

CHROM. 6232

VERSATILE ELECTROLYTIC CONDUCTIVITY DETECTOR FOR GAS CHROMATOGRAPHY

P. JONES AND G. NICKLESS

Department of Inorganic Chemistry, University of Bristol, Bristol, BS8 1TS (Great Britain)

(Received June 28th, 1972)

SUMMARY

The paper describes a relatively inexpensive gas chromatography detector system which may be constructed from easily obtainable components with a potential sensitivity between that of flame ionization and electron capture detectors. The use of a specially treated nickel catalyst produces reliable long-term operation, whilst replacement of a pure water system normally used by one employing very dilute electrolytes makes it possible to differentiate between nitrogen-, chlorine- or sulphur-containing compounds without recourse to gas "scrubbers".

INTRODUCTION

The use of an electrolytic conductivity system in conjunction with a micro combustion furnace for the detection of nitrogen, chlorine and sulphur compounds has been described by COULSON in 1965 (ref. 1). He demonstrated that oxidative or reductive pyrolysis of the eluants from a gas chromatographic (GC) column produced simple inorganic gases which when dissolved in water may be detected conductometrically with high sensitivity.

The most interesting feature of this detector is its potential in terms of high selectivity. For example, COULSON² produced a system which was completely selective for nitrogen compounds, by using the reductive mode in association with a strontium hydroxide "scrubber" to absorb unwanted acid gases, thereby producing peaks due to ammonia only. This was evaluated for nitrogen-containing pesticides by PATCHETT³. RHOADES AND JOHNSON⁴ went further and distinguished N-nitrosamines from other nitrogen compounds present in tobacco smoke by varying the furnace conditions.

A detector of this type should be of great value for the study of pesticide residues in complex matrices such as biological systems. Two important advantages are: (1) the qualitative data obtained can be used to supplement retention data for peak identification; (2) some tedious clean-up stages may be eliminated since a large number of compounds do not produce a response.

It will be shown that a relatively inexpensive detector system can be constructed from easily obtainable components, with a potential sensitivity between that of flame ionization and electron capture detectors. The use of a specially treated nickel catalyst gives reliable long term operation, and the substitution of the pure

water system by one using very dilute electrolytes makes it possible to differentiate between nitrogen, chlorine and sulphur compounds without the need for gas "scrubbers".

DETECTOR ARRANGEMENT AND OPERATION

All work with the detector was carried out in the reductive mode. The complete system is shown in Fig. 1 in schematic form. Hydrogen is mixed with the effluent from the GC column (carrier gas must not be nitrogen) through a capillary T-junction. The mixture is passed into a narrow-bore quartz furnace tube containing a nickel catalyst. Furnace temperature is maintained at around 800°. Breakdown of the eluant molecules to simple hydrides occurs, as follows, depending on the composition: NH_3 , HX (X = halogen), H_2S , PH_3 , H_2O , and simple hydrocarbons.

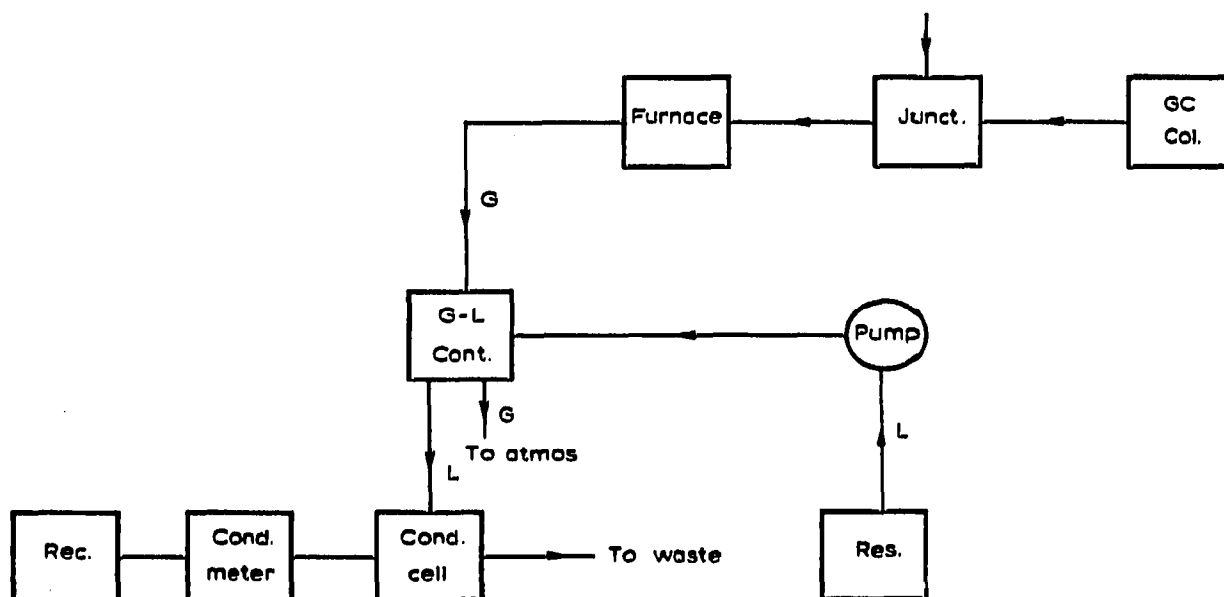


Fig. 1. General schematic outline of detector system. L = liquid; G = gas.

The issuing furnace gases immediately come into contact with a slow-moving stream of water. This is separated from the gas after a short contact time and drawn through a small-volume conductivity cell by siphon pressure. The electrical resistance of the solution is continuously monitored on a chart recorder via a conductivity meter. Any dissolved gases which ionize in solution will produce a peak similar to the concentration profile of the original eluant.

Figs. 2 and 3 show the more important components in greater detail.

Catalyst

The catalyst is a closely fitting (1.4-mm) nickel wire with a specially treated surface. Previous procedures utilized well packed tubes with a high surface area of nickel. It was found that even small nickel beads gave variable sensitivity and had a short lifetime (in terms of the number of samples injected) due to blockage by carbonization. Furthermore, the catalytic properties were not regenerated by

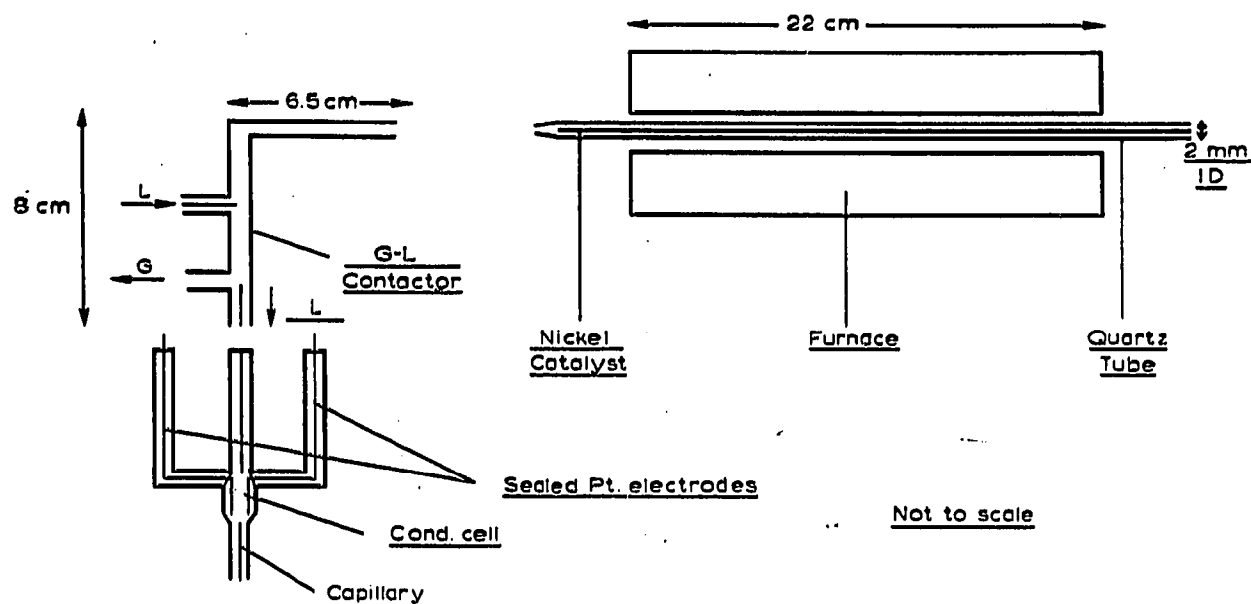


Fig. 2. Detailed magnified diagrams of components excluding junction and siphon system.

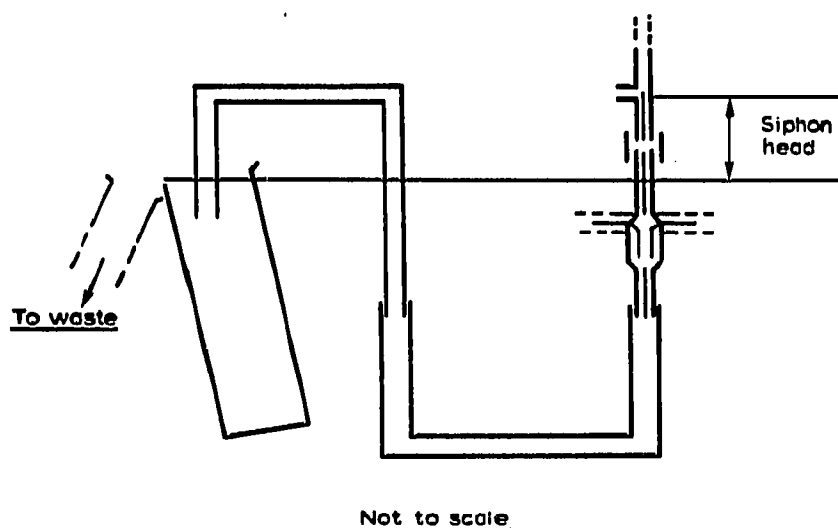


Fig. 3. Dimensions of siphon outlet system.

heating in a stream of air and then in a stream of hydrogen. Most of the trouble appeared to be caused by variable amounts of nickel oxide which were not reduced adequately in the hydrogen stream.

Nickel wire with a very clean surface gave the highest sensitivity with a much longer lifetime, the rate of carbonization being very low. The nickel surface was prepared by deliberately forming a layer of nickel oxide (heated to redness in air), then stripping off with hot "aqua regia" to produce a very bright pitted surface. To avoid oxidation this should not be heated or cooled in the furnace unless a stream of inert gas or hydrogen is flowing.

Gas-liquid contactor

The gas-liquid contactor was designed to facilitate a siphon outlet system and to reduce the liquid-dead-volume. The capillary inlet and outlet are essential

for reliable operation. The contactor is stored in "chromic acid" when not in use and soaked in 4% hydrofluoric acid for 10 min before operation to ensure 'even spread' of the water for maximum contact with the furnace gases.

Conductivity cell and electronic system

The conductivity cell and electronic system were obtained from the apparatus used for monitoring liquid or ion-exchange chromatography columns (LKB Produkter AB, Sweden). The cell (which was surrounded by a bath of water) had a volume of approx. 10 μl and a cell constant of 0.7 cm^{-1} . The conductivity meter (called Conductolyser, LKB 5300 A) could not measure resistances greater than 10,000 Ω , and since most solutions have resistances in excess of this, it necessitated a shunt across the cell (Decade box variable from 1-100,000 Ω). The detection limits were not affected by this change since the sensitivity of the Conductolyser can be increased to detect very small resistance changes much less than the noise levels encountered at present. Thus it can be seen that a high-purity water system ($R \approx 10^6 \Omega$) is not essential with this set-up and, more important, the effect of using very dilute electrolytes in the liquid flow system can be investigated without sacrificing sensitivity. This means simple chemical reactions between the furnace gases and the electrolyte may be utilized to extend the versatility of the detector (described later). Two important points arise, *viz.* (a) any dilute electrolyte solution can be used as long as its resistance is not less than 10,000 Ω , otherwise a rapid drop in sensitivity will be experienced; (b) the variable shunt should be set so that the resistance "seen" by the conductivity meter is approximately at its maximum limit of 10,000 Ω when the solution is flowing.

Flow system

The flow system is open-ended. The solution is supplied to the gas-liquid contactor using a peristaltic pump system (Watson Marlow Ltd.), usually operated at a flow-rate of 1-3 ml/min of water.

The siphon system is set so that all the liquid is flowing through the conductivity cell. This is easily stabilized by adjusting the siphon height. Static air bubbles should be cleared from the system for trouble-free operation.

DETECTOR PERFORMANCE WHEN CONNECTED TO THE GAS CHROMATOGRAPH

The detector was linked to a Microtek GC 2000R research gas chromatograph by 2 ft. of heated steel capillary tubing. The performance is most conveniently divided into three sections, depending on sample type.

Nitrogen compounds

Four simple types with different nitrogen environments were chromatographed (Fig. 4).

A 2-m by 0.2-cm I.D. stainless-steel column packed with 20% Carbowax 20M on AW Supasorb was used; the carrier gas was hydrogen at approx. 50 ml/min; subsidiary hydrogen was not needed; the temperature programme was 70-150°, approx. 7.5°/min; injection, 1 μl of 0.4% (v/v) solution. Detector conditions: junction temperature, 200°; furnace temperature, 800°; solution flow-rate, 3.0 ml/min; solution composition, 5 p.p.m. HCl in distilled water.

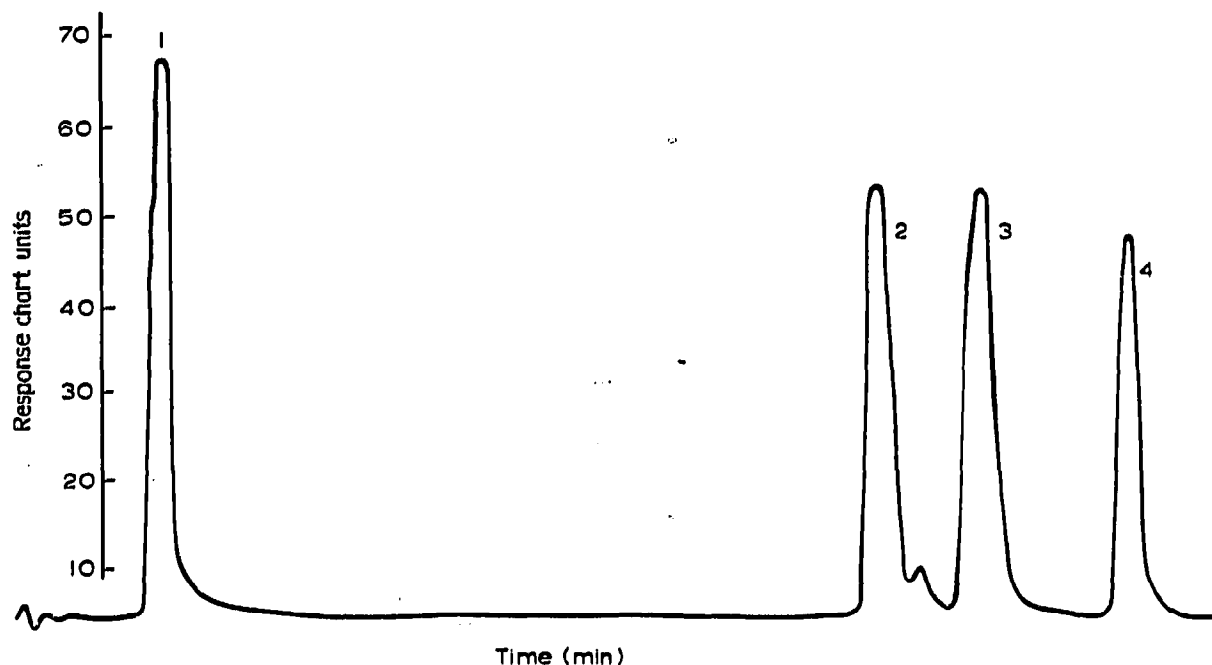
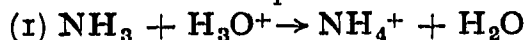


Fig. 4. Chromatogram of four nitrogen compounds, *viz.* (1) pyridine, (2) nitrobenzene, (3) *o*-toluidine, and (4) benzyl cyanide.

Peak shapes and base line stability were very good at the microgram level (Fig. 4). In this particular example a flow solution of very dilute HCl (5 p.p.m.) was used to dissolve the ammonia derived from the furnace, which produced an approximately four-fold increase in sensitivity compared with a non-reactive solution. The neutralization reaction (1) must produce a bigger change in conductance than simple dissolution and partial ionization of the ammonia (2).



For three compounds, nitrobenzene, *o*-toluidine, and benzyl cyanide, the detection limits, defined as a response equal to twice the peak-to-peak noise level, were from $2\text{--}5 \times 10^{-8}$ g. Noise produced by the pulsing action of the pump prevented lower limits of detection being attained.

Graphs of area or height against response were found to be reasonably linear in the 1- to 5- μg range.

Chlorine-containing compounds

In this case use was made of the hydrogen chloride produced in the furnace. No scrubber was employed in these tests, so that the detector would also respond to nitrogen and, to a much lesser extent, sulphur compounds.

Simple chlorine compounds

It was immediately apparent that the detector was much more sensitive to simple chlorine compounds than to nitrogen compounds. A simple comparison of the detection limits is given in Table I.

A 2-m \times 0.2-cm-I.D. stainless-steel column containing 3% Carbowax 20M on Celite was used; the temperature was 145° and the carrier gas, hydrogen at

TABLE I
COMPARISON OF DETECTION LIMITS

| Compound | Detection limit (g) |
|---------------------|---------------------|
| Nitrobenzene | 2×10^{-8} |
| Chlorobenzene | 1×10^{-9} |
| Chloronaphthalene | 5×10^{-10} |
| Hexachlorobutadiene | 5×10^{-11} |

approx. 60 ml/min. The detector conditions were: furnace, 800°; transfer, 200°; flow solution, 1 p.p.m. HCl at 1.5 ml/min; resistance, 10,000 Ω with 11,000 shunt. Quantitative work with chlorobenzene showed good linearity of response over the range 10^{-9} to 10^{-6} g.

Complex chlorine compounds

The performance of the detector was determined with organochlorine pesticides and polychlorinated biphenyls.

Organochlorine pesticides. The separation of a seven-component mixture is demonstrated, all 0.1% w/v in acetone; Lindane, Aldrin, Dieldrin, *p,p*-DDD, Endrin, *p,p*-DDE, and DDT (Tech.).

A 2-m \times 0.2-cm-I.D. stainless-steel column containing the mixed phase OV-17/QF-1 at 11% loading on Gas-Chrom Q was used; the temperature was 200° isothermal and the carrier gas, helium at 40 ml/min. The detector conditions were: furnace, 780°; transfer, 260°; subsidiary hydrogen, 50 ml/min; flow solution,

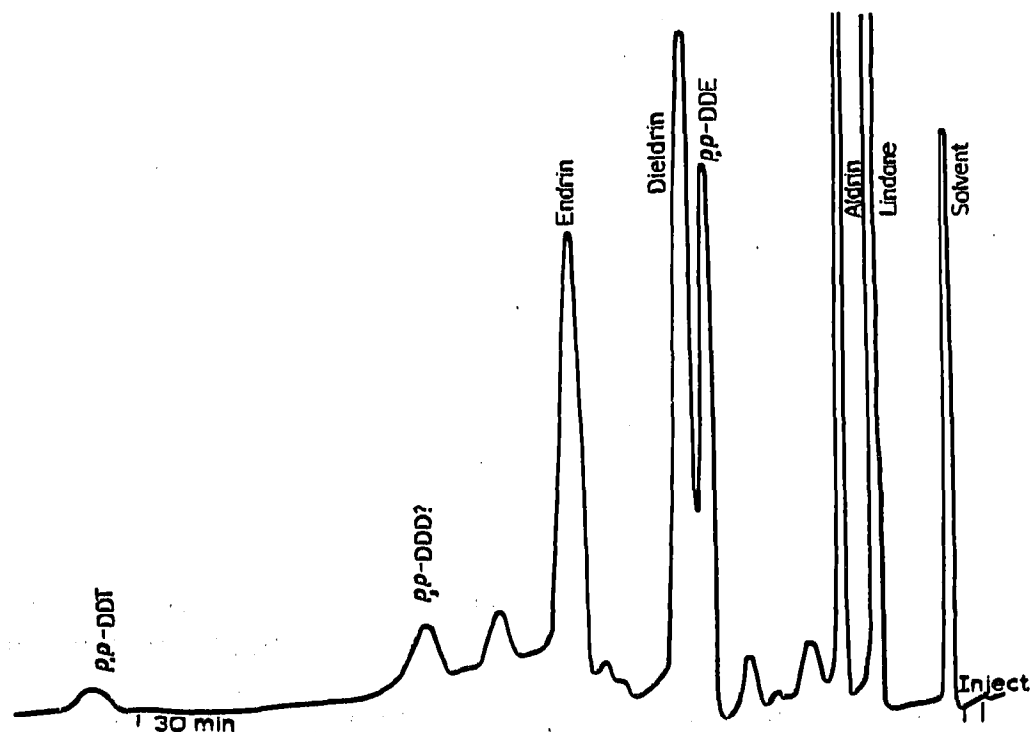


Fig. 5. Chromatogram of a seven-component mixture of organochlorine pesticides

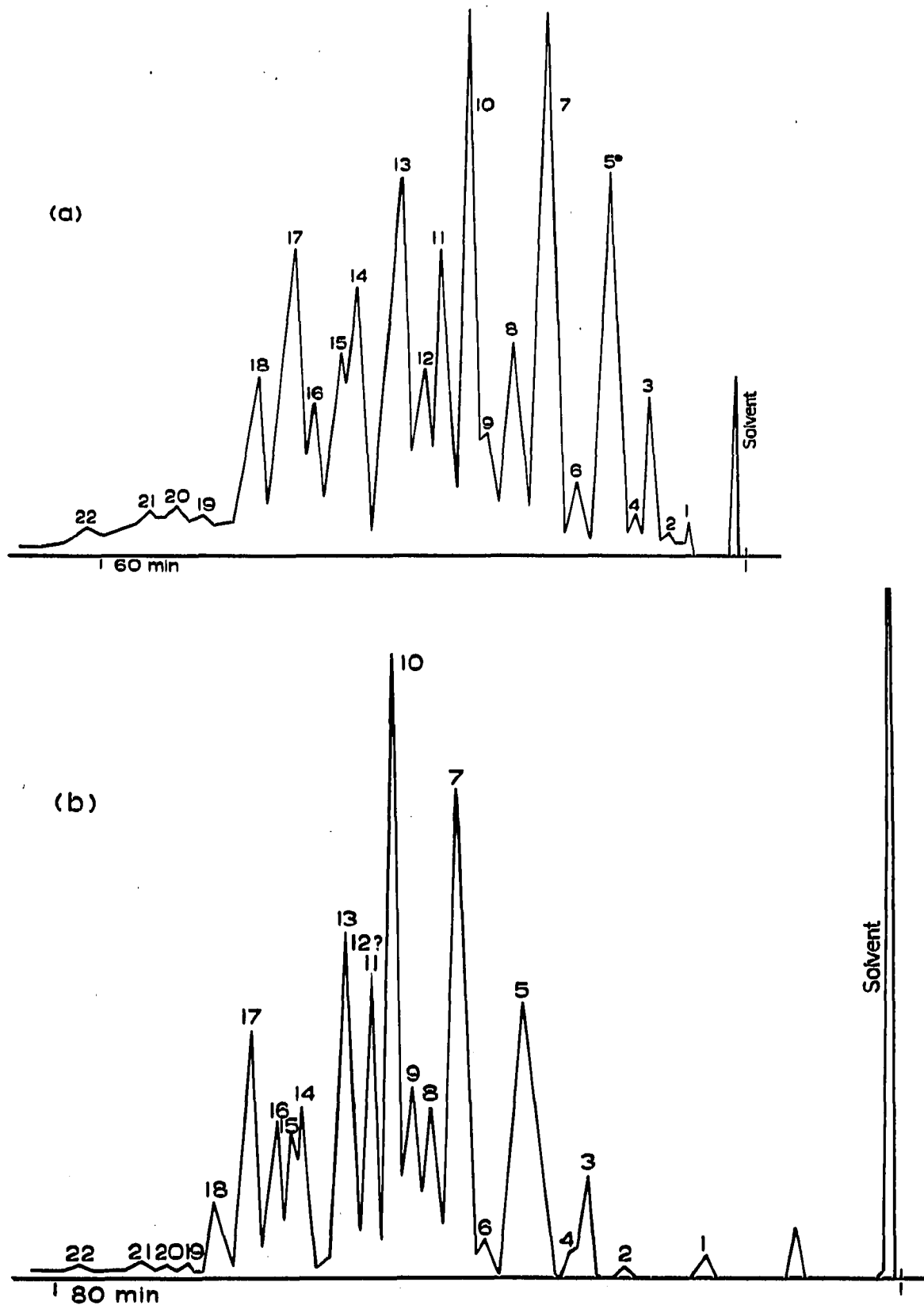


Fig. 6. Chromatogram of (a) An Aroclor 1242 mixture using the electrolytic conductivity detector, and (b) an Aroclor 1242 mixture using the flame ionization detector.

1 p.p.m. HCl at approx. 1.5 ml/min; resistance, set at 10,000 Ω ; chart speed, 16 in./h.

A good response was obtained with the Conductolyser at low sensitivity settings (Fig. 5). The good resolution of Dieldrin and *p,p*-DDE seems little affected by the number of processes involved in the detector where some peak broadening is expected to occur. (The small response for DDT is attributed to the long transfer line which has since been shortened.)

Polychlorinated biphenyls. A solution of the commercial Aroclor 1242 mixture was chromatographed using the conductivity detector and the chromatogram compared with one obtained using conventional flame ionization detection.

For electrolytic conductivity detection 2 μ l of a 2% solution of Aroclor 1242 in acetone were injected. The column was the same as that used for the pesticides. The temperature was held at 145° for 20 min and programmed to 200° at 1.3°/min. The carrier gas was helium at approx. 40 ml/min. Detector conditions: furnace, 820°; transfer, 250°; subsidiary hydrogen, 50 ml/min; flow solution, as for pesticides.

For flame ionization detection 1 μ l of a 5% solution of Aroclor 1242 in *n*-hexane was injected. The column consisted of 2-m \times 0.2-cm-I.D. borosilicate glass packed with 3% Carbowax 20M on Celite. The temperature was held at 105°, for 15 min, then programmed to 190° at 1.5°/min. The carrier gas was nitrogen at approx. 40 ml/min. A Standard Pye 104 detector was used with a sensitivity setting of 5×10^3 .

Care is needed when comparing the two chromatograms directly (Figs. 6a and b) due to different GLC conditions and scales. With the notable absence of the first peak in Fig. 6a (parent diphenyl would not give a response) there is a reasonable "fit" particularly with relative peak heights.

Choice of flow solution composition to improve selectivity and sensitivity

Differentiation of nitrogen- and chlorine-containing compounds. It has already been shown that using very dilute HCl to absorb ammonia produced from nitrogen compounds gave higher sensitivity. This solution can also be used to distinguish between chlorine and nitrogen compounds.

A nine-component mixture was prepared, all components being dissolved at the 0.05% v/v level in toluene. This was chromatographed using a 1 p.p.m. HCl flow solution in the detector with the recorder baseline set approximately in the centre of the chart.

A 2-m \times 0.2-cm-I.D. stainless-steel column containing 3% Carbowax 20M on Celite was used. The carrier gas was hydrogen at approx. 50 ml/min; the temperature programme was 75–170° at approx. 7.5°/min; injection, 1- μ l samples. Detector conditions: furnace, 800°; transfer, 200°; subsidiary hydrogen was not needed; flow solution, 1 p.p.m. HCl at approx. 1.5 ml/min; the baseline resistance was set at 10,000 Ω with recorder centre at chart division 40.

With reference to Fig. 7, the points are: (1) All nitrogen compounds produce peaks below the line because of decrease in conductance due to neutralization. (2) All chlorine-containing compounds produce peaks above the line due to general increase in conductance. (3) The partially resolved pyridine and chlorobenzene have a rapid change-over point. (4) The compound containing N and Cl in the

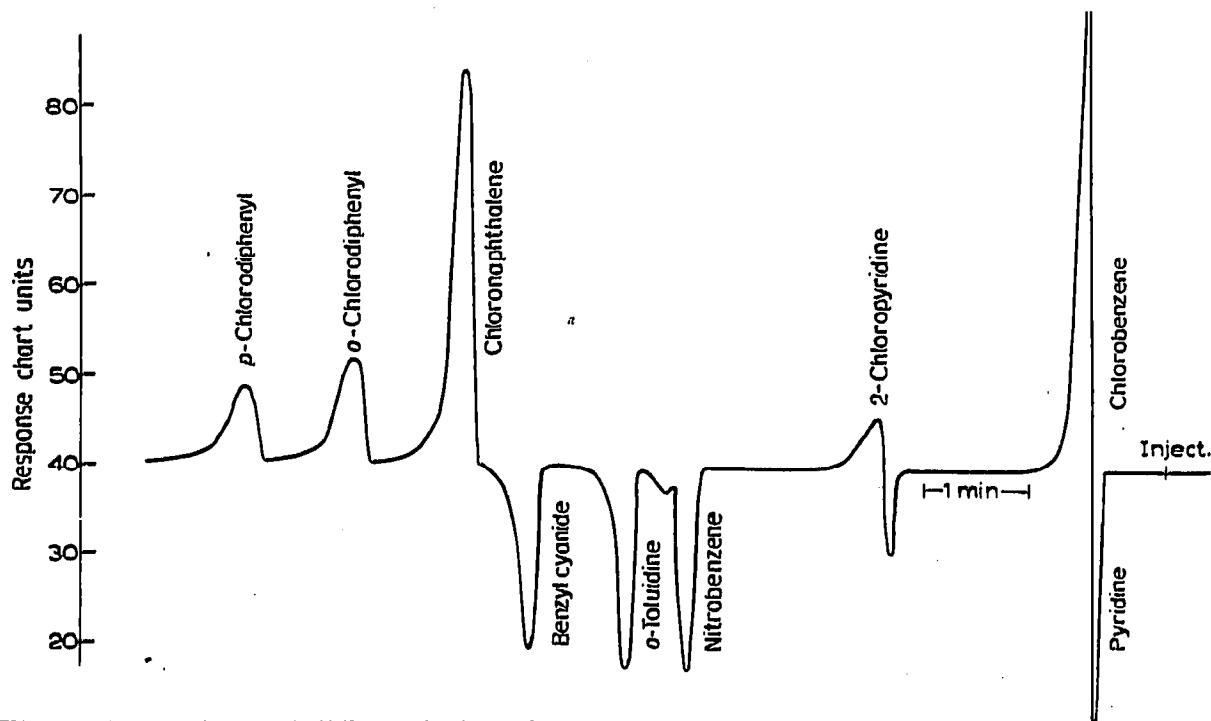


Fig. 7. Separation and differentiation of a nine-component mixture.

same molecule gives a double peak possibly due to different rates of desorption of HCl and NH₃ off the nickel catalyst.

Enhancement of response to sulphur compounds. Compounds containing sulphur are reduced to hydrogen sulphide in the furnace. This gives poor response in the detector with a non-reactive flow solution partly because of its low solubility and partly because of its poor degree of dissociation.

Dilute solutions of iodine were tried for H₂S absorption, hoping to utilize the rapid oxidation to sulphur:



Note the production of two highly conducting hydrogen ions per molecule of oxidised hydrogen sulphide.

Solutions of three sulphur compounds were prepared and the response compared with chlorobenzene using: (1) a detector flow solution of 1 p.p.m. HCl; (2) a flow solution of composition 0.04% I₂, 2% ethanol, and 1 p.p.m. HCl.

A 2-m × 0.2-cm I.D. glass column packed with the mixed phase 1.5% OV-17/1.95% QF-1 on a.w. Supasorb was used; the temperature was 100° and the carrier gas hydrogen at approx. 50 ml/min. Detector conditions: furnace,

TABLE II

RELATIVE RESPONSE OF SULPHUR AND CHLORINE COMPOUNDS USING DIFFERENT FLOW SOLUTIONS

| | <i>Chlorobenzene</i> | <i>Ethanethiol</i> | <i>Di-n-butyl sulphide</i> | <i>Carbon disulphide</i> |
|------------|----------------------|--------------------|----------------------------|--------------------------|
| Solution 1 | 1.0 | 0.30 | 0.15 | 0.12 |
| Solution 2 | 1.0 | 3.30 | 1.10 | 1.40 |

800 °; transfer, 200 °; flow solution, 1.5 ml/min; the resistance was set at 10,000 ohms.

The response of chlorobenzene was much higher when using solution 1 but became the smallest of the four when using solution 2 (see Table II). This iodine solution gave an increase of approximately ten-fold in terms of peak heights.

CONCLUSIONS

A detector system based on chemical modification of the eluants from a GC column with subsequent measurement using liquid conductivity methods is capable of high sensitivity with little distortion of peak shapes.

In the work shown the detector is operated entirely in the reductive mode where compounds containing C, H and O only give virtually no response and those containing N, Cl and S can be differentiated and their response enhanced using a dilute solution of electrolytes. Work on the detection of phosphorus-containing compounds has not yet been carried out. Absorption of phosphine in dilute silver nitrate appears to be a promising method for obtaining a response. This has been demonstrated by BURCHFIELD *et al.*⁵ using the microcoulometric method of detection.

The detector system itself can be further modified. A pulse-free pump giving highly stable flow-rates would reduce the detection limits much further. Modifications of the electronics to read conductance directly would also be an advantage to extend the linear range of quantitative response.

Finally operation in the oxidative mode, where volatile oxides are produced such as CO₂ and SO₂, must mean that the detector can be modified to respond to most compounds. The adsorption of CO₂ in dilute NaOH, for example, should give a reasonable response for all carbon-containing compounds.

ACKNOWLEDGEMENTS

We wish to gratefully acknowledge the award of a Science Research Council Advanced Studentship to one of us (P. J.) which made this work possible.

REFERENCES

- 1 D. M. COULSON, *J. Gas Chromatogr.*, 3 (1965) 134.
- 2 D. M. COULSON, *J. Gas Chromatogr.*, 4 (1966) 285.
- 3 G. G. PATCHETT, *J. Chromatogr. Sci.*, 8 (1970) 155.
- 4 J. W. RHOADES AND D. E. JOHNSON, *J. Chromatogr. Sci.*, 8 (1970) 616.
- 5 H. P. BURCHFIELD, D. E. JOHNSON, J. W. RHOADES AND R. J. WHEELER, *J. Gas Chromatogr.*, 3 (1965) 28.

J. Chromatogr., 73 (1972) 19-28