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EFFECT OF SOME OPERATING PARAMETERS ON THE RESPONSE OF THE COULSON CONDUCTIVITY DETECTOR

JAMES F. LAWRENCE
Food Research Laboratories, Health Protection Branch, Department of National Health and Welfare, Tunney's Pasture, Ottawa (Canada)

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SUMMARY

The variation in response with changes in operating conditions of the Coulson conductivity detector to some triazine herbicides was examined. Parameters such as water and hydrogen flow-rates as well as pyrolysis furnace temperature were investigated. Maximum response was obtained with equal flow-rates in the mixing chamber and siphon arm. However, tailing of peaks increased at slow water flow-rates. Hydrogen flow-rates of 30–70 ml/min produced the highest response. Sensitivity increased with increasing furnace temperature.

INTRODUCTION

The use of the Coulson conductivity detector system for the selective monitoring of nitrogen-, chlorine- or sulfur-containing compounds in the effluents from gas chromatographs has increased considerably in recent years. The detector is easily adaptable to most gas chromatography (GC) instruments and is simple to operate. While the choice of working parameters outlined in the Tracor Coulson conductivity detector operator's manual are generally acceptable for analysis, other operating conditions may be of more value for specific analytical problems. This was found to be so for the determination of amines and nitrosamines where conversion to ammonia took place at 400–600° as efficiently as at a normal furnace temperature of 850° (ref. 1). This lower temperature range offered a greater degree of selectivity since many other nitrogen-containing compounds did not form ammonia in this region. The effect of oven temperature and oxygen flow-rate on response of chlorine- and sulfur-containing compounds was recently studied[2]. It was found that response increased with increasing furnace temperature indicating a greater conversion to the corresponding acid gases, but decreased with an increase in oxygen flow-rate.

The present paper reports on the effect of water and hydrogen flow-rates, and furnace temperature on the response of the Coulson conductivity detector to some triazine herbicides.

EXPERIMENTAL

An Aerograph HY-FI Model 600C gas chromatograph (Varian, Palo Alto, Calif., U.S.A.) fitted with a Coulson Model C321 conductivity detector (Tracor, Austin, Texas, U.S.A.) was used. The 6 ft. × 6 mm O. D. glass columns were packed with 1% SP-525 (Supelco, Bellefonte, Pa., U.S.A.) on 80–100 mesh Chromosorb W HP (Supelco). Operating conditions were: injector temperature, 215°; column temperature, 185°; helium carrier gas flow-rate, 60 ml/min; pyrolysis furnace temperature, 450–840° (the range studied); transfer unit, 230°; helium sweep, 60 ml/min; hydrogen flow-rate, 0–100 ml/min (the range studied); d.c. bridge potential, 30 V. A 1-cm plug of strontium hydroxide coated glass wool was inserted at the exit of the quartz pyrolysis tube and a 50-strand nickel wire catalyst was placed in the center of the tube. A 1.0-mV strip-chart recorder operating at 0.25 in./min was used. Peak height was used to measure detector response.

The herbicides (all obtained from Ciba-Geigy, Basel, Switzerland) examined were atrazine (2-chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine), simazine (2-chloro-4,6-bis-(ethylamino)-*s*-triazine), propazine (2-chloro-4,6-bis-(isopropylamino)-*s*-triazine) and prometone (2-methoxy-4,6-bis-(isopropylamino)-*s*-triazine). One nitrogen-containing organophosphate, diazinon (O,O-diethyl-O-(2-isopropyl-4-methyl-6-pyrimidyl) phosphorothioate) (Ciba-Geigy) was also studied. Solutions of these were prepared in glass distilled methanol. Volumes of 2–5 μl were usually injected.

Gas flow-rates were measured at the end of the pyrolysis tube with a bubble flow-meter. The siphon flow-rate was measured first with the siphon arm exit exposed. Siphon flow-rates at higher reservoir water levels were calculated using the equation (see Fig. 1):

$$S_1 = \frac{S_x \times d_1}{d_x}$$

where

S_x = flow-rate with siphon arm exposed

d_x = vertical distance between siphon tube exit and entrance

d_1 = vertical distance between reservoir water level and siphon entrance.

The mixing chamber flow-rate was adjusted by drawing water up the water pressure control tube drain by applying suction to the water entrance after removing the pump tubing (see Fig. 1). When the water pressure control tube was completely filled with water, the suction was removed and the pump hose replaced. The pump was immediately started. The water level in the tube was adjusted by stopping the pump, removing the tube at the water entrance, allowing some air to enter the column, replacing the tube, and starting the pump.

RESULTS AND DISCUSSION

Chromatography

1% SP-525 (silicone polymer similar to OV-25 in polarity, maximum temperature 275°; Supelco) was found to be satisfactory for the separation of the compounds studied (Fig. 2). However, prometone, which appeared near atrazine, exhibited more tailing than the others. The column was stable over the period of use (approx. 2

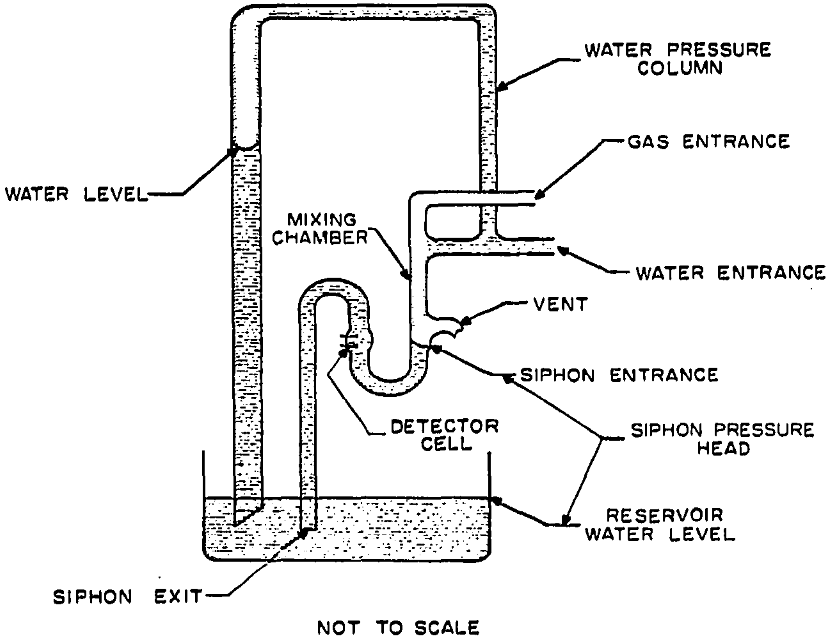

Fig. 1. Schematic diagram of the detector apparatus of the Coulson conductivity detector.

months). Reoplex 400 (polyester; Supelco) gave better separations at longer retention times but tended to bleed much more so than the SP-525, causing contamination of the pyrolysis tube with prolonged use.

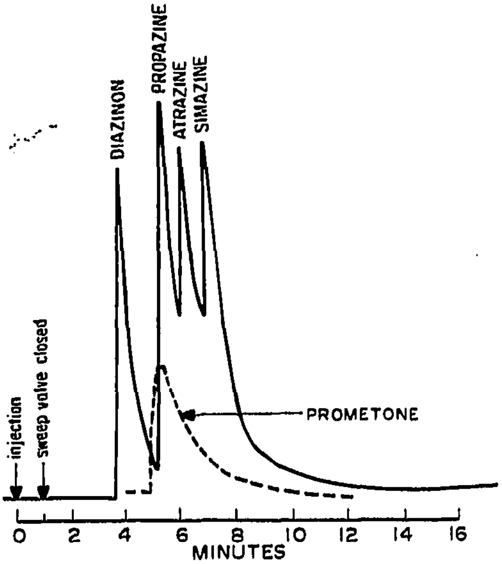

Fig. 2. Gas–liquid chromatography tracing showing the separation of four triazines and diazinon. Column conditions are described in the text.

Furnace temperature effect

Fig. 3 illustrates the effect of furnace temperature on detector response (peak height) for the compounds studied. Over the temperature range 450–840° a twofold gain in sensitivity was observed. This pattern was similar to that obtained for compounds in the pyrolytic mode[2]. The temperature used for further work in this report was 600°, which produced approximately 75% of the response at 850°.

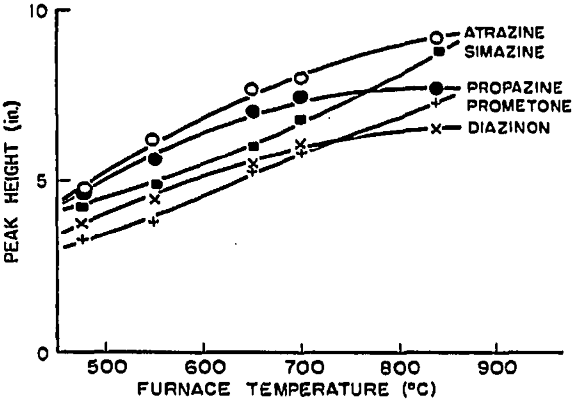

Fig. 3. Effect of pyrolysis furnace temperature on the detector response.

Influence of hydrogen flow-rate

Fig. 4 shows the results obtained when hydrogen flow-rate was varied from 0 to 110 ml/min at a constant carrier gas flow-rate of 60 ml/min. There was a sharp initial increase in response to a broad maximum at 30–60 ml/min followed by a gradual decrease. The pattern was similar for both peak area and peak height. A flow-rate of 50 ml/min was chosen for the remainder of this work.

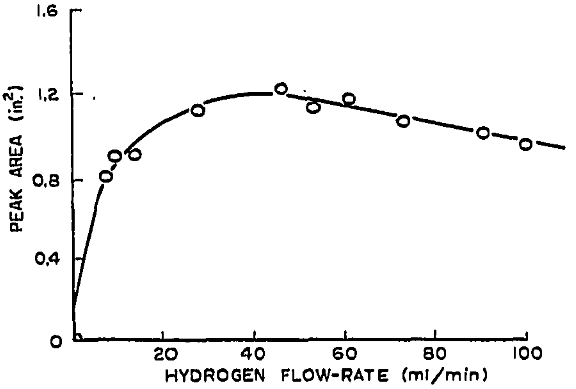

Fig. 4. Effect of hydrogen flow-rate for 10 ng atrazine.

Water flow-rate effect

During normal operation of the Coulson conductivity detector, the flow through the mixing chamber is about 3 ml/min while that through the detector cell (when the exit of the siphon arm is at or above the water level in the reservoir) is about 1 ml/min.

When the reservoir is filled to three-fourths as suggested by the operator's manual, the flow-rate is reduced to about 0.5 ml/min due to the loss in siphon pressure head (see Fig. 1). Thus only about one-sixth of the ammonia-containing water from the mixing chamber reaches the detector cell. The remainder is flushed out the vent tube. Fig. 5 illustrates the effect of reservoir water level on detector response at a mixing chamber flow-rate of 2.6 ml/min. The greatest detector response was observed at the lowest water level (just above the pump entrance). This level produced the greatest siphoning action which transported more ammonia-containing water from the mixing chamber to the detector cell.

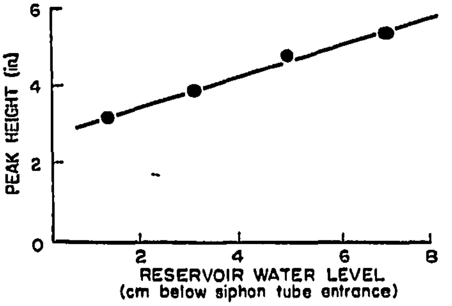

Fig. 5. Effect of reservoir water level on response to 20 ng propazine at a mixing chamber flow-rate of 2.6 ml/min.

The detector response was further improved by reducing the mixing chamber flow-rate to match the siphon flow so that no water escaped through the vent tube. Fig. 6 shows the variation of the detector response with changes in mixing chamber flow-rate at a constant siphon flow-rate of 0.5 ml/min. The maximum was obtained when the two flow-rates were matched. Matched flow-rates were also used in a conductivity cell described elsewhere[3]. When the mixing chamber flow-rate was less than the siphon rate, air bubbles were drawn into the detector cell causing excessive noise and irregular response. Fig. 7 compares peak size and shape for 30 ng of atrazine when the siphon flow-rate was 1 ml/min and the mixing chamber flow-rate was

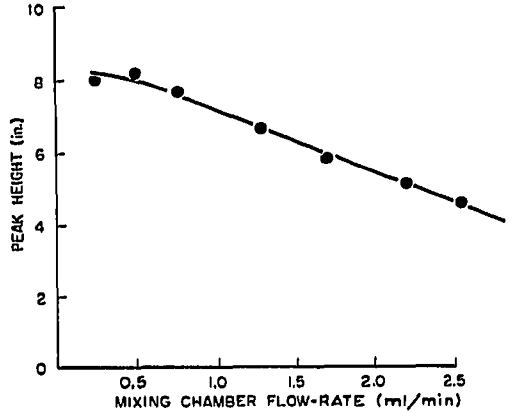

Fig. 6. Effect of mixing chamber flow-rate on response to 40 ng atrazine at a siphon flow-rate of 0.5 ml/min.

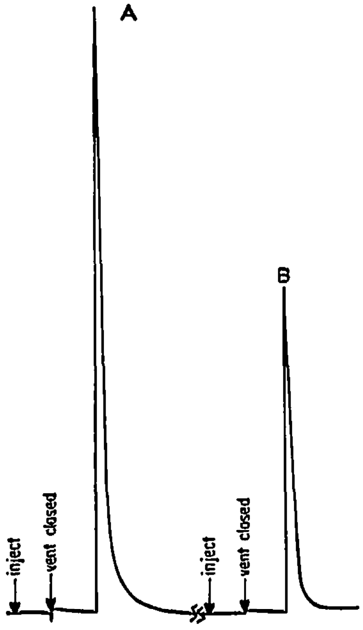

Fig. 7. Comparison of peaks of 30 ng atrazine with siphon flow-rate at 1 ml/min: (A) 1 ml/min mixing chamber flow-rate; (B) 2.6 ml/min mixing chamber flow-rate. Carried out on 4% SE-30 Chromosorb W HP at 195°; helium flow-rate, 60 ml/min.

(A) 1 ml/min and (B) 2.6 ml/min. The matched flow-rates (A) almost double the response.

The response of the detector to different flow-rates through the system (when both siphon and mixing chamber flow-rates were matched) was not greatly affected. Fig. 8 compares results obtained at matched flow-rates of 0.4 ml/min to 1.2 ml/min.

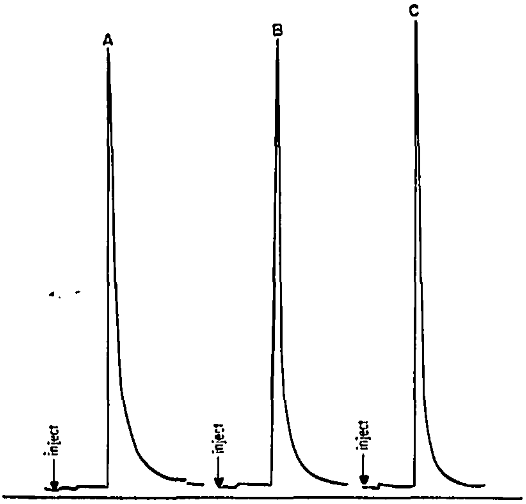

Fig. 8. Comparison of responses for 30 ng atrazine at different matched flow-rates: (A) 0.4 ml/min; (B) 0.8 ml/min; (C) 1.2 ml/min. GC conditions as in Fig. 7.

Peaks exhibited slightly more tailing at the slower flow-rates due to less efficient purging of the mixing chamber, siphon tube and detector cell (Coulson[4] found distorted peaks at slow flow-rates).

CONCLUSIONS

Water and hydrogen flow-rates as well as furnace temperature significantly affect the response of the Coulson conductivity detector to triazine herbicides. Hydrogen flow-rates between 30 and 60 ml/min and matched mixing chamber and siphon water flow-rates of about 1.2 ml/min gave the best response for the triazines. Small fluctuations in pyrolysis furnace temperature (± 10°) did not affect results.

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