Note

Thermionic detectors in gas chromatography

Selective detection of phosphorus, nitrogen, and sulphur compounds

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The thermionic detector (TD), sometimes referred to as an alkali flame ionisation detector or a nitrogen detector, has been used in combination with gas chromatography since 1964, when Giuffrida[1] thoroughly investigated its behaviour and determined the optimum operating conditions with respect to the selective detection of phosphorus and chlorine hetero atoms. Since then, the TD has been found capable of detecting nitrogen[2] and now it is used mainly for the selective detection of organophosphorus and organonitrogen compounds; its sensitivity towards phosphorus is several orders higher than that of the flame ionisation detector (FID) and it has a very high degree of selectivity with respect to hydrocarbons as well. The detector, it is claimed, also responds to silicon, sulphur, boron, arsenic, antimony, and bismuth, although to a much lesser degree[3].

This paper reports the use of a commercial TD (Pye Unicam) which has been tuned to give a high detection sensitivity towards organosulphur. The sensitivity is greater than that which can be obtained for nitrogen but less than that for phosphorus. It also shows the relationship between the hydrogen flow-rate and the optimum operating conditions for detecting sulphur, nitrogen, and phosphorus hetero atoms.

EXPERIMENTAL AND RESULTS

Our experiments were carried out on a Pye Series 104 Model 124 chromatograph, fitted with dual FID–TD. The TD[4] is a three-electrode detector where the salt, rubidium chloride, is pressed into a metal holder in the shape of a short tube. This coated metal tube is fitted between the burner and the collector electrode and acts as a ring electrode.

The separations were carried out on a 5 ft. × ¼ in. O.D. glass column packed with 10% Silicone Elastomer, E-301 on acid-washed Celite, 100–120 mesh at 175°. The effluent gas was split 1:1 to each detector. The electrometer attenuation settings were × 1000 for each detector.

Standard solutions

Standard 1 was a 0.01% (w/v) solution in hexane of each of the following

components listed in order of elution time (Fig. 1): *m*-chloroaniline, thionaphthene, *p*-dinitrobenzene, diphenylamine, tetradecane, and tris(isopropyl) phosphate.

Standard 2 was standard 1 diluted 10 times with hexane.

Standard 3 was standard 1 diluted 100 times with hexane.

Procedure

Using a constant carrier gas (nitrogen) flow-rate at 60 ml/min and an air flow-rate at 550 ml/min to each detector the hydrogen supply to the FID was set at 35 ml/min and to the TD was increased in small increments from 25–62 ml/min. Each hydrogen setting was tested with 1 μl of one or more of the standard solutions to obtain a less than full-scale peak for each component (Fig. 1). Because of the critical effect on response with hydrogen flow-rate setting the procedure was then repeated with an incremental reduction in hydrogen flow-rate and the mean peak heights were calculated (Fig. 2). Similar experiments were also carried out with air to the TD set at 300 ml/min.
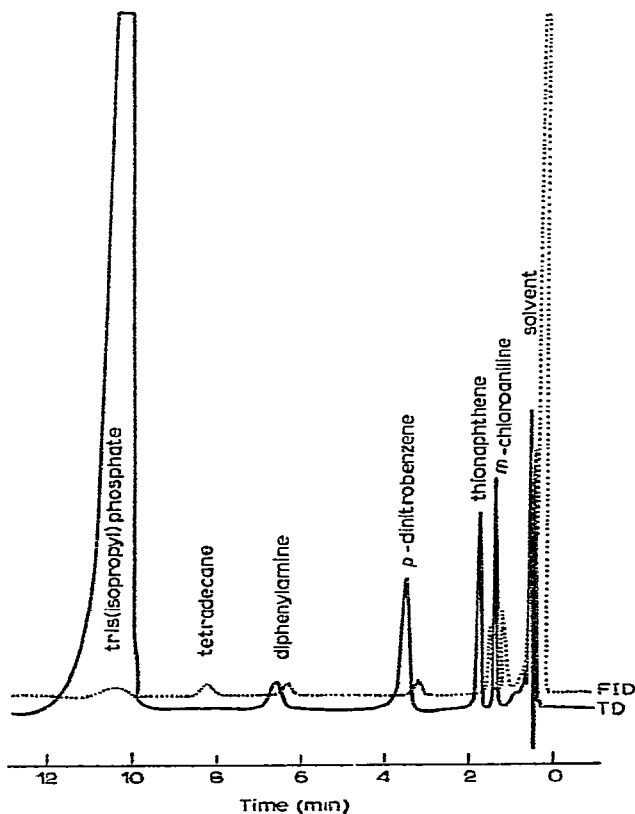

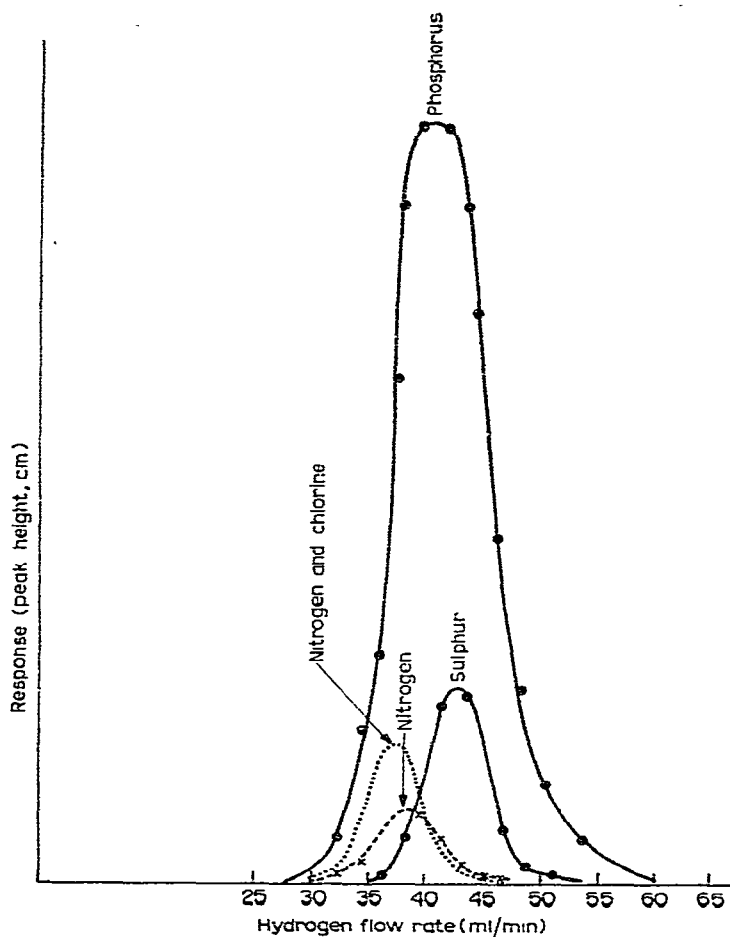Fig. 1. Typical chromatogram. Hydrogen flow-rate to TD, 40 ml/min.

Fig. 2. Effect on response with changes in hydrogen flow-rate.

DISCUSSION

Fig. 2 illustrates the change in response of the TD for each component (except tetradecane, which even with the strongest standard solution gave less than 1 % of full-scale deflection) with changes in hydrogen flow-rate. The responses are given as actual peak height measurements and are not therefore true relative responses. These results show there is a significant difference in the hydrogen flow-rates necessary to obtain optimum sensitivities for nitrogen and sulphur and that by careful control of the flow-rate a great deal of selectivity between these hetero atoms can be achieved. The response to phosphorus is much greater than to the other hetero atoms and there is a broad response with changes in hydrogen flow-rate that envelopes the responses from nitrogen and sulphur. This means that the detector cannot be tuned to distinguish between phosphorus and either of the other atoms. The hydrogen flow-rate required to give high sensitivity for phosphorus is relatively non-critical and con-

sequently the detector can be operated very satisfactorily for this purpose under routine analytical conditions.

In the detection of nitrogen the flow-rate necessary for optimum sensitivity is more critical and this confirms our general experience with the TD over the last year, which has shown that some operational expertise is necessary to obtain satisfactory sensitivity. The optimum hydrogen flow-rate was the same for both p-diphenylamine and dinitrobenzene and we also have satisfactorily operated the detector with a wide variety of other nitrogenous compounds, all of which have given responses approximately proportional to the amount of nitrogen introduced. At its optimum setting the detection sensitivity can be more than ten times greater than is obtainable with a FID.

This detector, fitted with a rubidium chloride, tip is known[4] to give a poor response to halogenated compounds and is rarely used for this purpose. The addition of m-chloroaniline to our test mixture was only made to check if the response to nitrogen could be influenced by the presence of chlorine. The results show a possible slight shift in the response peak but there is no indication that the presence of a halogen atom would affect the distinction that can be made between nitrogen and sulphur atoms.

The detection of sulphur-containing compounds requires a higher hydrogen flow-rate and at the optimum flow-rate for this hetero atom it is possible to distinguish it from nitrogen. Responses up to a hundred times greater than on an FID have been attained and a high degree of selectivity has been obtained with respect to non-sulphur- and phosphorus-containing organic compounds as well.

The high sensitivity makes it relatively easy to operate under routine conditions. We have now used the detector in the sulphur mode for about six months and it has proved indispensible in a number of problems, involving the determination of traces of sulphur compounds, e.g., isopropyl mercaptan, dimethyl sulphide and dimethyl sulphate, often in the presence of overlapping organic peaks. Because of the higher temperature of the salt plug associated with the increased hydrogen flow-rate, there is greater loss by vaporisation of rubidium chloride; some of this condenses in the upper part of the detector and it is necessary to brush between the salt disc and the probe each day.

When the experiments shown in Fig. 1 were repeated with the air flow-rate to the TD reduced to 300 ml/min, there was a slight shift in the optimum responses towards higher hydrogen flow-rates, but this did not affect the relative responses of nitrogen, sulphur and phosphorus.

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