

APPLICATION OF THE IONIZATION DETECTOR AND THE ALKALI FLAME IONIZATION DETECTOR IN CAPILLARY LIQUID CHROMATOGRAPHY

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A possibility is demonstrated of the use of the flame ionization detector (FID) and the alkali metal flame ionization detector (AFID) in capillary liquid chromatography. The minimum detectable mass flow rates for the FID and the AFID were $\approx 10^{-12}$ and $\approx 10^{-13}$ g s⁻¹, respectively. The detection time constant is about 1 s allows for operation with columns of inner diameters of 10–60 μ m and lengths above 1 m. The suggested design of the detector is described. The burner allows the total effluent from the column to enter the detector. The temperature of the end of the capillary column in the burner is controllable.

The optimization of the performance of capillary columns in liquid chromatography^{1–4} leads to a tendency to use columns of very low diameters ($\sim 1–15$ μ m). Limitations in this trend do not arise from the high pressure gradient at the column, as incorrectly supposed previously; however, constraints are imposed by the requirements of the detection of solute if the parameters of the apparatus are to be maintained. Detectors that would feature a sufficiently small volume, or a sufficiently low time constant of detection, are very difficult to design. Quite a number of detectors have been developed^{4–12} meeting these demands to various extents. Among detectors that proved satisfactory from the point of view of the time constant are also those based on the ionization of solute in a flame^{4,12}.

The application in liquid chromatography of detectors based on reactions occurring in a flame has been suggested recently^{13–15}. Similarly as in paper¹², a flame photometric detector has been used. Selective types of flame ionization detectors are advantageous by the possibility of employing a variety of mobile phases such as water, alcohols, or hydrocarbons.

The application of a flame ionization detector in capillary liquid chromatography is also feasible. Such a detector, interfaced to a capillary liquid chromatography apparatus, can be looked upon as a transport detector: after evaporation, pyrolysis, and, occasionally, conversion to the aerosol form¹⁶, the solute is transported with a nitrogen-hydrogen gas mixture into the flame ionization compartment, containing the detector electrodes. The transport is considerably faster than the passage of the

liquid mobile phase through the column. Consequently, the effective volume of the detector is smaller and the time constant shorter than as corresponds to the geometrical dimensions of the detector.

In the present work the flame ionization detection technique is applied to capillary liquid chromatography; the advantages of the introduction of the whole effluent into the flame, the possibilities of use of the flame ionization detector for reverse-phase systems, and the benefit resulting from the use of a dual alkali metal flame ionization detector are demonstrated.

EXPERIMENTAL

A flame ionization detector (FID) in the conventional desing for liquid chromatography was employed. The alkali flame ionization detector (AFID) was designed in the dual version^{17,18}. For both detectors the burner was adapted; a glass capillary column, inner diameter 5–20 μm and outer diameter 0.6–0.8 mm, was inserted into the quartz burner. A Chrom V (Laboratorní přístroje, Prague) or Vibron 33B (Electronic Instruments, Richmond, Great Britain) electrometric amplifier was used for the two detectors. The layout of the alkali flame ionization detector is shown in Fig. 1.

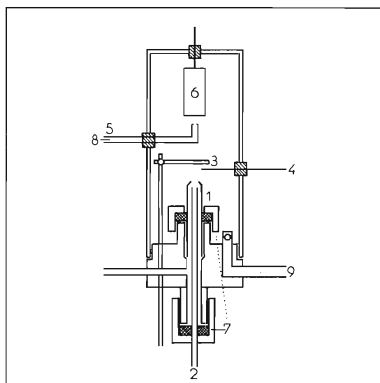


FIG. 1

Layout of the alkali flame ionization detector. 1 Quartz burner, 2 capillary column, 3 alkali metal source, 4 auxiliary electrode, 5 metal burner, polarization electrode, 6 cylindrical detecting electrode, 7 silicone rubber packing, 8 hydrogen-nitrogen mixture inlet, 9 air inlet

The bottom burner of the detector is constituted by a quartz tube with an inner diameter of 1 mm. The outlet end of the tube is either ground-in perpendicularly to the burner axis, or its diameter is reduced to 0.2--0.3 mm by sealing; the latter modification gave an enhanced response to the solutes measured as well as a lowered noise.

A hydrogen-nitrogen mixture passes about the end of the capillary column and burns at the end of the burner; the end of the column is thus cooled by the gas stream and simultaneously heated by the radiating burner. As a result, a sharper heat boundary at the end of the capillary column is attained. The temperature of the column end is determined by its distance from the burner edge. An identical burner design was used in the flame ionization detector and the alkali flame ionization detector.

The source of alkali metal for the AFID was a glass capillary (PN glass Jablonecké sklárny, Jablonec) submerged in molten KNO_3 for 16 h; the excess nitrate was removed from the surface and inside the capillary with distilled water.

The alkali metal source (3) (Fig. 1) is clamped on a special ungrounded beam enabling its vertical as well as horizontal setting. The auxiliary electrode (4) serves as the detecting electrode for the bottom burner (1). The detecting system proper is constituted by the top burner (5), made of metal (inner diameter 0.2 mm) and serving simultaneously as the polarization electrode for the auxiliary (4) and detecting (6) electrodes. The cylindrical detecting electrode (6) of the top burner (5) lies in the axis above the two burners. With this system the response of both detector flames can be recorded simultaneously.

The preparation of the glass capillary columns has been described⁴. The OV 101 or DC 505 silicone preparations or Tris III (1,2,3-tris(2-cyanoethoxy)propane) were used as the stationary phase; water, methanol, 2-propanol, or *n*-hexane or their mixtures served as the mobile phase.

The solutes were delivered to the columns by means of a six-way valve over a splitter¹⁹. The separation ratio was controlled in the region of $1 : 10^2$ to $1 : 10^4$.

RESULTS AND DISCUSSION

When using capillary columns, the whole of the effluent can be brought into the FID of AFID; this is made possible by the very low flow rate of the mobile phase in the capillary column, typically lying in the range of 10^{-3} – $1 \mu\text{l min}^{-1}$ in dependence on the column diameter and length. With such flow rates, the organic matter is brought into the burner in quantities as encountered in gas chromatography when applying higher temperatures to columns with liquid stationary phases. In gas chromatography, a gas mixture saturated by vapours of the stationary phase enters the detector. For instance, for Squalane coated on a commercial support, a temperature rise from 0°C to 70°C induces an increase in the base current of the flame ionization detector of an order of magnitude²⁰.

The dependence of the base current increment of the flame ionization detector on the mass flow rate of methanol, contained in the mobile phase, is shown in Fig. 2. The detector can be operated either at lower volume flow rates of the mobile phase and higher concentrations of methanol, or *vice versa*. With a column $15 \mu\text{m}$ in diameter, the detector is usable for methanol contents of $\varphi(\text{MeOH}) = 0.1$ and flow rates about $1 \cdot 10^{-3} \mu\text{l s}^{-1}$, which corresponds to a mass flow rate of methanol

of $0.57 \mu\text{mol s}^{-1}$. It is clear from Fig. 2 that under such conditions the base current of the detector increases by approximately an order of magnitude if the mass flow rate of methanol is increased from 0.5 to $4 \mu\text{mol s}^{-1}$.

As the content of methanol in the mobile phase is increased, the response of the flame ionization detector decreases. Examples are shown in Fig. 3. The slopes of the dependences are different for different solutes²¹. In all cases the sample was dissolved in the mobile phase.

The dependence of the drop in the response for phenol and 2-propanol exhibits a slope four times higher than as shown in Fig. 3 if the sample is dissolved in water and the solute is eluted from the column simultaneously with the solvent — water. This is consistent with Eq. (6) in paper⁴, indicating the possibility of increasing the base current of the detector, hence, of a negative response, at the moment that an incombustible substance passes through the detector. This takes place if the incombustible matter constitutes the solute and the mobile phase contains another component, methanol in our case, inducing a response of the detector. The changes in the detector response to water in dependence on the content of methanol in the mobile phase and on the inlet pressure of the latter are given in Table I.

Our experiments indicate that the major effect determining the changes in the response of the detector when the content of methanol is varied is the concentration changes taking place in the capillary column on the introduction of solute. To verify

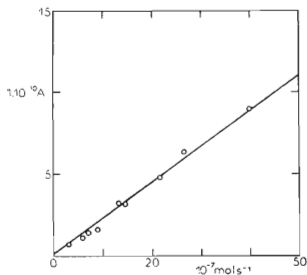


FIG. 2

Dependence of the base current of the flame ionization detector on the mass flow rate F_m of ethanol through the burner

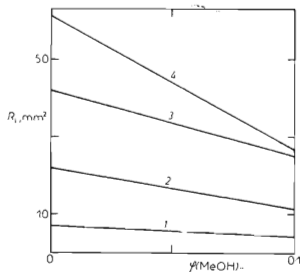


FIG. 3

Decrease in the response of the flame ionization detector in dependence on the volume fraction φ of methanol in the methanol-water mobile phase. 1 methanol, 2 2-propanol, 3 triethylene glycol, 4 phenol

this hypothesis we examined the changes in the detector response when the solute was introduced in the gaseous state in a carrier gas and simultaneously a liquid (water + methanol) was fed in. A gas chromatograph fitted with a flame ionization detector was used and the liquid was delivered into the burner. The nitrogen-hydrogen mixture was employed as the carrier gas. The separating column was packed with Chromosorb 102 (John Manville, Great Britain). Neither the water flow rate through the detector nor the flow rate of the 10% (V/V) methanol was observed to affect the detector response provided that the solute was delivered in the gaseous state (Table II).

The experiments evidence that the significant changes in the response of the flame ionization detector used in capillary liquid chromatography are due primarily to the changes in the concentrations in the liquid mobile phase rather than changes in the mechanism of formation of the ionized species in the flame. The dependence of the

TABLE I

Response of the flame ionization detector to water in dependence on the volume fraction of methanol in water $\varphi(\text{MeOH})$ and on the inlet pressure of the mobile phase P

$\varphi(\text{MeOH})$	Response, mm, at P (MPa)		
	1.0	2.0	3.0
0.02	25.6	28.6	32.9
0.05	31.9	33.9	86.9
0.10	41.7	59.7	86.9

TABLE II

Dependence of the peak height h for methane on the flow rate F_m of the liquid fed into the burner of the flame ionization detector

F_m^a $10^{-3} \mu\text{l s}^{-1}$	h mm	F_m^b $10^{-3} \mu\text{l s}^{-1}$	h mm
0.00	117.5	0.00	117.3
0.59	115.0	0.56	118.6
1.34	116.0	1.12	117.0
2.06	115.5	1.69	114.0

^a Liquid phase: water; ^b liquid phase: 10% (V/V) aqueous methanol.

detector response on the content of the organic substance in the carrier gas is considerably lower²², than as found for the use of capillary columns in liquid chromatography.

In the case of the alkali flame ionization detector in the dual arrangement, the effect of the composition of the mobile phase on the base current and the detector response is insignificant, provided that the mobile phase contains no element E to which the detector responds selectively. The detector response can be written²³ as

$$R_i = [K\alpha(\sum E_{\text{eff}}) + K'\alpha'(\sum C_{\text{eff}})] dm/dt, \quad (1)$$

where K and K' are constants of the apparatus, α and α' are the ionization efficiencies, E_{eff} s are elements to which the detector responds effectively and C_{eff} s are effective carbons; dm/dt is the mass flow rate of solute through the detector. In the dual arrangement,

$$K\alpha(\sum E_{\text{eff}}) \gg K'\alpha'(\sum C_{\text{eff}}), \quad (2)$$

and consequently the detector does not respond significantly to mobile phases that contain C_{eff} s only (alcohols, hydrocarbons, etc.) and are free of E_{eff} elements (halogenated hydrocarbons, phosphate buffers, etc.). In accordance with this, no substantial differences were observed between the responses for water, methanol, 2-propanol, or *n*-hexane as the mobile phase. The dependence of the ionization base current for the alkali flame ionization detector on the flow rate of the mobile phase is shown in Fig. 4. While the response in the electrode system of the bottom burner increases with increasing flow rate of the methanol-water 1 : 1 (V/V) mobile phase up to the

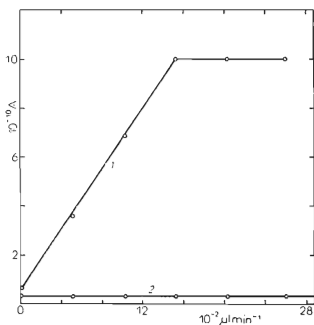


FIG. 4

Variations in the base current in dependence on the flow rate of the mobile phase ($\varphi(\text{H}_2\text{O}) = \varphi(\text{MeOH}) = 0.5$). 1 FID, bottom burner — auxiliary electrode system; 2 AFID, top burner — detecting electrode system

TABLE III

The minimum detectable mass flow rates of solutes for the FID and the AFID

Substance	Detector	Minimum detectable flow rate pg s^{-1}
Triethylene glycol	FID	3.0
<i>m</i> -Cresol	FID	1.5
Tributylphosphine oxide	AFID	0.17
Malathion	AFID	0.13
Naled	AFID	0.20
Methyltrithion	AFID	0.12
Phenitrothion	AFID	0.12
Chloroform	AFID	26
<i>p</i> -Dichlorobenzene	AFID	30

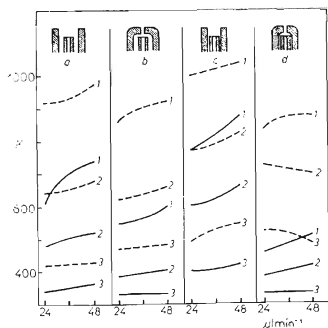


FIG. 5

Dependence of the temperature of the capillary column end on the gas flow rate through the burner. — $\text{H}_2 + \text{N}_2$ (1 : 1), - - - H_2 . Location of the capillary in the burner: 1 at the burner edge, 2 2 mm below the burner edge, 3—5 mm below the burner edge. Outer diameter of the capillary column 0.8 mm, inner diameter of the burner: *a*, *b* ≈ 1.2 mm, *c*, *d* ≈ 1.0 mm

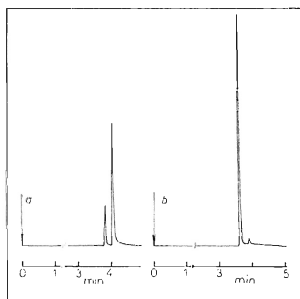


FIG. 6

Examples of response of the alkali flame ionization detector. *a* tributyl phosphate, *b* tributylphosphine oxide. Column: inner diameter 16 μm , length 3.5 m, stationary phase: DC 550, mobile phase: methanol-water 1 : 1 (*V/V*)

saturated current value in the same manner as in the flame ionization detector. the change in the base current of the AFID is considerably lower, amounting to 3% over the range examined.

A quantity relevant to the transfer of solute to the detector is the temperature of the capillary column end. While for volatile solutes this temperature is of minor importance, for low volatile solutes the temperature must be held high enough. Too high a temperature, however, can bring about decomposition of solute inside the column and a slow clogging of the column, ultimately resulting in a breakdown of the mobile phase flow.

The temperature of the capillary column end can be controlled *via* the composition of the nitrogen-hydrogen gas mixture and the spacing between the column end the flame. The temperature of the column end was measured with an iron-constantan thermocouple, introduced into the burner tube (1) (Fig. 1) parallel to the column (2) over the bottom rubber packing (7). The conditions and the temperature region are seen in Fig. 5. The temperature can be controlled from room temperature to approximately 1 000 K. In suitably chosen conditions, the rates of transfer of solutes to the detector for substances with boiling temperatures in the region of 350–600 K are identical. This fact was verified by measuring the band spreading for various solutes and various flow rates of the mobile phase⁴. The time constant of detection was established to be about 1 s.

The ionization efficiency of the flame ionization detector used, with respect to 2-propanol in the mobile phase ($\varphi(\text{MeOH}) = 0.05$ in water) was determined to be $0.02 \text{ C} \cdot \text{mol}^{-1}$. The values for other solutes lay in this range too. The minimum detectable mass amounts for various solutes are given in Table III. The lowest detectable mass flow rate was $8.7 \cdot 10^{-14} \text{ g s}^{-1}$ for phosphorus in Malathione (mobile phase: methanol). Examples of LC chromatograms obtained by using capillary columns and the alkali flame ionization detector are shown in Fig. 6.

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