

## Notes

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CHROM. 4110

### Anomalies in the flame ionization detector response

Carbon disulphide is usually qualified as a substance to which the flame ionization detector gives low or zero response<sup>1</sup>. From the theoretical viewpoint, carbon bound by two double bonds with sulphur atoms cannot be considered as the so-called effective carbon. On the basis of this, carbon disulphide is often recommended as a suitable solvent in analyses using F.I.D.<sup>2</sup>.

However, it was found by WALKER<sup>3</sup> that the F.I.D. response to carbon disulphide is dependent on the flow rates of the gases and that the response rises with an increasing hydrogen flow rate. The increase of the response to carbon disulphide has been attributed to the reduction conditions in the flame.

The author has found, while working with F.I.D. and carbon disulphide as a solvent, a response enhancement similar to that described by WALKER<sup>3</sup>; at the same time, it was ascertained that the enhancement depends on the detector geometry, particularly on the configuration of the electrodes with respect to the flame. In order to clarify this phenomenon, experiments were carried out with various types of collecting electrodes.

#### *Experimental*

Gas chromatographs CHROM 3 and CHROM 4 (Laboratory Equipment, N.E., Prague, Czechoslovakia) were employed. For the CHROM 3 apparatus, a 68-cm long column was used of 0.6 cm O.D. In the other case, the respective column dimensions were 200 and 0.3 cm. The column packing was 15 % of polyethylene glycol 400 on Sterchamol, and the column temperature was kept at 90°. The air flow rate was 600 ml/min; the nitrogen flow rates were 60 and 30 ml/min, respectively, with the columns of 0.6 and 0.3 cm O.D. The solvent (carbon disulphide, tetrachloromethane, trichloromethane, and dichloromethane) was injected in 0.5  $\mu$ l charges, the octane introduced amounted to  $6 \times 10^{-4}$  g.

Fig. 1 illustrates the geometry and circuitry of the F.I.D.s employed. In all cases, the distance of the collector from the jet was 6 mm.

In following the hydrogen flow rate dependence of the response to carbon disulphide, it was found that it was only with detectors (c), (d) and (e), *i.e.* with those having the collector placed just above the flame, that the response to the above compound was enhanced upon increasing the hydrogen flow rate. With all these detectors, a sharp increase in the background current occurs simultaneously. Both the increase in the response to carbon disulphide and the rise in the background current depend on the distance of the electrode from the flame. Both types of enhancement decrease upon increasing the distance. With the other detectors, the enhancement of the response did not occur within the limits of the hydrogen flow rates investigated (up to 100 ml/min).

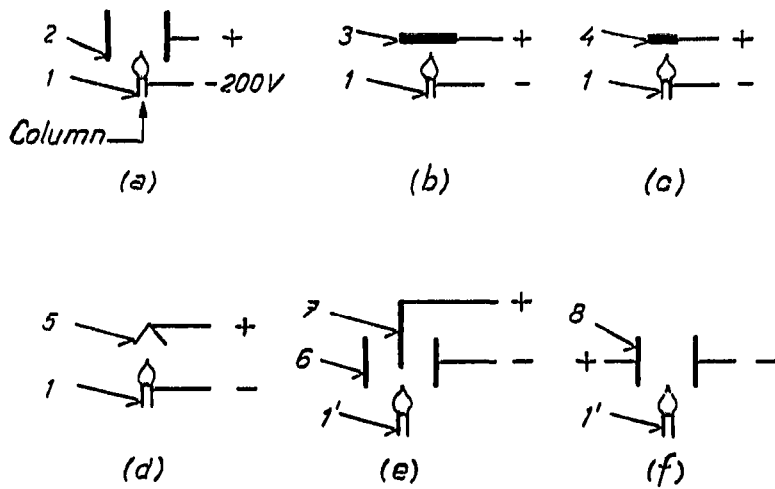


Fig. 1. Scheme of geometry and circuitry of the flame ionization detectors employed. (1) = jet connected as the polarizing electrode, (1') = jet, (2) = collecting electrode of the shape of a cylinder with 15 mm diameter, (3) = collecting electrode of the shape of a ring with 12 mm diameter, (4) = collecting electrode of the shape of a ring with 2 mm diameter, (5) = collecting electrode of the shape of a four-wire pyramidal roof, (6) = polarizing electrode in the shape of a cylinder with 10 mm diameter, (7) = collecting electrode in the shape of a bar, (8) = a cylinder with 10 mm diameter of which one axial half is the polarizing electrode and the other half is the collecting electrode.

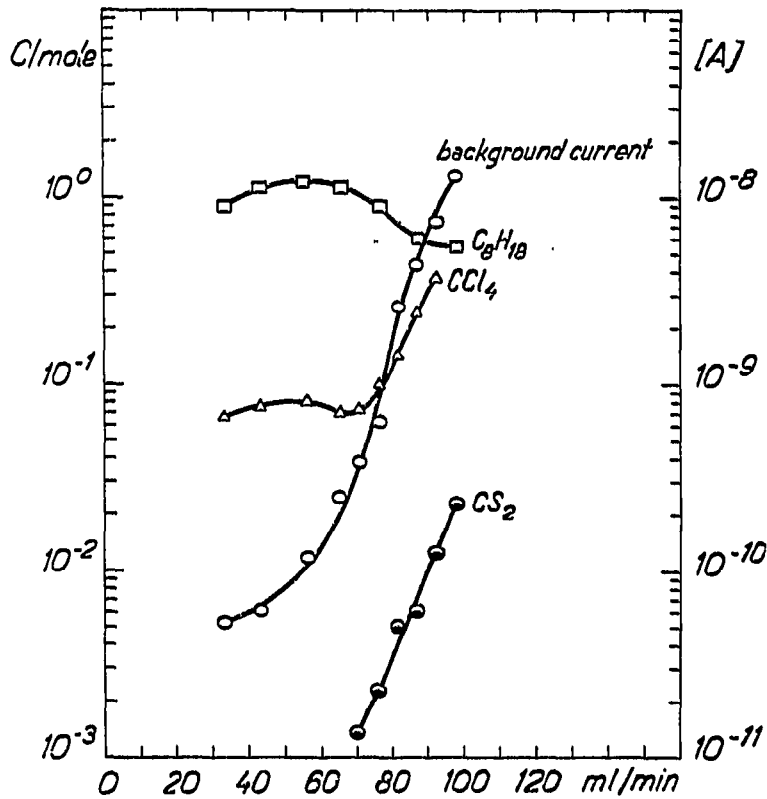


Fig. 2. Dependence of F.I.D. response and background current on the hydrogen flow rate.

In Fig. 2 are presented dependences on the hydrogen flow rate of the F.I.D. response to carbon disulphide, tetrachloromethane and octane, expressed in terms of ionization efficiency (coulombs per mole of the compound) for detector (d). It is evident that the response to the hydrocarbon has practically the normal course, while the response to carbon disulphide sharply increases.

The dependence of the response to tetrachloromethane shows a course different from that of octane. At low hydrogen flow rates the course is similar to the one encountered with hydrocarbons, but, at higher flow rates, the response rises and its course is similar to that for carbon disulphide. The dependence of the response to dichloromethane and trichloromethane is analogous to the response for tetrachloromethane; the only difference is the ionization efficiency. In Fig. 2 is quoted the increase in the background current in dependence on the hydrogen flow rate.

We thus believe that (1) the F.I.D. response to carbon disulphide will rise sharply upon increasing the hydrogen flow rate<sup>3</sup>, but only in the cases when the electrode is situated in such a way that it may be heated by the flame; (2) the increase of the F.I.D. response occurs also with di-, tri-, and tetrachloromethane; (3) a relationship exists between response enhancement and background current increase brought about by the electrons emitted from the heated electrode.

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