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HYDROCARBON AND WATER QUENCHING OF THE FLAME PHOTOMETRIC DETECTOR RESPONSE

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SUMMARY

The quenching effect for a flame photometric detector was examined. The range of response quenching was found to be affected by the temperature of the detector. At higher temperatures of the chromatographic column, the quenching effect can also be induced with a stationary phase background. Water does not cause response quenching; on the contrary, it leads to increased detector responses in certain cases. Response quenching due to hydrocarbons and water background does not affect the magnitude of the exponent n .

INTRODUCTION

In the cool flame of the flame photometer, the decomposition of sulfur- or phosphorus-containing substances produces excited S_2^* and/or HPO^* species. As the species revert to the ground state, they emit radiation characteristic of the hetero atom. The presence of a sulfur- or phosphorus-free compound in the cool flame causes a decreased response of this photometer^{1,2} and of that of the gas chromatographic flame photometric detector³⁻⁷. The decrease of the emission intensity quenching effect is ascribed to the deactivation of the excited states, to their combination or collision with organic compounds or with degradation products of the latter⁴. The intensity of the quenching effect in the flame photometric detector depends on the detector design⁷, on the oxygen:hydrogen flow-rate ratio through the detector⁷ and on the concentration of the quencher³⁻⁷. With equal concentrations of various quenchers, the intensity of emission quenching depends on the type of the quencher (hydrocarbon, ketone, alcohol)⁴, the effect of carbon dioxide being substantially smaller³. In the cool flames of molecular emission spectroscopy, the emission intensities of sulfur and phosphorus compounds are also decreased if acids are present^{1,8}.

The temperature of the detector affects the response⁹. Therefore, it was the aim of this paper to investigate whether the temperature of the detector also affects the quenching effect. The effect of column temperature on the quenching of the response was also studied. Because flame photometric detection has frequently been applied in environmental analyses with water present at various concentrations, the influence of water on the response was also examined.

EXPERIMENTAL

The flame photometric detector of the LFD-51 type¹⁰ constructed by the Special Designing Bureau at the Estonian Academy of Sciences, Tallin, U.S.S.R., with the emission chamber separate from the decomposition part, was used for the measurements. The emissions from the sulfur and phosphorus compounds were viewed through interference filters of 394 nm and 526 nm, respectively. The type Chrom-5 gas chromatograph (Laboratory Instruments, Prague, Czechoslovakia) was used. The glass column (250 cm × 3 mm I.D.) was packed with 3% SE-30 on Chromosorb W.

The temperature of the column was 85°C, the flow-rate of the carrier gas was 32 ml/min, the flow-rate of the air was 65 ml/min and that of hydrogen 60 ml/min. A 1- μ l volume of a solution of a sulfur and/or phosphorus compound was injected with a 1- μ l Hamilton microsyringe in *n*-nonane of $5 \cdot 10^{-7}$ to $5 \cdot 10^{-6}$ g/ml concentration.

Cyclohexane and methane were used to examine the influence of the presence of hydrocarbon molecules in the flame on the detector response and the exponent *n*. Methane (0.5 ml/min flow-rate) was added to the carrier gas. Cyclohexane was added to the nonane solution of thiophene. On the chromatographic column used, the retention time of cyclohexane is identical with the retention time of thiophene and this results in their simultaneous elution.

RESULTS AND DISCUSSION

The effect of detector temperature on quenching

The levels of the response to sulfur and phosphorus compounds differ greatly at different temperatures of the detector^{6,9}. Therefore, the detector temperature affects the processes connected with the excitation of the S₂ and HPO species and with their transition to the ground state. Consequently, the detector temperature can be supposed to affect the processes associated with the deactivation of the excited states caused by organic compounds, (*i.e.* quenching). Table I compares the peak heights of thiophene and the same heights for the simultaneous elution with cyclohexane at various temperatures. It can be seen that the intensity of the quenching effect varies with detector temperature. In the temperature range from 100 to 190°C, the peak

TABLE I
EFFECT OF THE DETECTOR TEMPERATURE ON RESPONSE QUENCHING

Cyclohexane concentration $4.67 \cdot 10^{-6}$ g/ μ l.

Detector temperature (°C)	Peak height (mm)	Peak height plus cyclohexane (mm)*	Variation (%)
100	151	34.4	5.70
130	108	49.2	11.39
160	61	27.0	11.07
190	67.5	27.0	10.00

* Amplifier sensitivity increased four-fold.

height varies between 5.7 and 10% of the initial peak height during simultaneous elution with cyclohexane.

The quenching effect with water

The retention time of the water peak maximum (29 sec) was first determined, using a catharometer, on the chromatographic column employed. The effect of water on the detector response was examined in the following way: a solution of model compounds of sulfur was injected into the chromatograph and, after a certain pre-determined time, 0.4 μ l of distilled water was injected. If the water was injected 29 sec prior to the retention time of the sulfur compound peak, the elution times of both peak maxima were the same (Fig. 1a). If this time interval exceeded 29 sec, the sulfur compound eluted only at the tail of the water peak (Fig. 1b).

Fig. 2 shows the quenching effect of water. Under the experimental conditions used, no decrease of the detector response to the sulfur compound occurred in the simultaneous presence of water molecules of the sample chromatographed. The response was the same in both the presence and the absence of water in the majority of cases (Fig. 2a and c). In the case of the sulfur compound eluting at the tail of the water peak (Fig. 2b), *i.e.* at a lower concentration of water vapour in the carrier gas, the detector response sometimes increased by *ca.* 12% for thiophene and *ca.* 25% for butylmercaptan. The reason for this irregular increase was not determined. The effect of water on the response of the phosphorus compounds in the P channel is identical with that of the sulfur compounds in the S channel. The detector noise during water elution remains unchanged (Fig. 2d).

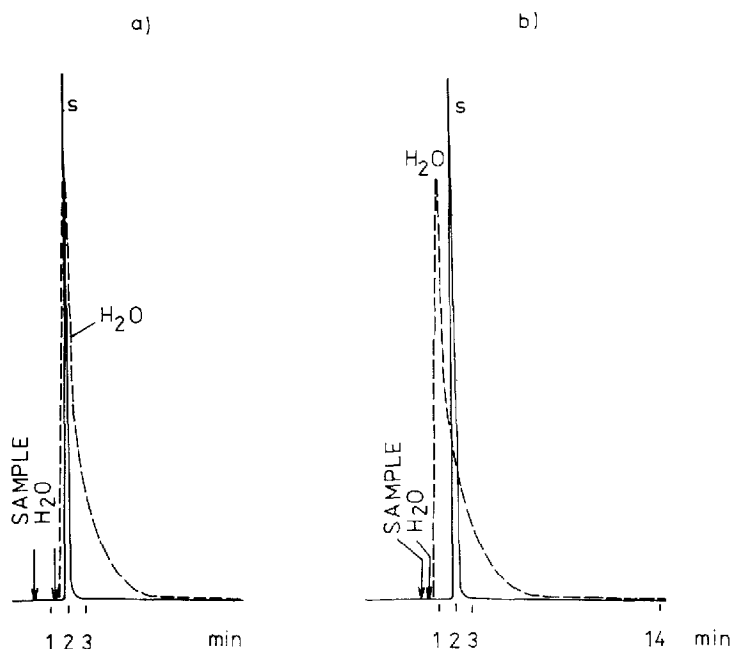


Fig. 1. Schematic representation of the injection of water and a solution of sulfur compounds. (—) sulfur compounds, measured by means of a flame photometric detector; (-----) water, measured by means of a catharometer.

The effect of quenching on n

In the expression for the dependence of the response R of the flame photometric detector on the amount of sulfur compound present $R = k[S]^n$, the value of the exponent n depends on the gas flow-rates^{11,12}, on the structure of the compound^{11,13}, and on the detector temperature⁹. Table II lists the results of measuring the effect of emission quenching on n ; these show that under various experimental

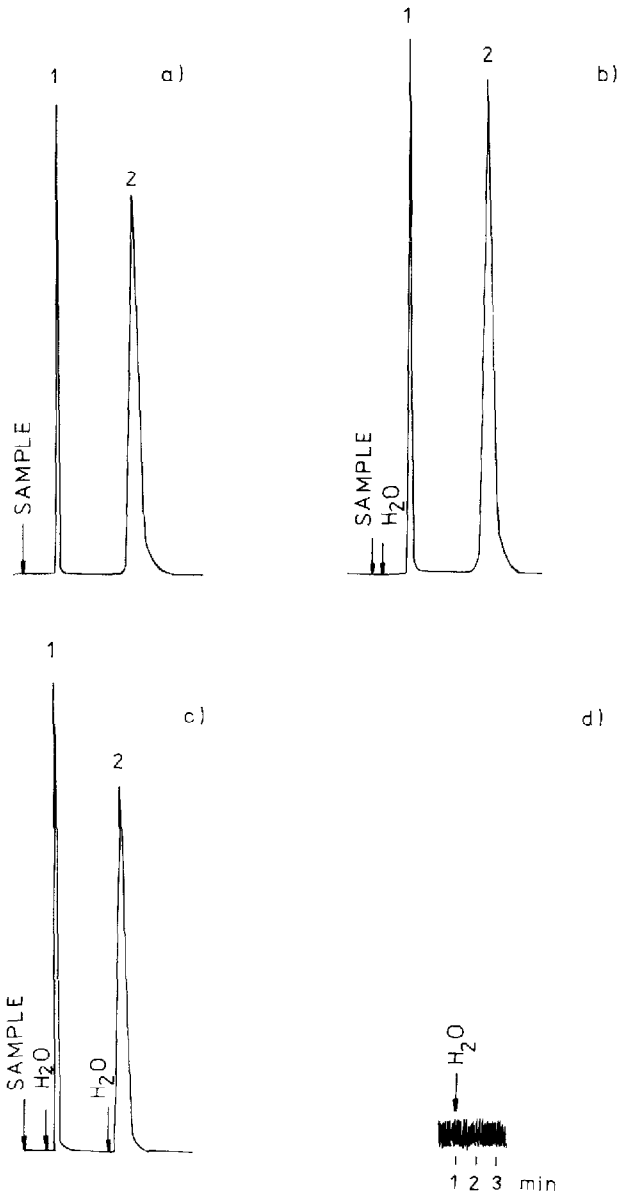


Fig. 2. Effect of water on flame photometric detector response. 1 = Thiophene; 2 = butanethiol. In (a) and (c) water was injected 29 sec prior to the sulfur compound.

TABLE II

EFFECT OF QUENCHING ON THE n VALUE OF THIOPHENE

(a) Flow-rates: air, 72 ml/min; hydrogen, 60 ml/min; cyclohexane at peak maximum, $7.78 \cdot 10^{-7}$ g/sec. Temperatures: detector, 90°C; column, 85°C.

(b) Flow-rates: air, 76 ml/min; hydrogen, 60 ml/min; methane, $5.97 \cdot 10^{-6}$ g/sec. Temperatures: detector, 130°C; column, 124°C.

Hydrocarbon added	n	Experimental conditions
—	2.06	<i>a</i>
Cyclohexane	2.04	
—	1.90	<i>b</i>
Methane	1.86	

conditions the value of n for thiophene remains the same, within the error range, in the following two cases: when methane is added to the carrier gas and also during the simultaneous elution with cyclohexane. The value of n for thiophene behaves in a similar way during simultaneous elution with water.

The effect of the stationary phase background

Maruyama and Kakemoto⁶ reported that the temperature of the chromatographic column does not affect the level of the detector response. With OV-1 or PEG 20 M stationary phases, the detector response to sulfur compounds, expressed by the

value of $\sqrt{H} \cdot w$ (H = peak height, w = peak width at half peak height; exponent $n = 2$), was constant in the temperature range from 60 to 220°C.

The temperature effect of the chromatographic column on the level of the LFD-15 response was examined for thiophene at column temperatures of 60 and 130°C (the detector temperature was maintained at 130°C). The experimentally determined exponent n is 1.97. The c_{130}/c_{60} concentration ratio of the substance in the peak maximum at temperatures of 60 and 130°C should be proportional to the w_{60}/w_{130} peak width ratio — 9.9 mm/3.8 mm in the case examined, *i.e.* 2.605. Thus, the thiophene peak height at a column temperature of 130°C is expected to equal 133.5 mm (peak height at 60°C) multiplied by 2.605 ^{n} , which gives 880.3 mm. However, this peak height is actually only 585.6 mm, *i.e.* it is smaller by 33.5%.

It is known that quenching of the flame photometric detector response begins only when the quencher reaches a certain concentration³⁻⁷. For the type LFD-51 detector employed, the quenching effect amounts¹⁴ to 22% with a cyclohexane mass flow-rate of $2.58 \cdot 10^{-8}$ g/sec, *i.e.* $4.3 \cdot 10^{-9}$ of effective carbon atom per second, while the quenching effect is not measurable with a cyclohexane flow-rate of $7.54 \cdot 10^{-9}$ g/sec ($1.26 \cdot 10^{-9}$ gC_{eff}/sec). If the mass flow-rate of the molecules of the stationary phase due to vaporization of the phase at the given column temperature were above *ca.* $1.5 \cdot 10^{-9}$ gC_{eff}/sec, then quenching could be brought about by the stationary phase. The background current of the SE-30 stationary phase used at a column temperature of 130°C measured by means of a flame ionization detector is $3.04 \cdot 10^4$ mm. The cyclohexane mass flow-rate in the peak maximum of $5.6 \cdot 10^{-8}$ g/sec ($9.3 \cdot 10^{-9}$ gC_{eff}/sec) gives a peak height of $1.49 \cdot 10^5$ mm. Thus, the stationary phase background at 130°C corresponds to a flow rate of $1.14 \cdot 10^{-8}$ g of cyclohexane per second,

i.e. $1.19 \cdot 10^{-9}$ gC_{eff}/sec. The mass flow-rate of the stationary phase molecules, at a column temperature of 130°C, is already in a region where it could cause response quenching.

The gas flow-rates and the detector temperatures are the same for both column temperatures. The calculation of the mass flow-rate of the stationary phase molecules, expressed in grams of effective carbon atoms per second, is not accurate because of the differences in the effective carbon atoms in the cyclohexane molecule and in the molecule of the stationary phase. The estimated flow-rate (with respect to the signal of the effective carbon atom in the cyclohexane molecule), however, occurs in a region where the quenching effect can already appear. The lower thiophene peak height at a column temperature of 130°C can be attributed to the quenching effect of the stationary phase molecules.

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