Benzene | 0·59 | 0·81 | 1·19 |

It should also be noted that Ray's equation 1 implies that in all experiments the same current flows in the detector. However, it is common practice to increase the current when using a carrier gas of higher thermal conductivity, so that the difference in temperature between hot wire and cell wall is kept constant. Under these conditions the approximate equation will be $dt/dx = -a(k_2 - k_1)/k_1$.

Relative sensitivities (Table 2) have been computed for this mode of operation. It is clear that helium is eminently superior to either argon or nitrogen. Thus, while it may be true that the use of a carrier gas of thermal conductivity much lower than that of any organic component to be analysed would exceed helium in sensitivity, no gas now available is applicable to the large variety of substances at present being analysed by gas chromatography.

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## Effect of the Carrier Gas on the Sensitivity of Thermal Conductivity Detectors in Gas Chromatography

It has recently been suggested[1] that the use of argon or other carrier gases of low thermal conductivity will lead to increased sensitivity of thermal conductivity detectors used in gas chromatography. While this may be so in certain special cases, it is by no means a general effect, and it is the purpose of this communication to point out some of the many disadvantages of carrier gases of low thermal conductivity. The effects we wish to discuss may be