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## NEW ELECTROLYTIC CONDUCTIVITY DETECTOR FOR CAPILLARY GAS CHROMATOGRAPHY

### ANALYSIS OF CHLORINATED HYDROCARBONS

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#### SUMMARY

An electrolytic conductivity detector for high resolution capillary gas chromatography has been constructed. By avoiding phase separation and with direct passage of the gas-liquid mixture through the conductivity cell, a high speed of response could be achieved. Doping of the auxiliary gas with vinyl chloride as a hydrogen chloride generator results in peaks free from tailing even at trace concentrations in the halogen-selective mode of operation. The detection limit for chlorine is  $1.5 \cdot 10^{-12}$  g/sec. The detector response is directly proportional to the chlorine content of the sample over a dynamic range larger than five orders of magnitude.

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#### INTRODUCTION

The first reported application of electrolytic conductivity detection (ECOD) for gas chromatography (GC) was to the analysis of carbon-containing compounds<sup>1</sup>. In principle, any separated component can be detected if it or a derivative acts as an ionic conductor in a suitable solvent. For example, palladium chloride has been used to convert molecular hydrogen into hydrogen chloride, and ECOD then used for the analysis of hydrogen isotopes<sup>2,3</sup>.

Coulson<sup>4</sup> described a commercially available electrolytic conductivity detector for selective detection of halogen-, sulphur- and nitrogen-containing compounds. ECOD was further improved by Jones and Nickless<sup>5</sup>, and Hall<sup>6</sup> reported a new design of the detector. Hall's system is commercially available as the Tracor Model 700 A Hall electrolytic conductivity detector. Various applications of this detector for selective analysis of halogen, sulphur and nitrogen in organics have been reported<sup>7-11</sup>.

In spite of its good performance, the electrolytic conductivity detector has not been widely used. One explanation for this could be its requirement of a phase separator. In all published designs, with the exception of Hall's device, it is difficult to separate the gas from the solvent stream. The price of Hall's improvements, however,

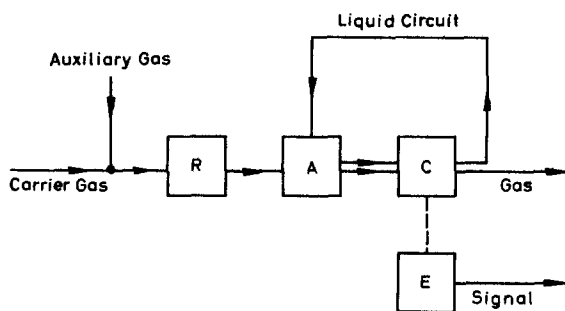


Fig. 1. Block diagram of the electrolytic conductivity detector. R = Reactor; A = gas-liquid contactor; C = conductivity cell; E = conductivity meter.

was a limitation of the speed of response, a disadvantage for applications in high-resolution capillary GC.

A new design of electrolytic conductivity detector is now described, which eliminates the phase separator and its associated disadvantages. Applications to the analysis of chlorinated hydrocarbons are also demonstrated.

#### DETECTOR DESIGN AND THE HALOGEN-SELECTIVE MODE OF OPERATION

A block diagram of the detector is shown in Fig. 1. The column effluent is mixed with a reaction gas and/or an inert make-up gas and transferred to the reactor (R). The gas stream is then passed to the phase contactor (A), where the reaction products are dissolved in water or another suitable solvent. Without phase separation the mixture of gas and liquid flows through the cell (C) and the change in conductivity is monitored by a conductometer (E).

#### Auxiliary gas

In order to optimize the hydrodynamics and the speed of response, a gas flow of 30 ml/min through the detector is established. At slower flow-rates, peak broadening occurs, whereas at high rates the contact time in the reactor is too short for complete reaction.

A hydrogen stream of 2 ml/min is necessary in the reductive mode of operation and it can be used as carrier in capillary columns with 0.32 mm I.D. If different carrier flows are preferred, the reaction gas is supplied together with helium as auxiliary gas.

Using a nickel wire as hydrogenation catalyst, hydrogen chloride formed from chlorinated hydrocarbons is partially adsorbed at the metal surface. Its slow desorption results in peak tailing, especially at very low solute concentrations. This disadvantage can be completely overcome by doping the auxiliary gas with *ca.* 20 ppm (v/v) vinyl chloride (VC). The generation of hydrogen chloride upon reduction of VC results in a higher baseline, and the flow of the auxiliary gas must be regulated in order to minimize noise and drift.

#### Reactor

The mixture of carrier gas and auxiliary gas flows through a quartz tube of

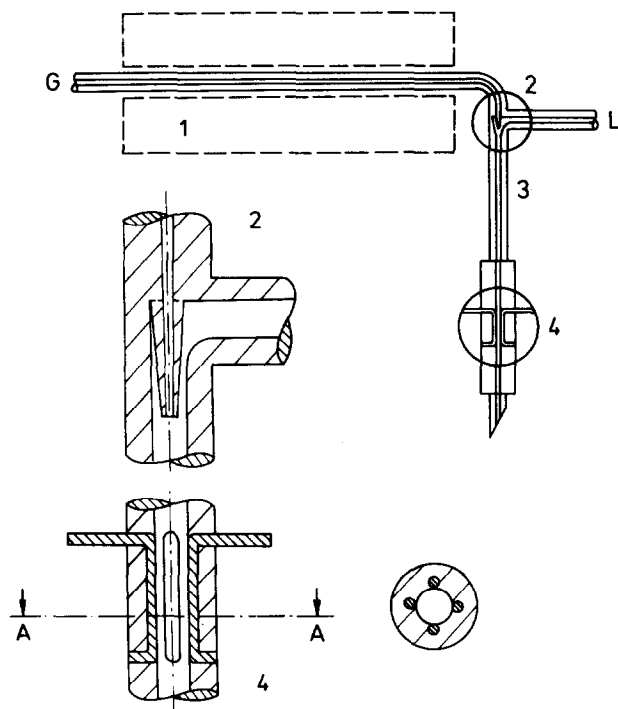


Fig. 2. Cross-section of the electrolytic conductivity detector. 1 = Furnace; 2 = T-piece for gas-liquid contact; 3 = gas-liquid contactor; 4 = conductivity cell; G = gas; L = liquid.

0.7 mm I.D., heated at 900°C (Fig. 2), containing a nickel wire, 25 mm long and 0.5 mm thick.

#### *Gas-liquid contactor*

The gas-liquid contact tube (40 × 1.3 mm I.D.) (3) is an extension of the reaction tube (1) (Fig. 2). In the T-piece (2) the gas is forced through a narrow opening (0.3 mm I.D.) in the quartz tube before it comes in contact with a water stream of 12 ml/min. The ratio of 2.5:1 for the gas and water flow-rates corresponds to optimal hydrodynamic conditions for regular bubble building.

#### *Conductivity cell*

The gas-liquid contactor is directly connected with a plastic glass cylinder (4) of 1.3 mm I.D. Four platinum wires, 10 mm long and 0.5 mm thick, are embedded at equal distances in the inside wall of this cell and opposite wires are connected to an electrode. The electrolytic conductivity is measured mainly in the liquid film on the cell wall. This film is not interrupted by the passage of gas bubbles and the noise is held at a low level.

#### *Liquid circuit*

Water is pumped through a column of mixed acid/base ion-exchange resins, the upper third of which comprises pure cationite. Above the lateral exit at the top

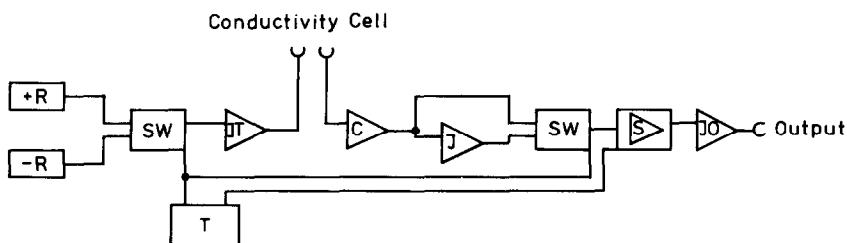


Fig. 3. Block diagram of the electrical circuit. R = Reference voltage; SW = field effect transistor switch; IT = impedance transformer; T = timing; C = comparison and gain; I = inverter; S = sample and hold; IO = impedance transformer and offset.

of the column an air buffer compensates for membrane pump pulsations. The resulting stream of deionized water flows at room temperature through the phase contactor and cell.

### Conductivity meter

An electrical circuit (Fig. 3) has been designed especially for this application<sup>12</sup>. It contains an adjustable source of reference voltage, and chopper-stabilized amplifiers and low-drift parts have been used on account of the high sensitivity.

### DETECTOR PERFORMANCE

#### Experimental

A fused-silica capillary column (30 m × 0.32 mm I.D.) coated with OV-1

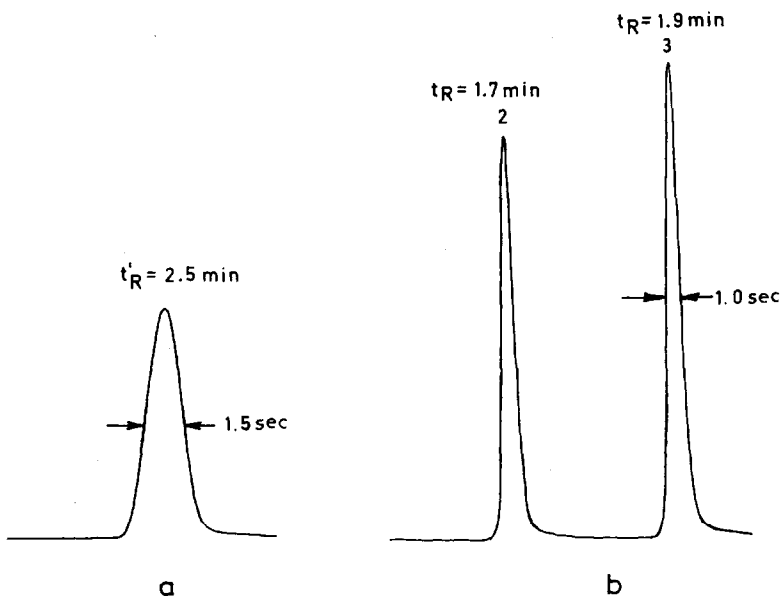


Fig. 4. Peak shape and speed of response. a, Lindane at 220°C; b, trichloroethylene (2) and carbon tetrachloride (3) at 30°C ( $t_R$  = retention time;  $t'_R$  = adjusted retention time; see the *Experimental* section for all conditions of analysis).

(J&W) is mounted in a Sichromat 2 gas chromatograph (Siemens) equipped with a split injector. The "live-circuit" of the gas chromatograph used as variable effluent splitter allows the connection of a flame ionization detector and an electrolytic conductivity detector. An uncoated fused-silica capillary (40 cm  $\times$  0.35 mm I.D.) connects the T-piece with the reactor tube. The capillary-interface is mounted in a stainless-steel tube (0.76 mm I.D., 1.6 mm O.D.) and is heated by means of the electric resistance of the steel tube. A Swagelok fitting insulated with graphite connects the quartz interface with the quartz reactor tube. Hydrogen is used as carrier gas and the auxiliary gas helium is introduced through the "live-circuit". By use of an electronic flow-regulator (Tylan), an additional helium stream of 13 ml/min, doped with 114 ppm VC, is introduced in the auxiliary gas. The VC-doped helium is delivered from a 10-l bottle at 150 bar (Messer-Griesheim). In this way the gas in the reactor is doped with 20 ppm VC.

A 10 cm long furnace BR-1.8/10 (Heraeus) and a low-voltage regulator REK 42 are used for heating the quartz reactor. The length of the horizontal part of the detector tube (Fig. 2) is 130 mm and that of the vertical phase contactor and the conductivity cell is 80 mm. The dimensions and the shape and alignment of the detector were adapted to the laboratory equipment which was available and could be varied as appropriate. Test runs with different arrangements led to the same results as with the device described here.

A membrane pump (CfG-Duramat) is used for water circulation. In addition to the home-made conductivity meter, a conductometer E 518 (Metrohm) has been examined, but the noise level of the latter was about ten-fold higher. The chromatograms are registered with a Kipp & Zonen recorder and the peak integration is carried out with a labor-automation-system 3353-A (Hewlett-Packard). The nickel catalyst was obtained from Puratronic and the exchange resins from Seral.

### Results

A decisive property of a detector for high resolution capillary chromatography is its speed of response. The influence of the electrolytic conductivity detector on the shape and width of peaks and, consequently, on the resolution has been examined. Fig. 4a shows the peak of lindane. It is free from tailing, and from the width at half-height of 1.5 sec, 55,000 effective theoretical plates are calculated. The same value was obtained with a flame ionization detector under identical conditions. The time delay between the entry of a component into the quartz reactor tube and its arrival in the cell is *ca.* 0.16 sec, and the time to change the cell contents of 9  $\mu$ l is 13

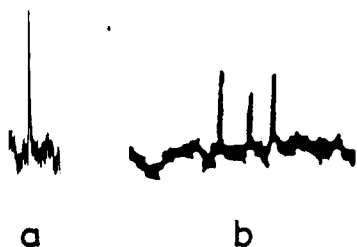


Fig. 5. Peak height and noise. a, Lindane (7.5 pg); b, chloroform, trichloroethylene and carbon tetrachloride (each 2.5 pg).

msec. In contrast to detectors employing phase separators and liquid bypassing, more rapid response is achieved by direct passage of the two phases through the cell.

A second important property of a detector used with capillary columns is its sensitivity. Because of the very high solubility of hydrogen chloride in water the electrolytic conductivity detector behaves like a mass-flow detector and its sensitivity is nearly independent of the gas:water ratio and of the gas flow-rate. The detection limit for chlorine is  $1.5 \cdot 10^{-12}$  g/sec and the linearity  $> 10^5$ . This corresponds to the sensitivity of the flame ionization detector for carbon. Fig. 5a shows the peak of 7.5 pg lindane and Fig. 5b the peaks of chloroform, trichloroethylene and carbon tetrachloride, respectively, each 2.5 pg.

The selectivity of this detector depends on the operation mode. Under reductive conditions, HX, H<sub>2</sub>S, NH<sub>3</sub>, CH<sub>4</sub> and H<sub>2</sub>O are formed from halogen-, sulphur-, nitrogen- and oxygen-containing compounds. Therefore, the detector is selective with respect to hydrocarbons and oxygen-containing compounds. The detection limit for H<sub>2</sub>S lies above 1 ng and accordingly the selectivity to chlorine relative to sulphur, Cl/S, is  $10^3$  at very low concentrations. As a consequence of the very low degree of dissociation of H<sub>2</sub>S, the selectivity increases to  $\text{Cl/S} \geq 10^4$  for  $\geq 100$  ng sulphur. At high sulphur concentrations the peak height of H<sub>2</sub>S is equivalent to 10 pg chlorine. Using an alcohol instead of water as solvent, the conductivity of H<sub>2</sub>S may be even more suppressed<sup>6</sup>.

At low concentrations, nitrogen-containing compounds give a negative peak, resulting from the neutralization effect of NH<sub>3</sub> on the doped HCl. At high nitrogen concentrations the signal direction can be observed to change twice, caused by the conductivity of excess of NH<sub>3</sub>. An unequivocal qualitative distinction between halogen- and nitrogen-containing compounds is therefore possible. The quantitation of halogen may be affected only by peak overlapping from nitrogen derivatives at insufficient resolution.

In the oxidative mode of operation, using air as reaction gas, the combustion products are CO<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub>, SO<sub>2</sub> and HX. Although no signal is produced by N<sub>2</sub> and the concentrations of nitrogen oxides are negligible, this mode of operation is less advantageous because CO<sub>2</sub> is formed from all organics and the selectivity Cl/C is much lower than in the reductive mode of operation<sup>13</sup>.

The different temperatures necessary for the hydrogenation of carbon-halogen bonds allow, in principle, a structure-selective mode of operation under reductive conditions and a distinction, *e.g.*, between pesticides from polychlorinated biphenyls (PCBs)<sup>7</sup>. Also hydrogen bromide and hydrogen iodide are produced at lower temperature than hydrogen chloride.

One of the outstanding properties of the electrolytic conductivity detector in the chlorine-selective mode is the proportionality of its response to the mass of chlorine. This means that a calibration of the detector with a substance of known chlorine content is sufficient for quantitative analyses of any chlorinated hydrocarbon of known elemental composition. In addition, the elemental composition of an unknown chlorinated hydrocarbon can be determined by successive use of the carbon-selective and chlorine-selective modes of operation or by parallel analyses with flame ionization and electrolytic conductivity detectors<sup>14</sup>.

Fig. 6 shows a chromatogram of a technical mixture of PCBs comprising 41% Cl.

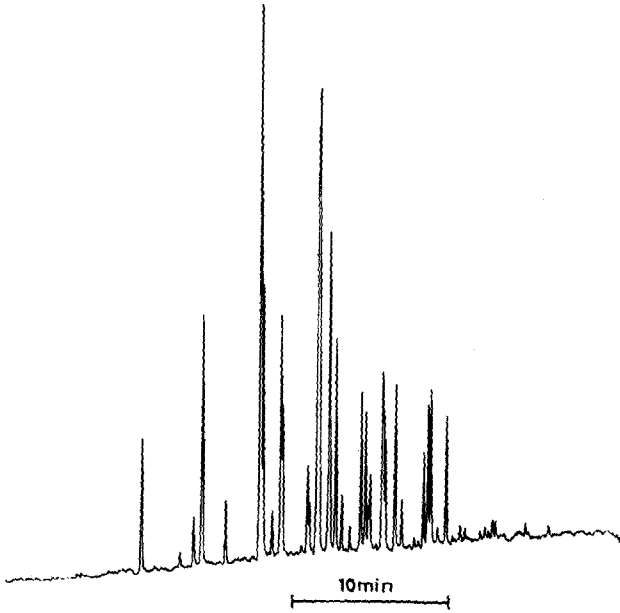


Fig. 6. Chromatogram of 5.4 ng PCB (41% Cl). Column programmed from 120°C to 250°C at 3°/min (see the *Experimental* section for all conditions of analysis).

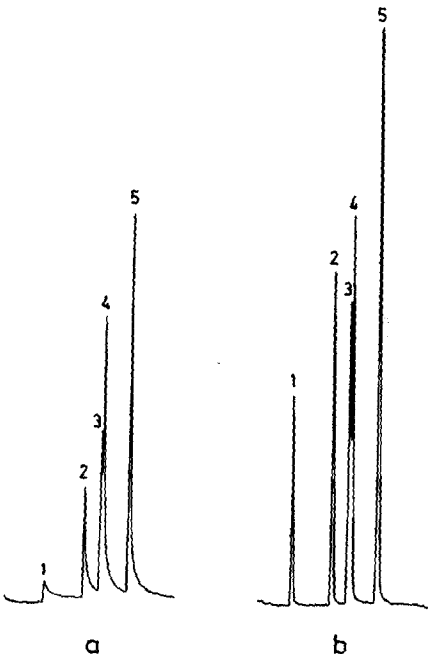


Fig. 7. Effect of doping on the peak shape. a, Undoped gas; b, auxiliary gas doped with 20 ppm vinyl chloride. 1 = 4-Chlorobiphenyl; 2 = 3,4-dichlorobiphenyl; 3 = 3,5-dichlorobiphenyl; 4 = 4,4'-dichlorobiphenyl; 5 = 2,4,5-trichlorobiphenyl.

Finally, the importance of gas doping with VC or another chlorine-containing compound must be emphasized. At very low electrolyte concentrations a non-linear relationship between the conductivity and electrolyte concentration has been observed previously. This could be corrected by adding an acid or base to the water<sup>13</sup>. On the other hand, at the high separation speed in capillary chromatography, especially at low solute concentrations, peak tailing has been observed as a result of the slow desorption rate of HCl from the surface of the nickel catalyst (Fig. 7a). This tailing effect produces a decrease in early-eluted peaks, or even the disappearance of the first peak in the chromatogram. The doping of the auxiliary gas with VC completely eliminates this effect and the peaks are free from tailing (Fig. 7b). In our device, however, the additional pure helium introduced through the live-circuit mounted in the gas chromatograph has only been pressure- and not flow-regulated; so a slow drift of the baseline occurs in the temperature-programmed analysis of PCBs (Fig. 6).

A trouble-free operation of this detector in quantitative analyses necessitates a solvent vent before the reactor entrance. This demand can be fulfilled without difficulty with the "live-circuit" of the Sichromat and with other available gas chromatographs.

With the new design of the electrolytic conductivity detector and the halogen-selective mode of operation, quantitative analyses of chlorinated hydrocarbons on high resolution capillary columns and, of course, on packed columns are possible. The analysis of monomers like VC, chlorinated compounds in water, pesticides, PCBs and other classes of halogenated compounds in the environment can be carried out. With the available methods of trace enrichment and on-column injectors for capillary columns, trace analysis can also be performed.

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