Design and optimization of a novel type nitrogen–phosphorus detector for capillary gas chromatography

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Abstract

The design and optimization of a novel type alkali flame ionization detector (AFID) for capillary gas chromatography is presented. The design differs in that the alkali salt is continuously introduced, as a solution in water, into the detector by means of a liquid chromatographic syringe pump. This design permits continuous refreshment of the enhancement source and circumvents the need of source replacement, thereby eliminating detector response fatigue over time.

Modification of an existing nitrogen–phosphorus detector (NPD) to allow direct introduction of the alkali salt into the detector will be described. Next, important operational parameters such as the location of introduction, type and concentration of the salt and the flow of the various detector gasses are optimized experimentally with regard to detector sensitivity, selectivity, minimum detectability and noise level. Moreover the linearity, reproducibility and stability of the detector are evaluated.

It will be shown that the new detector design exhibits excellent response characteristics for phosphorus compounds which are comparable to or better than those observed with commercially available AFIDs or NPDs. Finally, the performance of the detector will be demonstrated by two environmental applications.

Keywords: Nitrogen-phosphorus detection; Detection, GC; Alkali flame ionization detection; Azobenzene; Malathion; Octadecane; Alkali salts

1. Introduction

The nitrogen–phosphorus detector (NPD) is widely applied in capillary gas chromatography for selective detection of samples containing nitrogen and phosphorus compounds. The original design of this type of ionization detector is known as the alkali flame ionization detector (AFID) [1]. With the AFID enhanced response towards various heteroatom containing compounds is obtained by volatilizing an alkali metal salt into a hydrogen/air flame. The main disadvantages of the AFID are its poor stability and

the need for frequent replacement of the enhancement source due to its limited lifetime.

To overcome these drawbacks, many new detector designs have been proposed. An important improvement was reported in 1974 by Kolb and Bisschof [2]. The main difference of this new detector design, compared to the AFID, is the use of a nonvolatile enhancement source, incorporated in an electrically heated glass bead. Moreover, the hydrogen/air chemistry inside the detector differed from that in the AFID. In comparison with the AFID, this detector exhibited a much better stability and improved response characteristics. Moreover, the lifetime of the alkali bead was substantially extended. The Kolb

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and Bisschof design, commonly referred to as the NPD, served as the basic design for the NPDs which are currently applied in contemporary GC practice. Despite its frequent use in GC, there is still no consensus on the exact detection mechanism of the detector [2–8].

Although the current generation of NPD detectors shows good response characteristics, frequent replacement of the alkali metal source is still necessary. After source replacement, time-consuming detector stabilization and optimization is required. This can be disadvantageous in cases were minimal instrument down time is required.

In order to overcome the need for frequent source replacement, and to further improve detector stability and response over time, several approaches have been followed to alter the detector design in a way that continuous refreshment of the alkali source is allowed.

Brazhnikov et al. proposed and evaluated a detector design in which the alkali salt was introduced in the form of an aerosol [9]. The detector design used in this study consisted of a combination of a conventional FID with an alkali metal salt aerosol generator. Conte and Barry elaborated on this setup by presenting a similar design [10]. With both designs the need for source replacement is eliminated. Moreover, these new designs show good response characteristics and stable response. A disadvantage, however, is the complexity of the instrumental setup required.

In the present work an alternative approach for the introduction of the alkali salt is proposed and studied. The alkali salt is dissolved in water and is introduced into the detector sensing volume by means of a liquid chromatographic syringe pump. In this manner continuous refreshment of the enhancement source is allowed, thereby eliminating the need of source replacement. The main aim of the work is to describe the design and optimization of such a detector. First, it will be described how an existing NPD can be modified to allow direct introduction of the alkali salt solution into the detector. Next, important operational parameters such as the location of introduction of the salt, the flows of the various detector gasses and the salt type and concentration are optimized experimentally with regard to detector selectivity, sensitivity, noise level and minimum

detectability for phosphorus. Moreover, the linearity, stability and reproducibility of the detector are evaluated. The detector response towards nitrogen will be addressed briefly. Finally, the performance of the detector will be demonstrated by two environmental applications. All studies are of an empirical nature. It is not the goal of this work to investigate or elucidate the detection mechanism of alkali salt detectors.

2. Experimental

2.1. Gas chromatography

Gas chromatography was performed on a Fisons 8000 Series gas chromatograph (Fisons Instruments, Milan, Italy) equipped with a split/splitless injector, an on column injector, a flame ionization detector (FID) and a NPD-40 nitrogen–phosphorus detector. The column used in this study is a 25 m×320 μm I.D. fused-silica capillary coated with 100% methyl silicone, HP-1, film thickness 0.18 μm (Hewlett-Packard, Wilmington, DE, USA). The carrier gas pressure (helium) was 175 kPa (abs.). The make-up gas was nitrogen. All injections (injection volume, 1 μl) were performed in the split mode (split ratio, 1:104) unless stated otherwise. The injector temperature was 250°C. The oven was operated isothermally at 220°C. The detector temperature was 300°C both for the FID and the NPD. A Perkin-Elmer Nelson 1020 data system (Perkin-Elmer, Norwalk, CT, USA) was used for data acquisition and processing.

2.2. Detector design

Fig. 1 shows the detector design used in this study. From the NPD-40 nitrogen–phosphorus detector (Fisons Instruments) [11] the salt pellet was removed. At the position were normally the salt pellet is located, a metal ring (I.D. 8.1 mm, O.D. 10.5 mm, height 3 mm) is placed. In the ring a small orifice is drilled which allows a metal capillary (I.D. 0.25 mm, O.D. 0.45 mm) to enter the flame zone. In optimization of the detector, the position of this capillary relative to the flame jet is of utmost importance. In the setup proposed here, both horizontal and vertical positioning of the capillary is
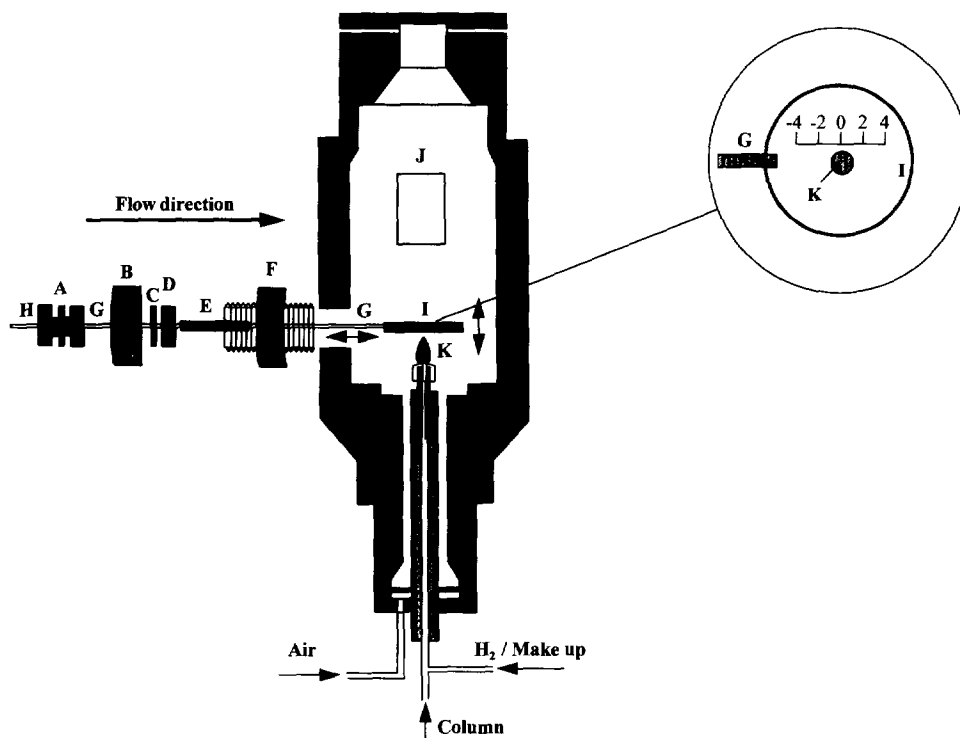
Fig. 1. Detector design: A=0.16 cm swagelock connector to connect metal capillary to fused-silica supply transfer line; B=brass nut; C=vespel ring; D=kalrez ring; E=ceramic feed-through; F=brass nut; G=metal capillary (I.D. 0.25 mm); H=fused-silica capillary (10 m×50 μm I.D.) I=metal ring; J=collector; K=flame jet. The arrows indicate the horizontal and vertical directions in which the capillary can be positioned. The inset shows a top view of the metal ring. Horizontal positions (in mm), used for optimization of the position of the metal capillary (G) relative to the flame jet (K), are indicated.

possible. The capillary enters the detector through a connecting nut which allows horizontal positioning of the capillary. This nut also provides a leak-tight connection. Vertical positioning is achieved by using the built-in calibration trimmer originally present on the NPD-40. A ceramic feed-through ensures electrical insulation of the capillary from the detector housing. To the capillary a voltage of −140 V is applied (using the original GC supply), while the flame jet is grounded. The inset of Fig. 1 shows an exploded top view of the flame zone. Indicated are the horizontal positions of the metal capillary which will be used for detector optimization (see Section 3.4). At position zero the end of the capillary is directly above the centre of the flame jet.

In Fig. 2 an overview of the instrumentation is presented. The alkali salt, dissolved in water, is fed to the detector via the metal capillary by means of a Varian 8500 syringe pump (Varian, Walnut Creek,

CA, USA). In this respect it is important to realize that the amount of water entering the detector must be carefully controlled. Too high flow-rates of water can adversely affect the detector flame. Operating the pump at too low a flow-rate, however, can result in instable operation of the pump due to too low a backpressure. To enable stable introduction of very small amounts of water into the detection zone, flow splitting was applied between the pump and the detector. For this purpose a combination of two fused-silica capillaries (10 m×50 μm I.D. and 1.5 m×50 μm I.D.) was used. In this way a stable flow of 3 μl/min could be introduced into the detector. The pump pressure in this case was 3000 kPa.

2.3. Test mixture and alkali salts

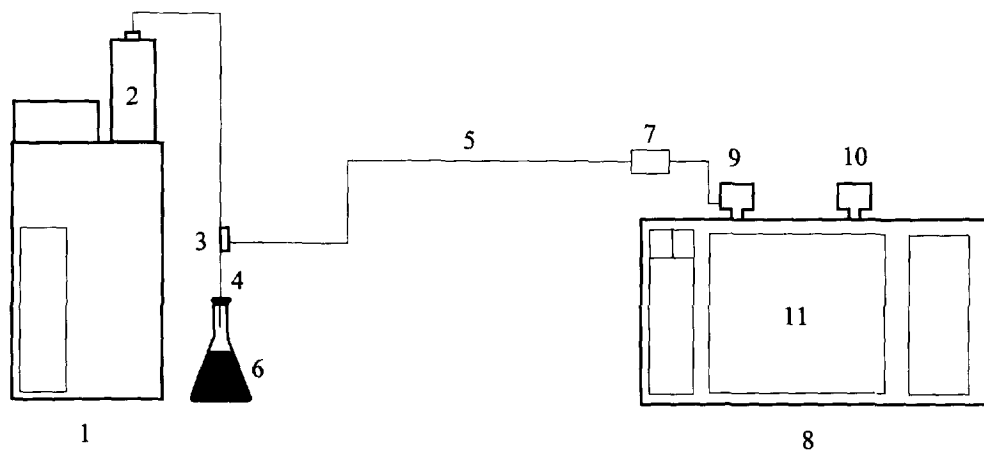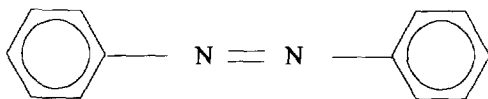Several alkali salts were used in this study. Sodium chloride and potassium chloride were pur-

Fig. 2. Overview of the instrumentation: 1=syringe pump; 2=salt solution reservoir; 3=split point; 4=fused-silica capillary (1.5 m×50 μm I.D.) to waste; 5=fused-silica capillary (10 m×50 μm I.D.) to detector; 6=waste flask; 7=0.16 cm swagelock connector to connect the metal capillary to the fused-silica capillary (see also Fig. 1.); 8=gas chromatograph; 9=detector (see Fig. 1.); 10=split/splitless injector; 11=column oven.

chased from Merck (Darmstadt, Germany). Lithium chloride, rubidium chloride and cesium chloride were obtained from Janssen Chimica (Geel, Belgium). The water, used to prepare the salt solutions, was freshly distilled before use. Detector optimization was performed with a solution consisting of a carbon, a nitrogen and a phosphorus compound. n-Octadecane and azobenzene, used as carbon and

(A)

(B)

Fig. 3. Structures of (A) azobenzene and (B) malathion.

nitrogen compounds, respectively, were purchased from Merck. Malathion (the phosphorus compound) was obtained from Riedel-de-Haën (Seelze, Germany). Fig. 3 shows the structures of azobenzene and malathion. All analytes were analytical grade. The solvent used to prepare the test mixture was analytical grade n-hexane (Merck). The test mixture consisted of 1.031 μg/μl n-octadecane, 0.865 μg/μl azobenzene and 88.0 ng/μl malathion. Taking into account the split-ratio, injection of 1 μl of this solution corresponds to introducing 8.42 ng carbon, 1.28 ng nitrogen and 79 pg phosphorus onto the column, respectively.

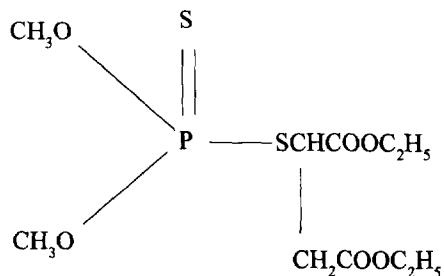## 3. Results and discussion

3.1. Response characteristics and optimization strategy

For a thorough optimization of the new detector design, the effect of operational parameters such as the location of introduction, type and concentration of the alkali salt and the flows of the various detector gasses must be explored in relation to important response characteristics as, e.g., detector sensitivity, minimum detectability, selectivity and noise level. The sensitivity to phosphorus atoms, S_p, can be calculated from:

$$S_P = \frac{A_P}{W_P} \qquad (1)$$

where A_P is the peak area of the phosphorus compound and W_P is the mass of phosphorus introduced onto the column. The minimum detectability, D_P, of a phosphorus compound can be calculated from:

$$D_P = \frac{2N}{S_P} \qquad (2)$$

where N is the peak-to-peak noise. The selectivity, $s_{P/C}$, of phosphorus compounds relative to hydrocarbons is defined as:

$$s_{P/C} = \frac{S_P}{S_C} \qquad (3)$$

where S_C is the sensitivity towards carbon atoms. In a similar way, the sensitivity, detectability and selectivity of the detector towards nitrogen can be defined.

As already mentioned in the introduction, the detector mechanism is still not fully understood and many interrelated operational parameters can affect detector response. For this reason the optimization strategy selected here is purely empirical. Although we realize that the use of optimization algorithms such as the well-known Simplex optimization can prove time-saving, we opted for a straightforward approach. By choosing this approach the possibility of converging into a local optimum can be circumvented. The straightforward empirical approach selected here results in a higher experimental load. It leads, however, to a more open-minded approach.

It is commonly recognized that the response characteristics of many types of AFIDs are highest for phosphorus compounds [12]. Therefore, also our work mainly focused on the phosphorus compound (malathion). Response towards azobenzene (the nitrogen compound) is addressed only briefly.

As mentioned before, the detector response is influenced by several factors. For clarity we discuss them separately in an arbitrary order.

3.2. Alkali salt type

As discussed by, e.g., Dressler [12] and Brazhnikov et al. [4], earlier studies using a conventional AFID/NPD clearly demonstrated that the nature of the alkali salt used as the enhancement source affects the performance of the detector. To evaluate the effect of using different types of alkali salts as the enhancement source 100 mg/l solutions of LiCl, NaCl, KCl, RbCl and CsCl in water were prepared and introduced into the detector by means of the syringe pump. For each salt the response characteristics of the detector were established by injections of the test mixture. The results of these measurements are presented in Fig. 4. This figure gives the experimentally observed detector characteristics for malathion using different alkali salts. The best performance found for each of the parameters is arbitrarily set to one. Other values are expressed relative to this value. From the figure it can be seen that the best performance is obtained using either RbCl or CsCl as the enhancement source. The use of RbCl yields the lowest minimum detectability (due to a high sensitivity, combined with a low noise level). CsCl shows maximum selectivity. Consequently, the detector can be tuned to optimal selectivity or minimum detectability by selecting the proper alkali salt as enhancement source. However, when CsCl is applied, a higher noise level is observed compared to RbCl. For this reason we use RbCl as the alkali metal source for further experiments.

3.3. Alkali salt concentration

In addition to the nature of the salt used, it can be expected that also the amount of salt introduced into the detector will influence the detector response. This was studied experimentally by introducing different concentrations of RbCl into the detector. The results of the measurements for malathion are presented in Fig. 5. From the figure it can be concluded that the best overall performance is obtained when using high salt concentrations. At a concentration of 150 mg/l RbCl (which corresponds, at a pump flow-rate of 3 μl/min, to introducing 0.45 μg RbCl per minute into the detector), the best selectivity is observed. Moreover, this concentration of salt gives the lowest minimum detectability, since the increase in noise is lower than the increase in sensitivity. The use of higher concentrations of RbCl was tested but was found to result in instable baselines, severe spiking
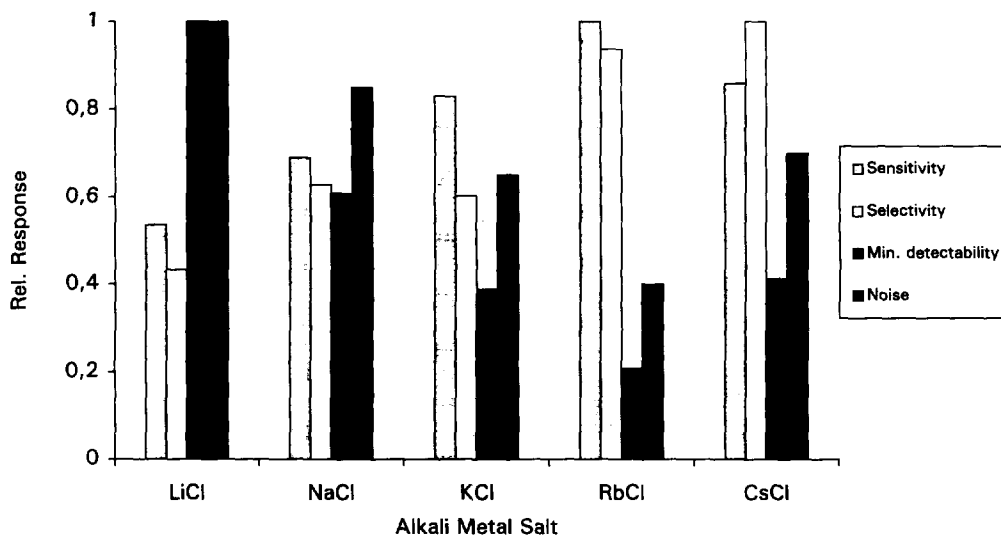
Fig. 4. Effect of alkali salt type on detector response for malathion. Alkali salt concentration, 100 mg/l; hydrogen flow, 80 ml/min; air flow, 250 ml/min; make-up flow, 5 ml/min. Supply capillary vertical position: 6 mm above flame jet; horizontal position: 0 mm relative to flame jet (see also inset in Fig. 1.).

and in an increase of the noise level. The instabilities observed were most likely caused by salt depositing inside the detector at these higher concentrations. Cleaning of the detector returns the response to its original value. In all further experiments a solution of 150 mg/l RbCl was used.

3.4. Optimization of the location of introduction of the alkali salt

In conventional AFID/NPD detectors, the position of the salt bead relative to the flame jet has a significant influence on the performance of the
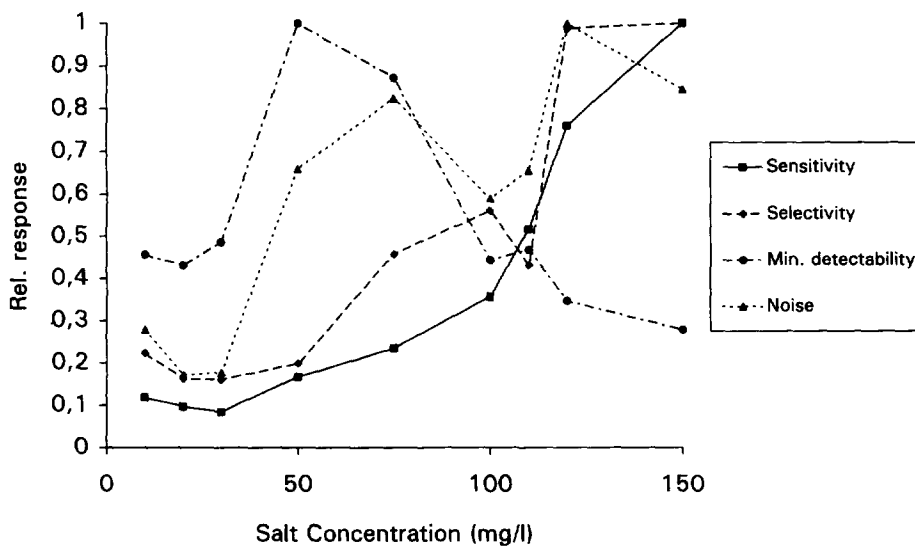

Fig. 5. Effect of RbCl concentration on detector response for malathion. Further conditions see Fig. 4.

detector. It therefore appears reasonable to assume that also with the present detector design the location were the salt is introduced will affect the performance of the detector. The effect of the location of introduction was investigated by studying the performance of the detector at several horizontal and vertical positions of the metal capillary inside the detector. The results of these experiments are presented in Fig. 6. The test solute is again malathion. From the figure it can be seen that optimal response is observed when the capillary is positioned 6 mm above the flame jet protruding into the flame (2 mm past the centre of the flame jet; for positions see also Fig. 1). In this position the capillary glows with a dull red colour. A possible explanation for the increased response observed at this position could be the increased alkali salt temperature as it leaves the capillary and enters the detector volume. It is commonly recognized that the temperature of the alkali source is one of the dominant factors determining the response of AFIDs and NPDs [4,12]. The position

where the capillary protrudes into the flame results in a higher salt temperature which in turn gives rise to a better performance.

In this respect, another important parameter, the influence of the detector temperature, was tested. Detector temperatures in the range of 250°C to 350°C were studied by injections of the test mixture. The results of these experiments showed no significant influence of the detector temperature to its response. For further experiments the capillary was positioned at the location specified above, i.e. 6 mm above the flame jet, protruding into the flame, 2 mm past the centre of the flame jet.

3.5. Optimization of the hydrogen and air flow

The hydrogen and air flow-rate entering the detector are key parameters determining the AFID and NPD response. The detector response at several hydrogen and air flows was determined experimentally. The results for malathion are depicted in Fig. 7.
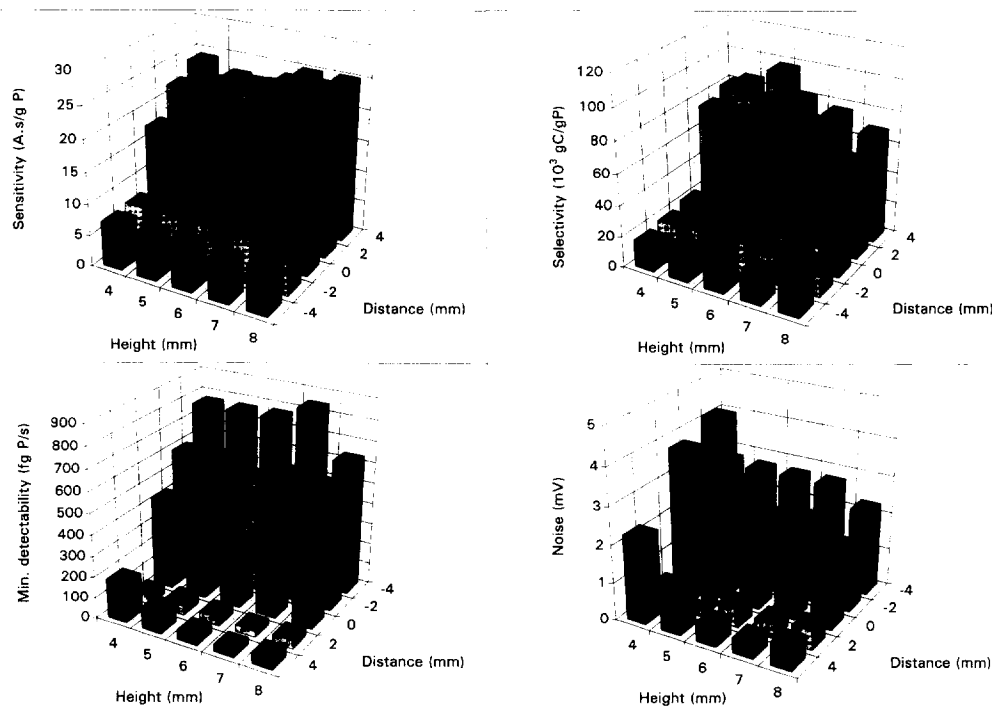

Fig. 6. Effect of the location of introduction of the alkali salt on detector response for malathion. Alkali salt: 150 mg/l RbCl. For reasons of clarity the figures on the x- and y-axes are not always in the same order. Further conditions see Fig. 4.

At the positions where no data are indicated, the noise level increased to too high levels and hindered detection of the carbon peak (*n*-octadecane). From the figure it can be seen that with increasing hydrogen and air flow-rates response characteristics improve significantly. A possible explanation could be that with increasing hydrogen flow-rate, the flame temperature increases and, as a result, the temperature of the alkali salt increases. This increasing temperature results in improved performance as mentioned in the previous paragraph. It can also be seen that the operating conditions that provide maximum sensitivity are not always the same as those that provide maximum selectivity. The same holds for the minimum detectability. It is interesting to see that in this respect the noise level plays a decisive role. For practical application it means that the best possible compromise between selectivity and sensitivity has to be selected depending on the requirements of the analytical problem at hand.

At the highest air flow-rates studied (330 ml/min) a high baseline instability was observed. For this reason a combination of 92 ml/min hydrogen and 295 ml/min air was selected for further experiments.

3.6. Make-up flow

The influence of the make-up gas flow (nitrogen) was investigated in a separate series of experiments. The results of these tests using malathion as the test solute are shown in Fig. 8. From this figure it can be seen that at increasing make-up flows the response characteristics deteriorate. This is mainly due to the relatively large increase of the noise level which hinders detection of the carbon compound (*n*-octadecane) at make-up flows exceeding 10 ml/min. For this reason no selectivity data are indicated at these points. The observed response behaviour is most likely the result of an increased instability in the flow pattern at higher make-up flow-rates. For
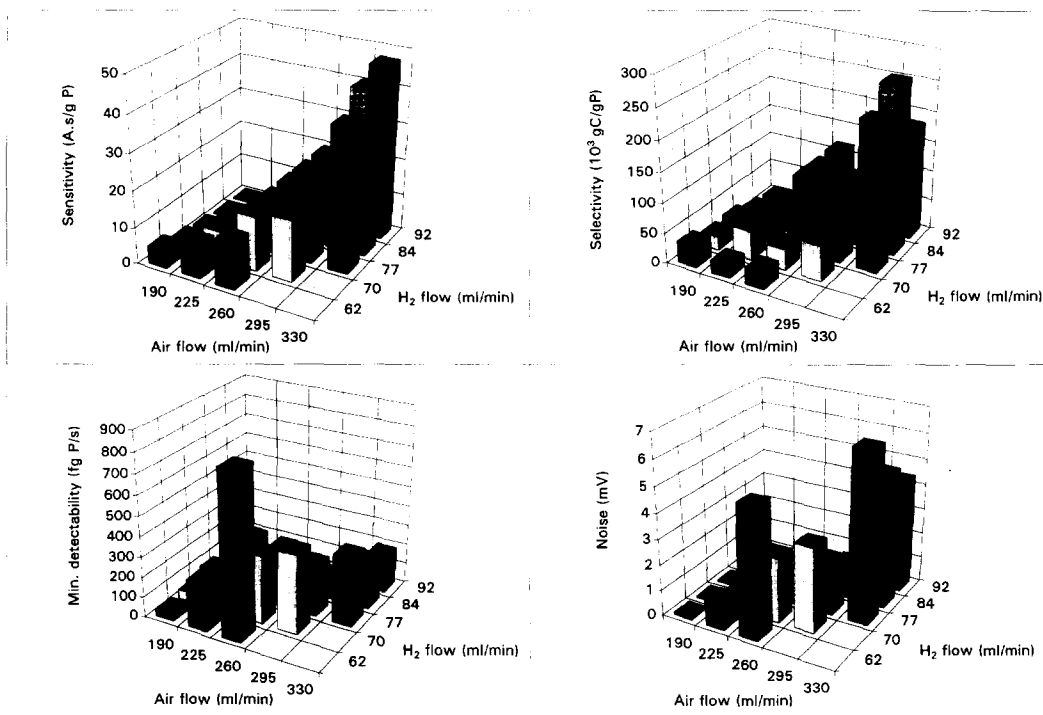

Fig. 7. Effect of the hydrogen and air flow-rate on detector response for malathion. Alkali salt: 150 mg/l RbCl. The supply capillary is positioned 6 mm above the flame jet and protrudes into the flame, 2 mm past the centre of the flame jet (see also inset of Fig. 1.). Make-up flow, 5 ml/min. Values not indicated were not measured due to a too high noise level which prevented the detection of the carbon peak (*n*-octadecane).
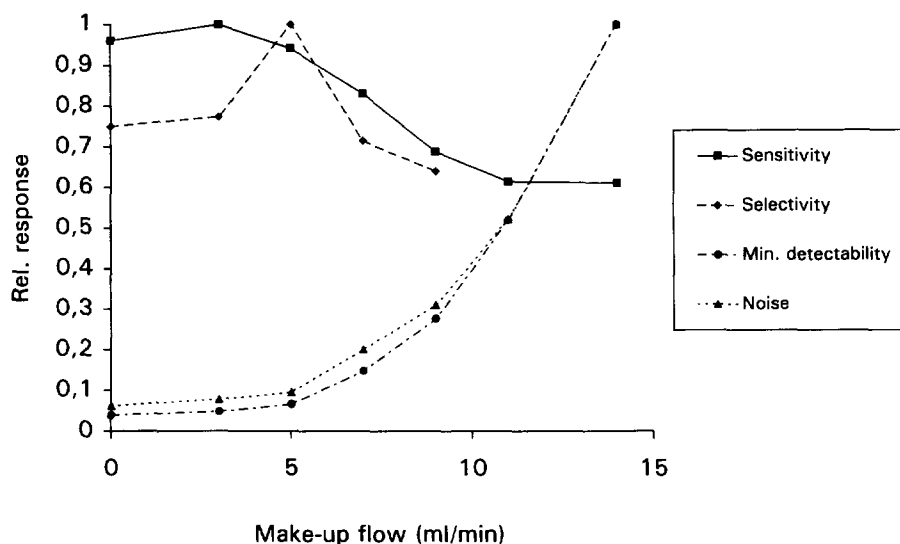
Fig. 8. Effect of make-up gas flow on detector response for malathion. Alkali salt 150 mg/l RbCl. The supply capillary is positioned 6 mm above the flame jet and protrudes into the flame, 2 mm past the centre of the flame jet (see also inset of Fig. 1.). Hydrogen flow, 92 ml/min. Air flow, 295 ml/min.

further experiments, a make-up flow of 4 ml/min was used. This value is low in comparison to typical make-up flow-rates in conventional AFIDs/NPDs. The experimentally found optimal operating conditions of the detector are listed in Table 1. Table 2 lists the corresponding response characteristics for the phosphorus and nitrogen compound. From the table it can be seen that the detector response towards phosphorus is comparable to or better than that observed with commercially available NPDs. The detector performance towards nitrogen will be discussed in more detail in Section 3.8.

3.7. Reproducibility, linearity and stability

At the settings listed in Table 1, the reproducibility of the system was verified by ten injections of the test mixture. This revealed a relative standard deviation of approximately 5%. Here it should be emphasized that this value represents the overall system reproducibility, which also includes the injection system. Since injections were performed manually in the split mode, which normally leads to relative large standard deviations, the reproducibility of the detector can be considered to be clearly satisfactory.

Table 1
Optimal detector operating conditions for phosphorus (malathion)

Parameter	Optimal value
Alkali salt type	RbCl
Alkali salt concentration	150 mg/l
Vertical position supply capillary	6 mm above flame jet
Horizontal position supply capillary	protrudes 2 mm past centre of flame jet
Hydrogen flow	95 ml/min
Air flow	295 ml/min
Make-up flow (nitrogen)	4 ml/min

For horizontal position see also inset of Fig. 1.

Table 2
Detector response characteristics for the phosphorus (malathion) and nitrogen compound (azobenzene), respectively

Parameter	P	N
Sensitivity	48 A.s/g P	0.4 A.s/g N
Min. detectability	51 fg P/s	8 pg N/s
Selectivity	152000 g C/g P	1125 g C/g N
Noise (mV)	1.50	1.50
Reproducibility (%)	5	–
Linear range	10^4	–

For operating conditions refer to Table 1. Carbon compound n-octadecane. Values not indicated were not determined.

For malathion, the detector shows linear behaviour over four decades, which was verified by injections of a diluted series of the test mixture.

The detector shows a good stability over a period of a few days to a week. The main cause of detector deteriorating is blocking or partial blocking of the metal salt supply capillary. Most likely, this can be avoided by the use of larger inner diameter capillaries.

3.8. Response characteristics towards nitrogen

From the results presented so far it can be concluded that the detector shows excellent response characteristics for phosphorus compounds. In parallel the performance towards nitrogen compounds was also explored, using the same approach followed for phosphorus. The results revealed that the optimal conditions equal the optimal conditions found for phosphorus (see Table 1). The final results are presented in Table 2. From this table it can be seen that the response for nitrogen compounds is substantially less than the response observed towards phosphorus compounds. The possibility to improve the detector response towards nitrogen compounds by varying experimental conditions such as detector voltages [11] is currently under investigation.

3.9. Applications.

To test the applicability of the new detector design two environmental samples were analyzed. A sample consisting of a number of components containing several heteroatoms was injected using both the NPD and the conventional FID. Injections were performed

using the on-column technique. The results are shown in Fig. 9. From this figure it can be seen that the phosphorus containing compounds (phorate and chloropyriphos, respectively) are selectively and sensitively detected. The nitrogen compounds exhibit a substantially lower response. The phenanthrene peak (carbon compound) is not detected when using the NPD. The observed retention time shifts are caused by the use of slightly different carrier gas inlet pressures due to reinstallation of the column inside the GC oven.

The excellent behaviour of the detector is further demonstrated by the analysis of diesel oil spiked with malathion. For analysis, the spiked diesel oil is diluted with n-hexane. The concentration malathion in the diluted oil is 60 pg/μl. The lower trace in Fig. 10 clearly demonstrates the selective and sensitive
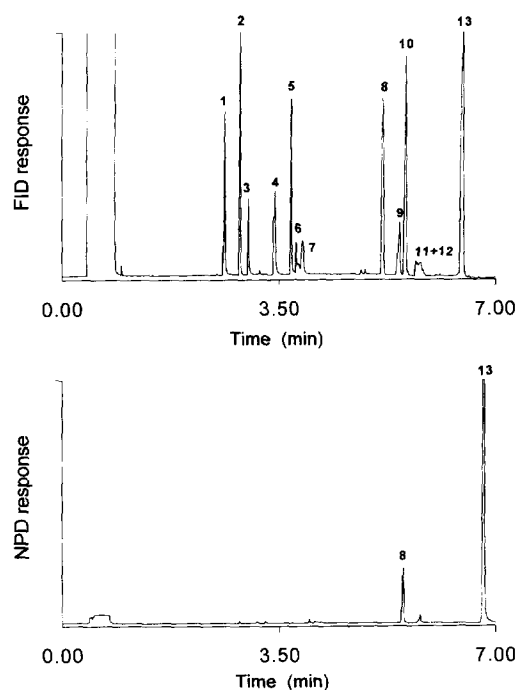

Fig. 9. Analysis of a test mixture consisting of compounds containing various heteroatoms. Solvent: methanol. Injection: on-column, 1 μl. Components: 1=2,6-dimethylphenol; 2=2,6-di-methylaniline; 3=p-chloroaniline; 4=indole; 5=nicotine; 6= 2,4,5-trichlorophenol; 7=p-dinitrobenzene; 8=phorate; 9= atrazine; 10=phenanthrene; 11=cafeine; 12=heptachlor; 13= chloropyriphos. Detector operating conditions as in Table 1. Oven temperature program: 40°C (3 min) → 20°C/min → 250°C. Upper trace range 0; lower trace range 1.
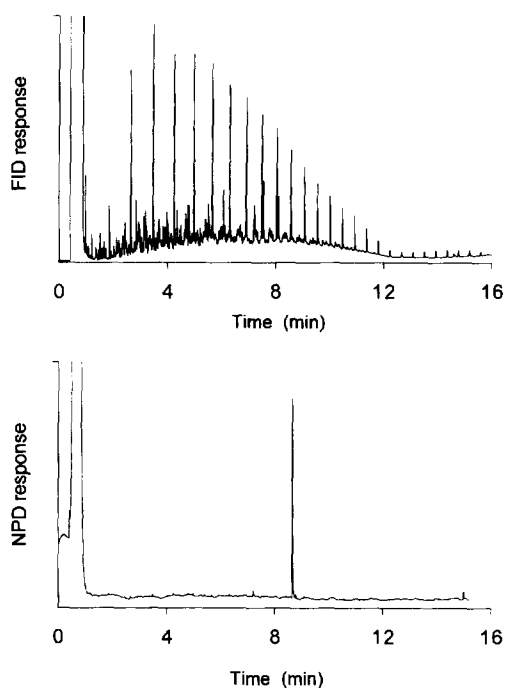
Fig. 10. Analysis of diluted diesel oil spiked with 60 pg/μl malathion. Solvent: *n*-hexane. Injection: on-column, 1 μl. For detector operating conditions see Table 1. Oven temperature program: 40°C (3 min) → 20°C/min → 250°C.

detection of only 60 pg malathion in an extremely complex matrix.

4. Conclusions

The new detector design exhibits excellent response characteristics for phosphorus compounds. Its performance is comparable to or better than that observed with commercially available AFIDs or NPDs. For optimal performance proper selection of the operating conditions is of utmost importance. Important parameters in the optimization are the alkali salt type and concentration, the location of introduction of the alkali salt and the hydrogen and air flow. Compared to conventional AFIDs or NPDs, continuous operation is allowed since there is no need for bead replacement. Due to its excellent sensitivity the detector is suited for selective trace detection in complex matrices. Future research should be directed to the improvement of the response towards nitrogen. Moreover, detector stability should be improved by examining alternative approaches to introduce the alkali salt solution into the detector.

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