

Short Communications

The nonlinearity of the signal response and the inversion effect in flame ionization detection

A further substantial development of gas chromatography has been achieved by means of highly sensitive detectors utilizing the ionization of gases and vapours. The flame ionization detector constitutes one of the important types^{1,2} of these detectors. Up to now, attention has been mainly devoted to the aspects of construction and the attainment of maximal sensitivity^{3,4}; in this stage, the detector has been used, primarily for qualitative analysis and for studying the separation features of the columns, etc.

Only recently have the working characteristics of the ionization flame detector been studied from the quantitative point of view⁵⁻⁷. Generally it has been stated that the relation between the magnitude of the signal and the concentration of the material in the carrier gas is linear²⁻⁴; recently, however, it has been reported that this linearity is roughly valid up to a concentration of 0.5 vol.% of the component in the carrier gas⁵. A negative deviation from linearity has been noticed at a concentration of 2% of the component⁸.

Some observations made during our own experiments⁷ with this detector are given in the following short communication.

The detector consisted of a steel capillary with an inner diameter of 0.5 mm and a wall thickness of 0.15 mm, above which two electrodes (made from 0.6 mm platinum wire) were placed across the center of the flame, perpendicular to its axis. The distance of the upper electrode from the burner was 10 and 15 mm, respectively. The distance of the lower electrode was variable. A voltage of 180 V was applied to the electrodes from an anode battery. Recording was made by means of a compensograph EZ-3, constructed by the National Plant "Laboratorní přístroje" (Laboratory Apparatuses), Prague (the input resistance was 500 k Ω and the scale 2 mV/280 mm). The flow rates of nitrogen as carrier gas and hydrogen as burning gas, fed directly into the inlet of the burner, are given in the legends to the figures.

It was found that in the case of low flow rates of the gases the inversion effect occurs at component concentrations above 0.6 vol.% (Fig. 1). The occurrence of nonlinearity of the detector signal response and the inversion of the chromatographic curves may be influenced by the flow rate, as well as by the position of the lower electrode. This effect is dependent on the form of the flame, however, especially on the form of the inner blue cone of the flame. The detector only functions correctly when the lower electrode is situated directly within the space where the oxidation of the

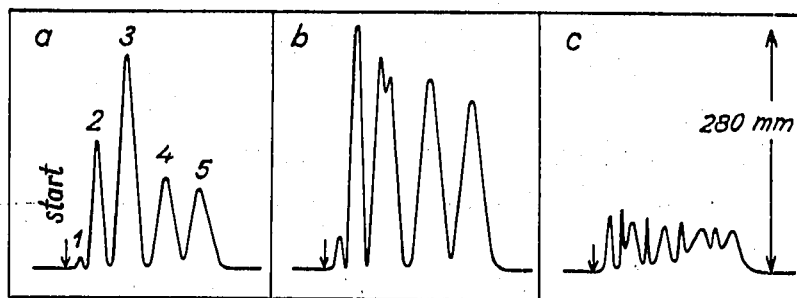


Fig. 1. Chromatograms of mixtures of methane (1), ethane (2), propane (3), isobutane (4) and *n*-butane (5). (a) sample volume 0.2 ml; reduction of the sensitivity of the compensograph 1:5; (b) sample volume 0.4 ml; reduction of the sensitivity of the compensograph 1:5; (c) sample volume 2.0 ml; reduction of the sensitivity of the compensograph 1:20. (45 g of 25% w/w Apiezon L on Sterchamol of 0.2–0.4 mm; temperature 90°; flow rate of nitrogen 0.3 ml/sec; additional hydrogen 0.25 ml/sec; distance of the lower electrode from the orifice of the burner 1.0 mm).

organic material begins, *i.e.*, when the burner serves as electrode^{3–5} and/or when the lower special electrode is inserted into the inner cone of the flame⁷. Under our experimental conditions the optimal ratio of the carrier gas (nitrogen) and the additional gas (hydrogen) was 1:1–2.

The estimated inversion effects appeared when the lower electrode was placed across the flame 1.0 mm above the orifice of the burner; at the same time, the top of the inner cone of the flame extended above the level of the inserted electrode. The inversions occurred at a concentration of 0.65 vol. % of propane and butane, respectively, at flow rates of 0.3 ml N₂/sec and 0.25 ml H₂/sec. If the flow rate of the carrier gas is increased the inversion effect disappears.

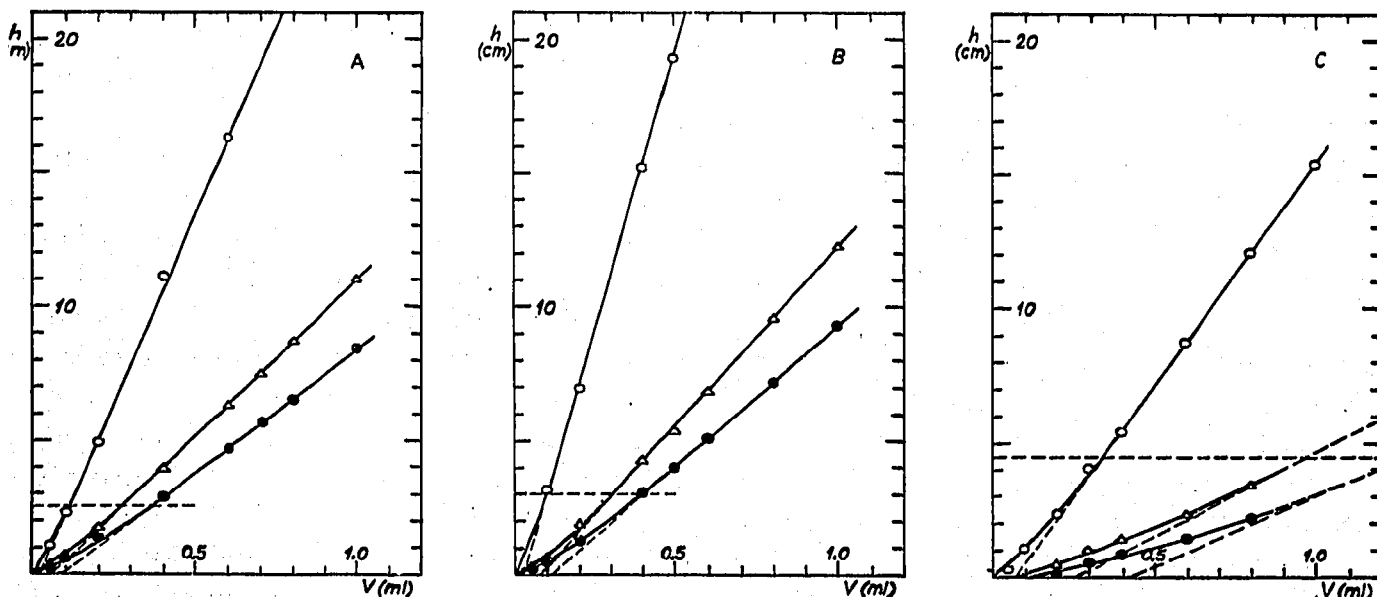


Fig. 2. Calibration curves for propane (o), isobutane (Δ) and *n*-butane (\bullet) at distances of the lower electrode above the orifice of the burner of: (A) 0.5 mm, (B) 1.5 mm and (C) 3.0 mm. (9 g of 25% w/w squalane on Sterchamol of 0.2–0.4 mm; temperature 22°; flow rate of nitrogen 0.7 ml/sec and of hydrogen 0.6 ml/sec; distance between the two electrodes 10 mm; voltage applied to the electrodes 180V; 1.00 ml of diluted sample contained 0.0075 ml propane, 0.0032 ml isobutane and 0.0030 ml *n*-butane; the concentration of the components in the carrier gas at the peak maximum was in 1.00 ml of the diluted sample in vol. %: propane 0.086% isobutane 0.020% and *n*-butane 0.015%).

The position of the electrodes, especially that of the lower one, with respect to the direction of the gas stream through the burner influences the linearity of the signal also in the range of small concentrations (Fig. 2). While the position and form of the upper electrode had practically no effect, either on the sensitivity or on the linearity of the signal, at variable positions of the lower electrode above the orifice of the burner, deviations from linearity were observed even with small concentrations of the vapours analysed. In Fig. 2, calibration curves for the same concentrations of gases and for different positions of the lower electrode of 0.5 to 1.5 and 3.0 mm above the orifice of the burner may be seen. The range of the nonlinearity of the signal increases with the distance of the electrode from the burner.

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Ninhydrin as a reagent for N-methyl-amino acids

In the course of work reported elsewhere¹ a method was needed for estimating valine and N-methyl-leucine in solutions containing both amino acids. N-Methyl-amino acids normally react weakly on paper chromatograms sprayed with ninhydrin² and except for sarcosine³ have not been observed to react in the test-tube^{4,5}. Because the use of ninhydrin would permit the estimation of both amino acids on the same chromatogram, conditions were sought under which both primary- and N-methyl-amino acids would react to give spots of satisfactory intensity.

In the reaction of most primary amino acids with ninhydrin, optimal colour yields are obtained using a buffer of pH 5³. Under similar conditions both sarcosine and N-methyl-leucine reacted optimally at pH 6.5, at which pH leucine also gave a satisfactory, although not maximal, colour yield. Based on these observations, a technique has been developed for the detection and estimation of primary- and N-methyl-amino acids on paper chromatograms. The study was limited to the N-methyl derivatives of glycine, valine, leucine and isoleucine.

Chromatograms on Whatman No. 3 MM paper are run in the solvent system

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