DESIGN OF A COMBINED PHOTOIONIZATION DETECTOR AND PHOTOIONIZATION-BASED ELECTRON-CAPTURE DETECTOR

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SUMMARY

A gas chromatographic detector based on photoionization with characteristics and performance comparable to conventional electron-capture detectors has been constructed. In the electron-capture mode of operation this detector uses a readily photoionizable dopant gas that is ionized by radiation from ultraviolet lamps, and the resulting electrons are collected at the anode under the influence of an applied electrical field. This gives a baseline current that is attenuated by the absorption of electrons by electron-capturing analytes. The detector functions quite satisfactorily, both as a photoionization detector and electron-capture detector. It provides a means of monitoring suitable analytes linearly from picogram to microgram levels.

INTRODUCTION

Since its introduction by Lovelock in 1960[1], the electron-capture detector (ECD) has been the subject of numerous publications. Its excellent sensitivity and selectivity for halogenated organic compounds deserve much of the credit for the current state of knowledge regarding environmental problems related to these chemicals.

Although the ECD has changed little in its basic design since it was introduced, attempts to enhance its sensitivity, linearity and selectivity has been reported[2–4]. Furthermore, extensive mechanistic studies dealing with physico-chemical processes occuring in the detector have been concluded[5–8]. All of the commercially available ECDs employ a radioactive foil as the internal ionization source, housed in an ionization cell constructed from a suitable insulating material such as PTFE, boron nitride, quartz, polyimide, etc. The radioactive foil, *e.g.*, ^{63}Ni on gold or ^{3}H sorbed to titanium, serves as a cathode while a stainless steel rod or cylinder is employed as an anode. Attempts to use other ionization sources have been made with varying degrees of success. The most promising of these are the heated-filament ECD reported by Sullivan[9] and photo-ECD reported by Wentworth *et al.*[10]. The performance of the heated-filament ECD has been found to be comparable to the conventional detectors in terms of sensitivity and selectivity; however, the stability of the detector was

poor. The detection limit for a strong electron absorber, carbon tetrachoride, was reported to be 50 pg with the photo-ECD when operated in the d.c. mode[10].

Based upon recent studies, an alternative mechanism for the d.c. electron capture response has been suggested by Aue and co-workers[12–14]. The alternative mechanism considers the combination of space charge resulting from the formation of anions in the detector. Later studies reported a rough quantitation of this effect. These studies led to the conclusion that a detector based upon photoionization with performance comparable to the conventional ECD could be constructed. This paper is a report on the construction and performance of such a detector. In addition to its ECD capability, the detector was designed to function as a well performing photoionization detector (PID), thus giving a gas chromatographic (GC) detector system which combines the high sensitivity and selectivity of the ECD (in the ECD mode) with the wide dynamic range of the PID (in the PID mode).

EXPERIMENTAL

Fig. 1 is a schematic of the. detector. The detector housing was a 304 stainless-steel block with an 11 mm deep cavity 7 mm in diameter. Into this cavity five openings were drilled; two served as electrode ports, two served as inlets (designated inlet 1 and inlet 2) and the last opening served as the outlet. A boron nitride (BN) detector cell was made to fit tightly into the stainless-steel block. Two cylindrical stainless-steel electrodes were made to fit into the BN detector cell. The ionization sources were commercially available vacuum UV lamps (HNU System, Inc.) with
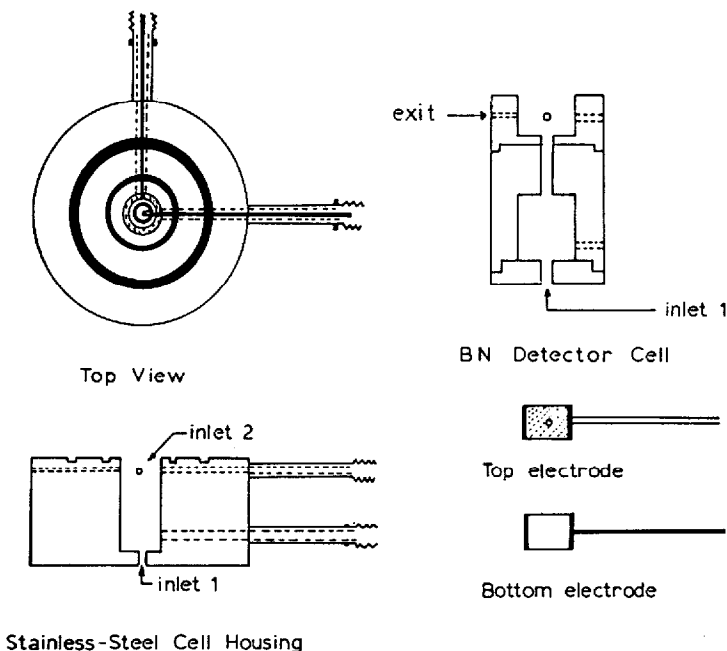

Top View

BN Detector Cell

Top electrode

Bottom electrode

Stainless-Steel Cell Housing

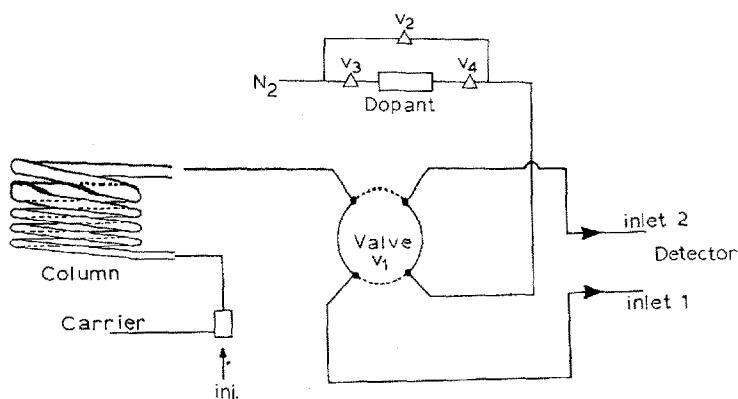Fig. 1. Schematic of combined PID–ECD.

Fig. 2. Schematic of gas flow switching system.

peak energy outputs at 10.2 and 9.5 eV. The gas-tight seal was obtained between the lamps and detector housing with PTFE or polyimide "O" rings.

During operation in the ECD mode, the column effluent was introduced at the bottom of the detector through inlet 1 and a readily ionizable organic material (*i.e.*, one with a low ionization potential) was introduced with a nitrogen stream through the top inlet in close proximity to the MgF_2 window of the UV lamp. Operation in the PID mode required reversal of the inlets so that the column effluent was introduced through the top inlet. This flow-switching was accomplished by the use of a high temperatue four-port switching valve (Valco Valves, Houston, TX, U.S.A.). The schematic of the switching valve and other plumbing arrangements is shown in Fig. 2.

The detector system was mounted on a Bendix Model 2500 gas chromatograph. A 150 × 0.2 cm U-shaped borosilicate glass tube packed with 3% OV-101 on Chromosorb W HP (80–100 mesh) served as the chromatographic column. The column flow-rate was maintained at 30 ml/min. Nitrogen was used as the carrier gas. The dopant carrier flow was kept at 20 ml/min. The detector temperature was regulated at 250°C.

RESULTS AND DISCUSSION

The aim of this study was to explore the feasibility of developing a GC detector system which could act as both an electron-capture and a photoionization detector. Toward this end, conclusions drawn from studies dealing with the alternative electron-capture response mechanism were taken into consideration.

The UV lamps employed as ionization sources in the detector employed for this study cannot bring about the ionization of the carrier gas. Instead, a readily ionizable material, such as aliphatic/aromatic amines or aromatic hydrocarbons in nitrogen, needs to be introduced into the detector cell in close proximity to the UV lamp window. In this study naphthalene and tri-*n*-propylamine were used as the dopant, which acted as the source of electrons in the electon-capture mode of operation. In this mode the bottom electrode (the farthest from the lamp) was polarized with a d.c. power supply and acted as the anode. The electrode closest to the lamp was connected to an electrometer.

A kinetic model for the photo-ECD has been presented by Wentworth *et al.*[10]. Applying Wentworth's model to the detector used in this study, the dopant gas (DP) is ionized by the UV radiation and the resulting electrons are collected at the anode under the influence of the applied field. The resulting current is the baseline current of the detector. The absorption of electrons by solutes in the column effluent leads to anion formation with a corresponding decrease in current below the baseline current. In the classical model this electron capture is thought to be directly linked to the response due to accelerated neutralization. The alternative mechanism for d.c. electron-capture response proposes that the *modus operandi* is the increased impedance offered by the heavy anions formed by electron capture. It was further postulated that since the mobilities of these anions are comparable to the mobilities of the cations, a better estimate of response for a given detector could be obtained by measuring the difference between the voltage needed to collect a certain current, I, under a "reverse field" condition, V_I^+, and the voltage required to collect the sample current under a "normal field" condition, V_I^{-}[12]. Thus, the response, R, is proportional to the difference between V_I^+ and V_I^-:

$$R \propto V_I^+ - V_I^-$$

This relationship was observed to hold for the detector under various configurations tried. Optimum results, *i.e.*, maximum response with lowest noise, were observed for the concentric cylinder design adopted in the prototype detector.
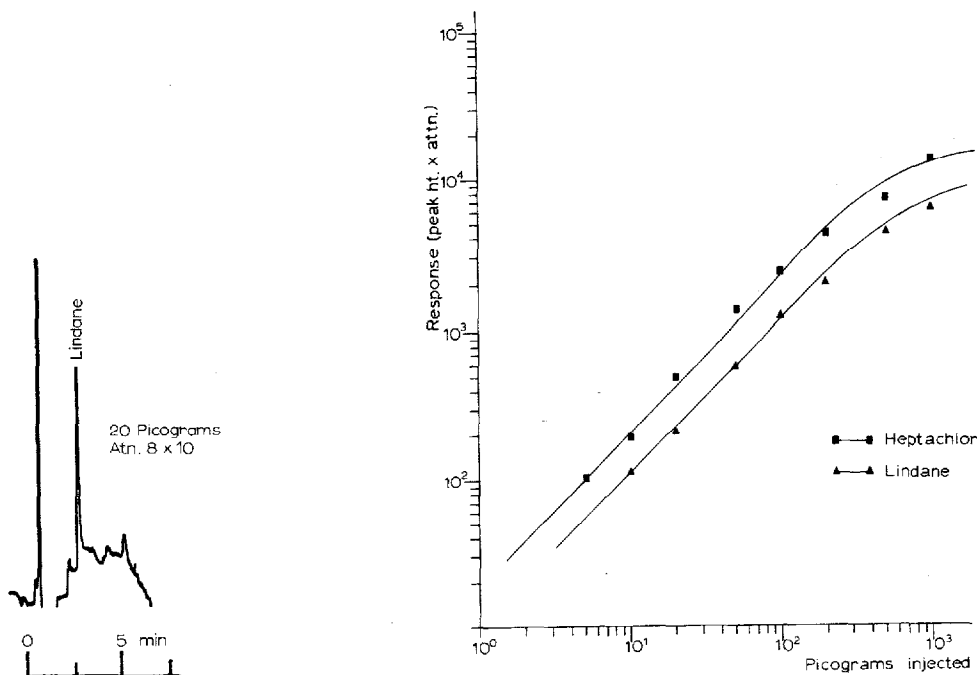

Fig. 3. Chromatography of 20 pg lindane in the ECD mode. Column temperature 170°C.

Fig. 4. Calibration curves for lindane and heptachlor obtained in the ECD mode. Chromatographic conditions as in Fig. 3.

The performance of the detector in the ECD mode is shown in Figs. 3 and 4. Fig. 3 is a chromatogram of 20 pg of lindane (the λ isomer of hexachlorocyclohexane). The detection limit for the compound was found to be approximately 1 pg. Calibration curves for two model compounds, lindane and heptachlor, are shown in Fig. 4. The linearity of the detector was found to be similar to that of a conventional ECD operating under d.c. or constant pulse conditions.

The current density of the prototype detector was found to be dependent upon the nature and the amount of dopant added, the intensity of the lamp and the condition of the MgF_2 window. The concentration of the dopant was varied by changing the flow of purging gas and the temperature of the dopant trap. In order to obtain currents of the magnitude found in the conventional ECD ($1 \cdot 10^{-8}$ A), approximately 1 $\mu g/min$ of naphthalene dopant was added. An accurate determination of the dopant concentration in the detector could easily be made by operating the detector in the PID mode.

The operation of the detector in the PID mode was accomplished by rotating the switching valve, V_1, such that the column effluent entered the detector cell through the jet in proximity to the UV lamp. The dopant flow was stopped by turning valves V_3 and V_4 off. The polarizing potential applied to the bottom electrode was increased from $+20$ to $+300$ V. Under these conditions the detector functioned as a PID with performance comparable to the PIDs described in the literature[14].

The chromatographic separation and photoionization detection of two model compounds, naphthalene and anthracene, at the 500-pg level is shown in Fig. 5. The detection limit for such compounds was discovered to be approximately 100 pg. The linear dynamic range of the detector in this mode extended over more than three orders of magnitude as shown in Fig. 6, which depicts the calibration curves for anthracene and heptachlor.
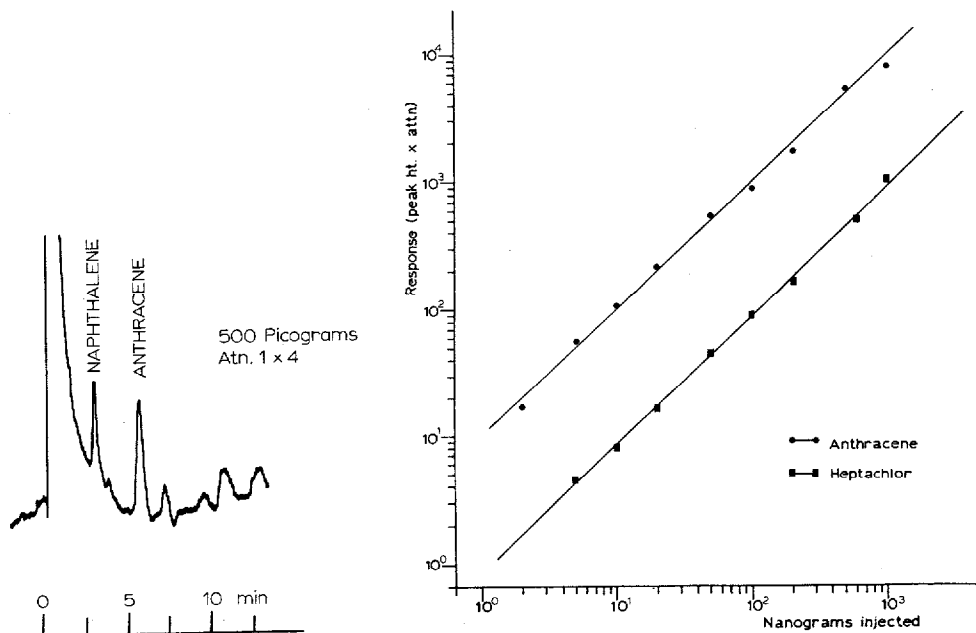

Fig. 5. PID response for 500 pg of naphthalene and anthracene. Column temperature 130°C.

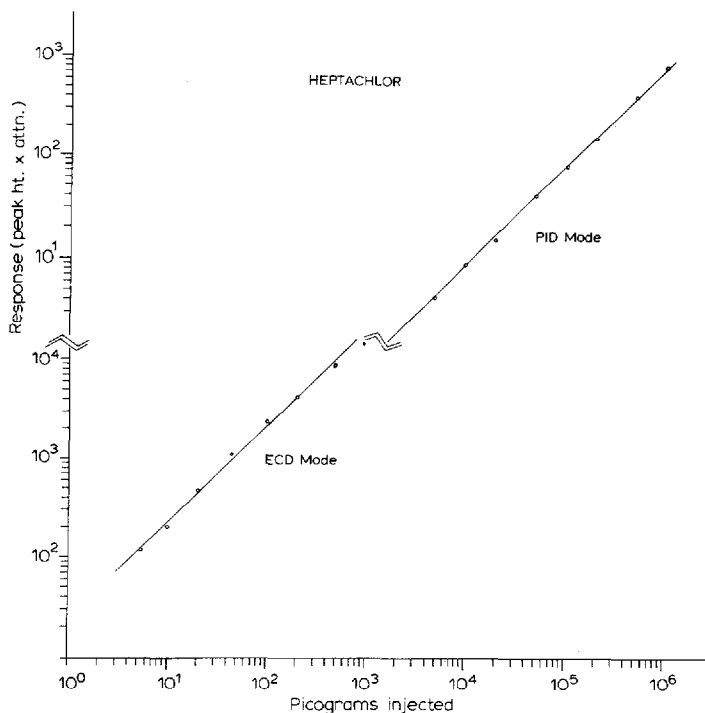Fig. 6. Calibration curves for anthracene and heptachlor obtained in the PID mode.

Fig. 7. Combined calibration curve for heptachlor obtained in ECD and PID modes.

These results illustrate that the detector described in this study functions quite satisfactorily, both as an ECD and a PID. Furthermore, such a detector gives a means of monitoring suitable solutes from picogram to microgram levels, as shown in Fig. 7.

It is expected that further improvement in the detector performance can be brought about by optimizing the design parameters to give a detector which would truly combine the sensitivity and selectivity of an ECD with the wide dynamic range of the PID.

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