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Note

Comparison of the Coulson and Hall electrolytic conductivity detectors for the determination of nitrogen-containing pesticides

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Since the introduction of the Coulson electrolytic conductivity detector (CCD) in 1965[1] a number of workers have evaluated its response in various modes of operation in an effort to improve its sensitivity and selectivity[2–6]. Patchett[2] incorporated a number of refinements to extend the nitrogen response of the CCD down to about 0.1 ng. Cochrane and Wilson[3] determined the amounts needed for 1/2 full-scale recorder deflection (1/2 f.s.d.) of a number of pesticides in the nitrogen mode and compared these responses to those obtained with an electron capture detector.

Cochrane *et al.*[4] also investigated the effect of furnace temperature and oxygen flow to find the optimum parameters for the determination of sulphur- and chlorine-containing compounds. In general, response increased with increasing temperature, whereas the optimum oxygen flow-rate was dependent upon the structure of the compound being determined.

More recently, Lawrence[5] investigated the variation in response of the Coulson detector to some triazine herbicides with changes in water and hydrogen flow-rates as well as furnace temperature. He found that equal flow-rates in the mixing chamber and siphon arm produced maximum response, with some peak tailing occurring at slow water flow-rates. Response increased with increasing temperature and hydrogen flow-rates. Dolan and Hall[6] also determined and optimized the factors influencing sensitivity and selectivity of the Coulson detector to chlorinated hydrocarbon pesticides.

In 1974, Hall[7] published a description of a Selective Microelectrolytic Conductivity Detector with a sensitivity of 20 to 50 times that of the CCD. This detector is now being produced commercially instead of the CCD. The Hall detector operates on the same basic principles as the Coulson detector and is essentially a refinement over its predecessor. The quartz reaction tube has been decreased to a diameter of 0.25 in. to reduce adsorption and subsequent peak tailing. More precise control over furnace temperature is also provided. The conductivity cell is greatly reduced in size and consists of a precision-drilled PTFE block which acts as a gas–liquid contactor and houses stainless-steel concentric electrodes. A 50% mixture of isopropanol and water is used as the circulating solvent instead of water and an a.c. bridge circuit is used to measure conductivity.

Although Hall[7] claims an increase in response of at least ten times over the CCD for sulphur- and chlorine-containing compounds, a comparison with results obtained by Cochrane *et al.*[4] reveals only a four fold increase. They found that 20 ng

of Diazinon was required for 1/2 f.s.d. while Hall required only 5 ng for the same response. Hence a factor of 4.

The factors that can be controlled and influence detector response include furnace temperature, reactant gas flow-rate, solvent flow-rate and composition, length of nickel catalyst and cell voltage. In this study, the effects of hydrogen flow-rate, solvent flow-rate and furnace temperature were determined in the nitrogen mode of operation and optimized using the herbicide atrazine. The response of some nitrogen-containing pesticides was then compared with those obtained by Cochrane and Wilson[3] using the CCD.

EXPERIMENTAL

A Microtek MT 220 gas chromatograph equipped with a Tracor Model 310 Hall Electrolytic Conductivity Detector and containing a 4-ft. glass column packed with an equal mixture of 4% OV-101 and 6% OV-210 on Chromosorb W HP was used. Operating conditions were: injector temperature, 225°; column temperature, 205°; transfer line temperature, 250°; helium carrier flow-rate, 70 ml/min; conductivity meter setting, 1 μmho; attenuator, $\times 1$. The circulating solvent used was a 50% isopropanol–water mixture. Peak areas were measured using an Infotronics Model 204 digital integrator set at 1000 counts per millivolt second. Pesticide standards were prepared as previously described[3].

RESULTS AND DISCUSSION

Fig. 1 shows the results obtained when the hydrogen flow-rate was varied from 0–100 ml/min. The furnace temperature was maintained at 820° and the solvent flow-rate at 1 ml/min. There was a sharp increase in response to a maximum at 30 ml/min followed by only a slight increase with further hydrogen flow. The maximum in the response curve was also observed by Lawrence[5] at 30 to 60 ml/min and by Cochrane *et al.*[4] at 80 ml/min of oxygen in the sulphur and chloride mode. Dolan and Hall[6] attribute this effect to the increase in response with additional hydrogen flow up to a point where total flow-rates are high enough to decrease residence time in the reaction tube causing a decrease in response. If this is the case it may be possible to increase response by switching to hydrogen carrier gas or increasing the length of the reaction tube and nickel catalyst. Baseline noise increased slightly at higher flow-rates but was still tolerable.

The variation in response with changes in solvent flow is shown in Fig. 2. In this case the furnace temperature was 820° and the hydrogen flow-rate was 30 ml/min. The solid line represents the response of atrazine in counts/ng and the dashed line is the peak to peak noise in mm. The vertical axes are entirely different for each curve. From 2.0 down to about 1.0 ml/min, the response is constant at 4,000 counts/ng with a baseline noise of less than 1 mm. This noise is almost undetectable since the pen width itself is almost 1/2 mm. Below 1.0 ml/min, however, the response increased sharply to 40,000 counts/ng at 0.2 ml/min (a tenfold increase). Unfortunately the baseline noise also increased sharply to about 20 mm peak to peak at 0.2 ml/min. The response remained fairly constant from day to day, but the noise did vary. It was possible to operate as low as 0.6 to 0.7 ml/min on some occasions but, in general,

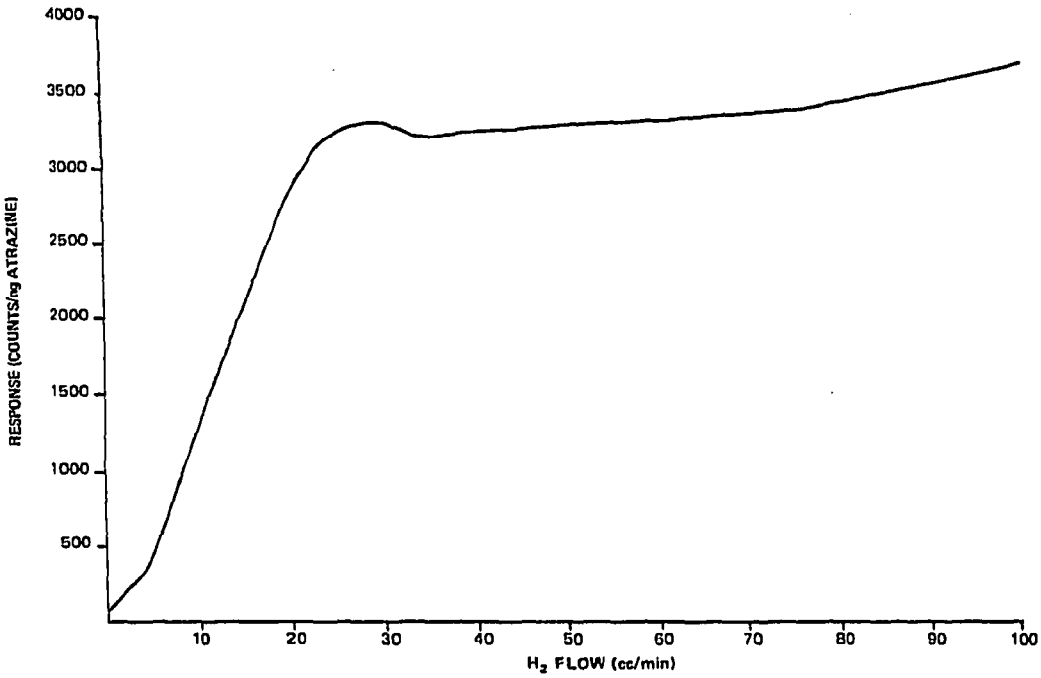


Fig. 1. Variation in response with increase in hydrogen flow-rate.

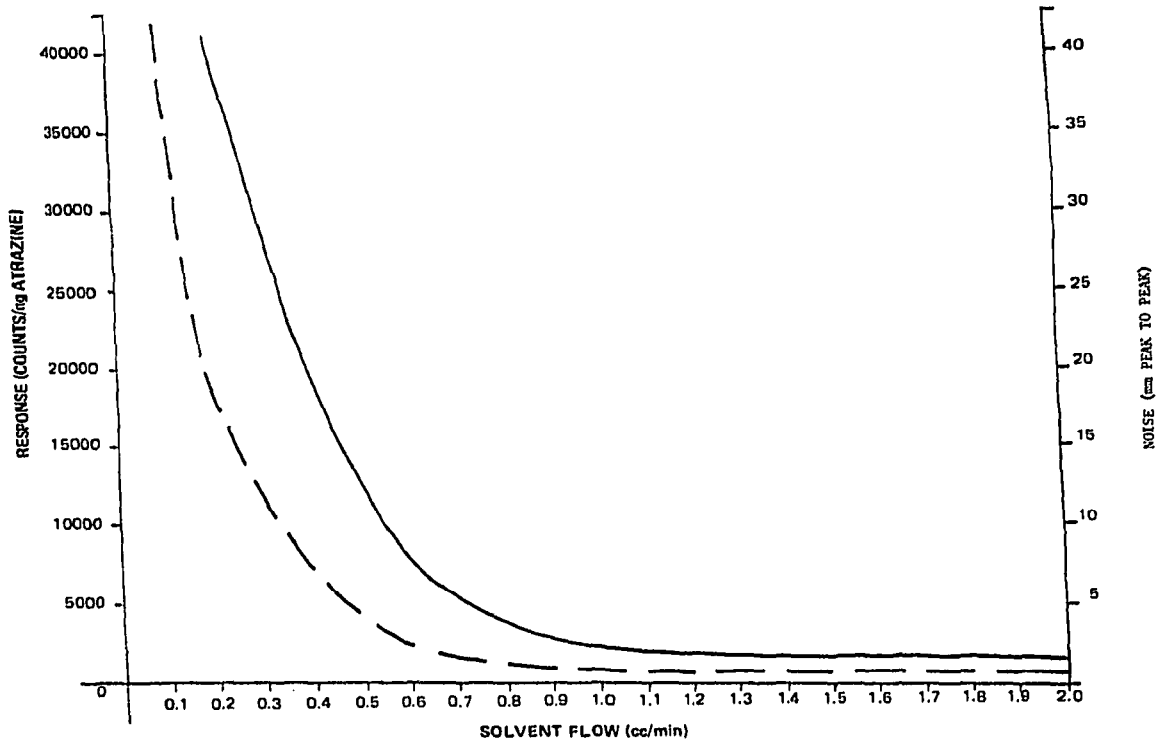


Fig. 2. Variation in response with increase in solvent flow-rate. ———, Atrazine; — — —, noise.

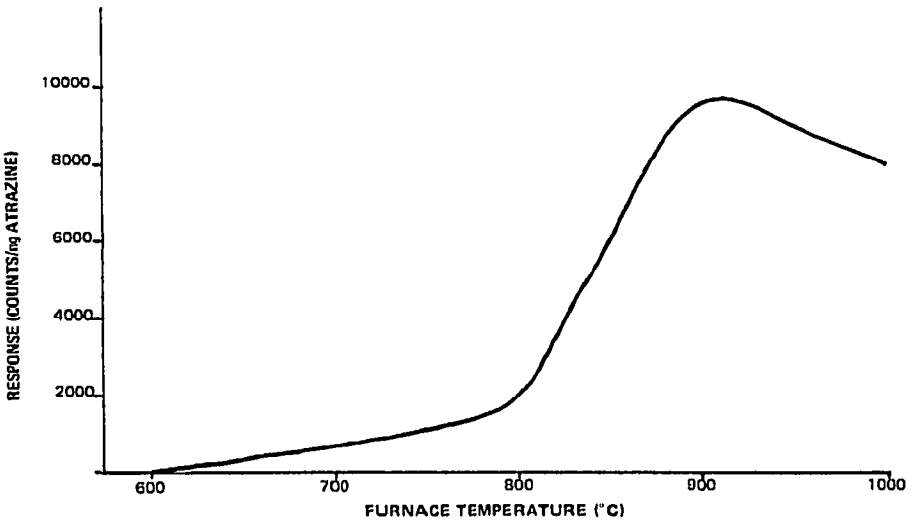


Fig. 3. Variation in response with increase in temperature.

a flow-rate of 0.7 to 0.8 ml/min was chosen for an optimum signal-to-noise ratio.

Fig. 3 depicts the variation in response with changes in furnace temperature. Here the solvent flow-rate is 0.7 ml/min and the hydrogen flow-rate is 30 ml/min. Below 600° no response is observed, even for 500 ng of atrazine. From 600 to 800° the response increases gradually. Above 800° the response increases sharply to a maximum of 10,000 counts/ng at 900° and then decreases above that temperature. There was only a slight increase in baseline noise above 900°.

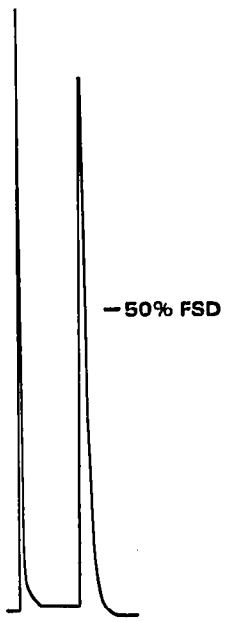
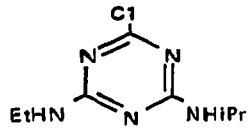
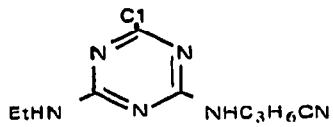
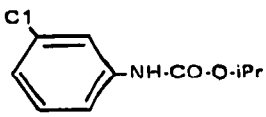
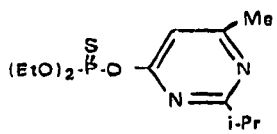
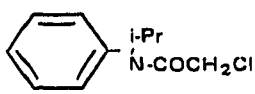
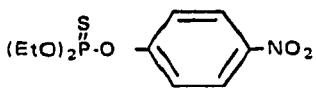


Fig. 4. Chromatogram of 1.9 ng atrazine on 4% OV-101/6% OV-210 at 205°.

From the three response curves the optimum conditions of 900° furnace temperature, 30 ml/min hydrogen flow-rate, and 0.7 ml/min solvent flow-rate were chosen. Under these conditions 1.9 ng atrazine gave an 85% f.s.d. (Fig. 4) and a 1/2 f.s.d. of 1.1 ng. The responses of some nitrogen-containing pesticides are shown in Table I and compared to the 1/2 f.s.d. previously obtained with the CCD in the

TABLE I

RESPONSE OF COULSON AND HALL DETECTORS TO SOME NITROGEN-CONTAINING PESTICIDES

Compound	*Structure*	*½ f.s.d. (ng)*		R_p*
		Coulson	*Hall*	
Atrazine		7	1.1	0.31
Bladex		15	1.1	0.54
Chlorpropham		75	6.0	0.24
Diazinon		25	4.5	0.31
Ramrod		50	6.5	0.31
Parathion		150	20.0	1.00

* 4% OV-101, 6% OV-210 at 205°, Parathion t_R = 6.2 min.

nitrogen mode. In each case a significant increase in response was observed and ranged from a low one of 3.8 times for Bladex to a high one of 12.5 times for Chlorpropham. Overall, the response was increased by an average factor of 7.2.

Work is continuing to evaluate the effects of solvent composition and catalyst length on the nitrogen response of this detector. The greatest potential for increased sensitivity, however, lies in effective noise reduction, since an immediate tenfold increase is available at slower solvent flow-rates if the accompanying noise can be suppressed.

In summary then, the new Hall Electrolytic Conductivity Detector offers an immediate increase of about seven times the sensitivity of the Coulson detector for nitrogen-containing compounds with the potential for a greatly increased response once the noise problem has been overcome.

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