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## EFFECT OF DETECTOR TEMPERATURE ON FLAME PHOTOMETRIC DETECTOR BEHAVIOUR

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### SUMMARY

Detector temperature was studied as a parameter affecting the behaviour of the flame photometric detector towards sulphur and phosphorus compounds using 394 and 526 nm filters, respectively. It was found that while the peak heights of sulphur compounds decrease along with increasing temperature of the flame photometric detector, the peak heights of phosphorus compounds increase. At the same time, the exponent  $n$  in the dependence of the peak height on the amount of sulphur compounds also decreases. As the detector noise also increases with the detector temperature, the minimum detectable amount of sulphur compounds increases *ca.* 2.5 times, while that of phosphorus compounds remains approximately the same. The detector temperature also affects the detection selectivity, the P/S ratio increasing six times in one channel over the temperature range 80–160°C. At a constant detector temperature, the selectivity varies with the air flow-rate by *ca.* two orders of magnitude.

It was shown that errors in the quantitative analysis which had not taken into consideration the effect of the detector temperature on the flame photometric detector response can reach values greater than 100%.

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### INTRODUCTION

The flame photometric detector (FPD) was used in gas chromatography for the first time in 1966 by Brody and Chaney<sup>1</sup>. In view of its wide use for the detection of sulphur and phosphorus compounds, in particular in environmental analysis, the factors affecting the FPD response to these compounds have been intensively studied.

The response of the FPD to sulphur and phosphorus compounds depends on the working conditions, such as the flow-rates of gases through the detector<sup>2-5</sup>, the structure of the compounds undergoing analysis<sup>3,5-8</sup> and, with sulphur compounds, also on the detector temperature<sup>4</sup>. The dependence of the peak height,  $h$ , on the amount of sulphur compound,  $c$ , is given by relationship  $h = ac^n$ . With regard to the fact that S<sub>2</sub> species in the excited state are responsible for the emission of light

quanta ( $S_2^* \rightarrow S_2 + h\nu$ ) the exponent  $n$  ought theoretically to be equal to two. Some measurements confirm this assumption both for FPD<sup>4</sup> in gas chromatography and for cool flames in molecular emission spectroscopy<sup>9</sup>. However, a series of experiments has shown that  $n$  ranges between one and two (*e.g.* refs. 5 and 6). The exponent  $n$ , similar to the response, is dependent on the flow-rate of hydrogen, on the ratio of flow-rates  $O_2/H_2$  and  $O_2/N_2$ <sup>2,7,8</sup> and also on the structures of the compounds<sup>3,6-8</sup>.

In the present work, the effect of the detector temperature on the response of phosphorus and sulphur compounds, the detector noise, the minimum detectable amount, the exponent  $n$  and the detection selectivity was studied.

## EXPERIMENTAL

A Chrom 5 gas chromatograph (Laboratory Instruments, Prague, Czechoslovakia) and an LFD-4<sup>10</sup> FPD (Special Designing Bureau, Estonian Academy of Sciences, Tallin, U.S.S.R.; the decomposition section of the detector is separated from the emission space) were used for all the measurements. The emission of both sulphur and phosphorus compounds was measured by means of a photomultiplier via 394 and 526 nm interference filters, respectively. A glass chromatographic column, (250 cm  $\times$  3 mm), was packed with 3% SE 30 on Chromosorb W. Aliquots (1.4  $\mu$ l) of the solution of sulphur compounds and  $PSCl_3$  in nonane were injected at concentrations of  $1.0-6.0 \cdot 10^{-10}$  g/ $\mu$ l with the aid of a 5- $\mu$ l Hamilton microsyringe.

While the dependence of the peak height of the FPD used on the hydrogen flow-rate shows a plateau from a certain flow-rate, the same dependence on the air flow-rate shows a maximum. Hydrogen and air flow-rates through the detector, unless stated otherwise, were therefore selected to be in a range where the response was approximately at a maximum, *i.e.*, 52 and 72 ml/min, respectively.

## RESULTS

### *Detector response to sulphur compounds*

The peak heights for the sulphur compounds decrease to a minimum with increasing detector temperature over the range 80 to *ca.* 160°C (Fig. 1) and then begin to increase again as the temperatures rises up to 200°C. The course of this dependence varies with both the air flow-rate and the structure of the compound being studied (*cf.* thiophene and butanethiol). At the same time, the background current and the detector noise also increase.

Columns 3-5 of Table I show the differences in the peak heights for thiophene expressed as percentages when compared with the peak heights at one selected detector temperature; the differences are both positive and negative and reach up to 200%.

### *Detector response to phosphorus compounds*

In contrast to sulphur compounds, the peak heights for the phosphorus compounds increase linearly over the range of temperatures studied, 80-200°C (Fig. 2). At the same time, the detector noise again also increases.

If the change in FPD response with detector temperature is not considered,

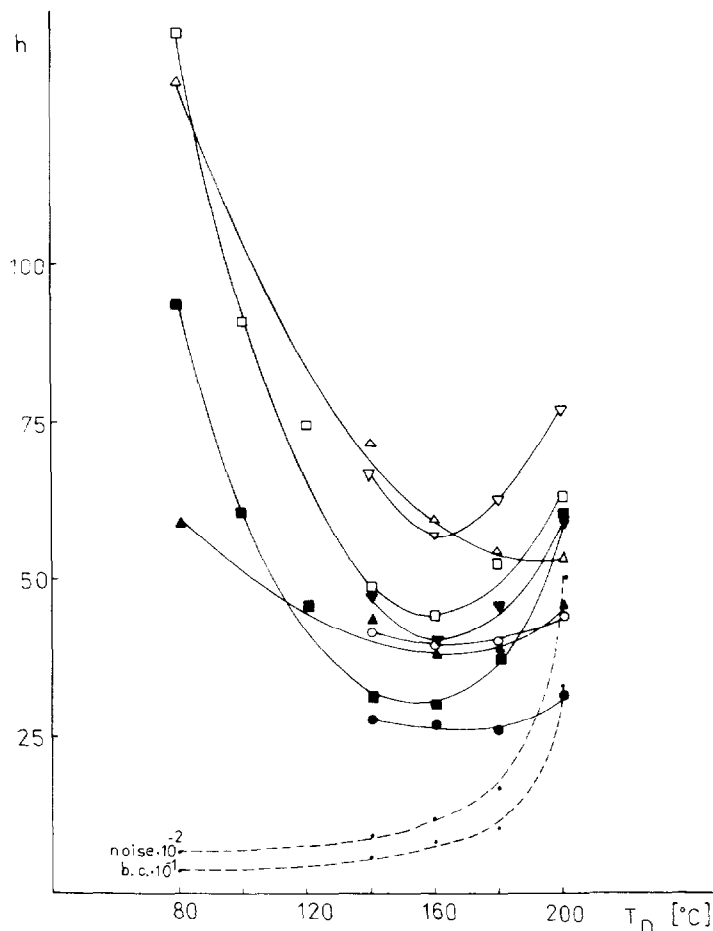


Fig. 1. Effect of the FPD temperature on peak heights ( $h$ , in arbitrary units) of sulphur compounds, detector background current and noise.  $\circ$ ,  $\triangle$ ,  $\square$  and  $\nabla$  refer to thiophene;  $\bullet$ ,  $\blacktriangle$ ,  $\blacksquare$  and  $\blacktriangledown$  refer to butanethiol. Air flow-rates (ml/min):  $\circ$ ,  $\bullet$  = 22;  $\triangle$ ,  $\blacktriangle$  = 35.3;  $\square$ ,  $\blacksquare$  = 46.2;  $\nabla$ ,  $\blacktriangledown$  = 72.3. Injection: 1.2  $\mu\text{l}$ , except for an air flow-rate of 46.2 ml/min when 1.4  $\mu\text{l}$  was injected. b.c. = background current.

the amount of the substance found differs substantially from the real value. Table II shows amounts of  $\text{PSCl}_3$  and their relative errors when single temperatures only are used in the calculations, *i.e.*, when the calculations do not take into consideration various detector temperatures. The error due to this can be up to 140%.

#### Detector response to hydrocarbons

Fig. 3 illustrates peaks for nonane (1.4  $\mu\text{l}$ ) at various detector temperatures. Nonane is eluted only after all the compounds studied, with an elution time of *ca.* 7 min. A complete chromatogram of a nonane solution of thiophene is shown at a detector temperature of 80  $^{\circ}\text{C}$ , while only the section of the chromatogram containing the solvent peak is shown for other temperatures. Under the experimental conditions used, the character of the detector response to nonane changes. While at lower de-

TABLE I

ERRORS IN THE QUANTITATIVE DETERMINATION OF THIOPHENE WITH THE USE OF VARIOUS FPD TEMPERATURES, CAUSED BY THE USE OF THE CALIBRATION GRAPH FOR ONE DETECTOR TEMPERATURE ( $T_D$ )

Injected amount:  $1.50 \cdot 10^{-10}$  g. Detection temperatures ( $T_D$ ) taken as basis: a,  $160^\circ\text{C}$  ( $n = 1.68$ ); b,  $120^\circ\text{C}$  ( $n = 1.86$ ); c,  $80^\circ\text{C}$  ( $n = 1.91$ ).

$T_D$ ( $^\circ\text{C}$ )	Peak height (arbitrary units)	Difference in peak heights (%)			Calculated amounts $g \cdot 10^{-10}$			Relative error (%)		
		a	b	c	a	b	c	a	b	c
80	136	+212.6	+83.8	—	2.956	2.085	—	97.1	39	—
100	90	+106.9	+31.6	-33.8	2.313	1.665	1.209	54.2	11	19.4
120	74	+70.1	—	-45.6	2.058	—	1.091	37.2	—	27.3
140	47.5	+9.2	-35.8	-65.1	1.581	1.185	0.866	5.4	21	42.8
160	43.5	—	-41.2	-68.0	—	1.125	0.827	—	25	44.9
180	51.5	+18.4	-30.4	-62.1	1.659	1.230	0.902	10.6	18	39.9
200	62	+42.5	-16.2	-54.4	1.852	1.365	0.995	23.5	9	33.7

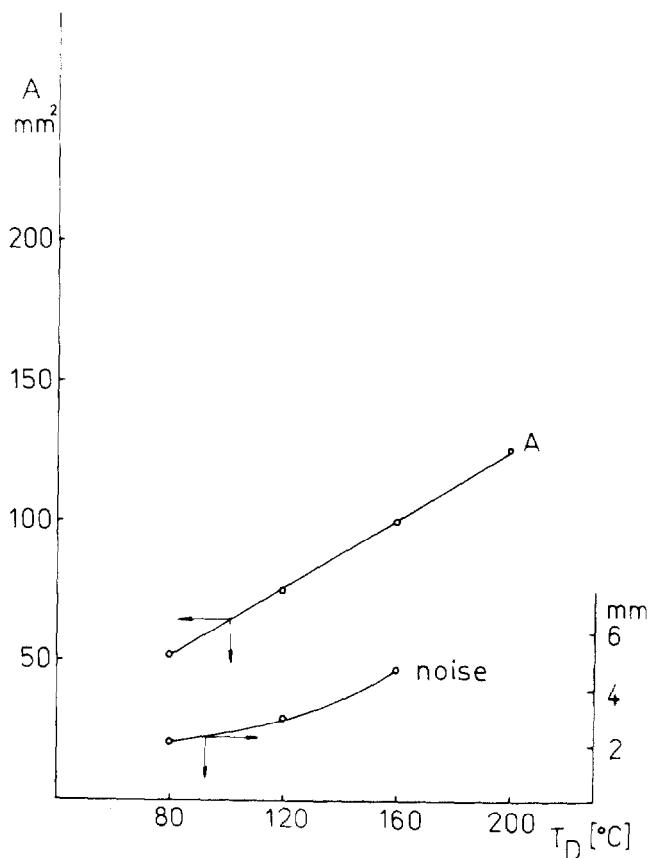


Fig. 2. Effect of the FPD temperature on the peak area of  $\text{PSCl}_3$  and the detector noise. Noise:  $1 \text{ mm} = 2 \cdot 10^{-12} \text{ A}$ .

TABLE II

ERRORS IN THE QUANTITATIVE DETERMINATION OF  $\text{PSCl}_3$  WITH THE USE OF VARIOUS FPD TEMPERATURES, CAUSED BY THE USE OF THE CALIBRATION GRAPH FOR ONE DETECTOR TEMPERATURE

Injected amount:  $2.24 \cdot 10^{-10}$  g. Detection temperatures ( $T_D$ ) taken as basis: a, 80°C; b, 120°C; c, 160°C; d, 200°C.

$T_D$ (°C)	Peak area (arbitrary units)	Calculated amounts ( $g \cdot 10^{-10}$ )				Relative error (%)			
		a	b	c	d	a	b	c	d
80	52	—	1.553	1.165	0.932	—	30.7	48	58.4
120	75	3.231	—	1.680	1.344	44.2	—	25	40.0
160	100	4.308	2.987	—	1.792	92.3	33.3	—	20.0
200	125	5.385	3.733	2.8	—	140.4	66.7	25	—

tector temperatures the response is positive, peak inversion gradually occurs with increasing detector temperature; at a temperature of 200°C the response is negative.

#### Dependence of the peak height on the amount of material

It is obvious from Table III that the detector temperature has also an influence on the exponent  $n$  in the expression for dependence of the peak height on the amount of the material in the detector. The exponent  $n$  decreases with increasing detector

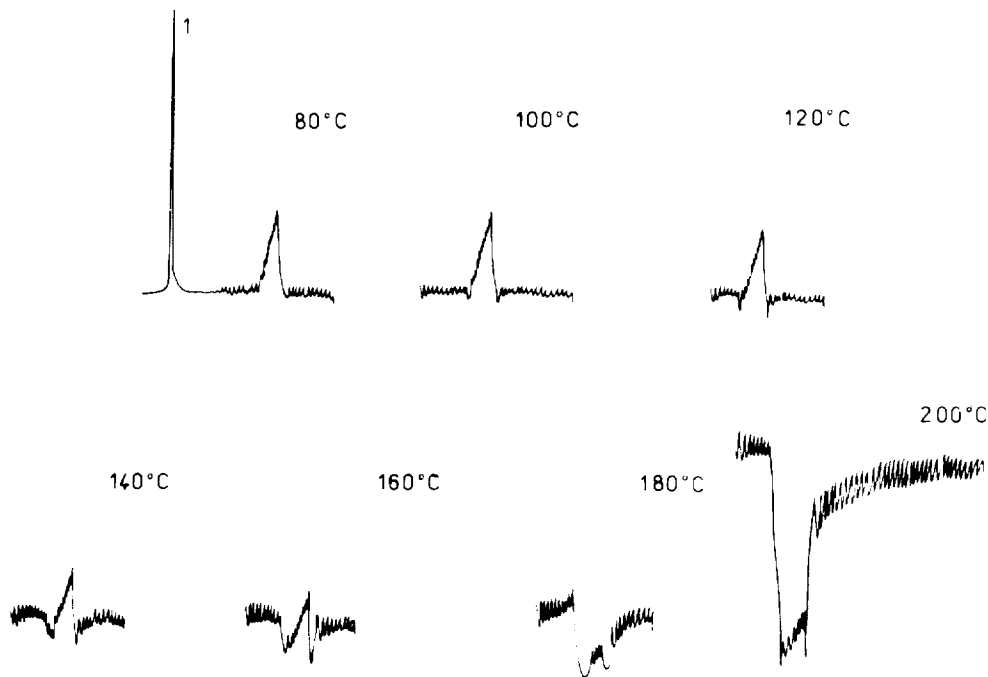


Fig. 3. Nonane peak shape at different detector temperatures. Peak 1 = thiophene. Injection:  $2.4 \cdot 10^{-10}$  g of thiophene in  $1.4 \mu\text{l}$  of nonane. Amplifier sensitivity: thiophene,  $\times 64$ ; nonane,  $\times 8$ .

TABLE III  
EFFECT OF THE DETECTOR TEMPERATURE ON  $n$

$T_D$ (°C)	<i>PSCl<sub>3</sub></i>		<i>Thiophene</i>		<i>Butanethiol</i>	
	$n$	Change in $n$ (%)	$n$	Change in $n$ (%)	$n$	Change in $n$ (%)
70	1.79		1.93		1.86	
114	1.80		1.88	97.4	1.70	91.4
152	1.66	92.7	1.70	88.1	1.55	83.3
190	1.19	66.5	1.47	76.2	1.24	66.7

temperature, with a varying rate of decrease for different types of sulphur compounds. This fact, together with the change in peak height at different detector temperatures, must be taken into consideration when carrying out quantitative evaluations. The amounts of the substance calculated without taking into account these changes are shown in Table I for thiophene (columns 6-8) together with the relative error of one such calculation, which can be up to 100% (columns 9-11).

For the phosphorus compounds the dependence of the FPD response remains linear at various detector temperatures (Fig. 4).

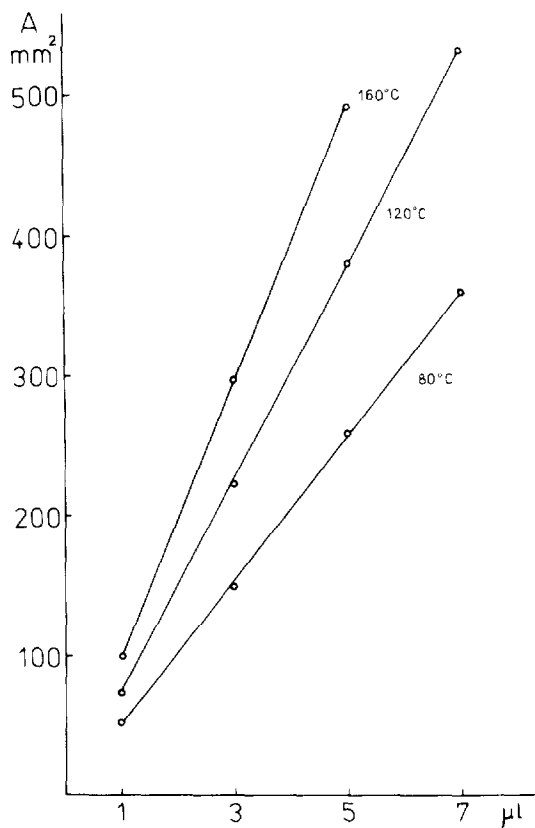


Fig. 4. Dependence of the peak area on the injected volume of  $PSCl_3$  for various detector temperatures. Concentration:  $1.7 \cdot 10^{-10}$  g/ $\mu$ l.

TABLE IV  
CHANGES IN THE FPD SELECTIVITY

S = Thiophene; P =  $\text{PSCl}_3$ ; C = nonane.

$T_D$ (°C)	Air flow-rate (ml/min)	Change in selectivity		
		$P/S^*$	$S/C$	$P/C$
80	46.2	1 ×	3.1 ×	1 ×
120		2.8 ×	1.7 ×	1.44 ×
160		6.3 ×	1 ×	1.92 ×
200		5.5 ×	0.5 ×	0.80 ×
120	35.3		132.4 ×	
	46.2		47.0 ×	
	61.2		19.1 ×	
	72.3		15.6 ×	
	81.1		2.7 ×	
	92.3		1 ×	

\* In the same channel.

### Selectivity

The selectivity of the response also depends on the detector temperature (Table IV). The ratio of peak heights of thiophene to nonane decreases over the temperature range 80–200°C (the selectivity at 160°C was taken as the basis for the comparison, as at this temperature the dependence of the peak height of thiophene on the detector temperature is at a minimum). In contrast, the ratio of the peak heights for  $\text{PSCl}_3$  to those for nonane increases over the above-mentioned temperature range (the selectivity at 80°C was taken as the basis) except for a detector temperature of 200°C, at which the detector response to hydrocarbon is approximately three-fold that at 80°C and, moreover, negative (see Fig. 3).

The ratio of the peak heights for  $\text{PSCl}_3$  to those for thiophene in one channel also varies with detector temperature with the maximum occurring at *ca.* 160°C. The selectivity of the FPD response towards hydrocarbons depends considerably on the air flow-rate through the detector. Over a range of flow-rates of 35–92 ml/min the selectivity decreases with increasing air flow-rate.

### DISCUSSION

Maruyama and Kakemoto<sup>4</sup> found out that the response of the FPD to sulphur compounds decreases with increasing detector temperature; the dependence of  $w_{\frac{1}{2}}$  (peak width at the half height) against the detector temperature is linear with the response decreasing by about one third over the range of 100–300°C. As may be seen from Fig. 1, the dependence of the peak heights for the sulphur compounds for the detector used also has a tendency to decrease with increasing detector temperature. However the course of this dependence is different, at certain temperature showing a minimum. The increase in response at the higher detector temperatures may be due to the releasing of a certain amount of sulphur from the detector (see background current in Fig. 1). In this case, the response on a higher sulphur background is larger<sup>11</sup>. However, no source for the sulphur contamination was found in the detector. The course of the above dependence is influenced by the air flow-rate through the detector. Both background current and detector noise increase exponentially with increasing detector temperature, and the minimum detectable amount of sulphur

compounds thus increases from  $1.6 \cdot 10^{-12}$  g of sulphur per second at a detector temperature of  $80^{\circ}\text{C}$  to a value of  $3.8 \cdot 10^{-12}$  at  $152^{\circ}\text{C}$ .

The FPD response to the phosphorus compounds, in contrast to the sulphur compounds, increases with increasing detector temperature. As at the same time the background current and the detector noise also increase, the minimum detectable amount is approximately the same, *i.e.*,  $1 \cdot 10^{-13}$  g of phosphorus per second at a detector temperature of  $80^{\circ}\text{C}$  and a value of  $1.1 \cdot 10^{-13}$  at  $160^{\circ}\text{C}$ .

Various authors have found the ratio of FPD responses to certain pair of sulphur compounds to be entirely different, sometimes even opposite. Sugiyama *et al.*<sup>6</sup> found that the response to sulphides is greater than to disulphides, while Mizany<sup>8</sup> found a greater response to disulphides. The difference is given by the fact that the exponent  $n$  in the expression for the dependence of the peak height for sulphur compounds on the amount of compound present is affected by the structure of the compounds; hence in comparisons of the responses of sulphur compounds of two different types the difference depends on the concentrations of the compounds at which the experiments are carried out<sup>3</sup>. The fact that  $n$  is also dependent on the detector temperature suggests that, in comparative measurements, the FPD temperature must also be taken into consideration for sulphur compounds. For phosphorus compounds, no change in the linear dependence of the response on the concentration with change in the detector temperature occurs.

The fact that the exponent  $n$  for sulphur compounds is influenced by the detector temperature when the FPD is used must be seriously taken into consideration when quantitative evaluations of analyses are carried out (this has not been so until now). Errors caused by neglecting these changes can be very large (*i.e.* in tens of percentages).

The detection selectivity of the FPD is not constant. Because the response increases exponentially with the amount of sulphur compounds, but only linearly with that of phosphorus compounds, the ratio of responses, P/S, obviously depends on the concentrations of these compounds. However, it is obvious from Table IV that the FPD selectivity also depends on the detector temperature. With regard to the fact that the detector response to hydrocarbons is approximately constant at various detector temperatures, the selectivity varies as the peak height of a particular compound increases or decreases depending on the detector temperature (except for at  $200^{\circ}\text{C}$ , where the peak height of the hydrocarbon is approximately three fold). The peak heights of phosphorus compounds increase as the detector temperature increases, while they decrease for sulphur compounds; the P/S selectivity in one channel thus varies with increasing detector temperature in favour of phosphorus compounds. In addition the FPD selectivity towards hydrocarbons also varies with the air flow-rate through the detector. Over a range of flow-rates of 35–92 ml/min it changes by two orders of magnitude.

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