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GAS CHROMATOGRAPHY OF NITROGEN- AND PHOSPHORUS-CONTAINING COMPOUNDS

A NEW, HIGH-SENSITIVITY, VARIABLE SELECTIVITY DETECTOR*

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SUMMARY

Gas chromatographic analysis of nitrogenous and phosphorated compounds is simplified by the use of thermionic detectors which respond selectively to these substances.

The new detector described here works on the principle of thermionic detection, showing high sensitivity and marked selectivity towards phosphorus and nitrogen containing molecules, and discriminating well between them. The selectivity factor between the two heteroatoms may be varied by changing the geometrical arrangement of the electrodes. The detector lends itself to numerous applications, one particularly interesting field being the determination of inorganic compounds containing nitrogen and phosphorus.

INTRODUCTION

In 1964 Karmen and Giuffrida[1–3] demonstrated that the conventional flame ionization detector (FID) shows much greater sensitivity to organic compounds containing phosphorus or halogens if the flame is doped with sodium salt vapours. A special sodium thermionic detector was built, in which a ring electrode, coated with molten sodium sulphate, was placed around the flame. These detectors, known as thermionic, alkali-flame, etc., were immediately put to use to determine phosphorated and chlorinated pesticide traces.

Later investigations into the selective behaviour of this detection system, depending on the type of alkali metal salts used, showed that the detector response could be enhanced towards other heteroatoms such as nitrogen, arsenic[4] and sulphur[5]. The chemico-physical mechanism by which this is achieved is still not altogether clear. However, from the point of view of gas chromatography applications, the thermionic detector is of great interest in solving analytical problems requiring maximum sensitivity and selectivity. The detector response is enhanced for organic phos-

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phorus- and nitrogen-containing substances, and is therefore extremely useful for both research and routine analysis. It may be applied meaningfully for the determination of pesticide residues, either phosphorated or nitrogenous, herbicides, or in the fields of toxicology, forensic medicine, pharmacology, etc., or wherever high sensitivity and selectivity are required and the active components are almost always nitrogenous.

The analysis of phosphorus-containing substances does not represent a big problem, since the thermionic detector is especially sensitive to this element: analysis of nitrogen compounds is slightly more complicated, because it calls for an optimisation of operative parameters, providing some difficulty in ensuring a controlled, repeatable, and specific response coupled to a high sensitivity.

The detection system is, however, simple, and is suitable for a broad range of applications, thus explaining the interest it has aroused over the last 10 years. Numerous detectors have been produced, with widely varying geometry, single or double flames, and different alkali metal salts. The commercially available thermionic detectors for phosphorus and nitrogen offer many original features, but not all are equipped to exploit fully this detection principle, and may suffer some analytical limitations.

THE NITROGEN-PHOSPHORUS SELECTIVE DETECTOR (NPSD)

Description

The detector is designed to ensure that all the thermionic detection operative parameters are independent and easily controlled. A schematic diagram of the NPSD is shown in Fig. 1. The alkali source, the heart of the thermionic detector, is a potas-

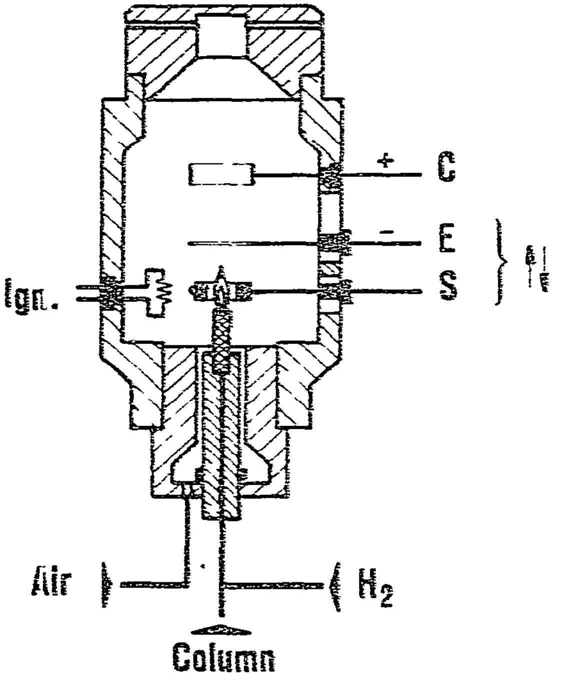


Fig. 1. Schematic diagram of the NPSD. C = Collector electrode. E = adjustable height polarization electrode: S = adjustable height alkali salt source.

sium chloride pellet. This particular salt has been chosen for the following reasons: it requires a low hydrogen flow-rate, suppresses the response to halogenated compounds, gives an enhanced response to phosphorus, and works equally well with nitrogenous compounds. The alkali source can be shifted over the flame to give the maximum ionization current, or lowered beneath the flame allowing typical FID operations. The polarization electrode is also movable and can be shifted vertically to alter the electric field in which the complex ions generated by the detection mechanism are collected, thus considerably increasing the analytical range of the detector. The hydrogen flow-rate is adjusted by the pressure reducers already mounted on the gas chromatograph.

Operation

The alkali source having been positioned to give maximum electrical conductivity of the flame, the standing current can be reduced as shown in Fig. 2 by adjusting the position of the polarization electrode. Detector sensitivities (signal-to-noise ratios) for the nitrogen and phosphorus operation modes are achieved from different standing current levels. In the right conditions, the charges producing the standing current cause a minimum of interference, and the ions formed can be collected "cleanly". The results of a trial with the NPSD appear to be in agreement with the mechanism suggested by Cremer[6] whereby complex ions of increased and different lifetimes are

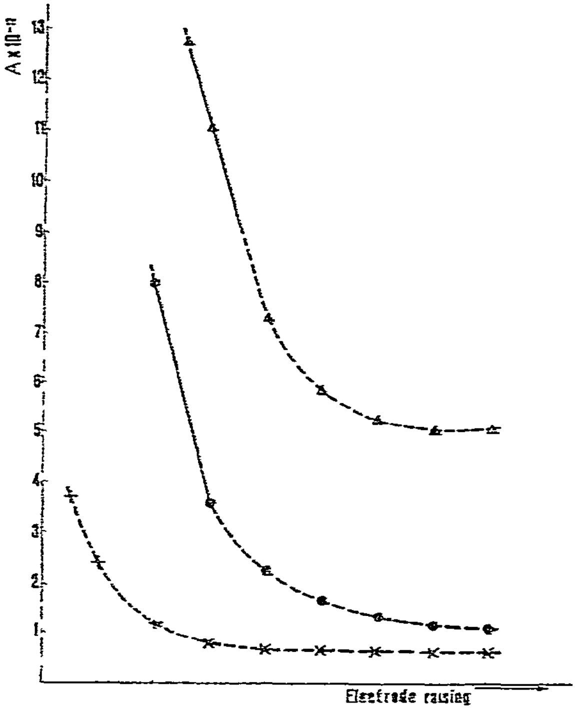


Fig. 2. Standing current patterns following upward displacement of the polarization electrode. Full line: optimum sensitivity range. Hydrogen flow-rate: ▲, 39 ml/min; ●, 36 ml/min; ×, 30 ml/min.

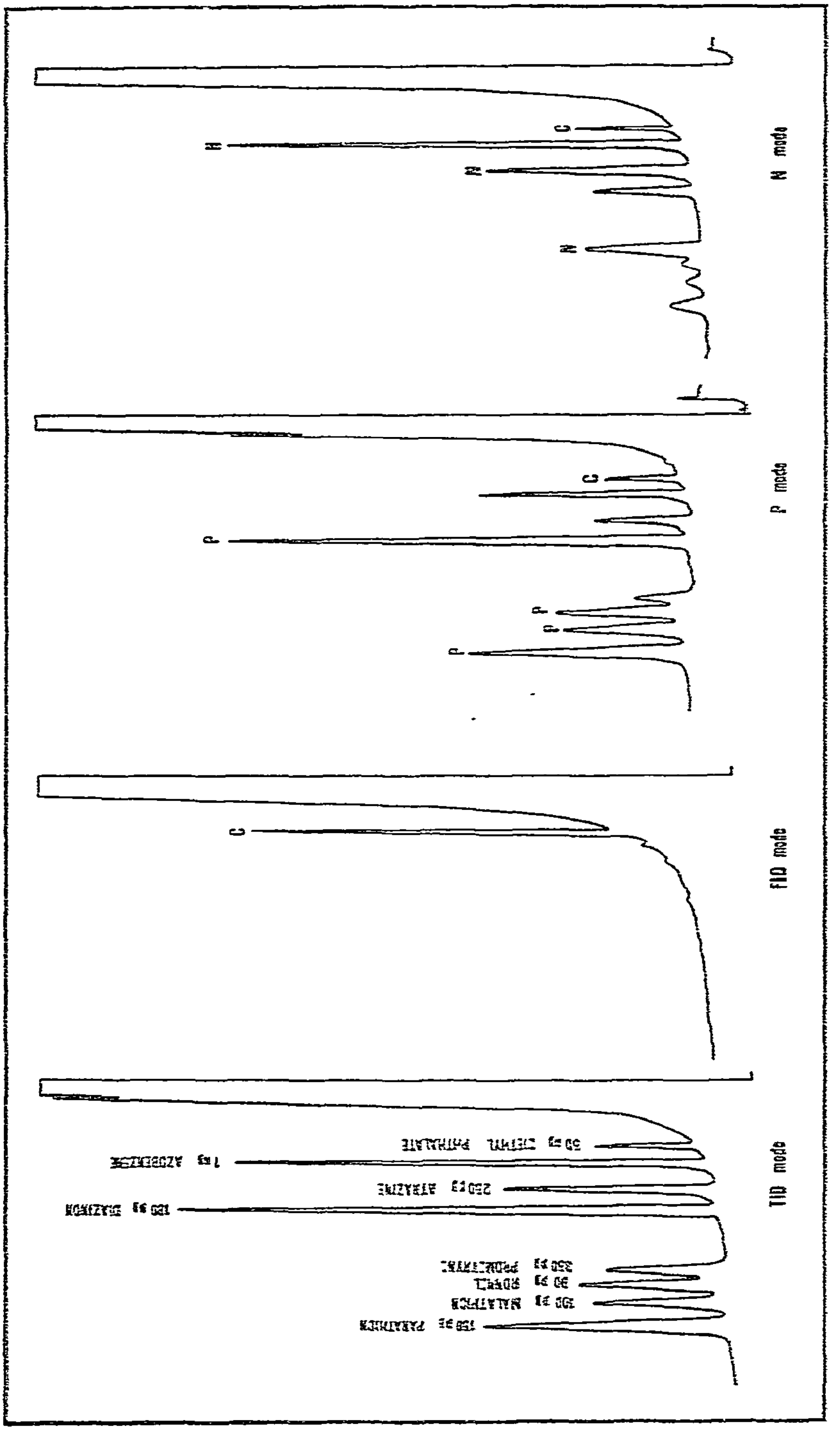


Fig. 3. Different NPSD responses to a standard solution containing nitrogen and phosphorus compounds and diethyl phthalate. Column: 2 m × 3.5 mm I.D., 5% OV-1 on 80–100 mesh Gas Chrom Q; column temperature: 210°; carrier gas: nitrogen, 50 ml/min.

formed by interaction between alkali ions and ionized or neutral radicals containing heteroatoms.

Altering the geometry of the electrical field[7] by shifting the polarization electrode, the charges can be collected more selectively either for phosphorus or for nitrogen. Moving the electrode towards the flame, and increasing the standing current, gives a better phosphorus/nitrogen (P/N) signal ratio, while if the electrode is moved away from the flame, the standing current drops and the P/N signal ratio improves in favour of nitrogen.

To underline the detector's ability to be selective for one or other of these two heteroatoms, a solution containing nitrogen and phosphorus compounds, and diethyl phthalate as organic reference substance, was analysed with the detector in four different modes. Fig. 3 shows the chromatograms obtained with a 2 m glass column of 5% OV-1 on Gas Chrom Q at 210° using nitrogen as carrier gas, and demonstrates the possibility of changing the selectivity ratio towards either nitrogenous or phosphorated compounds. To obtain the FID tracing, the potassium chloride pellet was lowered beneath the flame.

The optimum hydrogen flow-rate depends on the carrier gas type: using helium, the hydrogen flow-rate should be set at 25–30 ml/min, and at 35–40 ml/min when nitrogen is used (with the carrier gas flow-rate in the range 40–50 ml/min).

The detector behaves quite differently with nitrogen and helium. This effect appeares to be related to the different thermal conductivities of helium and nitrogen which changes the environmental conditions of the flame (temperature and ion concentration). Using helium, the selectivity ratio against carbon is about 100 times greater for phosphorus and 10 times greater for nitrogen; sensitivity, in terms of minimum detectable amount, is increased about ten-fold for phosphorated compounds while being slightly decreased for nitrogen-containing compounds (Fig. 4).

DETECTOR PERFORMANCE

Sensitivity and selectivity

Compared to the conventional FID, the NPSD offers improved sensitivity, ranging from 50 to 100 times for nitrogen substances, and from 500 to 1000 times for phosphorated substances, according to the amount of nitrogen and phosphorus in the molecule. Table I gives the detection limit for some nitrogen- and phosphorus-containing compounds.

It is to be noticed that the detector gives the best absolute sensitivity for phosphorated compounds: as shown in Fig. 5, parathion and malathion can be detected easily in quantities below 10^{-12} g. In view of this extreme sensitivity to phosphorus, analytical techniques might be developed involving the formation of phosphorated derivatives[8–10], allowing determination of traces of organic substances which would otherwise not be detectable. The selectivity of response to carbon varies from 10^3 for nitrogen compounds and 10^4 for phosphorated substances, the selectivity being moveable, as already described, towards phosphorus or nitrogen, just by raising or lowering the electrode over the flame.

Some properties of the NPSD

It is interesting to note that in case of substances containing both phosphoru

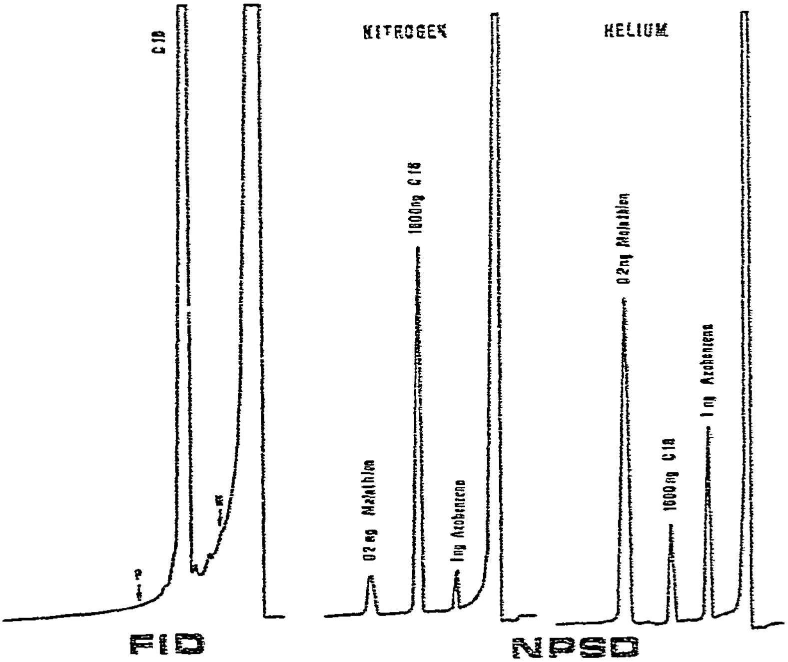


Fig. 4. Dependence of NPSD behaviour on carrier gas type (nitrogen and helium) compared with FID response.

TABLE I

DETECTION LIMIT FOR SOME NITROGEN- AND PHOSPHORUS-CONTAINING COMPOUNDS

Compound	*Detection limit (g/sec)*	*Per cent heteroatom*	*Detection limit to heteroatom*
Dimethylnitrosamine	7×10^{-13}	N = 37.82	2.6×10^{-13}
Caffeine	3×10^{-13}	N = 28.85	1×10^{-13}
Atrazine	1.5×10^{-13}	N = 32.58	5×10^{-14}
Prometryne	3×10^{-13}	N = 29.02	9×10^{-14}
Diazinon	1×10^{-14}	P = 10.18	1×10^{-15}
Malathion	2×10^{-14}	P = 9.38	2×10^{-15}
Parathion	1.5×10^{-14}	P = 10.64	1.6×10^{-15}

and nitrogen, such as diazinon (2N = 9.20%; 1P = 10.18%) the detector responds as if only phosphorus were in the molecule. The detector behaviour is similar when compounds containing only nitrogen and those containing only phosphorus emerge from the column with the same retention time.

Also, for substances containing phosphorus and chlorine, such as ronnel (3 Cl = 33.08%; 1P = 9.63%), the detector is phosphorus-sensitive. On the other hand, compounds containing only chlorine do not respond, or give negative peaks, if large amounts are present.

The presence of phosphorus is therefore sufficient to identify the molecule as phosphorated, regardless of whether other detectable heteroatoms are also present.

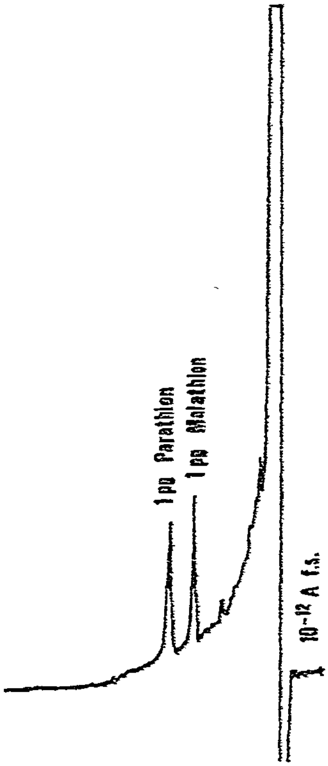


Fig 5. High sensitivity determination of organophosphorus pesticides.

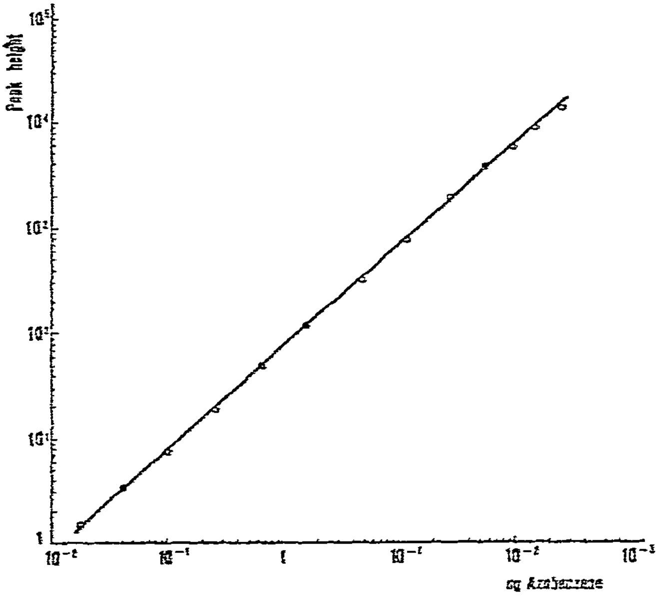


Fig. 6. NPSD response linearity for azobenzene.

Linearity

The NPSD gives a linear response over a wide range of concentration. Fig. 6 shows a linear plot for azobenzene to within 10^4. For phosphorated compounds, a similar degree of linearity is obtained.

Analytical applications

For the determination of pesticide residues in fruit, vegetables, soil, etc., phosphorated pesticides must be identified rapidly, together with any nitrogenous ones such as carbamates or triazine herbicides.

The NPSD is not only very sensitive to these substances, but is also useful in the identification of phosphorus or nitrogen peaks. The same detector operated as in the FID mode allows the identification of the organic co-extracts also present. Fig. 7 gives the gas chromatographic results for an extract of a culture medium treated with igran, a triazine herbicide. A 2 m column of 5% OV-1 was used, with a temperature program of 20°/min from 180 to 240°. Shifting the detector response to "N mode" and "P mode", and comparing the chromatograms obtained, at least four phosphorated pesticides were detected whose presence in the sample was not suspected. The FID tracing, obtained under the same conditions, shows peaks for organic co-extracts which the NPSD totally suppresses.

The high sensitivity of this detector, and its selective response reduces the "clean-up" needed before the GC analysis. The determination of the caffeine residue in decaffeinated coffee is an example. Fig. 8 shows the chromatogram of a water–

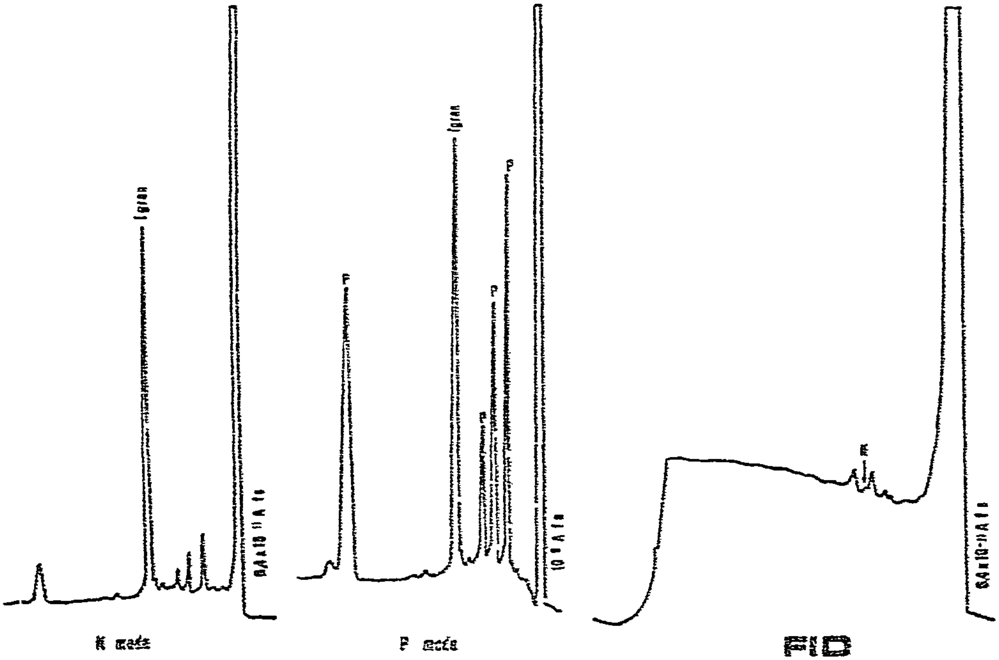


Fig. 7. Identification of a nitrogenous herbicide (igran) together with phosphorated and organic co-extracts ("P mode" and FID tracings).

acetone extract of coffee powder treated with magnesium oxide in comparison with the FID chromatogram, which here appears absolutely inadequate for quantitative purposes.

Using the NPSD and FID mounted in parallel at the column outlet, qualitative and quantitative results can be immediately obtained from biological extracts. The nitrogenous substances can be identified by simply comparing the two chromatograms, and determined quantitatively with a sensitivity roughly in agreement with the nitrogen content. Fig. 9 shows an example of a barbiturate (veronal) analysis extracted from organic material and chromatographed without any special "clean-up". A 2 m column of 3% OV-17 on 80–100 mesh Gas Chrom Q was used, with a temperature program of 5°/min from 160 to 280°. Compared to the FID, the NPSD chromatogram is extremely clean, and baseline drift due to the temperature program is almost totally absent.

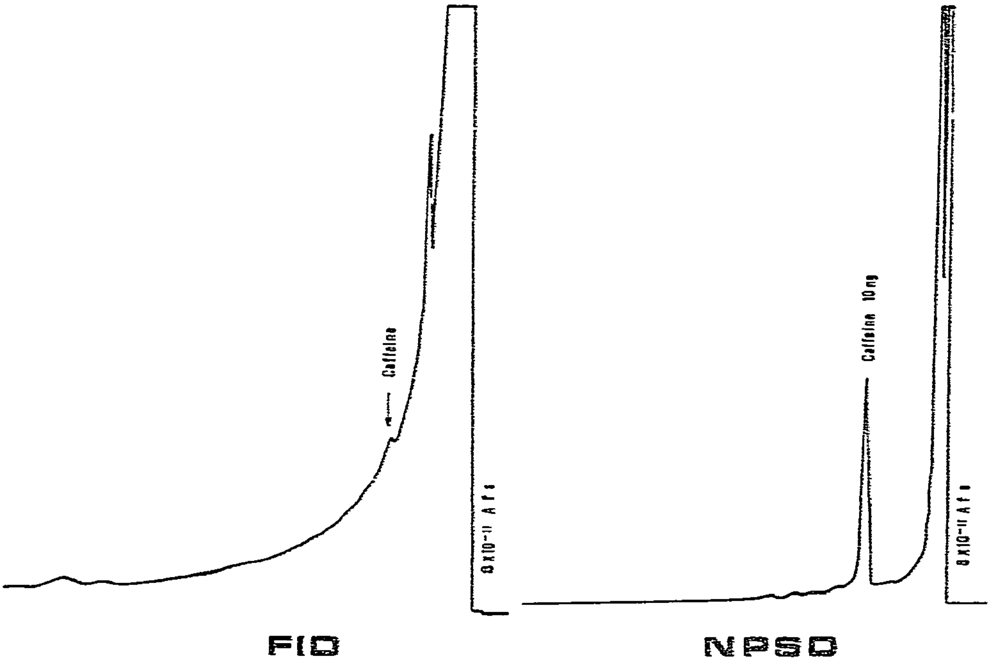


Fig. 8. Caffeine residue in a water–acetone extract of decaffeinated coffee chromatographed with NPSD and FID mounted in parallel.

The performance of the detector with inorganic compounds containing phosphorus of nitrogen has been also investigated. Fig. 10 shows traces of PCl_3 in diethyl ether, and Fig. 11 and 12 show the analysis of N_2O in nitrogen and NH_3 in an aqueous solution. The detector sensitivity towards these substances, which contain no ionizable carbon, is good —in any case much better than a thermal conductivity detector. This confirms that the detection mechanism is not the same as in a conventional flame ionization detector, where the response depends on the formation of ions as a result of carbon oxidation. It might be interesting to go into this question further, analysing different inorganic substances and assessing detector efficiency, both with regard to sensitivity and linearity of response.

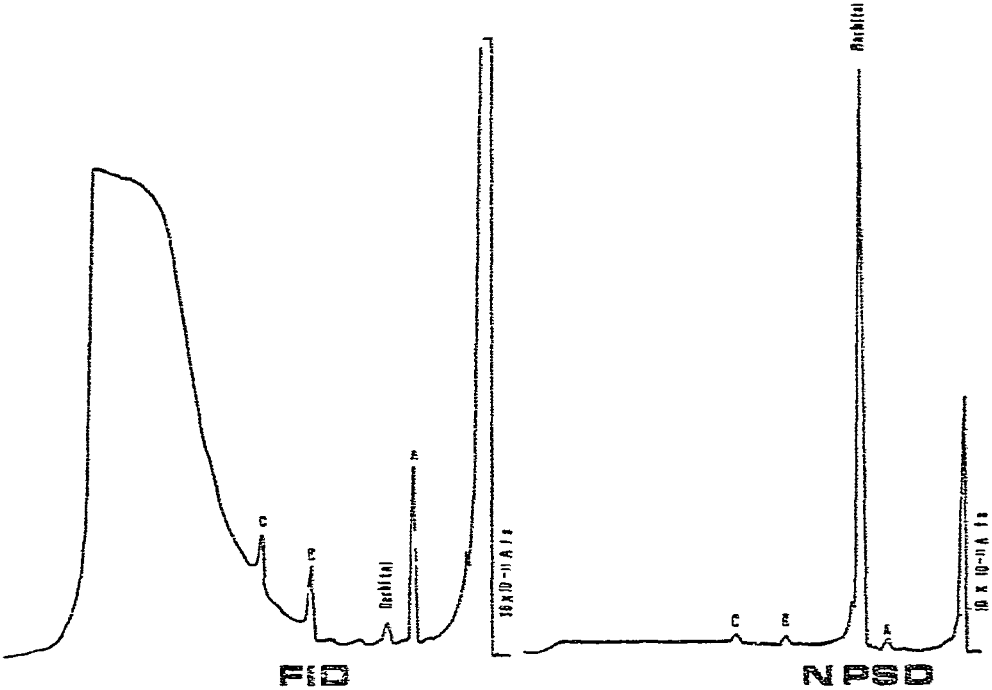


Fig. 9 Temperature programmed chromatograms (NPSD and FID) of a barbiturate extracted from organic material without any special clean-up. Column: 2 m × 3.5 mm I.D., 3% OV-17 on 80–100 mesh Gas Chrom Q, column temperature: 160–280°, 5°/min, carrier gas: helium, 45 ml/min.

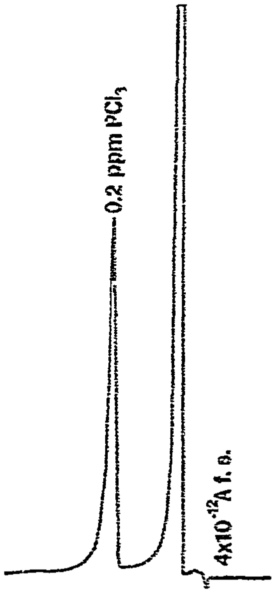
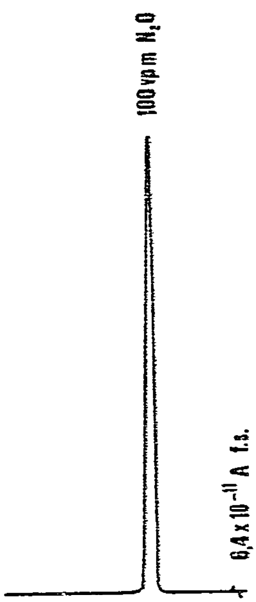


Fig. 10. Determination of PCl_3 in diethyl ether. Column: 2 m × 3.5 mm I.D., 7% DC 200 on 80–100 mesh Gas Chrom Q; column temperature: 60°; sample injected: 1 μl.



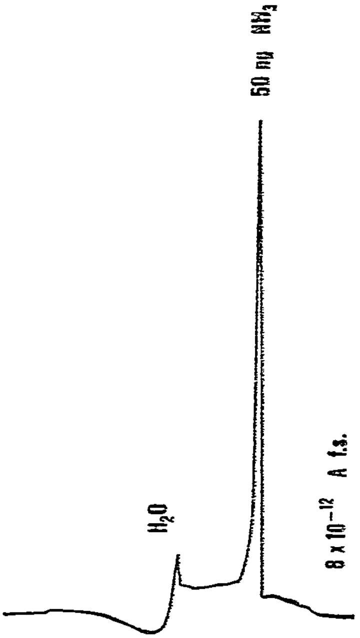


Fig. 11. Detection of N_2O in nitrogen. Column: 2 m × 3.5 mm I.D., 80–100 mesh Chromosorb 102: column temperature: 50°; sample injected: 2 ml.

Fig. 12. Determination of NH_3 in aqueous solution. Column: 2 m × 3.5 mm I.D., 80–100 mesh Chromosorb 103: column temperature: 120°.

CONCLUSIONS

The new nitrogen–phosphorus detector described in this paper has significant advantages in terms of sensitivity, selectivity and versatility. The detector's capability of distinguishing molecules containing nitrogen from those containing phosphorus, and detecting them in extremely small amounts, is expected to be useful in solving many analytical problems. The NPSD possibilities for detecting inorganic substances containing nitrogen or phosphorus are of particular interest, as they demonstrate the high versatility of the detector.

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