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DESIGN OF AN UNEXTINGUISHABLE FLAME PHOTOMETRIC DETECTOR AND ITS MEASUREMENT PROPERTIES

STEFAN HASINSKI

Research and Development Centre of Measurement and Electronic Automation, Mera-Elmat, Wroclaw (Poland)

SUMMARY

The construction of a dual flame photometric detector (FPD) is described. The new design of the body of the detector, which comprises the luminescence and burner parts, separated from each other by a thermal insulation plate, enables easy changes in the geometric arrangement of the system which is responsible for such parameters as signal-to-noise ratio, background noise (flame on) and detector sensitivity to carbon compounds. The contruction also allows independent thermal control of both parts of the detector, which is important regarding the possibilities of limiting and maintaining the dark current of the photomultipliers at a constant level.

The flame is not extinguished by solvent peak volumes of up to 30 μl over a wide range of air and hydrogen flow-rates (at a 1:1 ratio). The measurement properties of the new FPD in chromatographic and non-chromatographic systems are described.

INTRODUCTION

Flame photometric detectors (FPD) belong to the group of chromatographic detectors which have recently become a centre of interest to analysts and manufacturers of chromatographic equipment.

Since Brody and Chaney's contribution[1] concerning the construction and properties of such a detector, an increasing number of new applications and constructions have been described. However, the measurement properties of FDPs are not yet as well recognized as those of other chromatographic detectors, and thus much caution is required in the interpretation of results obtained. The commonly known drawbacks of FPD are:

(1) Extinguishing of the flame in some types of burner constructions at the moment of solvent peak elution. Relighting the flame causes disturbances in the baseline, and it is possible that components with short retention times may not be recorded. Automatic relighting of the flame appears to be only a partial solution, because only the manual operations are eliminated and not the interruption in the recording of the chromatogram.

(2) Drifting of the baseline due to thermal instability of the photomultipliers.

(3) Damping of luminescence by the presence of other compounds, e.g., hydrocarbons[2-4]. This effect may lead to a partial or even entire loss of the essential feature of a detector, i.e., its specificity.

(4) There is considerable controversy about the dynamic range of the detector for sulphur compounds; this problem will also be discussed in this paper.

Some of the above drawbacks may be eliminated by suitable mechanical and geometrical design of the detector.

EXPERIMENTAL

As a result of the requirements discussed above we have designed a detector which is shown schematically in Fig. 1.
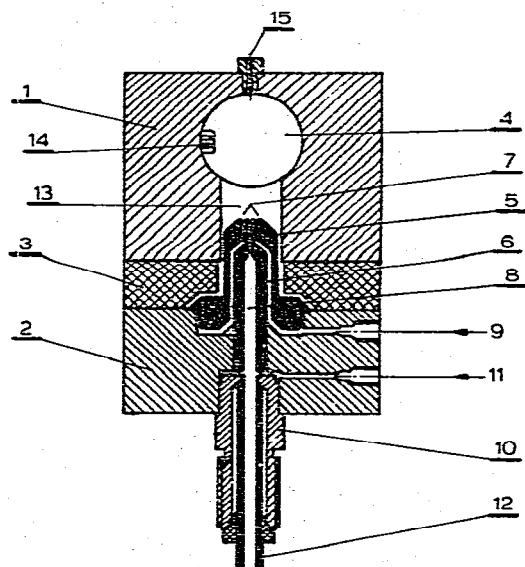

Fig. 1. Schematic view of the FPD construction. 1 = Luminescence part; 2 = burner part; 3 = plate of thermal insulator; 4 = luminescence-chamber; 5 = external cylinder; 6 = internal nozzle; 7 = gap; 8 = mixing chamber; 9 = air inlet; 10 = column joints; 11 = hydrogen inlet; 12 = column; 13 = burner cavity; 14 = ignition; 15 = exhaust of gases.

The detector body is divided into luminescence (1) and burner (2) parts, separated from each other by a thermal insulation plate (3). The thickness of the plate determines the distance between the burner outlet and the lower edge of the luminescence chamber (4). Owing to the easy exchange of the insulator, the geometrical arrangement of the system which is responsible for such measurement parameters as signal-to-noise ratio, background current (flame on), and detector sensivity to carbon compounds containing no sulphur or phosphorus (P/C and S/C specificity), may be varied. Thermal separation of the luminescence chamber to which the photomultipliers are connected allows it to be maintained at a constant temperature, independent

of the variable temperature of the burner. Thus the temperature of the luminiscence chamber is controlled independently and is kept at a constant value of 100° to prevent water vapour condensation. With such a construction, the cooling of the photomultiplier housing, by means of complicated electronic systems or by cooling media, appears to be quite unnecessary. An air radiator with a double layer of thermal insulation in the multiplier housing (not shown in Fig. 1) makes it possible to stabilize the temperature of the interference filters and the head of the photomultiplier at 35°, independent of the necessary changes of temperature of the burner part, which may be varied from 40 to 250° by an independent thermal controller. Under these conditions the dark current and drift are at a low level and are only slightly dependent on variations in the environmental temperature.

The burner part (2) of the detector body comprises the burner itself, the joints of the glass column and the gas inlets. The burner is formed as a nozzle (6), being an extension of the chromatographic column (12) and surrounded by an external cylinder (5) concentric to the nozzle. The gap formed between the top of the cylinder (5) and the outlet of the nozzle (6) is 0.2 mm wide (2.5 mm O.D.) and a crown-like flame is produced to here. Air supplied through the inlet (9) flows around the internal nozzle and hits the gap. Hydrogen is fed through the inlet (11) and meets the carrier gas at the outlet of the chromatographic column. Thus a mixture of the carrier gas and hydrogen reaches the outlet of the internal nozzle at the gap.

For air and hydrogen flow-rates of 100–250 ml/min (1:1) solvent volumes of up to 30 μl do not extinguish the flame. A different hydrogen-to-air ratio can be used provided the condition of stoichiometric excess of hydrogen is fulfilled. The volume of solvent not extinguishing the flame may then be lowered or raised.

Any gas, including hydrogen, may be used as carrier gas. If the total amount of hydrogen required can be supplied through the chromatographic column as the carrier gas, the hydrogen inlet (11) is closed. The required amount of hydrogen may also be divided in any ratio between the column (carrier gas) and the inlet (11) (make-up line). If gases other than hydrogen are used as carrier gas in the chromatographic separation, the total amount of hydrogen required is supplied through the inlet (11).

The FDP described above has been installed on the head of a gas chromatograph using the following equipment: a Model N-503 gas chromatograph (Mera-Elmat); a Model P-704 electrometer (Mera-Elmat); a Model M-159 recorder (Hitachi-Perkin-Elmer); a Model D-24 integrator (Perkin-Elmer); interference filters (Carl Zeiss Jena) $\varnothing$ 50 JP525 ($\lambda_{max.}$ = 522 nm, $T_{max.}$ = 34%) and $\varnothing$ 50 JP400 ($\lambda_{max.}$ = 402 nm, $T_{max.}$ = 47%); Model M10FQS29 photomultipliers (Carl Zeiss Jena, polarized with 700 V.

A similar detector was installed in a monoparametric, total sulphur analyser, Model Mera-Elmat. In this case a Carl Zeiss Model S12FS35 photomultiplier was used, polarized with 850 V, as well as the interference filters described above.

Slightly porous tubes filled with liquid SO_2 were used as the SO_2 source in the preparation of the standard mixtures of SO_2 and n-butane using a 5% precision analytical calibrator (Mera-Elmat).

RESULTS AND DISCUSSION

The detector is characterized by its variable geometry. A change in the thick-

ness of the thermal insulator lowers or raises the burner in the cavity, thus changing the parameters of the detector mentioned above. The flame is not extinguished over a wide range of hydrogen- and air-flow intensities. Since the measurement parameters of the detector are dependent on the ratio and flow-rates of hydrogen and air and also on the possible change of detector geometry, a wide range of these values may be selected according to one's own requirements and needs.

Parameters in the phosphorus mode

Noise level (flame on). 10^{-12}A, at a distance of 7 mm between the top of the burner and the lower edge of the luminescence chamber, and flow-rates of 200 ml/min H_2 and 200 ml/min air.

Detection limit. 10^{-12} g/sec for trimethyl phosphate. The detection limit may be lowered to the value of 10^{-13} g/sec by changing the type of photomultiplier, increasing the feed voltage, using an interference filter with greater T-value and optimizing the geometry in relation to the flow-rates of the gases.

Specificity P/C. 10^5, may be increased by a change in geometry and gas flow-rates.

Specificity P/S. 7–25. The specificity depends on the ratio of the masses, P/S.

Base-line drift. 1% per h at constant ambient temperature and with an electrometer sensitivity of 10^{-9} a.f.s. Under these conditions no baseline noise is observed.

Linear dynamic range. 10^4, *i.e.* from 10 pg to 200 ng for trimethyl phosphate.

Parameters in the sulphur mode

Some general remarks should be made before discussing FPD parameters when working in this mode. Results published to date are insufficient, and sometimes even contradictory, in their description of detector characteristics. In various cases the detector response has been described as exponential[1], as following a square law[4], or else as linear[5]. The frequently employed term "approximately" seems to be appropriate to the difficulties of measurements occurring during the determination of detector characteristics in the sulphur mode. An interesting discussion concerning the differences between linear and square-law detection has been given by Moss[4]. He finds that a square-law detection in which the response is proportional to the square of concentration is an uncommon phenomenon and as a result is not well understood. He finds the exponent to be between 1.5 and 2. An important contribution to avoid measuring errors is also pointing to the fact that, for above-mentioned characteristics, the area of elution band recorded is dependent on retention time[4].

It is my opinion that contradictory descriptions of the detector characteristics have been based on certain misconceptions:

(a) When an FPD is used for analysis of sulphur compounds in a chromatographic system, the results are interpreted either in the relationship current–mass (measured by the peak height) or in the relationship charge–mass (measured by the peak area). In this case the shape of the eluted peak exerts a decisive influence on the detector characteristic, which may be considered as square-law-like.

(b) When the detector is used without a chromatographic column, *e.g.*, in total sulphur analyses, the results are interpreted in the relationship current–concentration. In this case, a predominant influence on the detector characteristic is exerted by the mass of the sample passing through the detector per unit time. Thus the detector

characteristics may be considered as linear over a strictly determined range of concentrations.

Both of these cases have been investigated in the present study.

(a) FPD parameters in a chromatographic system: S mode. Assuming as a criterion the peak height, a twofold increase of injected sample resulted "approximately" in a fourfold increase in peak height. This ratio (4:2) has been maintained for dimethyl sulphoxide but not for lauryl mercaptan, for which at the detection limit level considerably lower values (3:2) were obtained. The measurements of the peak areas (for sharp peaks) by means of an integrator confirmed the fourfold increase of peak area resulting from a twofold increase of injected sample. The results of these determinations are shown in Fig. 2.
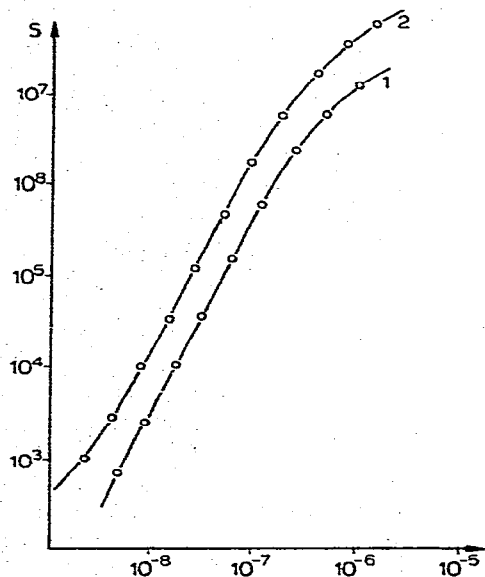

Fig. 2. Calibration curves for the FPD in the sulphur mode. 1 = Lauryl mercaptan; 2 = dimethyl sulphoxide. Column, 1 m × 4 mm I.D., 5% Triton on Chromosorb W, 30–60 mesh; carrier gas (H_2) flow rate, 60 ml/min.

A straight line is obtained in the range of two orders of mass if the results are plotted on a log-log system (the values of the integrator bits are plotted on the y axis).

The other detector parameters in the chromatographic mode are as follows: noise level —10^{-11} A, flow-rates as for the P mode; detection limit —10^{-11} g/sec for dimethyl sulphoxide; specificity S/C —10^5; specificity S/P —350–1000, dependent on the ratio of the masses, S/P.

(b) FPD parameters in a non-chromatographic system: S mode

A standard mixture of SO_2 in air was sucked through the detector at a rate of 115 ml/min by means of an ejector pump at the detector exhaust outlet. The flow lines for the gas mixture were made of PTFE. The exhaust gases from the detector
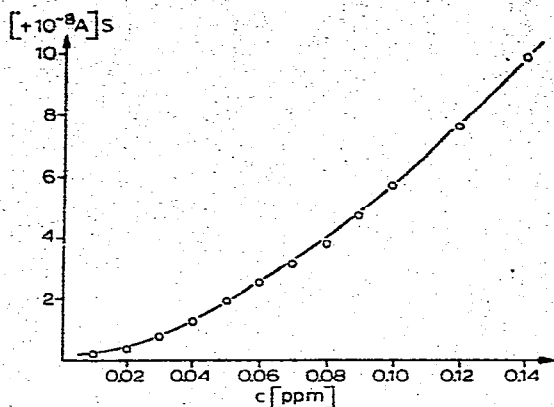
Fig. 3. Characteristics of the FPD working without a GC column in the concentration range 0.01–0.15 ppm SO_2.

were diluted with air above dew point. The hydrogen flow-rate was fixed at 120 ml/min. The measurements of SO_2 concentration in air were determined in the range 0.01–1.1 ppm. From a trial run it appeared advisable, with this detector, to divide the range into two subranges, 0.01–0.15 and 0.20–1.1 ppm. The results of the measurements are shown in Figs. 3 and 4.
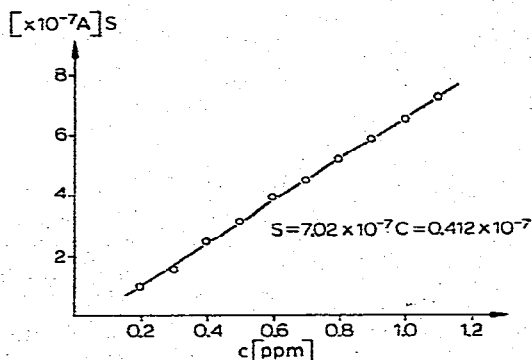

$$S = 7.02 \times 10^{-7} C = 0.412 \times 10^{-7}$$

Fig. 4. Characteristics of the FPD working without a GC column in the concentration range 0.2–1.1 ppm SO_2.

It was found that the function was not linear in the concentration range 0.01–0.15 ppm, but that it was linear in the range 0.20–1.1 ppm. Thus, in the latter range there is agreement with published results[5]. At concentrations above 1.1 ppm the function loses its linearity.

The noise level under the described conditions is of the order of 10^{-11} A. At an electrometer sensitivity of $1 \cdot 10^{-9}$ a.f.s. the detector signal for a 0.01 ppm concentration is more than 80 times higher than the noise level. This corresponds approximately to a detection limit of 1 pg/sec.

Damping of the luminescence signal by hydrocarbons

The detector system, working without a chromatographic column, creates the most favourable conditions for measurement of the damping effect. Butane is added to the standard mixture of 0.5 ppm SO_2 in air. A 150 ppm butane concentration caused a 50% damping of the SO_2 signal, while a 50 ppm butane concentration caused 25% damping. At butane concentrations below 10 ppm, the damping effect was within the limits of analytical error. It was subsequently found that not only hydrocarbons but carbon-containing compounds in general are responsible for the damping effect. The effect can be reduced by increasing the hydrogen and air flow-rates for as long at the dark current value can be kept sufficiently low.

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