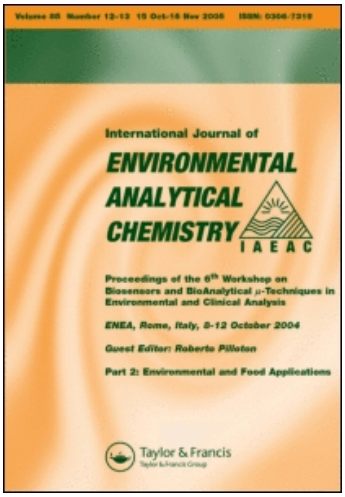


International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

# The Application of a Flame Photometric Detector in Packed Microcapillary Liquid Chromatography: Detection of Organophosphates

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**To cite this Article** Kientz, Charles E. and Verweij, Albert(1987) 'The Application of a Flame Photometric Detector in Packed Microcapillary Liquid Chromatography: Detection of Organophosphates', International Journal of Environmental Analytical Chemistry, 30: 4, 255 — 263
**To link to this Article: DOI:** 10.1080/03067318708075474
**URL:** http://dx.doi.org/10.1080/03067318708075474

*Intern. J. Environ. Anal. Chem.*, 1987, Vol. 30, pp. 255–263
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Printed in Great Britain

# The Application of a Flame Photometric Detector in Packed Microcapillary Liquid Chromatography: Detection of Organophosphates

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(*Received November 19, 1986; in final form January 12, 1987*)



A commercially available flame photometric detector (FPD) designed for gas chromatography has been investigated for its applicability in microcolumn liquid chromatography. The column effluent is evaporated and subsequently introduced into the detector using a home-made interface. The influence of the mode of effluent introduction into the flame, and the composition and flow rates of the flame gases and eluent on the detector performance are discussed.

KEY WORDS: Micro HPLC, organophosphates, flame photometric detector.

## INTRODUCTION

The development of miniaturized HPLC has allowed the direct introduction of the entire liquid effluent into gas chromatographic detectors, which has led to the successful implementation of phosphorus-sensitive detectors in small bore HPLC. Among these detectors, the thermionic detector (TID) recently received considerable attention. Basic research in this field was done[1–4] using packed microcapillary columns coupled via a nebulization interface introducing the effluent directly into a dual-flame TID. A different

approach was made[5–7] using narrow-bore columns and an interface to vaporize the LC effluent before entering the single flame TID.

However, the use of a flame photometric detector (FPD) in microcolumn liquid chromatography has been described only in few papers. A miniaturized FPD was described by McGuffin *et al*[8] who was able to detect 2 ng of phosphorus by means of direct introduction of the column effluent into the flame. At the tenth International Symposium on Column Liquid Chromatography in San Francisco (1986) the Varian Instrumentation Group presented a dual flame micronebulizer-FPD as an HPLC detector.[9] In our laboratory we are dealing with the analysis of polar, acidic and other high-boiling phosphorus containing compounds. Generally, HPLC-UV detection and GC analysis are not suitable for such compounds. Therefore we are investigating the possibility of coupling packed capillary fused silica columns to a commercially available FPD detector to determine phosphorus directly in the HPLC effluent. Some preliminary results are given in this paper.



## EXPERIMENTAL

### Instrumentation

The system was assembled from a Shimadzu LC-5A pump, a Valco sample valve with 60 nl internal volume and a Tracor FPD 100 AT. The fused silica capillaries were packed with Lichrosorb RP 18 particles (10 $\mu$m) according to the procedure of Gluckman *et al.*[10] The inlet side of the capillary column was directly connected to the injector using a finger-tightened PTFE ferrule and nut (Hibar, Merck, F.R.G.). The column performance was tested separately using a home-made 40 nl micro flow UV-cell.[11]

### Materials

The solvents were of HPLC-grade quality supplied by Merck (Darmstadt, F.R.G.). Trimethyl phosphate (TMP, b.p. 197°C; Merck, Darmstadt, F.R.G.), triethyl phosphate (TEP, b.p. 215°C; BDH Ltd, Poole, England), tributyl phosphate (TBP, b.p. 289°C; UCB, Brussels, Belgium) and triphenyl phosphate (TPP, b.p. 245°C 11 mm Hg; Aldrich Europe, Beerse, Belgium) were of analytical grade. The adhesives used were epoxy glue (UHU, Linger + Fischer GmbH) and Silcoset 151 (Ambersil Ltd, England).

## Construction of the interface

The design of the interface between the LC fused silica capillary column and the FPD detector is shown in Figure 1. The packing at the end of the column was confined by a porous Teflon frit 0.2 mm secured by two internally close-fitting fused silica capillaries.[11]

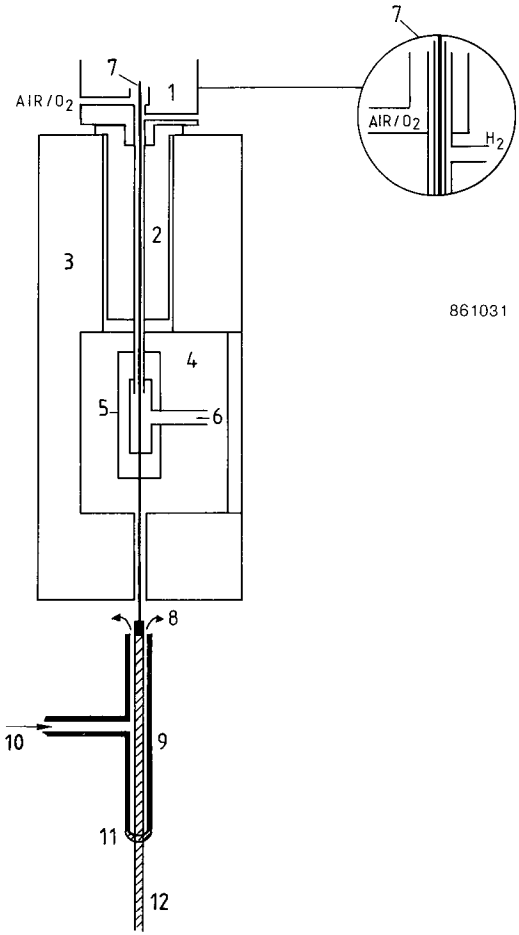


**Figure 1** Column-detector interface. 1 = burner base, 2 = aluminium cylinder (length 80 mm), 3 = detector oven body, 4 = detector oven, 5 = T-piece, 6 = nitrogen purge, 7 = tip of flame base with fused silica capillaries (0.32 mm I.D., 0.1 mm I.D.), 8 = end of 12, 9 = cooling device (GC-splitter), 10 = air cooling, 11 = Silcoset adhesive, 12 = packed capillary column.

The column [12] is fixed with Silcoset 151 adhesive [11] in a cooling device derived from an original GC-splitter. The purpose of the cooling device is to prevent too premature an evaporation of the effluent outside the hot detector oven body [3] due to heat radiation. The column end [8] is connected to a fused silica capillary (I.D. 0.1 mm) which is inserted through the detector oven [4] and the burner base [1] directly into the flame jet. Besides a nitrogen purge [6] flowing through a fused silica capillary of 0.32 mm I.D. [7] is added by means of a T-piece [5].

## RESULTS AND DISCUSSION



The performance of the micro HPLC-FPD system was investigated by varying parameters such as the adjustment of the effluent into the flame jet, the flame gas and LC eluent flow rates, and the eluent composition. A characteristic chromatogram of a mixture of four organophosphates is shown in Figure 2.

The observed reduced plate height ($h$), peak asymmetry ($A$) and detector sensitivity ($Sm$)[12] of the phosphorus compounds are listed in Table I. Under identical LC conditions using a 40 nl microflow UV cell at 260 nm[11] the reduced plate height of TPP was 7.9. This value corresponds with those of TMP and TEP given in Table I. This may indicate that on application of the micro LC-FPD equipment the increased peak-broadening, peak asymmetry and the detector sensitivity for TBP and TPP are probably due to insufficient evaporation of these relatively high-boiling compounds in the interface used.

**Table I** Micro LC results as presented in Figure 2

| Compound | $h$ | $A$ | $Sm$(ng $P/s$) |
|---|---|---|---|
| 1 TMP | 7.4 | 1.0 | 5.7 |
| 2 TEP | 7.0 | 1.0 | 6.4 |
| 3 TPP | 15.2 | 1.5 | 9.5 |
| 4 TBP | 15.7 | 3.8 | 7.8 |

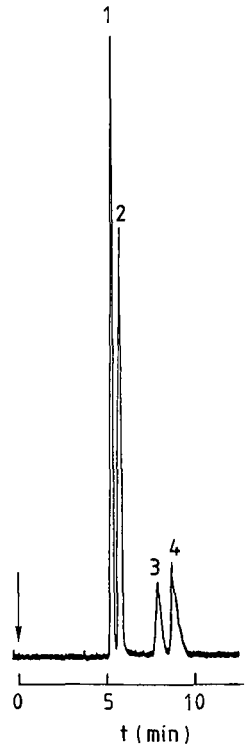


**Figure 2** LC-FPD Chromatogram of a mixture of four organophosphates. Column 500 mm × 0.5 mm × 0.32 mm (L × O.D. × I.D.) packed with Lichrosorb RP 18, 10 μm.; mobile phase acetonitrile/water 9:1; flow 5 μl/min; interface temp. 310°C; air flow rate 250 ml/min; hydrogen flow rate 360 ml/min; oxygen flow rate 5 ml/min.; compounds: 1 = TMP, 2 = TEP, 3 = TPP, 4 = TBP.

## Adjustment of the fused silica capillary into the flame jet

The adjustment of the effluent outlet (Figure 1, item 7) near the flame jet appeared to be very critical as can be seen from Figure 3. Placing the end of the capillary 40–50 mm below the flame tip will be a compromise in the optimization of the different responses.

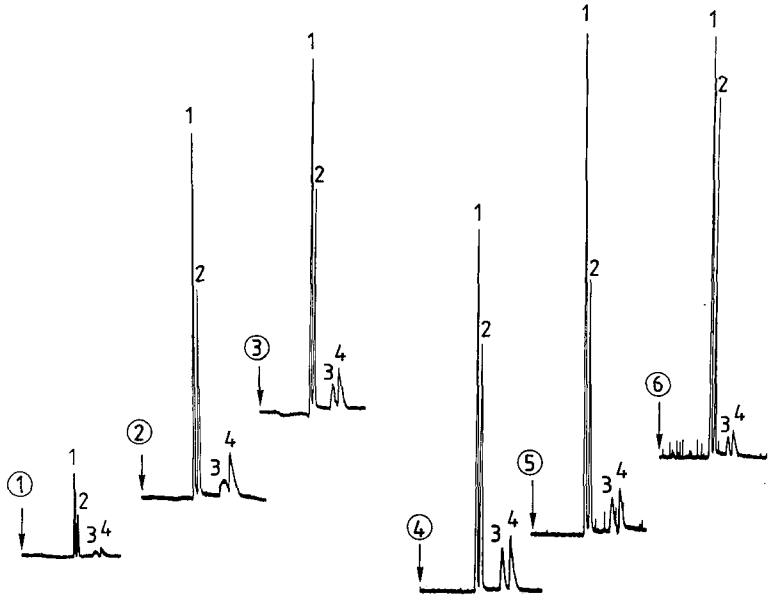


**Figure 3** Influence of column-end positioning on FPD responses. 1 = in the top of the flame jet, 2 = 20 mm, 3 = 30 mm, 4 = 40 mm, 5 = 50 mm, 6 = 60 mm below the flame jet. For other conditions see Figure 2.

## Flame gas flow rates

The performance of the FPD was evaluated varying the hydrogen, air and oxygen flow rates. The influence of different hydrogen flow rates on peak shape and sensitivity of the organophosphates was insignificant. A stable flame was obtained over 170 ml/min, below 170 the flame extinguished. The air flow rate proved to be an important parameter influencing the peak height as presented in Figure 4.

From experiments represented in Figure 4 it can be seen that when the air flow increased the response of TMP (peak 1) improved a factor of 30. When the oxygen flow was subsequently increased to a total hydrogen-to-oxygen ratio of 3.6 the peak height improved additionally a factor of 10. This hydrogen-to-oxygen ratio is in accordance with the optimum value given by McGuffin *et al.*,[8] which is comparable with the value when using this detection system in gas chromatography.

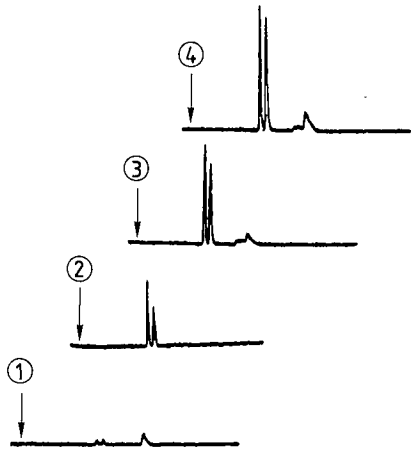


**Figure 4** Influence of air flow rate on detector response. 1 = 110 ml/min, 2 = 140 ml/min, 3 = 175 ml/min, 4 = 215 ml/min (H2/02 ratio is 8.4); hydrogen flow = 360 ml/min; for other conditions see Figure 2.

## Eluent composition

Two eluent compositions were compared: acetonitrile-water and methanol-water, ratio 8:2. Comparable signal-to-noise ratios were obtained on analysing TMP and TEP using both eluent compositions as can be seen from Table II.

**Table II** Influence of eluent composition on signal-to-noise ratio

| Compound | Eluent composition | |
|---|---|---|
| | Acetonitrile/water 8:2 | Methanol/water 8:2 |
| | Signal/noise | Signal/noise |
| TMP | 11 | 13 |
| TEP | 3 | 3 |

In both cases a similar noise level of 1.5% full scale (att. $10^4 \times 2$, recorder 1 mv) was measured at flow rates of 20 $\mu$l/min. Injected amounts 14 $\mu$g TMP and 6 $\mu$g TEP.

The result from Table II differs from those obtained by McGuffin[8] and Chester[13,14] who found increased background noise substituting methanol for acetonitrile even at very low 1–5% concentrations in aqueous mixtures.

## Eluent flow rate

From the detector sensitivity values for TEP given in Table III it can be concluded that the FPD response depends on the eluent flow rate. Additionally, it was found that by decreasing the flow rate an improvement in response could be obtained both for TMP and TEP, whereas TPP and TBP gave poorly shaped peaks. The strong dependence of the FPD response on the flow rate indicates that especially for quantitative purposes a very stable eluent flow will be necessary.



**Table III** Influence of eluent (acetonitrile: water 8:2) flow rate on detector[a] sensitivity (*Sm*) of TEP

| Flow rate (μl/min) | *Sm*(ng *P*/s) |
|---|---|
| 1 | 0.1 |
| 2 | 1.6 |
| 20 | 110.0 |

[a]H2/O2 ratio = 3.6.

## Nitrogen purge

Addition nitrogen purge flow showed an improved peak height and shape of the phosphorus containing compounds.

## EVALUATION

In view of the above-mentioned preliminary and orientating experiments with the micro LC-FPD equipment further investigations will be concentrated on improving the interface to obtain sufficient

evaporation of high-boiling phosphorus-containing compounds and subsequently, efficient introduction into the flame. The distance between column and flame tip, the hydrogen-to-oxygen ratio, the eluent flow rate and nitrogen purge flow rate are important parameters to be studied more thoroughly.

## Acknowledgement

We are indebted to Jan de Bruin for his experimental assistance.

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