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## PRACTICAL ASPECTS OF FAST GAS CHROMATOGRAPHY ON 50 $\mu\text{m}$ I.D. CAPILLARY COLUMNS: COMBINATION WITH ELECTRON-CAPTURE DETECTION

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### SUMMARY

A sensitive test is described for measuring the residual activity of 50- $\mu\text{m}$  I.D. capillary columns deactivated by polysiloxane degradation. The combination of these columns with electron-capture detection is reported. A detection limit of *ca.*  $10^{-15}$  g was found for Dieldrin, using a 4.1 m  $\times$  55  $\mu\text{m}$  I.D. OV-1 column having 70,000 theoretical plates. Fast chromatograms of a test mixture of chlorinated pesticides and of Arochlor 1260 are shown, the analysis times being of the order of 10 min.

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### INTRODUCTION

In 1962, Desty *et al.*<sup>1</sup> demonstrated that the speed of analysis in capillary gas chromatography can be greatly increased by reducing the column inner diameter. This approach was recently further investigated by, among others, Gaspar *et al.*<sup>2,3</sup>. Promising results were obtained by Schutjes *et al.*<sup>4</sup>, also with very complex samples, for which a proportional decrease of the analysis time with the column diameter was found. A gasoline could for example be separated within 7 min on an 8 m  $\times$  50  $\mu\text{m}$  I.D. borosilicate SE-30 column having 150,000 theoretical plates<sup>4</sup>. Until now, the flame ionization detector has been the only detector used with these very narrow bore columns. In this paper, the coupling of a 55- $\mu\text{m}$  I.D. column to an electron-capture detector is described.

### EXPERIMENTAL

A Pye-Unicam (Cambridge, U.K.) Model 104 gas chromatograph equipped with a laboratory-made split mode injector, a Veriflo (Richmond, CA, U.S.A.) Model IR 503 carrier gas pressure regulator and an electron-capture detector (Pye-Unicam, Series 795012), was used. The injector and detector were both kept at 250°C. The flow-rate through the splitter vent was 1.5 ml/min. The detector was equipped with a <sup>63</sup>Ni source of 10 mCi and was operated with a pulse technique, the applied voltage and the time interval between successive pulses being kept constant. A mixture of 5% methane in argon was used for the detector make-up gas. The time constant of

the amplifier was 0.1 sec. A SP 4100 (Spectra-Physics, Santa Clara, CA, U.S.A.) computing integrator coupled to a DCC-D-116 E minicomputer was employed for data acquisition and data handling.

Fused-silica capillary tubing of 55  $\mu\text{m}$  I.D. was obtained from SGE (Melbourne, Australia). The tubing was rinsed with an aqueous solution of 2% hydrofluoric acid and 2% nitric acid for 30 min, and was then flushed with 2% hydrochloric acid and with distilled water. The columns were dehydrated for 3 h at 280°C under a flow of nitrogen, filled with 0.6% (v/v) OV-1 in pentane, flame-sealed at one end, enclosed in an aluminium box purged with nitrogen and heated for 1 h at 420°C. After being rinsed with pentane the columns were statically coated.

## RESULTS AND DISCUSSION

Owing to its high sensitivity, the electron-capture detector is able to detect sub-picogram amounts of halogen-containing compounds. For the proper separation of such small amounts, well deactivated capillary columns are required. In a previous paper<sup>5</sup> a suitable deactivation method for 50  $\mu\text{m}$ -I.D. columns, based on polysiloxane degradation, was described. To obtain a high coating efficiency the deactivation had to be carried out in a solvent, thus preventing the build-up of unwanted solid deposits on the column wall. Surprisingly, the reported method gave best results when one side of the capillary column was left open during the polysiloxane degradation step at 420°C, thus allowing the solvent to escape gradually. Additional studies on 50- $\mu\text{m}$  I.D. columns have confirmed this observation. The method however failed for columns with diameters greater than 80  $\mu\text{m}$ , for reasons which are not yet known.

To evaluate the residual adsorptive activity of the deactivated, non-coated column inner wall, the capacity ratios of a series of test compounds were measured. The capacity ratio, which can be assessed with a much greater precision than the peak area or the peak asymmetry, is employed as a quantitative measure of the residual adsorption. To facilitate the interpretation of the data the columns were tested at 100°C, at which temperature the test compounds are normally chromatographed. Some of the results are listed in Table I, which shows the activity of untreated fused-silica tubing and the effect of the rinsing step with distilled water on the activity of the deactivated column. Rinsing with distilled water appears useful.

On well deactivated columns, a capacity ratio very close to 0 was obtained for all the compounds studied. Columns giving capacity ratio values very close to 0 normally also gave the best Grob tests after being coated. The reported activity test thus apparently provides very practical information in a simple way.

The cell volume of an electron-capture detector is a well known source of extra-column contributions to peak dispersion. The detector is normally purged with a make-up gas to eliminate this effect. Unfortunately, the response of the detector is then decreased, owing to dilution of the compounds eluting from the column. To restore the sensitivity, we tried to reduce the amount of make-up gas needed by reducing the detector outlet pressure, thus enhancing the purging. Air leakages initially prevented the detector from working under these conditions. After careful elimination of all leakages by enclosing the detector in a stainless steel housing, the detector operated well at outlet pressures down to 0.4 bar abs, with 50- $\mu\text{m}$  I.D. capillary columns as well as with a conventional 36 m  $\times$  0.31 mm I.D. persilylated borosilicate

TABLE I

CAPACITY RATIOS ON UNTREATED FUSED-SILICA COLUMNS AND ON DEACTIVATED COLUMNS, WITH AND WITHOUT THE RINSING STEP WITH DISTILLED WATER

Values are the averages obtained with three different columns, measured at 100°C. Compounds:  $C_{10}$  = *n*-decane; DMA = 2,6-dimethylaniline; DMP = 2,6-dimethylphenol; ol = 1-octanol; S = 2-ethylhexanoic acid; Am = dicyclohexylamine.

Treatment	Capacity ratio					
	$C_{10}$	DMP	DMA	ol	S	Am
None	0.0	0.25	0.35	0.4	1.0	2.1
Deactivated, no water rinse	0.0	0.0	0.05	0.1	0.1	0.5
Deactivated, water rinse included	0.0	0.0	0.0	0.0	0.0	0.1

SE-54 column. For maximum sensitivity, the position of the column outlet inside the detector had to be carefully optimized.

Contrary to our expectations, reduction of the detector outlet pressure gave no improvement of the sensitivity, as the amount of make-up gas needed was found to be approximately independent of this pressure. However, analysis was quicker with the 36 m × 0.31 mm I.D. column. This is illustrated in Fig. 1, showing plate height curves measured for *p,p*-DDT ( $k = 5.4$ ) at 215°C, with helium as the carrier gas. The optimum linear carrier gas velocity was shifted from 27 cm/sec at atmospheric outlet pressure to 33 cm/sec at 0.4 bar, decreasing the analysis time by 20%, in accordance with theory<sup>6</sup>. An improvement of the column efficiency was also observed, indicating that flushing of the detector cell with carrier gas alone is impaired when a glass column with a comparatively large outer diameter (1.0 mm) is installed.

Since 50- $\mu$ m I.D. capillary columns have to be operated with an elevated inlet pressure, their speed of analysis is not noticeably increased when the outlet pressure

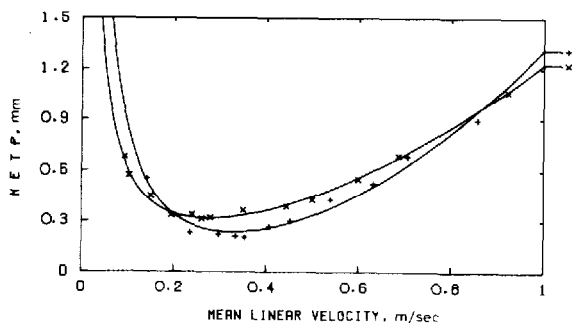


Fig. 1. Plate height (HETP) versus average linear carrier gas velocity measured for *p,p*-DDT ( $k = 5.4$ ) at 251°C with helium, on a 36 m × 0.31 mm I.D. SE-30 column, using an electron-capture detector operated at 1 bar, abs (×) and at 0.4 bar, abs (+). Make-up gas flow-rate, 50 ml/min and 100 ml/min (converted to 1 bar), respectively.

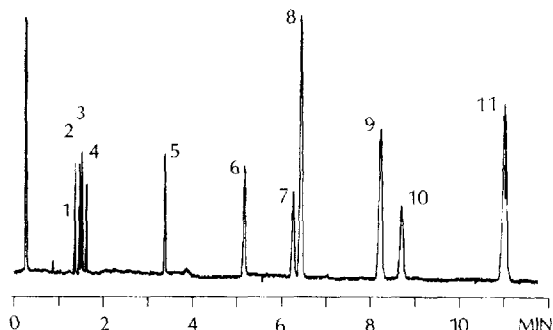


Fig. 2. Separation of a standard mixture of chlorinated pesticides (150–170 ppb, dissolved in hexane) on a 4.1 m  $\times$  55  $\mu$ m I.D. capillary OV-1 column, employing electron-capture detection. Peaks: 1 =  $\alpha$ -HCH; 2 = HCB; 3 =  $\beta$ -HCH; 4 =  $\gamma$ -HCH; 5 = Aldrin; 6 = *o,p*-DDE; 7 = Dieldrin; 8 = *p,p*-DDE; 9 = *p,p*-DDD; 10 = *o,p*-DDT; 11 = *p,p*-DDT.

is decreased below 1 bar<sup>4,6</sup>. The coupling of such a column to the electron-capture detector was therefore mainly investigated under atmospheric outlet pressure conditions. A 4.10 m  $\times$  55  $\mu$ m I.D. deactivated fused-silica OV-1 column was employed. Helium was the carrier gas, the column inlet pressure being 5 bar (gauge).

Firstly, a synthetic mixture of chlorinated pesticides was studied, at 220°C. Starting with a small flow, the make-up gas flow-rate was gradually increased, until the peak widths of the earliest eluting compounds ceased to decrease. A flow-rate of 60 ml/min appeared to be necessary. A chromatogram of the mixture is illustrated in Fig. 2. For Dieldrin ( $k = 25$ ), *ca.* 70,000 theoretical plates were obtained, which is 95% of the theoretically predicted plate number. The detection limit for Dieldrin was *ca.*  $10^{-15}$  g.

The column was subsequently used for the isothermal separation, at 222°C, of Arochlor 1260 (Fig. 3). This took 8 min: analysis times exceeding 30 min are normally reported in the literature<sup>7,8</sup> for Arochlor 1260.

The decrease of the inner diameter of a capillary column is known to be accompanied by a large decrease of its sample capacity. With a flame ionization detector, overloaded peaks are generally observed when more than 2 ng of a compound are applied to a 50- $\mu$ m I.D. column. However, the electron-capture detector is gen-

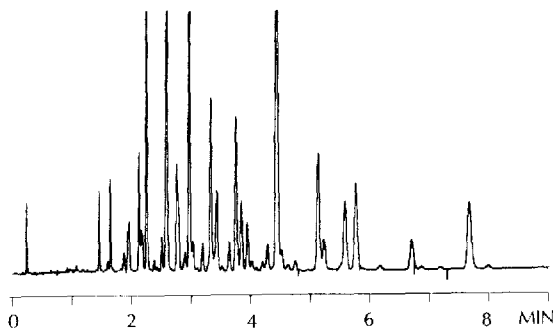


Fig. 3. Arochlor 1260, analysed at 222°C on a 4.1 m  $\times$  55  $\mu$ m I.D. fused-silica OV-1 column, employing electron-capture detection. Carrier gas, helium.

erally used to detect sub-nanogram amounts. During our investigations, overloaded peaks indeed did not occur. The electron-capture detector thus appears eminently suitable for use with very narrow bore columns, as are nowadays employed in fast capillary gas chromatography.

The coupling of a 50- $\mu\text{m}$  I.D. capillary column to a mass spectrometer has recently also been realized. A Finnigan (Sunnyvale, CA, U.S.A.) Model 4000 quadrupole GC-MS instrument connected to a minicomputer was used. Because of the high speed at which the compounds eluted from the column, the fastest available scanning rate (10 scans per sec) was needed. As an example, mass spectra obtained with 2,6-dimethylphenol (DMP) and 2,6-dimethylaniline (DMA) are illustrated in Fig. 4. Using the sophisticated MSRR search program developed by the Research group of Chemometrics, Laboratory of Analytical Chemistry, State University of

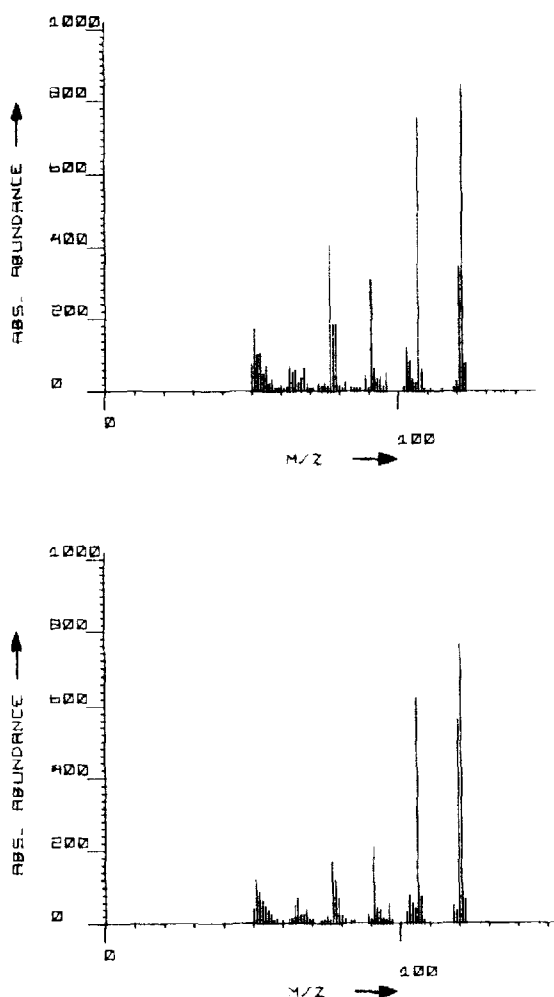


Fig. 4. Mass spectra of 2,6-dimethylphenol (top) and 2,6-dimethylaniline (bottom), obtained with a 4 m  $\times$  50  $\mu\text{m}$  I.D. fused-silica OV-1 column coupled to a quadrupole mass spectrometer.

Utrecht, Utrecht, the Netherlands, the DMP spectrum was compared with the Wiley-McLafferty reference file, containing spectra of *ca.* 30,500 different compounds. The DMP spectrum was correctly identified. The DMA spectrum was not identified, because DMA was not present in the reference file.

Some preliminary GC-MS results with the 50- $\mu\text{m}$  I.D. capillary columns have been published elsewhere<sup>9</sup>. Further work is in progress.

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