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A DUAL-CHANNEL FLAME PHOTOMETRIC DETECTOR WITH A SEPARATE COMBUSTION CHAMBER*

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SUMMARY

A new version of the dual-channel flame photometric detector is described for compounds containing phosphorus and sulphur. The sample is mixed with hydrogen before introduction into the detector. The burner is formed as a specific combustion chamber, which is separated from the emission chamber of the detector. Interference signals in the P-channel, caused by sulphur-containing compounds (crosstalk signals) are damped electrically. Thus the selectivity to hydrocarbons is increased by a factor of up to 10^7 , crosstalk signals are reduced by a factor of 10^3 and flame stability is guaranteed (there are no flame-outs caused by amounts of up to $50 \mu\text{l}$ of liquid samples).

INTRODUCTION

In spite of the good technical characteristics of the flame photometric detectors (FPD) for detecting compounds containing phosphorus and sulphur, there are some specific limitations which are typical particularly of the classical Brody-Chaney FPD¹. These are: (1) the flame is extinguished by small amounts of liquid samples (even less than $1 \mu\text{l}$)^{2,3}; (2) the optimum flow-rates of feed gases are different for detecting phosphorus- and sulphur-containing compounds^{4–6} the sensitivity of the S-channel increases when the hydrogen flow-rate is reduced until the flame becomes extremely unstable^{5,7,8}); (3) sulphur produces interference (crosstalk)** signals on the P-channel at a relatively high level; the crosstalk factor is *ca.* $3 \cdot 10^{-2}$ (refs. 9–12); (4) the sensitivity of both channels decreases if amounts of more than 10^{-7} g/sec of hydrocarbons are present (the “quenching effect”)^{8,11,13,14}.

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** The penetration of signal transmission from one channel to another, and the resulting confusion of information.

EXPERIMENTAL AND RESULTS

Experiments have shown^{3,15} that when the effluent is passed to the detector by means of the hydrogen line, and not by means of the oxidant line, the dose of liquid sample may be increased by up to 50 μl or more without damaging the flame. Such quantities of sample overcome the capabilities of analytical columns and injectors. Thus, solvent-venting devices or automatic igniters, used in the classical version of FPD¹⁶, are not needed. Moreover, mixing the column effluent with hydrogen enables some methods of eliminating the quenching effect to be used, *e.g.*, the oxidation¹³ or hydrogenation⁸ of the sample before its introduction by the hydrogen line.

A new version of the dual-channel FPD has been designed in which the sample is mixed with hydrogen before its introduction into the detector and where the burner is formed as a specific autonomous combustion chamber, separated from the emission chamber of the detector (Fig. 1). The column effluent mixed with hydrogen is fed into the combustion chamber (1) via the channel (2). In the side wall of the combustion chamber there are orifices (3) for introducing the oxidant (air or oxygen) mixed with an inert gas (nitrogen, helium or argon).

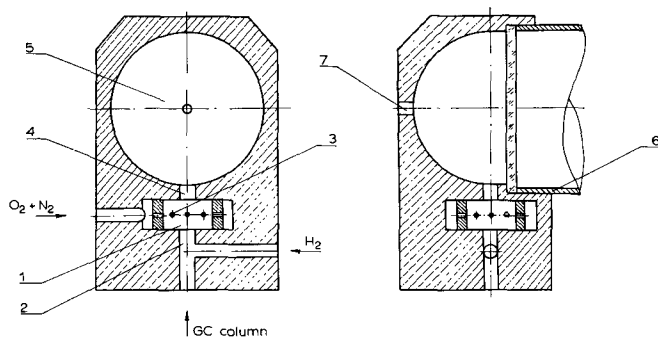


Fig. 1. The FPD with the separate combustion chamber: 1 = combustion chamber; 2 = effluent and hydrogen conduit; 3 = oxidant and gas inlet orifices; 4 = evacuation channel; 5 = emission chamber; 6 = light conductor; 7 = exhaust.

In the hydrogen-rich medium of the combustion chamber at each oxidant inlet orifice (3) a homogeneous flame is formed. In the burning zone, the phosphorus- and sulphur-containing molecules are decomposed, and the excited molecules are formed¹⁷ during various reaction stages. The reacting substances are blown by the flow of gases from the combustion chamber via channel (4) into the emission chamber (5) where the excited molecules HPO^* and S_2^* emit light energy corresponding to their molecular emission bands. The inert gas added to the oxidant is used to speed up the evacuation of the reacting substances from the combustion chamber.

The emission chamber is connected to a dual-channel photometric block (not shown in Fig. 1) by means of the light conductor (6). The reaction products are blown out via the channel (7). Since the FPD must be fed from several gas sources, there is the problem of the dependence of the detector sensitivity on changes in the gas flow-rates. Fig. 2 shows how the relative sensitivity of the described detector depends on the gas flow-rates. Unlike the classical version of detector, our version gives broad maxima for each feed gas.

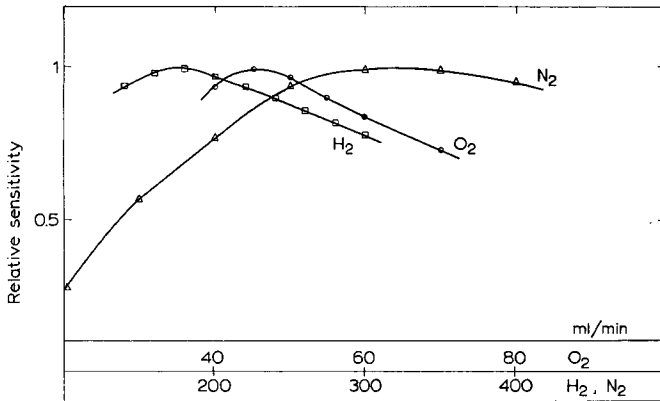


Fig. 2. Dependence of the relative sensitivity on the gas flow-rates: combustion gas, hydrogen; oxidant, oxygen; speeding-up gas, nitrogen.

Of particular importance is the fact that the optimum flow-rates for phosphorus- and sulphur-containing compounds are equal. Consequently, optimum flow-rates can be determined, and minimal changes in gas flows do not cause any changes in sensitivity. This enables the crosstalk problems in the two-channel version to be solved by electrical compensation (Fig. 3). The detector (1), with the separate combustion chamber, is connected to the photometric block (2) by the light conductor (3). In the photometric block there are a light divider (4), interference filters (5) and photomultipliers (6). Output signals from the photomultipliers are amplified by electrometric amplifiers (7). Crosstalk in the P-channel is damped as follows. The output signal of the S-channel amplifier is processed by means of the signal divider (8) to give a value corresponding to the crosstalk factor which is then passed to the separating network (9) on the output of the P-channel amplifier. The network (9) separates the crosstalk from the P-signal and thus only the pure P-signal is recorded by the recorder 10P. The interference in the S-channel caused by phosphorus-containing compounds is negligible with a crosstalk factor of $ca. 10^{-3}$ (ref. 9) and no

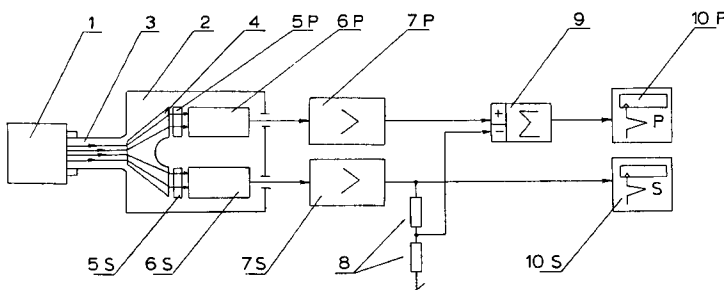


Fig. 3. Dual-channel FPD system with the S-interference compensator: 1 = FPD; 2 = dual-channel photometric block; 3 = light conductor; 4 = light divider; 5 = interference filters; 6 = photomultipliers; 7 = electrometric amplifiers; 8 = signal divider; 9 = separating network; 10 = recorders.

damping is needed. The S-signal from the output of the amplifier 7S is recorded directly by the recorder 10S.

Fig. 4 demonstrates the action of the compensator. Chromatograms of two pesticides, dimethoate and prometryne, were recorded with the compensator in the modes "on" and "off". Prometryne does not contain phosphorus. In the first chromatogram (with the compensator "off") prometryne is detected on the P-channel as a result of crosstalk. The second chromatogram is run with the compensator "on" and no prometryne is observed.

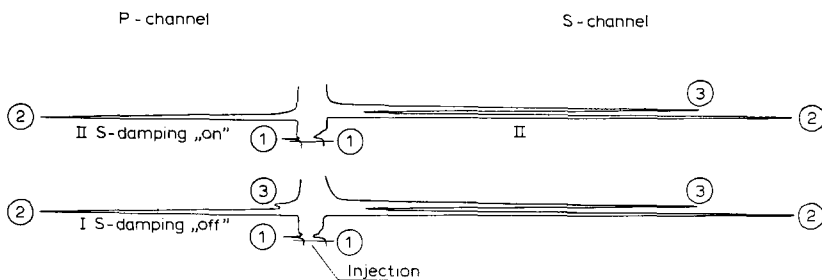


Fig. 4. Arrangement of the compensator for pesticide analysis. I = Chromatograms with S-damping "off"; II = chromatograms with S-damping "on". Peaks: 1 = solvent ($8 \mu\text{l}$ of ethanol); 2 = dimethoate ($3.2 \cdot 10^{-7}$ g); 3 = prometryne ($3 \cdot 10^{-7}$ g). The complete absence of peak 3 in the P-channel chromatogram II is to be noted.

The limits of detection, dynamic range and calibration graphs for the above detector are generally the same as those for the classical version of FPD⁹, but the selectivity factor to hydrocarbons and to alcohols reaches 10^7 . In Fig. 5 are shown P- and S-channel chromatograms of some pesticides (each of *ca.* 0.01% in ethanol). Approximate calculations on the basis of these two chromatograms show that the detector is 10^7 times more sensitive to the phosphorus- and sulphur-containing pesticides than to ethanol.

The extraordinary high selectivity to hydrocarbons enables the quenching effect to be used for the qualitative detection of hydrocarbons, alcohols, etc. which are used as solvents. For this purpose a constant background of the element (P or S) must be generated by mixing, for example, sulphur dioxide with air in the air-flow line or by use of permeation tubes^{18,19}. The recommended background value is 5–20 times the noise level. Owing to the quenching effect, the hydrocarbons are detected as negative peaks in the constant background current. The detection level for such a mode is *ca.* 10^{-7} g/sec. In Fig. 6 a chromatogram is shown of the injection of $0.02 \mu\text{l}$ of *n*-nonane containing 0.05% of allyl sulphide using the constant-background mode. Of course, when the dose of hydrocarbons is increased greatly, the peaks will be distorted.

CONCLUSIONS

The FPD with the separate combustion chamber is a reliable detector for phosphorus- and sulphur-containing compounds. The advantages of this detector

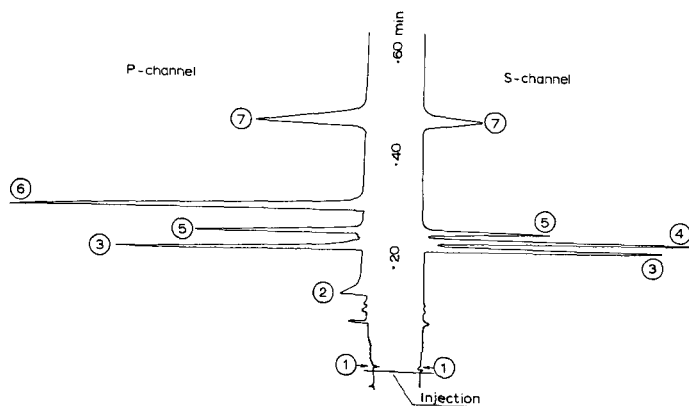


Fig. 5. Pesticide standard analysis. The chromatograms were run with S-damping "on". Peaks: 1 = ethanol ($2.6 \mu\text{l}$); 2 = dylox ($1.03 \cdot 10^{-7} \text{ g}/\mu\text{l}$); 3 = dimethoate ($6.6 \times 10^{-8} \text{ g}/\mu\text{l}$); 4 = prometryne ($1.25 \cdot 10^{-7} \text{ g}/\mu\text{l}$); 5 = malathion ($6.71 \cdot 10^{-8} \text{ g}/\mu\text{l}$); 6 = gardona ($2.26 \cdot 10^{-7} \text{ g}/\mu\text{l}$); 7 = phosalone ($6.70 \cdot 10^{-8} \text{ g}/\mu\text{l}$). Glass column ($2 \text{ m} \times 4 \text{ mm I.D.}$), packed with 3% OV-17 on Chromosorb W AW-DMCS (80–100 mesh). Temperatures: column programmed at 80 to 210° at $12^\circ/\text{min}$ and then from 210 to 240° at $2^\circ/\text{min}$; detector, 250° ; injector, 250° . Carrier gas (nitrogen) flow-rate, $70 \text{ ml}/\text{min}$. Attenuation, $1/10$ in both channels.

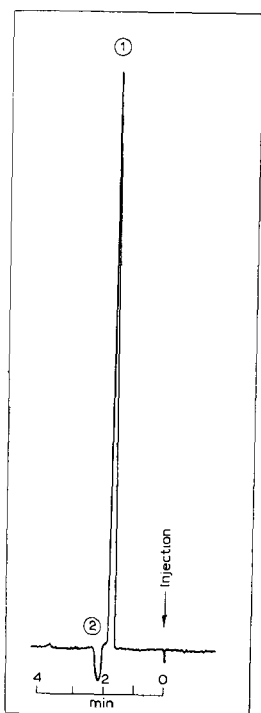


Fig. 6. Analysis with the FPD in the constant-background mode, S-channel chromatogram. Peaks: 1 = allyl sulphide (1 ng); 2 = *n*-nonane ($0.02 \mu\text{l}$).

are: the extremely high selectivity to hydrocarbons, the very stable flame and the equal optimum flow-rates of feed gases for the P- and S-modes. The high selectivity to hydrocarbons enables the detector to be used in the constant-background mode for the detection of hydrocarbons, alcohols, etc. The stable flame permits the dose of liquid sample to be increased to 50 μl . Equal gas flow-rates ensure the stability of the maximum sensitivity of both channels in the dual-channel version of the detector, and it is possible to eliminate the crosstalk by electrical compensation.

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