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WIRE DETECTOR WITH AN ALKALI FLAME IONIZATION SENSING ELEMENT FOR LIQUID CHROMATOGRAPHY

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SUMMARY

A detector with a wire mass transfer was modified for the analysis of thermally labile halogen derivatives of tetrahydrofurans. The wire and eluate enter a combustion oven directly and the combustion products are carried by a stream of air into a double-burner alkali flame ionization sensing element.

INTRODUCTION

Transport detectors represent an independent category of detectors in liquid chromatography. A substantial difference, when compared with detectors based on binary mixtures analysers such as, *e.g.*, refractometers, capacitance detectors and spectrophotometers, is that the effluent does not enter the sensing element of the detector directly from the column but is transported through a thermal zone which removes the mobile phase and through a zone where either vaporization or pyrolysis of the sample takes place. Vapours of the substance under analysis or its pyrolysis products are then detected by sensing elements commonly used in gas chromatography. A wire transporter¹⁻⁴ is used in most of the different effluent transporters (chains⁵, belts⁶, disc⁷, etc.) that have been designed and used. The non-selective flame ionization detector (FID)¹⁻⁷ is used most often of all the sensing elements.

The use of the non-selective FID necessitates that the mobile phase should be eliminated from the effluent being transported. The analytical characteristics in flame ionization detection of an organic mobile phase are often similar or identical with the analytical characteristics of the component under study. Elimination of the mobile phase from the portion of the effluent that is transported by the wire brings about substantial technical difficulties and some disadvantages. The quality of the elimination of the mobile phase depends on the period of time during which the transporter with the effluent is in the oven, on the temperature of the oven and on the boiling point of the mobile phase being used. If the mobile phase is completely eliminated, losses of sample and a consequent decrease in detection sensitivity occur. An imperfect elimination of the mobile phase always increases the background current on which the detector operates and the noise and decreases the signal-to-noise ratio.

The situation is somewhat simpler if a mobile phase is used that causes no re-

sponse of the FID. For example, if water is used as mobile phase, it need not be eliminated too carefully. However, without the elimination of the mobile phase, the noise of the detector increases.

The use of a selective detector in such a way that it does not respond to the mobile phase⁸ is considered to be the most suitable solution. For this work, on the analysis of halogen derivatives of tetrahydrofurans, the flame ionization detector with an alkali metal (AFID) could, therefore, be used to advantage.

The response (R) of the FID⁹ is known to be

$$R = K\alpha (\Sigma C_{\text{eff}}) (dN_{i \text{ eff}}/dt) \quad (1)$$

where K is the proportionality constant, α is the ionization efficiency, ΣC_{eff} is the number of effective carbon atoms and $(dN_{i \text{ eff}}/dt)$ is the number of solute moles, i , that are transported into the detector during time t . The following expression is used to express the response of the AFID⁸.

$$R_i = [K\alpha^* (\Sigma E_{\text{eff}}) + K_1\alpha (\Sigma C_{\text{eff}})] (dN_{i \text{ eff}}/dt) \quad (2)$$

where ΣE_{eff} is the sum of effective elements to which the AFID responds. At the same time

$$N_{i \text{ eff}} = \beta (N_{i \text{ d}} - N_{i \text{ s}}) \quad (3)$$

where β is the efficiency of the pyrolytic process, $N_{i \text{ d}}$ is the number of moles that were taken by the transporter into the detection device and $N_{i \text{ s}}$ is the number of moles that are carried by the carrier gas from the wire during the evaporation.

By comparing the ionization efficiencies of the FID and the AFID, it is found that

$$K\alpha \ll K_1\alpha^*$$

The effluent that is carried out on the wire was burnt off in a stream of air in the present device, carbon being thus converted into carbon dioxide, which is not detectable. Then it is possible to write for the AFID response:

$$R_{i \text{ e}} = K_1\alpha^* (\Sigma E_{\text{eff}}) (dN_{i \text{ eff}}/dt) \quad (4)$$

EXPERIMENTAL

The detector described is similar to devices described in the literature⁴ as far as construction is concerned. The detector with the sample transporter (Fig. 1) operates as follows. The wire is reeled off from a storage coil (1), passed via rollers (2,3) through an activation oven (4), which is heated to 750° to purify it from impurities and led through a coating block (5). Here it takes a part of the effluent from a column (12). The amount of the liquid carried depends on the speed of the wire feed and mobile phase flow-rate. This amount represents 0.5% under the present conditions of measurement. The wire then passes through a combustion oven (7) heated to 700°. Air is led into the combustion oven through the sides and carries the combustion products into the AFID (8). 50% of the total air amount that is introduced is taken to the sensing

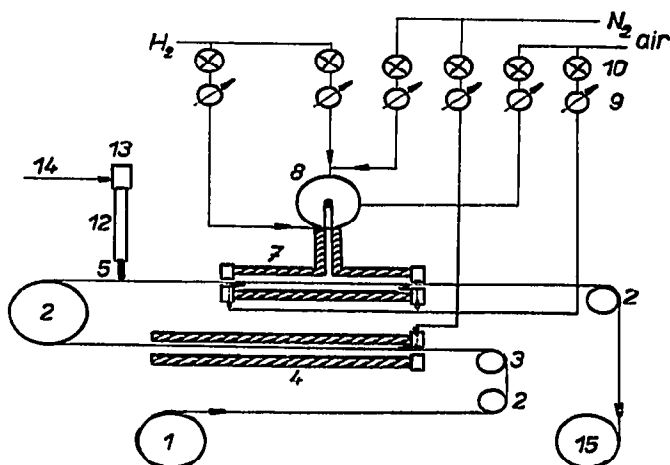


Fig. 1. Diagram of the detector with AFID. For description, see text.

element. The flow-rates of the gas can be adjusted by needle valves (10) and controlled by manometers (9).

A diagram of the AFID sensing element is given in Fig. 2. The stream of combustion products passes through a lower burner, where eventual residues of the mobile phase and solute are combusted. The gases then proceed round the jet to an upper burner with an alkali metal. The tip (1) was made of compressed sodium sulphate. Ionization current from the sensing element is led through an amplifier (Vibron C 33; Electronic Instruments, Richmond, Great Britain) to a recording device.

The chromatographic part of the equipment used for the investigation of the detector described consisted of a reservoir of mobile phase, a piston micropump (Model MC 300; Mikrotechna, Prague, Czechoslovakia), a pressure-pulse damper (after Locke¹⁰), a membrane sampler (13), and a stainless-steel column (12).

Experimental conditions for the measurement of detector characteristics are given in Table I.

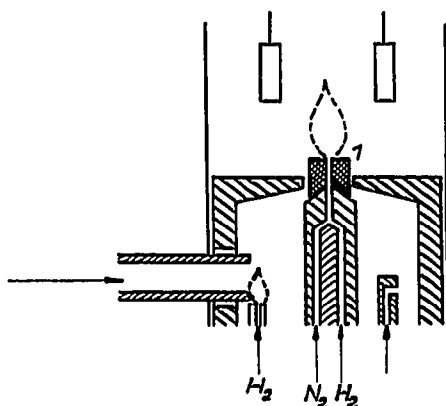


Fig. 2. Diagram of the AFID sensing element used. For description, see text.

TABLE I

CONDITIONS FOR THE MEASUREMENTS OF THE DETECTOR CHARACTERISTICS

Column	500 mm × 2 mm
Packing	Glass beads, 140–160 mesh
Mobile phase	<i>n</i> -Hexane
Flow-rate, ml/min	0.37
Wire feed, cm/sec	15
Sampling method	Syringes, 1, 5, 40 μ l
Points on the graphs	Average from four measurements

RESULTS AND DISCUSSION

The operating conditions were optimized for the detector described. Signal-to-noise ratios were studied relative to flow-rates of hydrogen through the burner with the alkali metal, hydrogen through the lower burner and air through the combustion oven. Characteristic graphs are shown in Fig. 3. The gas flow-rate through the sensing element is plotted on the *x*-axis and the signal-to-noise ratio (*R/N*) is plotted on the *y*-axis. The temperature of the flame, and thus also the emission of the alkali metal, increases as the hydrogen flow-rate through the burner with the alkali metal increases. This leads to an increase in the background ionization current, which affects both the value of response, *R*, and the level of noise, *N*. The dependence of response-to-noise ratio on the flow-rate of hydrogen reaches a maximum.

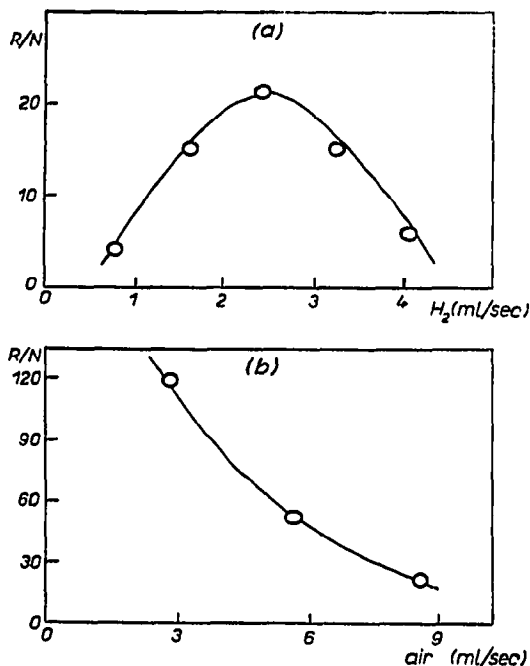


Fig. 3. (a) Dependence of *R/N* ratio on hydrogen flow-rate; air flow-rate, 8.5 ml/sec. (b) Dependence of *R/N* ratio on air flow-rate through the combustion oven; hydrogen flow-rate 2.4 ml/sec. Injection: 1 μ l of 2-*tert.*-butoxy-3-chlorotetrahydrofuran.

The response-to-noise ratio decreases with the air flow-rate through the combustion oven. This phenomenon is caused by the diffusion of molecules from the air stream into the flame of the burner. More gas is taken from outside the flame at the higher flow-rates. The flame in the burner extinguishes at flow-rates smaller than 2.5 ml/sec.

The response-to-noise ratio is almost unaffected by the hydrogen flow-rate through the lower burner, which is evidence for the perfect combustion.

The optimal flow-rates of hydrogen and air through the burner with the alkali metal were found to be 2.4 ml/sec and 2.9 ml/sec, respectively.

The responses for several tetrahydrofuran derivatives were determined under optimal conditions. The response is proportional to the content of halogen, as can be seen from Fig. 4. A derivative containing two halogen atoms has a response twice as large. The lower response of 2-methoxy-3-chlorotetrahydrofuran can be explained by a higher volatility when compared with other derivatives. On the wire entering the combustion oven, air passes in the opposite direction and picks up part of the effluent.

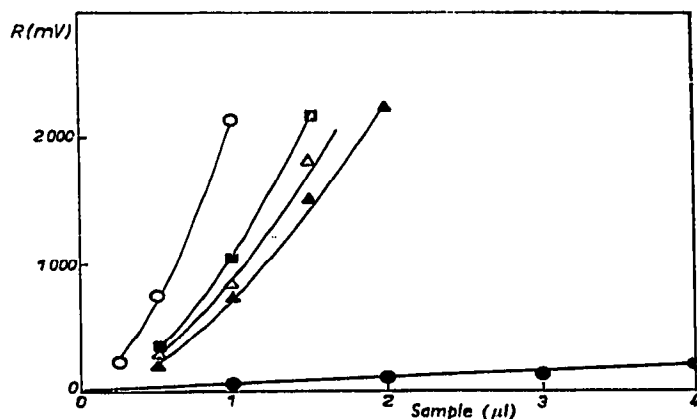


Fig. 4. Responses of the AFID to some derivatives of tetrahydrofuran with hydrogen flow-rate of 2.4 ml/sec and air flow-rate of 2.9 ml/sec. For further experimental conditions, see Table I. ○, Bis(3-chloro-2-tetrahydrofuranyl) ether; ■, 2-phenyl-3-chlorotetrahydrofuran; △, 2-*tert.*-butoxy-3-chlorotetrahydrofuran; ▲, 2-(*n*-hexyl)oxy-3-chlorotetrahydrofuran; ●, 2-methoxy-3-chlorotetrahydrofuran.

2-*tert.*-Butoxy-3-chlorotetrahydrofuran was selected for the determination of the sensitivity and ionization efficiency of the detector. The sensitivity was determined by extrapolating the value of the response-to-noise ratio to 2. The minimum detectable amount of 0.02 μl was found if the above derivative was injected. The sensitivity of 3×10^{-7} g/sec corresponds to this amount.

The ionization efficiency of the detector of 3×10^{-3} C per mole of Cl was calculated for the butoxy derivative. The response measured for the injection of 1 μl was taken for the calculation. Considering that under the conditions given 0.5% of the eluate is transported by the wire into the detector and that 50% of air passing inside comes into the sensing element, the ionization efficiency for the AFID thus obtained is 1.2 C per mole of Cl, which can be compared to the value of 1.4 C per mole of Cl for the AFID used in gas chromatography⁸.

The selectivity for hydrocarbons was determined by injecting squalane. The response could not be noted even when injecting 40 μ l. Hence the selectivity coefficient can be estimated to be greater than 2000 for the halogen derivatives under study.

The reproducibility of the results over six measurements was $\pm 10\%$.

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