

Effect of detector temperature on the flame ionization detector response

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Abstract

The effect of the detector temperature on the flame ionization detector response of *n*-alkanes (nonane, decane, undecane, dodecane), *n*-octanol and dimethylphenol was studied for four different detector designs. Both absolute and relative response changes were found. They are dependent on the detector design and the solute type.

1. Introduction

The flame ionization detector (FID) is the most frequently used gas chromatographic detector. Since its origin [1–3] its properties have been studied many times. Parameters such as the mechanism of ion formation [4,5], carrier gas, hydrogen and air flow-rates [5–9], column temperature programme [10], carrier gas type [9,11], electrode geometry [5–8], voltage level [5–9], response linearity [6,8,12] and functional groups [5,12] have been studied in connection with FID response and noise. Only several of the oldest references are given here as examples, of course. For determinations the relative response factors have been published. The concept of effective carbon number has been developed [5], consisting in the constancy of the contribution of different carbon atom types in the solute mole-

cule to the overall solute response. The effect of hydrogen and carrier gas flow-rates on the FID relative molar response has been published [13]. Many anomalous FID responses for different types of compounds have been described (e.g., [14–16]).

The detector temperature has been considered mentioned only exceptionally. FID is generally considered not to be very sensitive to temperature changes (e.g., [17]). Only Maggs [18] and Teplý and Dressler [19] have presented some temperature response effect. Maggs found about a 1.3-fold increase in the molar and mass responses without any changes in the relative response within the temperature range 30–150°C. Teplý and Dressler found a small response increase for the FID using steam as the carrier gas within the temperature range 150–280°C.

In this work we studied the effect of the detector temperature on the FID response in greater detail within a wide temperature range and for different detector designs.

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2. Experimental

Four flame ionization detectors were studied: Carlo Erba (Milan, Italy) (HRGC 5300 Mega Series gas chromatograph), Phillips Scientific (Cambridge, UK) (PU 4400), Laboratory Instruments (Prague, Czech Republic) (Chrom 5) and Hewlett-Packard (Avondale, PA, USA) (5980 A). Their configurations are given in Fig. 1. A jet is the electrode in the Carlo Erba (Fig. 1a) and Hewlett-Packard (Fig. 1b) detectors and a coil around the jet in the Phillips detector (Fig. 1c). In the Laboratory Instruments detector (Fig. 1d) two electrodes in the form of semi-cylinders

insulated from one another are situated above the jet. Between these two electrodes and the detector wall a PTFE barrier is placed, directing the gas flow to the space between both the semi-cylinders.

The column and injector temperatures were equal for all four detectors, 110 and 220°C, respectively. Packed columns were used with the Phillips and Laboratory Instruments chromatographs and capillary columns with the Carlo Erba and Hewlett-Packard instruments. The flow-rates of hydrogen and air through all the detectors studied were similar, 25 and 350 ml min⁻¹, respectively (air in Laboratory Instru-

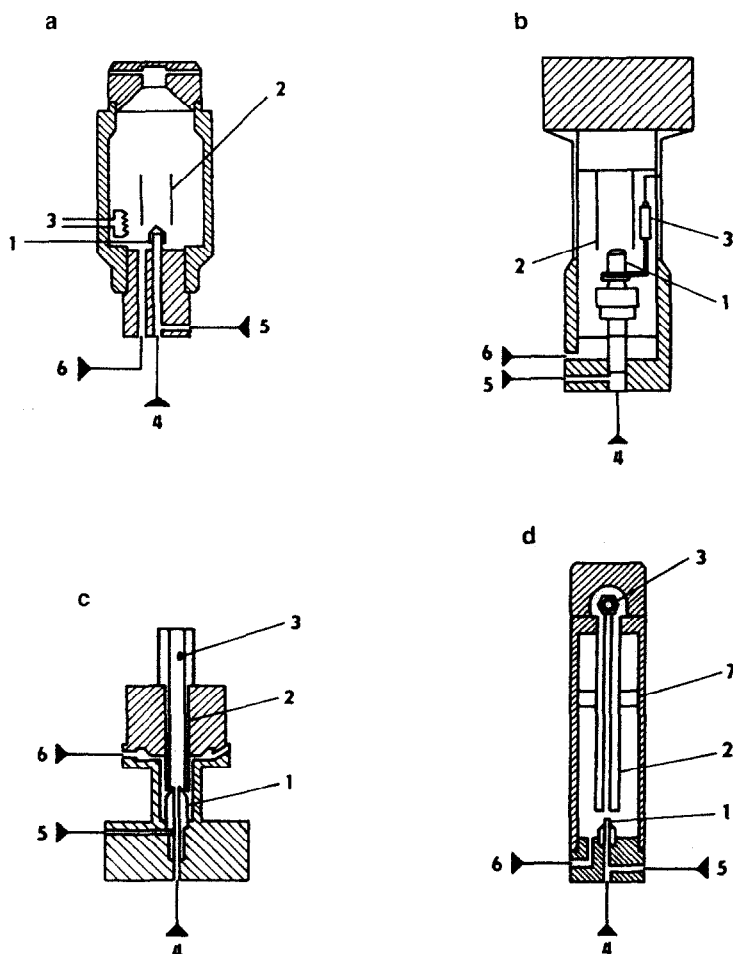


Fig. 1. Schematic diagrams of the flame ionization detectors. (a) Carlo Erba; (b) Hewlett-Packard; (c) Phillips; (d) Laboratory Instruments. 1 = Jet; 2 = collector electrode; 3 = ignition; 4 = carrier gas inlet; 5 = hydrogen inlet; 6 = air inlet; 7 = PTFE barrier.

ments chromatograph at 450 ml min^{-1}). The nitrogen make-up gas flow-rate was set in such a way as to obtain the same overall nitrogen flow-rate through the detector. The injection splitting ratio for the capillary columns was always 50:1.

The chromatographic conditions were as follows:

Carlo Erba: HP-5 column, $30 \text{ m} \times 0.53 \text{ mm}$ I.D.; film thickness, $0.88 \mu\text{m}$; flow-rates of nitrogen, carrier gas 3 ml min^{-1} , make-up gas 29 ml min^{-1} ;

Hewlett-Packard: Ultra 2 column, $25 \text{ m} \times 0.2 \text{ mm}$ I.D.; film thickness, $0.3 \mu\text{m}$; flow-rates of nitrogen, carrier gas 0.9 ml min^{-1} , make-up gas 31 ml min^{-1} ;

Phillips: column, $3.1 \text{ m} \times 4.0 \text{ mm}$ I.D., Chromosorb W AW ($149\text{--}177 \mu\text{m}$) with 10% of SE-54; nitrogen carrier gas flow-rate, 32 ml min^{-1} ;

Laboratory Instruments: column, $1.1 \text{ m} \times 3.0 \text{ mm}$ I.D., Chromosorb W AW ($149\text{--}177 \mu\text{m}$) with 4% of SE-54; nitrogen carrier gas flow-rate, 32 ml min^{-1} .

Alkanes ($n\text{-C}_9\text{--C}_{12}$), *n*-octanol (OH) and dimethylphenol (DMP) were used as test solutes. A $1\text{-}\mu\text{l}$ volume of methylene chloride solution (about $0.1 \mu\text{g}$ of each solute) was always injected.

For processing the detector signals an HP 3393A integrator (Hewlett-Packard) was used. The given response values are the arithmetic averages of three parallel measurements. The relative responses are peak-area (or peak-height) ratios of the solute tested with respect to decane.

3. Results

3.1. Carlo Erba FID

The FID response for $\text{C}_9\text{--C}_{12}$ alkanes and octanol increases slightly within the temperature range $120\text{--}130^\circ\text{C}$. The response at 320°C is about 14% higher than that at 120°C . The DMP response increases between 240 and 280°C , the maximum response being ca. 19% higher (Fig. 2).

The alkane and OH relative responses do not

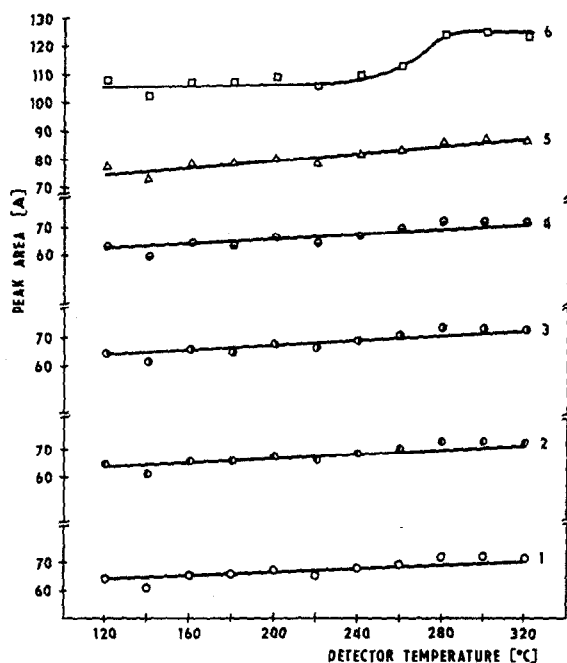


Fig. 2. Effect of detector temperature on Carlo Erba FID response. 1 = C_9 ; 2 = C_{10} ; 3 = C_{11} ; 4 = C_{12} ; 5 = OH; 6 = DMP. A = arbitrary units.

change with the detector temperature. The DMP relative response decreases slightly from 120°C , having the lowest value at about 230°C , then it increases again up to 320°C . The maximum–minimum response differences are 3% and 6% for 120 and 320°C , respectively (Fig. 3).

3.2. Phillips FID

The temperature dependence of the response exhibits a maximum for all the compounds studied (Fig. 4). The temperature maximum is, however, different for alkanes and octanol plus DMP. For alkanes it is about 230°C and for octanol and DMP about 200°C . The response at 340°C is always lower than that at 120°C . The maximum response for alkanes is about 6% and 21% higher in comparison with the response at 120 and 340°C , respectively. For DMP these differences are about 20% and 39% higher and for OH about 13% and 35% higher.

The alkane relative response is the same for all detector temperatures studied (Fig. 5). It is not

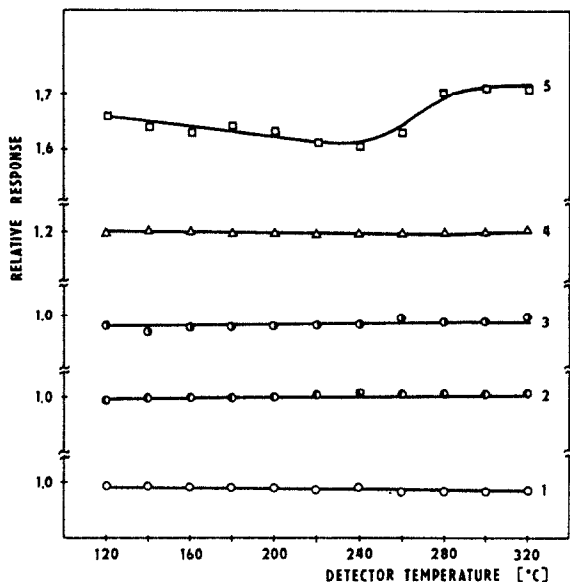


Fig. 3. Effect of detector temperature on Carlo Erba FID relative response. 1 = C₉/C₁₀; 2 = C₁₁/C₁₀; 3 = C₁₂/C₁₀; 4 = OH/C₁₀; 5 = DMP/C₁₀.

so for DMP and OH. The maximum relative response for both compounds occurs at about 190°C. It is about 14% higher than that at both 120 and 340°C for DMP and about 10% higher for OH.

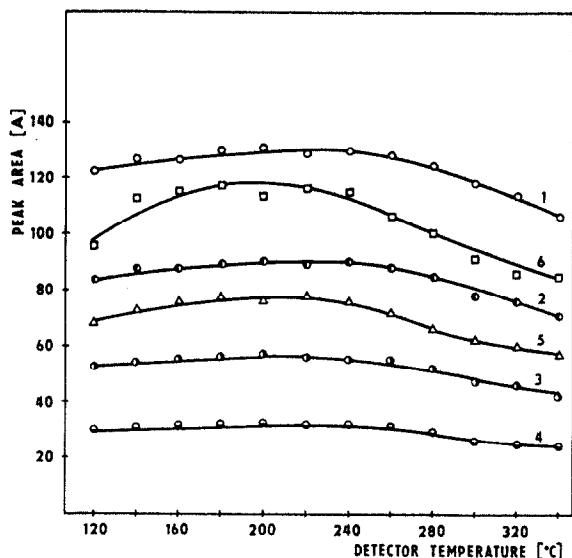


Fig. 4. Effect of detector temperature on Phillips FID response. Identification as in Fig. 2.

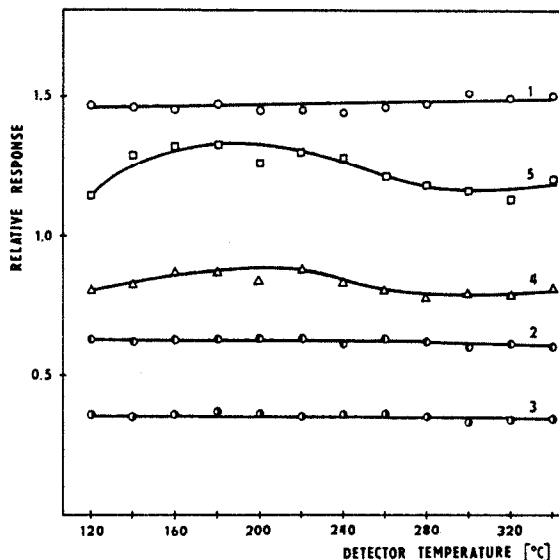


Fig. 5. Effect of detector temperature on Phillips FID relative response. Identification as in Fig. 3.

3.3. Hewlett-Packard FID

During the experiments with the Hewlett-Packard FID some time-dependent differences in the octanol and dimethylphenol responses were noticed. The first measurements are presented in Fig. 6a. The responses for C₁₀, OH and DMP increase within the temperature range studied. The highest response values were about 35% higher than the lowest values. Three months later, the responses for the same temperature range remained constant (Fig. 6b). The results obtained were compared with those for another instrument of the same type (Fig. 6c). The temperature dependences of the response for the second instrument were different. The response for all solutes increase beginning at about 160°C. The OH and C₁₀ response reach a constant maximum value at about 240 and 305°C, respectively. The DMP response shows a maximum at about 250°C.

The temperature dependence of the relative response is maximum at about 230°C for both DMP and OH and the response difference to a temperature of 120°C is about 7% (Fig. 7a). Three months later, the relative responses remained constant (Fig. 7b). The temperature

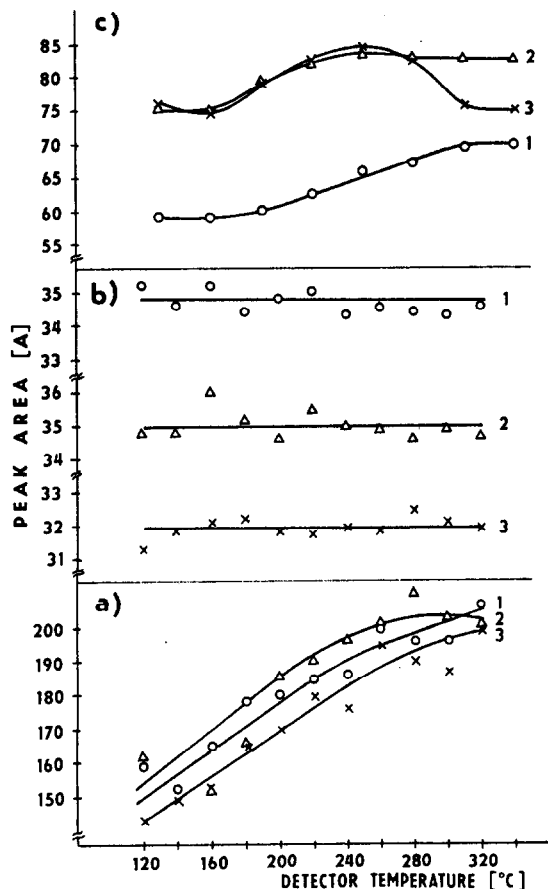


Fig. 6. Effect of detector temperature on Hewlett-Packard FID response. (a) first instrument, first measurements; (b) the same 3 months later; (c) second instrument. 1 = C₁₀; 2 = OH; 3 = DMP.

dependences are again different for the second instrument (Fig. 7c). Starting from about 250°C the relative response decreases. For a temperature of 340°C it equals 6% and 23% for OH and DMP, respectively. We have no explanation for this effect; it was not observed with the other FIDs studied.

3.4. Laboratory Instruments FID

The temperature dependences for this type of FID differ to a great extent from those for the other detectors studied (Fig. 8). Starting from 140–160°C a response decrease occurs for all the compounds studied. A very deep response de-

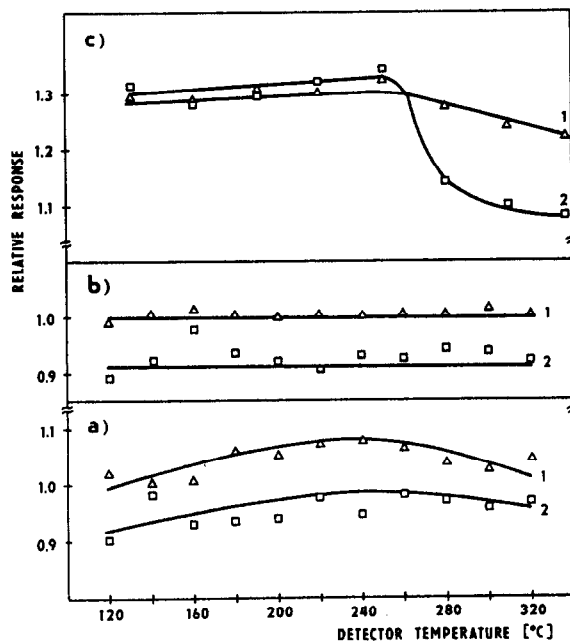


Fig. 7. Effect of detector temperature on Hewlett-Packard FID relative response. (a) First instrument, first measurements; (b) the same 3 months after; (c) second instrument. 1 = OH/C₁₀; 2 = DMP/C₁₀.

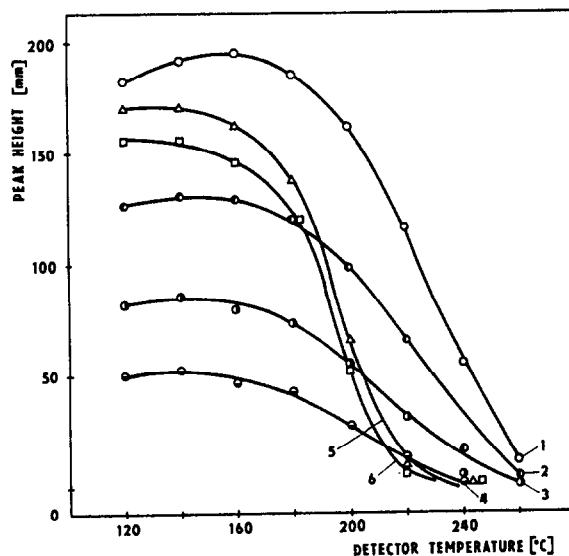


Fig. 8. Effect of detector temperature on Laboratory Instruments FID response. Identification as in Fig. 2.

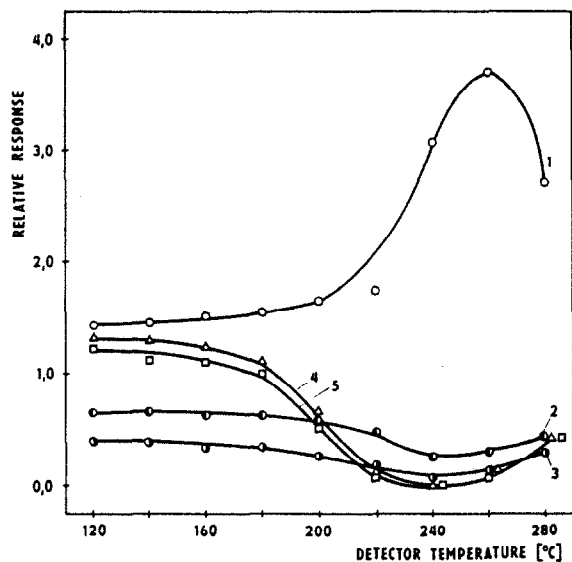


Fig. 9. Effect of detector temperature on Laboratory Instruments FID relative response. Identification as in Fig. 3.

crease, of about two orders of magnitude, appears at temperatures higher than ca. 230 and 240°C for DMP + OH and alkanes, respectively.

None of the relative responses are constant

within the temperature range studied, including *n*-alkanes (Fig. 9). Up to 160°C the relative response changes are small. The level of the relative response changes depends on the alkane used as a standard. The response behaviour of this type of FID is abnormal, especially at temperatures above ca. 160°C.

3.5. Temperature inside the detector body

The FID is not thermostated separately but is heated from its bottom base. We measured with a thin thermocouple the real temperatures inside the detector body at different distances from the detector base at different set detector temperatures for two of the detectors studied (Table 1). Real jet temperatures for one FID were also measured.

The real temperature inside both FIDs followed at each distance is always lower than the temperature set. The higher the set temperature, the higher are the relative temperature differences. The real temperature decreases with increasing distance from the detector base. A greater decrease was found with the Laboratory

Table 1
Temperature inside the detector body

Temperature set (°C)	Temperature measured (°C)					Detector
	Position				Jet	
	1	2	3	4		
120	72	69	67	65	145	I ^a
160	94	84	83	82	170	
200	112	105	103	101	201	
240	140	135	131	129	226	
280	171	165	162	160	253	
320	198	190	186	184	278	
120	101	117	125			II ^b
160	131	133	147			
200	175	167	153			
240	203	185	164			
280	230	211	170			
320	260	228	185			

^a I = Carlo Erba FID. Position = distance from the base (in the free "gas" detector volume, between the wall and the flame): 1 = 4 mm, 2 = 16 mm, 3 = 28 mm, 4 = 40 mm; jet orifice is 8 mm above the detector base.

^b II = Laboratory Instruments FID. Position: 1 = 4 mm, 2 = 24 mm, 3 = 42 mm; jet orifice is 9 mm above the detector base.

Instruments FID. The jet temperature increases with increasing detector temperature. This difference is about 130°C for a detector temperature change from 120 to 320°C.

4. Conclusions

Both the absolute and relative FID response depends on the detector temperature. The level and the character of these changes depend on the detector design and on the solute type.

The response values differ for different detector temperatures by up to several tens of per cent, and for one detector studied even by two orders of magnitude.

The relative response for *n*-alkanes seems to be constant within the temperature range 120–340°C. The relative response for DMP and OH can depend on the detector temperature. The differences are usually up to 23%, with the exception of one detector studied for which it was several hundred per cent.

The absolute and relative responses for one of the detectors studied changed during the experimental period and they were different for two different instruments.

Our results show that for compounds containing heteroatoms the effective carbon number need not be constant within the FID temperature range used. For some special FID designs it can be valid even for hydrocarbons. The effective carbon number can even depend on the detector type (with the same instrument type) and/or on the detector “life”.

It is difficult to explain why the effects of response changes with FID temperature are observed and further experiments are needed. However, the temperatures around the FID

flame (both “gas” and jet) are different at different FID set temperatures. This means that, e.g., the diffusion conditions for oxygen and other molecules and/or radicals vary.

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