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IONIZATION DETECTOR FOR GAS CHROMATOGRAPHY WITH SWITCHABLE SELECTIVITY FOR CARBON, NITROGEN AND PHOSPHORUS

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SUMMARY

An ionization detector for gas chromatography is described, the selectivity of which can be changed such that it can be operated as a universal detector with the same properties as a flame-ionization detector, as a specific phosphorus detector and as a selective detector for both nitrogen and phosphorus. The last operational mode is also used for operation as a selective nitrogen detector. The changeover between all three operational modes is rapid and needs no manipulation of the detector itself, as all necessary operations are effected at the control unit only.

INTRODUCTION

Element-specific detectors are very useful in gas chromatography, particularly for trace analysis. For such an application, it is often desirable to analyze a sample with both a universal detector, such as the flame-ionization detector (FID), and an element-specific detector. An important application of such a combination is the determination of the retention index of an unknown compound that has been found in a specific chromatogram and requires identification. It is an inherent weakness of specific detectors that retention indices based on the retention of the homologous series of *n*-alkanes cannot be determined, as the hydrocarbons are not detected if the detector is of high efficiency. With a selective detector, the hydrocarbons must be added at such high concentrations that the peaks are overloaded and no longer symmetrical, and thus useless for retention index calculations.

In order to overcome this problem, the combination of both an FID and an element-specific detector is possible by using an outlet splitter and operating both detectors simultaneously. Such a combination, however, is particularly difficult to achieve with glass capillary columns in an all-glass system. With an alkali flame-ionization detector it is further possible to remove mechanically the alkali source from the detector, as most alkali flame detectors are modified FIDs, and to repeat the analysis with a standard FID after having recorded the selective chromatogram. This possibility is obviously less suitable for rapid, routine analyses, as manipulation at the hot detector is necessary. A detector, the selectivity of which can be changed easily and rapidly by push-button operation only, would therefore be ideal.

The detector described here, namely the nitrogen-phosphorus detector (NPD), has such a switchable selectivity, because it can be operated as an FID [flame-ionization (FI) mode], as a specific phosphorus detector [phosphorus (P) mode] and in an operational mode where both nitrogen- and phosphorus-containing compounds are detected [nitrogen-phosphorus (NP) mode]. The changeover between these three operational modes is rapid and is performed by operating electrical switches and pneumatic valves at the control unit only. This detector therefore approaches the ideal of a universal detector with push-button operated selectivity.

Actually, this detector is an alkali flame-ionization detector and some of its properties have already been described and compared with other thermionic detectors with respect to both the instrumental design and the theory of the possible reaction mechanism¹. Some practical applications, mainly for the use as a selective nitrogen detector, have also been given²⁻⁴, but the operational mode as a universal FID and the changeover possibilities have not been described previously and are considered here in detail.

DESCRIPTION OF DETECTOR

The NPD (Fig. 1) differs from a standard FID with respect to the alkali source, which is a small glass bead between the jet and collector electrode, and an isolation disc, which divides the detector housing into two electrically independent parts. The glass bead, which contains the alkali mainly as a rubidium silicate, is fused on to a platinum wire and is always at a negative potential of -180 V relative to the collector electrode, as is the upper part of the detector housing, while the lower part, including the jet, can be made positive by an external switch at the control unit. The glass bead can be heated electrically and is thus independent of the flame as a source of thermal energy.

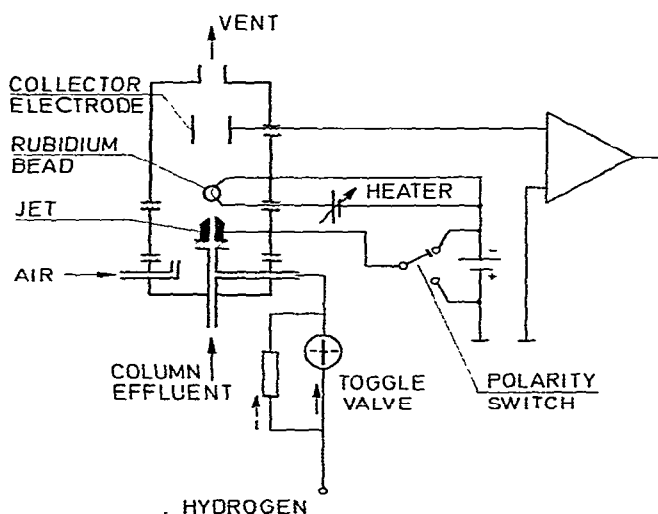


Fig. 1. Schematic of the nitrogen-phosphorus detector (NPD).

OPERATIONAL MODES OF THE NPD

The three possible operational modes of the NPD are discussed here in terms of the example as shown in Fig. 2.

A high-boiling ester oil was analyzed for its content of both nitrogen- and phosphorus-containing additives, using a short glass column packed with OV-1 as the stationary liquid phase. An outlet splitter was used and both the FID and the NPD were operated simultaneously, both chromatograms being traced with a dual-pen recorder. In Fig. 2 (a-d), therefore, two chromatograms are always shown together, the lower chromatogram resulting from the FID, which is presented here in order to permit a comparison between the selective and the universal chromatograms. The upper chromatogram shows the different chromatograms from the NPD as a result of the particular operational modes. Also shown in a diagrammatic form are the distribution of the polarities and the type of flame for each operational mode.

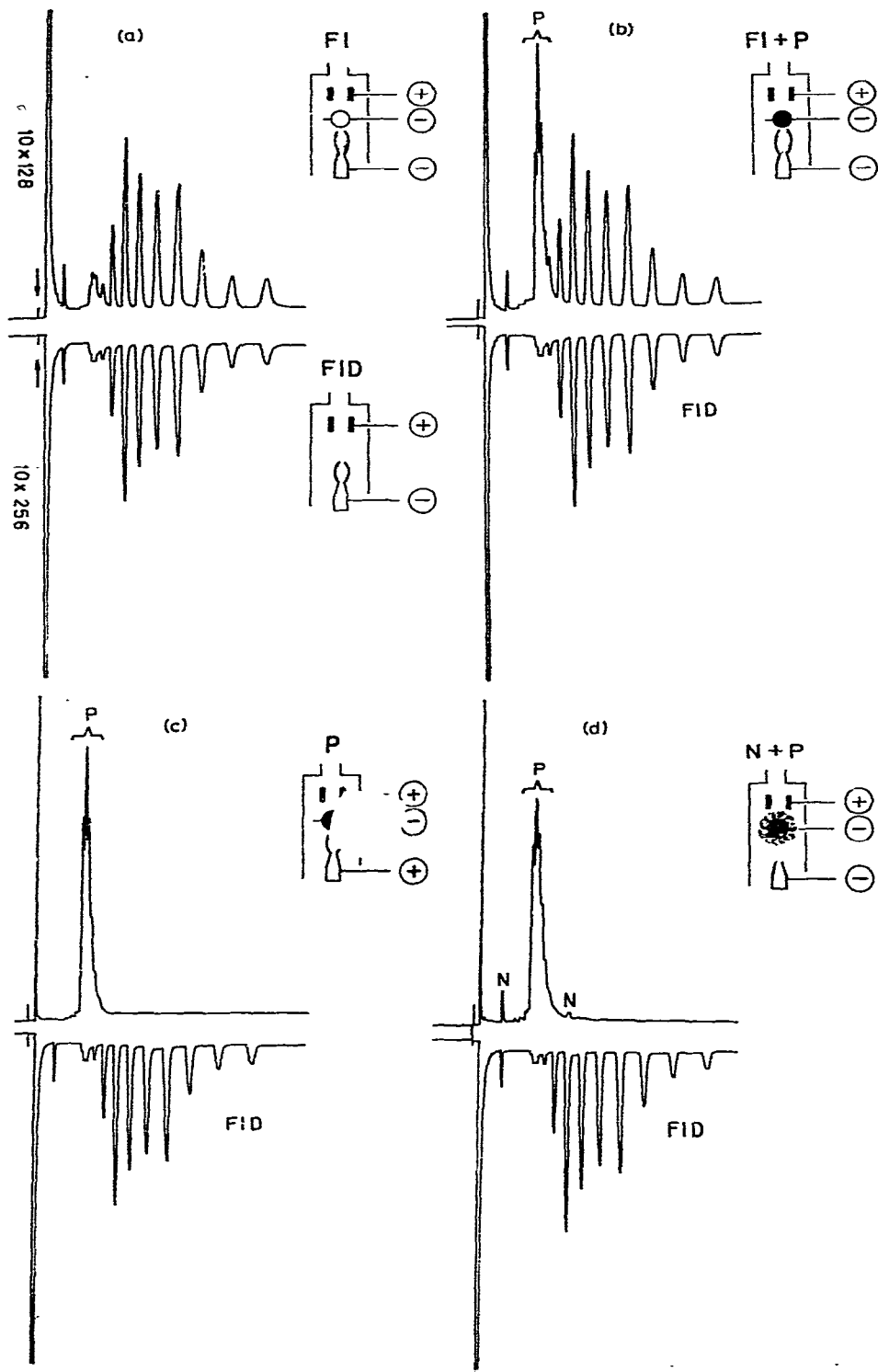
Flame-ionization operational mode

The conditions for running the NPD as an FID are the same as for an FID; the flow-rates of the fuel gases are the same as with an FID and the jet polarity is also at a negative potential. The only difference from an FID is the presence of the glass bead between the flame and the collector electrode. Provided that the bead is not heated, no alkali is emitted and no enhanced sensitivity for certain elements is achieved. The bead has, in fact, no influence on the result and the chromatogram is identical with that from the standard FID, as shown in Fig. 2a. Only if the bead is sufficiently near to the flame (< 2 mm) to be heated is some alkali emission produced and, as a result, a slightly enhanced sensitivity for phosphorus compounds may be caused. The chromatograms in Fig. 2a show mainly the homologous series of esters in the high-boiling ester oil.

Phosphorus operational mode

The alkali emission can be initiated by heating the bead electrically to dull-red and the increased alkali emission results in an increased sensitivity for phosphorus compounds, as shown in Fig. 2b. At the beginning of the chromatogram there is a group of fused peaks that is much higher than that in the FID chromatogram. These peaks are due, in fact, to an isomeric mixture of tricresyl phosphates. In this operational mode the detector is sensitive to phosphorus, but not selective.

It is now desirable to make the detector selective by eliminating all other signals, which can be achieved extremely simply by earthing the jet. The result is demonstrated in Fig. 2c, where only the phosphorus-containing compounds remain unchanged, all other peaks having disappeared. This effect is best explained by the geometrical arrangement of this detector. The bead, which is always at a negative potential, works as a grid. The electrons from the usual C, H combustion in the flame below this grid cannot overcome the potential of the grid and are conducted to earth by the earthed jet. Contrary to these electrons are the thermionic electrons, which result from the reaction of the combustion products of phosphorus with the alkali of the bead in a reaction mechanism that has already been described⁴. As this reaction takes place at the surface of the bead and thus at least partly above the grid, the



resulting electrons can be collected by the collector electrode, and are therefore responsible for the selective response for phosphorus. The jet is earthed by switching the polarity over on the control unit. This working mode is the P mode, which differs from the FI mode in having the the earthed jet and the electrically heated bead..

Nitrogen-phosphorus operational mode

The NPD can also be operated as a nitrogen detector, with additional sensitivity for phosphorus. For this purpose, it is necessary to change the flame conditions such that organic nitrogen compounds are pyrolyzed, forming cyanide radicals as intermediates, rather than being oxidized in the normal way¹. Such flame conditions are best achieved by reducing the hydrogen flow-rate to about 10% of the value that is necessary to maintain the flame for both the FI and P modes. This reduction in flow-rate is achieved by means of a valve in the control unit, by which the hydrogen flow is directed through an additional flow restrictor. A similar reduction of the air flow-rate to about 80–100 ml/min is recommended, but is not so important so far as the detector properties are concerned. Such a low hydrogen flow-rate is sufficient neither to heat the bead to the necessary temperature nor to maintain a stable flame burning at the jet. The bead is heated electrically to compensate for the loss in thermal energy and, as a result, the hydrogen is therefore burns around the glowing bead. If the detector is switched to the NP mode, the flame jumps automatically from the jet to the bead.

As the decreased hydrogen flow is further diluted by the carrier gas, we can assume that there is a cold and diluted flame zone around the bead and further that the resulting energy is no longer sufficient to cause ionization of the C, H compounds. This effect would explain the selectivity in the NP mode, while in the P mode the geometry of the earthed jet and the negative bead with the flame in between cause the selectivity.

The result of applying the NP mode to the test sample is shown in Fig. 2d. Two small peaks are now present in addition to the phosphorus peaks, which correspond to nitrogen-containing additives in the ester oil. The first of the two peaks was found to be due to diphenylamine, while the second could not be identified.

Fig. 2. Operational modes of the NPD, exemplified by the analysis of an ester oil with nitrogen- and phosphorus-containing additives. Perkin-Elmer F22 chromatograph with a 1-m glass column packed with 3% OV-1 on Chromosorb W-HP; carrier gas (nitrogen) flow-rate, 20 ml/min; outlet splitter, 1:1; temperature programme, 270° to 300° at 8°/min; attenuation, FID 10 × 256 and NPD 10 × 128. Compounds: P = P-containing additives (tricresyl phosphates); N = N-containing additives (first N peak: diphenylamine. In (a)–(d) with FID: H₂ = 35 ml/min; air = 400 ml/min. (a) NPD, FI mode: H₂ = 35 ml/min; air = 400 ml/min; heating position "off". (b) NPD, P + FI mode: H₂ = 35 ml/min; air = 400 ml/min; heating position 250; (c) NPD, P mode: H₂ = 35 ml/min; air = 400 ml/min; heating position 280. (d) NPD, NP mode: H₂ = 2 ml/min; air = 100 ml/min; heating position 710.

TABLE I
CHARACTERISTIC OPERATIONAL SPECIFICATIONS OF THE NPD

Characteristic	FI Mode (carbon)	P Mode (phosphorus)	NP Mode	
			Phosphorus	Nitrogen
Sensitivity	$5 \cdot 10^{-3}$ Cb per g of C	1 Cb per g of P	5 Cb per g of P	0.5 Cb per g of N
Detection limit	$3 \cdot 10^{-12}$ g of C per sec	$5 \cdot 10^{-14}$ g of P per sec	$1 \cdot 10^{-14}$ g of P per sec	$1 \cdot 10^{-13}$ g of N per sec
Linearity	$2 \cdot 10^7$	10^5	10^5	10^5
Selectivity	—	10^6 g of C per g of P	$1.25 \cdot 10^5$ g of C per g of P	$2.5 \cdot 10^4$ g of C per g of N

CHARACTERISTICS OF THE DETECTOR

The characteristic detector specifications in the P and NP modes have already been published¹, but are summarized again in Table I, together with the properties of the NPD in the FI mode, for the purpose of comparison.

It can be seen that the NPD is even more sensitive towards phosphorus compounds in the NP than in the P mode. The latter mode is therefore recommended only in instances when specificity is of more interest than sensitivity or if, in a chromatogram that has been recorded in the NP mode, some unknown peaks have to be identified unambiguously as nitrogen- or phosphorus-containing compounds, as is demonstrated in the examples in Fig. 2. Hence the possibilities of the P mode make the NPD a specific and not only a selective detector.

A comparison of the detector properties in the FI mode with that of a standard FID is shown in Table II. Both the values of the detection limit and of the linear range are identical.

Another very important specification is the short stabilization time after having changed the operational mode. The idea of "push-button" operation, as outlined above, is realistic only if the detector follows the changes of the operational conditions rapidly enough. If a long stabilization time is necessary, the detector itself could be exchanged equally well. Fig. 3 shows such an example of changing from the FI to the NP mode. It can be seen that the stabilization time is short enough to enable the next analysis to be carried out a few minutes after having changed the operational mode.

The chromatogram in Fig. 3 shows the analysis of a urine extract from an athlete, which was obtained in a doping test using a 25-m glass capillary column. The extract was prepared according to the procedure of Dadisch *et al.*⁵. The chromatogram on the right, recorded in the FI mode, shows the homologous series of hydrocarbons as the basis for retention index calculations, while the chromatogram in the NP mode (left) shows the urine extract, which contained pyridine-3-carboxydiethyl-

TABLE II
PROPERTIES OF THE NPD IN THE FI MODE COMPARED WITH A STANDARD FID

Property	FID	NPD/FI mode
Detection limit (g of C per sec)	$3 \cdot 10^{-12}$	$3 \cdot 10^{-12}$
Linearity	$2 \cdot 10^7$	$2 \cdot 10^7$

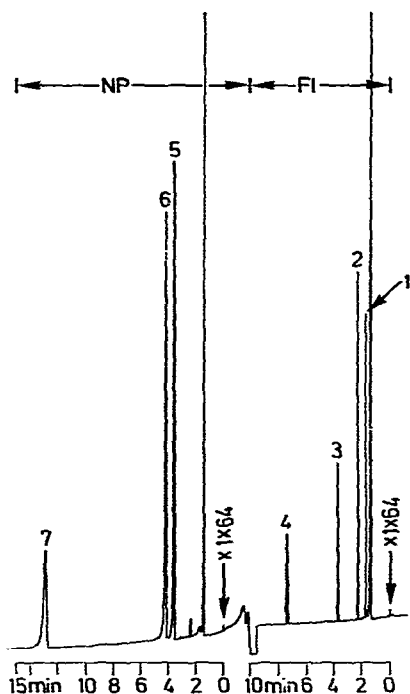


Fig. 3. Switchover between FI and NP operational modes for the identification of compounds in a urine extract by retention index calculation. Perkin-Elmer F22 chromatograph with a 25-m glass capillary column with Apiezon L as the stationary liquid phase operated isothermally at 180° with helium as the carrier gas at a flow-rate of 2 ml/min and a splitting ratio of 1:50. Compounds: 1 = *n*-dodecane; 2 = *n*-tetradecane; 3 = *n*-hexadecane; 4 = *n*-octadecane; 5 = pyridine-3-carboxydiethylamide (nikethamide); 6 = metabolite; 7 = caffeine.

amide (nikethamide) and its main metabolite together with caffeine. The possibility of a rapid changeover enables retention indices to be determined by consecutive analyses of the sample and the hydrocarbon test sample.

The chromatogram in Fig. 3 therefore demonstrates the ease of operation, which makes this detector suitable for routine application, such as in doping tests. The reliability and long-term stability were demonstrated during the 1976 Olympic Games in Innsbruck⁵ and Montreal⁶, where this detector was used in doping tests.

REFERENCES

- 1 B. Kolb and J. Bischoff, *J. Chromatogr. Sci.*, 12 (1974) 625.
- 2 M. J. Hartigan, J. E. Purcell, M. Novotný, M. L. McConnell and M. L. Lee, *J. Chromatogr.*, 99 (1974) 339.
- 3 R. Pigliucci, W. Averill, J. E. Purcell and L. S. Ettre, *Chromatographia*, 8 (1975) 165.
- 4 M. J. Hartigan and J. E. Purcell, *Chromatogr. Newsl.*, 3 (1974) 23.
- 5 G. L. Dadisch, W. Vycudilik and G. Machata, *Forensic Sci.*, in press.
- 6 M. Bertrand, G. Sanchez, C. Vaziri and R. Dugal, *ACS Centennial California Section Diamond Jubilee Meeting*, San Francisco, 1976.