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Note

Performance characteristics of a system containing a capillary column and an electron-capture detector

L. REJTHAR* and K. TESAŘÍK

Institute of Analytical Chemistry, Czechoslovak Academy of Sciences, 66228 Brno (Czechoslovakia)

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The extreme sensitivity and selectivity of the electron-capture detector (ECD) and the high separation efficiency of capillary columns cannot be combined with advantage owing to the large dead volume of commercial ECDs. A reduction in the separation efficiency of up to 50% with such combined systems has been reported[1], and even with the use of a special detector[1] the decrease is up to 20%. With a micro-packed column[2], the decrease in the efficiency was found to be 11%. Other papers[3–5] in which the performance characteristics of combined capillary column–ECD systems have been discussed did not report comparative results for other detectors for the same compound obtained under identical operating conditions, and therefore an adverse effect of the ECD on the separation characteristics cannot be evaluated.

As little work appears to have been carried out on this subject, we tried to verify the influence of the working volume of a commercially available ECD on the efficiency of a capillary column, on the magnitude of the detector response and on the linear range of the response under the conditions necessary for the use of the capillary column.

EXPERIMENTAL

All measurements were carried out on a Fractovap 2300 AC chromatograph (Carlo Erba, Milan, Italy) equipped with a standard injector for capillary columns, a splitter and an ECD HT-20 electron-capture detector or an FID-20 flame-ionization detector.

A glass capillary column, 24 m long × 0.3 mm I.D., was first etched in the gas phase[6] and then silanized[7]. The capillary was coated by the dynamic method with a 10% solution of OV-101. The column was conditioned for 24 h at 513 °K and at a flow-rate of 0.5 ml/min of nitrogen without the detector. It was then mounted in the chromatograph by means of PTFE seals and its function was tested by using the FID. All parts of the chromatograph and the detector were used without any special modifications.

The operation conditions were as follows. The carrier gas was nitrogen, flow-

* Present address: Institute of Vertebrate Zoology, Department of Experimental Ecology, Czechoslovak Academy of Sciences, 67502 Studenec, Czechoslovakia.

rate 0.50 ml/min, linear velocity 11.8 cm/sec; temperatures of the injector and column, 498 and 485 °K, respectively; splitting ratio, 1:20. The operation conditions for the ECD were: temperature, 523 °K, pulse mode with pulse width 3 μsec, pulse interval 100 μsec and pulse voltage 50 V; scavenger gas, nitrogen at flow-rates of 21.5 ml/min for the measurement of linearity of the response and for the determination of the minimal detectable amount and 5–140 ml/min for the measurement of the dependence of the separation efficiency on the amount of gas passing through the detector.

RESULTS AND DISCUSSION

Using the FID, the efficiency of the capillary column was determined for lindane (a solution containing $4.8 \cdot 10^{-7}$ g of lindane in 0.5 μl of *n*-hexane, *i.e.*, $2.4 \cdot 10^{-8}$ g of lindane for the column and the detector, was injected). An efficiency of 70,000 theoretical plates for $k = 5$ (Fig. 1a) was measured.

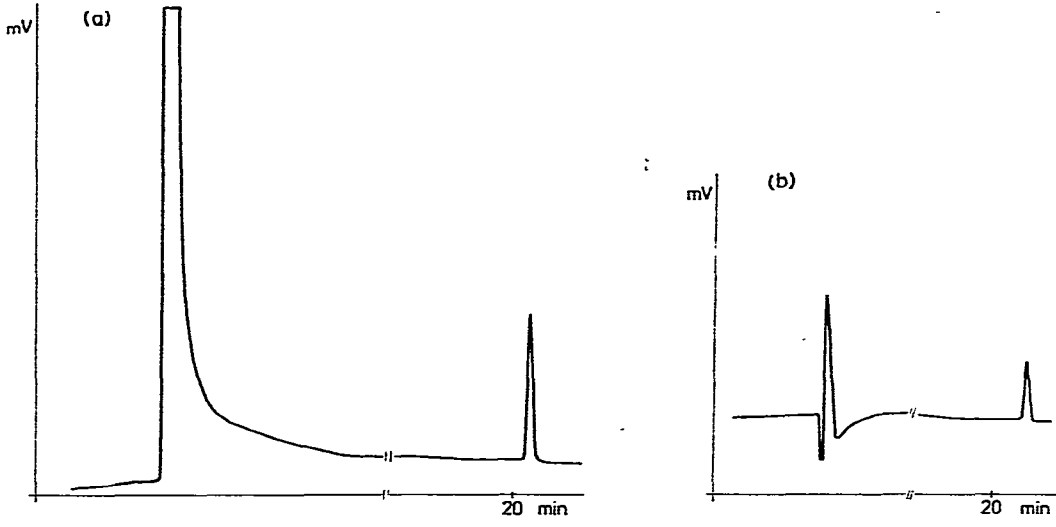

Fig. 1. (a) Chromatogram obtained for lindane ($2.4 \cdot 10^{-8}$ g), detection with the FID, column efficiency 70,000 theoretical plates (k = 5). (b) Chromatogram obtained for lindane ($2.4 \cdot 10^{-10}$ g), detection with the ECD, column efficiency 63,000 theoretical plates, scavenger gas flow-rate 140 ml/min.

After determining the separation efficiency of the capillary column with the FID, the detector was replaced and the efficiency of the system containing the same capillary column and the ECD was measured as a function of the amount of gas passing through the detector. The operating conditions (temperature and flow-rate of the carrier gas) were maintained constant during this determination; the amount injected was $4.8 \cdot 10^{-9}$ g of lindane in 0.5 μl of *n*-hexane (*i.e.*, $2.4 \cdot 10^{-10}$ g for the column and the detector). The results are summarized in Fig. 2. As the flow-rate of the scavenger gas increases, the negative effect of the volume of the detector on zone broadening decreases. At a flow-rate of nitrogen of about 28 ml/min, the system acquires about 80% of the efficiency measured for the column with the FID. A further increase in the amount of scavenger gas causes a slow, approximately linear increase

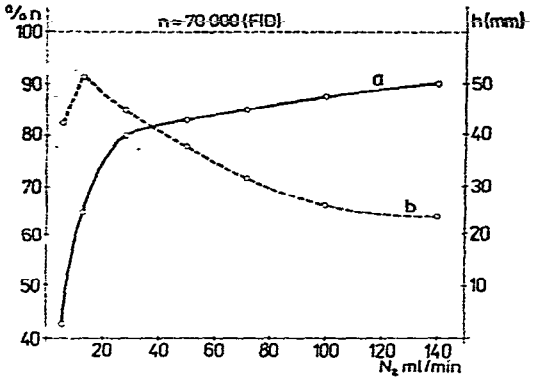

Fig. 2. Dependence of (a) the efficiency of the capillary column (theoretical plates, n) and (b) the height of the peak of lindane on the amount of gas passing through the detector.

in the efficiency up to 90% of that measured for the FID at a flow-rate of nitrogen of 140 ml/min (Fig. 1b).

The detector response corresponding to the passage of $2.4 \cdot 10^{-10}$ g of lindane through the detector was determined simultaneously with the efficiency and the results are shown in Fig. 2. The peak height changes with the amount applied, depending on the separation efficiency of the system and on the degree of dilution of the solute in the detector. The increase in the separation efficiency of the system leads to an increase in the peak height, while dilution of the solute with the scavenger gas causes a decrease in the peak height. At the front part of the peak, the effect of the increase in the separation efficiency prevails, while at the back of the peak the effect of the dilution of the solute prevails.

With a compromise in the selection of the operating conditions, *i.e.*, at a flow-rate of gas through the detector (carrier gas plus scavenger gas) of 22 ml/min,

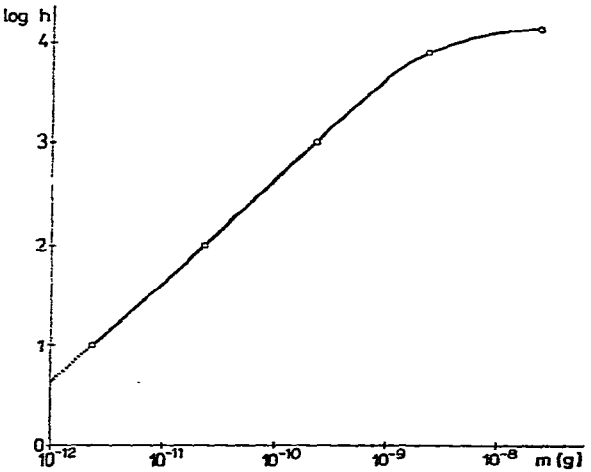

Fig. 3. Calibration graph for lindane. Operating characteristics of the system: column efficiency n = 56,000 theoretical plates; sensitivity = 94% of maximal sensitivity (see Fig. 2).

when the column efficiency is *ca.* 80% of that measured with the FID and the detector response is relatively high (94% of the maximal response for the given amount), the linear range of the detector response and the minimal detectable amount of lindane were measured. The results are given in Fig. 3. The minimal detectable amount of lindane is about 1 pg and the response expressed as the peak height remains linear for amounts of lindane passing through the detector varying between 2.4 pg and 1.0 ng. The peak height for 2.4 ng of lindane is already 20% lower than would correspond to a linear calibration graph. From the course of the calibration graph it is obvious that the system used is sufficiently sensitive and useable over a relatively wide range for quantitative purposes.

CONCLUSION

The results indicate that a commercial ECD can be combined with an efficient capillary column if the operating conditions are selected correctly. The decrease in the resolving power leads, depending on the conditions used, to a decrease of 10–20% in the separation efficiency in comparison with the maximal values measured with an FID. The combined ECD–capillary column system provides both high sensitivity and a linear response over a wide range.

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