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NARROW-BORE WALL-COATED OPEN-TUBULAR COLUMNS FOR FAST HIGH-RESOLUTION GAS CHROMATOGRAPHIC SEPARATIONS OF TOXICANTS OF ENVIRONMENTAL CONCERN

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SUMMARY

High-resolution gas chromatographic columns with 100 μm I.D. can achieve better separations than presently used 250-μm I.D. wall-coated open-tubular (WCOT) columns in about half the total time. However, these columns also produce narrower solute peaks that require low dead volume gas chromatographic systems. This paper describes a new technique for static coating of such columns and their adoption for cold on-column injections and interfacing with mass spectrometer and electron-capture detectors. They can be used with present gas chromatographic equipment, usually without any system modifications. A number of questions relating to the use of these new columns were examined experimentally. The results show no compromise in GC performance. A number of applications of narrow bore WCOT columns are presented, including comparisons of separations with corresponding 250 or 320-μm I.D. columns. It is shown that many difficult environmental separations can be resolved using narrow bore WCOT columns.

INTRODUCTION

In recent years the use of wall-coated open-tubular columns (WCOT) has increased significantly in almost all areas where gas chromatography (GC) can be applied. High-resolution GC has become a very popular method for analyzing complex mixtures in environmental analyses. Despite the broad area of applications of these techniques and the tremendous amount of work devoted to preparation of reproducible, thermally stable, non-active surfaces, little effort has been made to investigate the optimum diameter of WCOT columns.

In 1975, Grob and Grob[1] utilized both the packed and WCOT column on the same river water extract and demonstrated clearly the distinct advantage of WCOT columns. They showed that number of resolved peaks on the wide-bore WCOT column (600-μm I.D.) was approximately three times as many as the packed column but only 67% of the number obtained on a 250-μm I.D. WCOT column. The conclusion is not surprising, since Desty in the early 1960's demonstrated the advantages of a 140-μm I.D. column in the separation of nine C_7-paraffin isomers in just under 1 h.

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Recently, Schutjes *et al.*[2,3] and Gonnord *et al.*[4] demonstrated that narrow-bore WCOT columns can produce high resolution analytical separation of complex samples. More than 250.000 theoretical plates (TP) can be generated on relatively short, narrow-bore WCOT columns (25 m) that are commercially available (Quadrex, New Haven, CT, U.S.A.). These columns can be used effectively with electron-capture and mass spectrometer as GC detectors. Theoretical studies of Guiochon[5] show that the time of analysis is proportional to the column diameter. Schutjes *et al.*[2,3] and Gonnord *et al.*[4] also demonstrated that a reduction in column diameter yields a proportional decrease in analysis time.

The purpose of this paper is to show experimental consequences of using narrow bore WCOT columns and to discuss injection techniques and the detector performances when picogram quantities are introduced onto the narrow bore column.

EXPERIMENTAL AND RESULTS

Preparation of narrow bore WCOT columns

Various chemical and physical treatments have been evaluated in order to produce an ideal glass surface. By far the most popular treatment for borosilicate and fused-silica capillary tubing is leaching. It employs an etching solution consisting of 2.26% hydrofluoric acid and 2.15% HNO_3 at 30°C for a maximum of 1 h, followed by a rinse with 1% hydrochloric acid and flushing with distilled and deionized water. With both ends of the capillary tubing connected to the oven the capillary is heated under nitrogen at 280°C for 2 h. Then the nitrogen flow is stopped and mild vacuum (10–50 mmHg) is applied during the cooling period which lasts approx. 30 min.

Silanization

Several researchers have used silanization both in the liquid and gaseous phases of the inner wall with wide variety of silylating agents. This has been done both instead of, and as a complement to, etching[6,7]. It is known that the thermal stability and non-extractability of polysiloxane stationary phases is improved by cross-linking reactions. The use of cross-linking agents, such as peroxides, for various polysiloxane stationary phases has been recommended by Grob *et al.*[8] and many other authors[9–11]. Organic peroxides producing free radicals have been widely used as initiators of polymerization. Of the peroxides, those most commonly used are benzoyl peroxide and dicumyl peroxide which decompose thermally to give radicals, which in turn, can lose carbon dioxide to give phenyl or tolyl radicals, as shown:

$$C_6H_5\text{–}COO\text{–}OOC\text{–}H_5C_6 \rightarrow 2C_6H_5\text{–}COO^{\cdot} \rightarrow 2C_6H_5^{\cdot} + 2CO_2$$

Either of these radicals is capable of initiating polymerization and it has been shown that this indeed happens. However, peroxides generally show some tendency to undergo side reactions with other radicals in the system. Consequently, the order of decomposition is not quite unity. It has also been reported that dicumyl peroxide causes oxidation of tolyl and cyanopropyl functional groups during cross-linking[12].

We have been using azo compounds instead of peroxides. These componds decompose unimolecularly with elimination of nitrogen[13]. They are not subject to any side reactions as far as is known and apparently decompose at the same rate

regardless of the solvent used. However, while Richter *et al.*[12] recommend various azo-alkanes, we prefer commercially availabele 1-*tert*-butylazo-1-cyanocyclohexane (Luazo-96; Pennwalt Lucidol, Buffalo, NY, U.S.A.) or 2-*tert*.-butylazo-2-cyanobutane (Luazo-79) and 2-*tert*.-butylazo-2-cyanopropane (Luazo-82).

We consider 1-*tert*.-butylazo-1-cyanocyclohexane as a reliable source of free radicals generated at controllable rates for polymerization. The new cross-linked polymer is no longer completely soluble under the usual conditions. The macromolecules formed are tied to each other and cannot be completely separated by solvent. Usually, appropriate volumes of a 1% (w/w) solution of the initiator in methylene chloride is added to 20 mg of SE-52 containing 1% vinyl groups.

Static coating procedures

The Luazo-96 was doped directly into the coating solution for a maximum of 20 min prior to use. After coating, the WCOT columns were purged with nitrogen, their ends sealed in a flame, and then heated to 150°C for 1 h. The columns were then installed in a GC oven and purged for 1 h at 50°C. Finally, the WCOT columns were washed with 20 ml of methylene chloride and 10 ml *n*-hexane.

Recently, Volkov *et al.*[14] described a variation of the static method which was improved and modified at our laboratory as it is discussed in detail here for the fused-silica column variant.

In this technique the fused-silica capillary tubing is filled with a coating solution containing an appropriate concentration of a liquid phase, preferably silicone gums, Apiezon greases or Superoxes and 0.4–4% of 1-*tert*.-butylazo-1-cyanocyclohexane in methylene chloride. A short length (less than 5 cm) of the capillary tubing is not filled with the solution. This end is flame-sealed. At least 30 cm of the other end of capillary tubing is also left empty. This end is later clamped to the metallic cylinder which is placed on a horizontal shaft driven by a d.c.-electric motor geared to a variable speed shaft of 1 to 5 rpm. The shaft can be demounted easily from the motor by a bayonet type connector. The drum is immersed into a silicone oil bath, which is located on a hot plate stirrer. Its proper adjustment will permit the capillary tubing to be driven smoothly into the silica tube heater. The latter consists of the high temperature resistor (200Ω and 5 W) positioned over the silica tube, which is well isolated by asbestos tape. The bath temperature and the tube heater are heated to 140 and 300°C respectively. The evaporation runs continuously. The process can be easily monitored visually by observing fine bubbles of the solvent leaving the capillary tubing. Evaporation of the solvent is very even, since the oil bath provides a pressure head which eliminates vigorous bumping during evaporation. It takes approx. 60 min to coat a 50-m capillary column. When less than one loop remains outside the bath, the seal is broken away and the fused-silica column is connected to an ultra-pure nitrogen cylinder. The carrier gas is passed through the column at a low flow velocity of 0.5 to 1 ml/min for 30 min. Curing occurs during this period of time. The apparatus is shown in Fig. 1.

Universal static coating apparatus

This static coating apparatus has been designed to accommodate both fused silica and glass capillary tubings. It consists of a hollow alumium cylinder, 355 mm × 114.3 mm in diameter. The wall thickness is 3 mm, and it has a stainless steel shaft

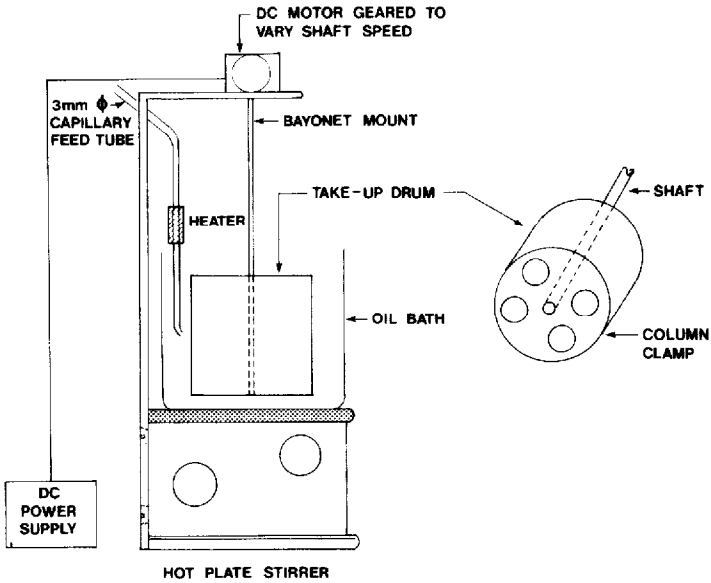

Fig. 1. Static coating apparatus for fused-silica columns.

down the centre fixed at both ends. One end of the shaft which protrudes 45 mm beyond the cylinder, has a thumb screw mount. Attached to the shaft, inside the cylinder, near each end, is an expanding spider. One arm of each spider is connected to one of the three grooved Lexan strips each allowing their diameter to be adjusted from that of the aluminum cylinder to 12.5 mm larger to properly fit and hold the glass capillary tubing.

To mount a column, the Lexan strips are retracted and the capillary tubing is slipped over the cylinder, which is then set horizontally in a holding stand. The spiders are expanded until Lexan strips protrude above the surface of the cylinder sufficiently for the loops to be positioned into each groove, or every other groove, depending on the spacing desired. Each Lexan strip has 160 grooves (2.5 mm deep by 1 mm wide) spaced 2 mm apart, centre to centre.

Once the capillary tubing is positioned, the cylinder is mounted to the rack gear, which is attached to a 990-mm tall stand. A constant speed timer motor attached to a pinion driving gear moves the rack gear downward at 2 cm/min immersing the capillary tubing at a uniform rate into a heated silicone oil bath. The motor has an automatic shut off switch and is connected to the rack and pinion gear through a bayonet clutch which allows the rack gear and cylinder to be moved manually when required. The immersed capillary tubing is connected to a water aspirator to continuously remove solvent vapours. The apparatus is shown in Fig. 2.

This devices are much simpler in design than that of Jennings[15] and Volkov[14]. They allow the use of any solvent from pentane to toluene, if proper pre-heating and evaporator bath temperatures are used.

The most important advantages are the speed of coating and the fact that any stationary phase can be applied. The coating apparatus is relatively inexpensive and may be used for coating and crosslinking at the same time.

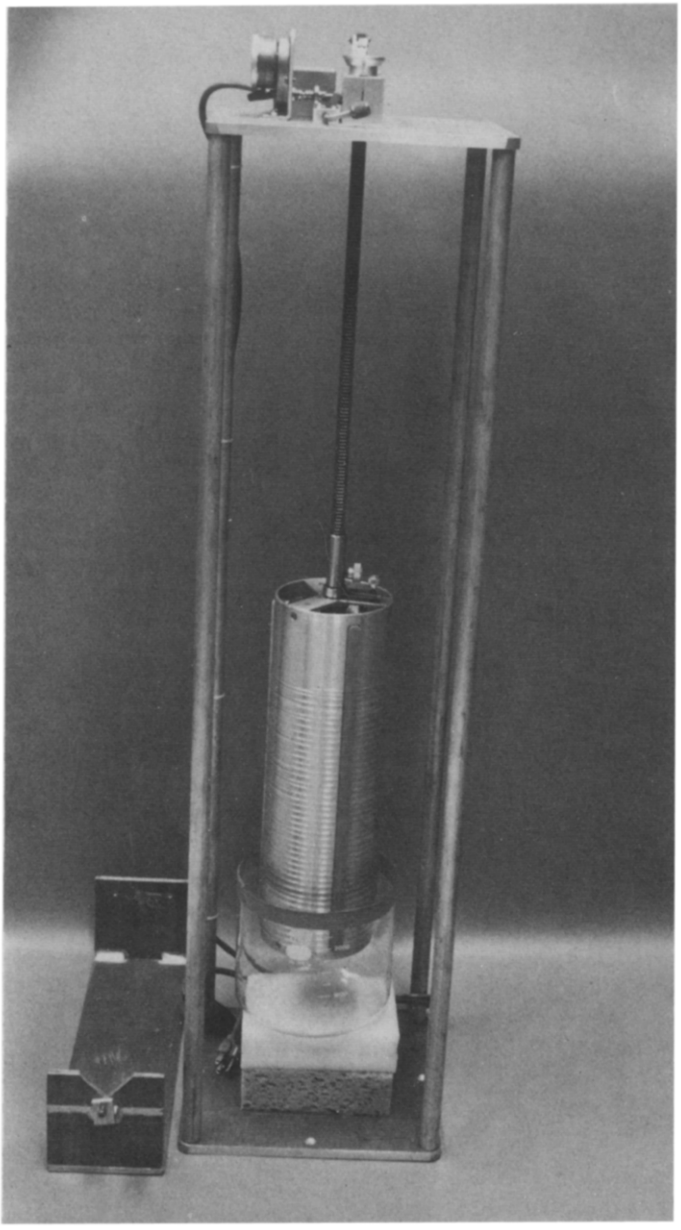

Fig. 2. Universal static coating apparatus.

We recommend establishing coating conditions experimentally using a short fused-silica WCOT column (with a maximum of 5 m in length) filled with the solvent only. The data will indicate the correct feed-rate. A rule of the thumb is that the bath temperature should be twice the boiling point of the solvent and the tube-heater temperature should be 100°C above the bath temperature.

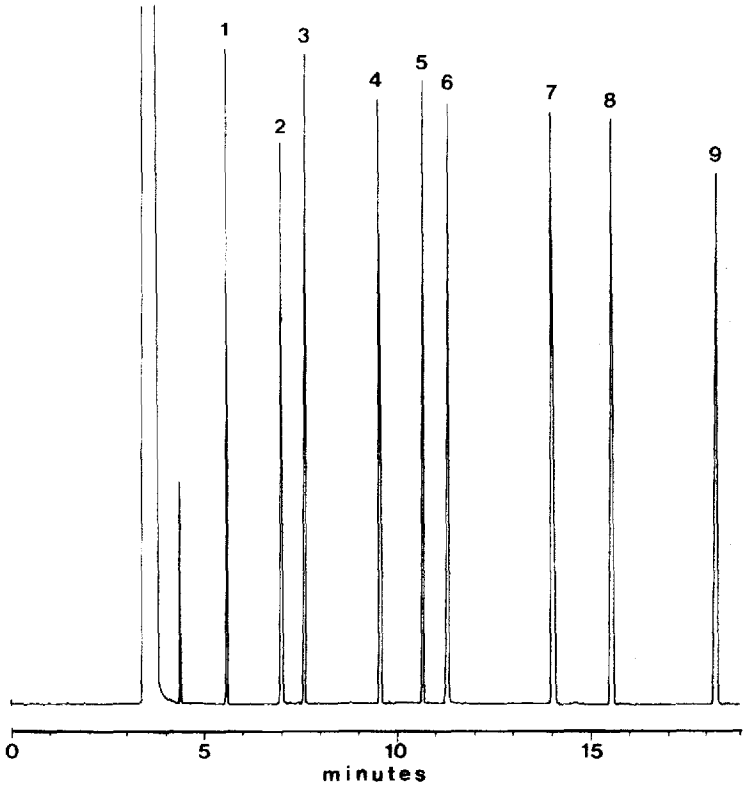

Fig. 3. Chromatogram of the Grob's test mixture. Column OV-1 methylsilicone, 25 m × 104 μm I.D., d_f = 0.2 μm; hydrogen as a carrier gas at 345 kPa; isothermal at 100°C. 1 = Nonane; 2 = 2-octanone; 3 = *n*-decane; 4 = 1-octanol; 5 = 2,6-dimethylphenol; 6 = undecane; 7 = 2,4-dimethylphenol; 8 = naphthalene; 9 = dodecane.

Stationary phases can be deposited on the inner walls of WCOT columns under these conditions. Excellent deactivation is obtained using the procedure described above as shown in Figs. 3–5 for cross-linked OV-1 and Silar 10 C narrow-bore WCOT columns.

Injection techniques

Narrow-bore fused-silica (FS) WCOT columns of 100 μm I.D. can be connected to any known injection devices except for the cold on-column injector without any modification. However, it is recommended that the volume of the injector should be minimized with a well-deactivated glass insert. This should be cleaned to avoid adsorption of some components or decomposition after contact with active centres.

Split injection

Our experience shows that for environmental samples this type of injection is not suitable since environmental samples are very dilute. Band broadening is rarely a problem and reproducibility of Kovats indices is relatively high. Especially when

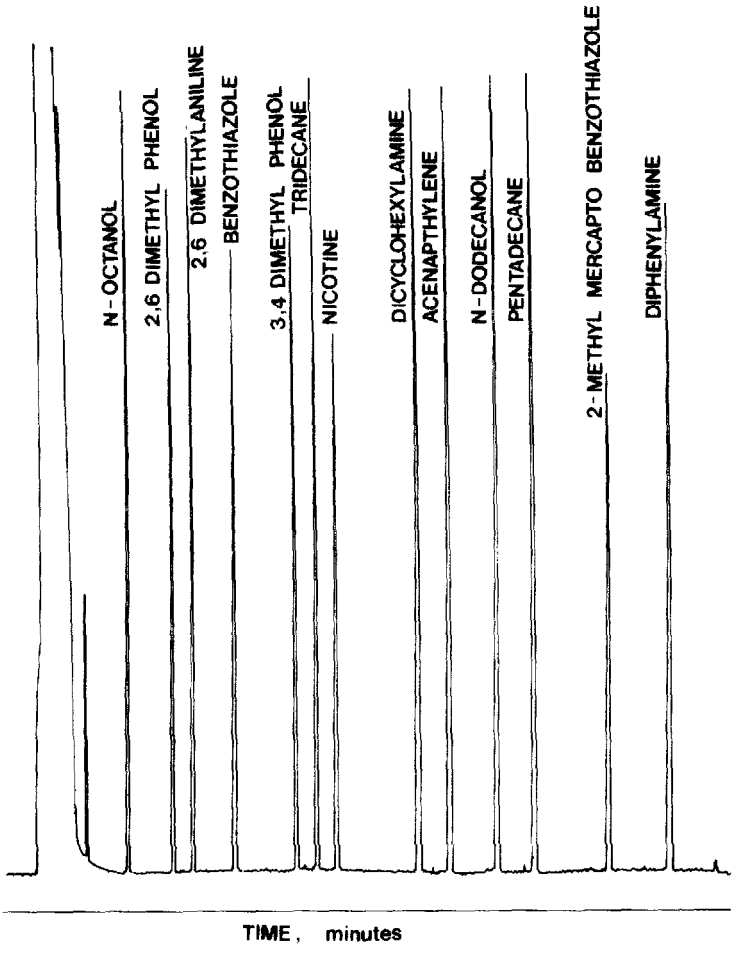

Fig. 4. Chromatogram of modified test mixture. Column OV-1 methylsilicone, 25 m × 104 μm I.D.; d_f = 0.2 μm; temperature programmed from 110 to 150°C at 3°C/min. Hydrogen as a carrier gas at 350 kPa.

hydrogen is used, it is not practical and safe to vent large volumes of hydrogen to atmosphere.

Splitless injection

Splitless injection is a better sample introduction technique in environmental trace analyses. It provides a high dynamic range sensitivity but it requires a significant time for optimizing conditions for introducing a sample into the injector. We have observed that contrary to previous recommendations of bringing the injector to 280°C, the temperature should be optimized for the particular sample, usually in the range of 190 to 230°C. Even for PCB analyses 210°C is sufficient to evaporate the sample. Narrow-bore FS-WCOT columns are not significantly influenced by sample transfer problems. In this mode of operation using narrow-bore columns the split should be set to 1 to 20 maximum and the splitless period should be at least 40 sec[16].

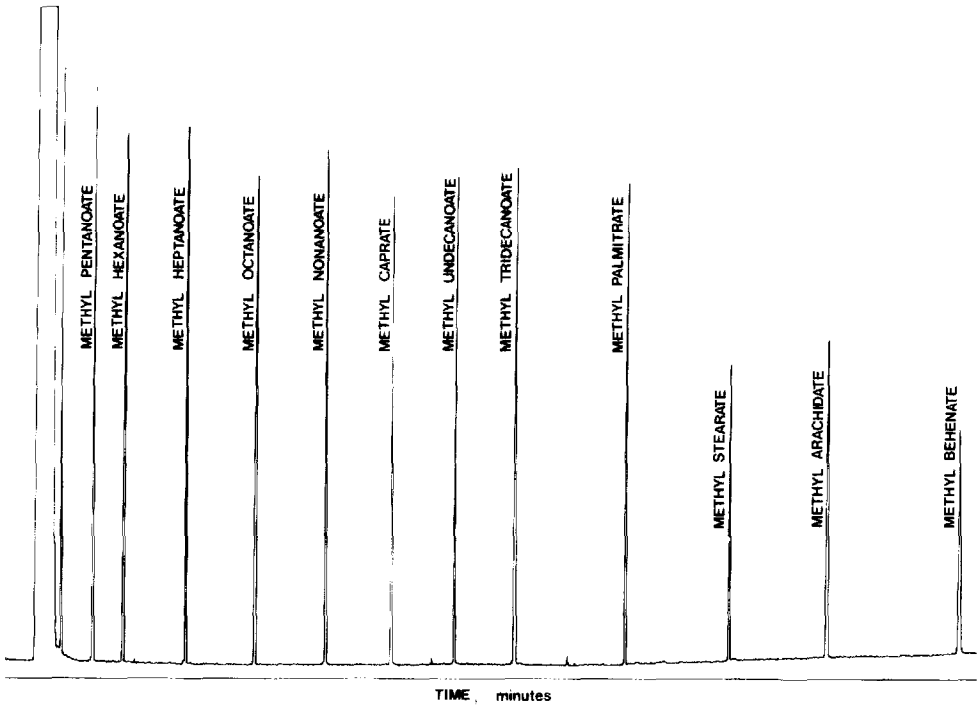

Fig. 5. Chromatogram of fatty acids methyl esters. Column Silar 10 C, 25 m × 100 μm I.D., d_f = 0.18 μm; temperature programmed from 150 to 200°C at 4°C/min; hydrogen as a carrier gas at 350 kPa.

The injection of a large amount of solvent (over 3 μl) may cause undesired solvent effects which can result in solvent peak broadening. The technique allows for quantitation based on internal and external standardization. It should be emphasized that the column temperature must be lowered to 50°C for *n*-hexane and 75°C for isooctane in order to achieve effective sample transfer.

Cold on-column injection

As has already been postulated[16,17], the vaporization of the sample inside the syringe needle and in the injector vaporization tube, as well as the splitting and transfer of the aerosol formed in the injector, may cause problems in quantitative analysis[18]. Cold on-column injection allows deposition of the entire sample directly into the WCOT column of larger diameter tubing. As there is no discrimination of

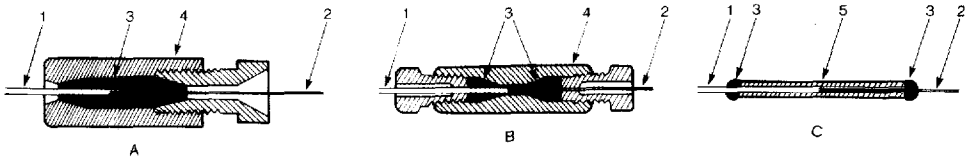

Fig. 6. The types of connectors for two different diameter columns. (A) The butt connector (Supelco); (B) the no dead volume connector (Quadrex Corp.); (C) the glass connector. 1 = Wide-bore capillary; 2 = narrow-bore capillary; 3 = ferrules; 4 = connector body; 5 = glass capillary envelope.

solutes the results are highly accurate[19]. However, when 100-μm I.D. WCOT columns are employed, it is impossible to introduce the sample directly onto the column. We overcame this problem by connecting a short piece of wide-bore capillary to the front of a narrow-bore column. There are three ways, at the moment, to connect a wide bore (*e.g.* 320 μm I.D.) fused-silica tubing, which has not been coated with a liquid phase to obtain a retention gap[20]. The retention gap speeds-up migration of sample components and allows them to be concentrated to the front of the narrow-bore WCOT column in the stationary phase. Since we usually inject 2-μl samples, an approximately 2-m long piece of a fused-silica tubing of 320-μm I.D. is sufficient.

As shown in Fig. 6 both ends must be positioned inside the connector. However, it is not easy to verify the proper position of the ends. This can be done by measuring the length of the connector and the length of each capillary tubing inserted in it. On the other hand, one can use the technique proposed by Sandra *et al.*[21]. Instead of a small polyimide cylinder, a deactivated piece of a glass capillary or fused-silica tubing is used. The wide-bore fused-silica capillary should fit into the glass bore first, and a drop of polyimide is applied on top of the glass capillary. Polymerization is carried out at 110°C for 20 min as recommended[21]. Afterwards, another FS-WCOT column end (narrow-bore capillary) is properly positioned inside the wide-bore capillary with a maximum of 1 mm inside) and polyimide prepolymer is applied in the same manner as the first time. The polymerization step is repeated. When both seals are inspected and no leak is observed a third coating should be applied to cover the entire connector.

Electron-capture detector and mass spectrometer as GC detectors

The electron-capture detector and mass spectrometer are very sensitive, highly specific detection systems. They have been extensively applied in environmental laboratories[19]. Two different detector cell designs are suitable for narrow-bore WCOT column GC. Displaced coaxial cylinder cell geometry and asymmetric concentric cylinder cell may have a total volume of 300 μl employing 8 mCi ^{63}Ni source as described by Patterson[22]. Because of the small elution peak volume obtained from narrow-bore WCOT columns, both detectors must be purged with makeup gas to diminish extra-column contribution to peak broadening.

The requirements for the mass spectrometer in a GC–MS system are more complicated. To obtain adequate qualitative information about the purity of a chromatographic peak and to obtain representative mass spectra, the mass spectrometer should be able to register at least 6 mass spectra per GC peak. A scanning time of 0.1 to 2 sec per decade is required for scanning sharp peaks eluting from narrow-bore WCOT columns. In environmental analyses determination of ultra trace quantities is often required. To meet this requirement, means must be made available to avoid having to cycle the system through the complete mass range but instead focus the mass spectrometry on a few selected masses of interest. This technique of selected ion monitoring (SIM) can be realized even with narrow-bore columns. The narrow-bore column is directly interfaced to the ion source of a mass spectrometer.

Practical applications of the narrow-bore WCOT columns

The primary practical advantage of narrow-bore WCOT columns is that they can provide faster separations than their larger bore counterparts. This leads to the

possibility of fast separation of relatively complex mixtures or simply a general decrease in analysis time for most samples. The narrow-bore columns should replace the wide-bore columns and give faster separations, and in fact will separate same components which could not previously be separated. The change can be made at minimal cost since the same GC instrumentation can be used for both, wide-bore and narrow-bore columns.

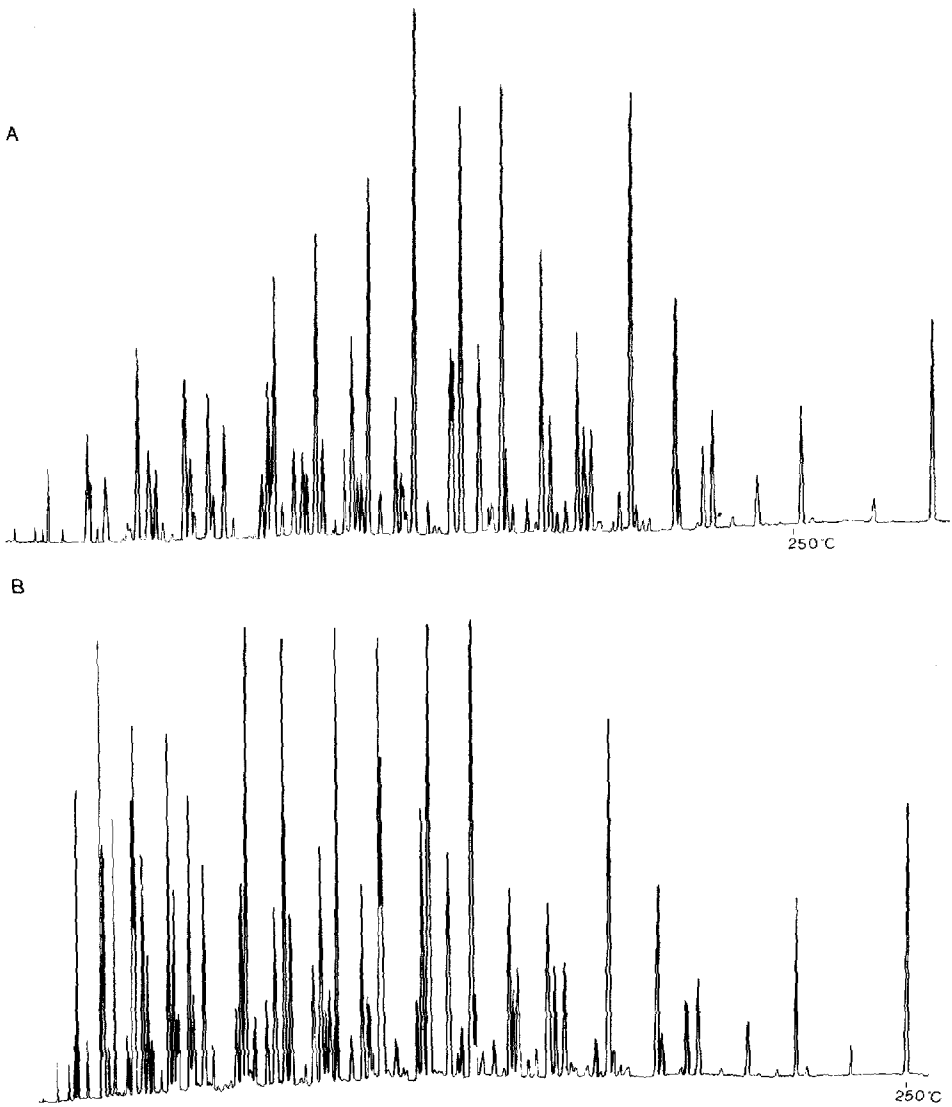

Fig. 7. Chromatograms of a PCB mixture at 600 pg/μl level. (A) OV-1 50 m × 300 μm I.D. column; temperature programmed from 75°C (hold for 2 min) after ballistically heating to 120°C (hold for 2 min) than at 2°C/min to 240°C; hydrogen as a carrier gas at 180 kPa; (B) OV-1 25 m × 104 μm I.D. column; temperature programmed from 100°C (2 min hold) to 210°C at 40°C/min and to 230°C at 2°C/min; hydrogen as a carrier gas at 350 kPa.

We have carried out several model separations which illustrate the ability of narrow-bore WCOT columns to achieve the above objectives using standard Varian Vista 6000 GC equipment.

Polychlorinated biphenyls

The first comparison has been carried out on chromatograms obtained using a 50 m × 300 μm I.D. FS-WCOT column coated with OV-1, having 155,000 theoretical plates at $k' = 4.9$ for C_{12}-hydrocarbon, and separation repeated under similar conditions with the 25 m × 104 μm I.D. FS-WCOT column coated with OV-1. The column has 275,000 TP for C_{12}-hydrocarbon at $k' = 4.4$. Column temperature in both cases was 100°C. A polychlorinated biphenyl (PCB) mixture containing Aroclors 1242, 1254, 1260 (1:1:1) at 600 pg/μl was introduced onto the column using cold on-column injection technique. Chromatograms are shown in Fig. 7a and b. Fig. 7a shows separation of PCB mixture at 600-pg/μl level on a 300-μm I.D. column. The separation time was approximately 60 min. Fig. 7b shows the separation of a similar sample on the 104-μm I.D. column. The separation time on this column was only 35 min or about half that required earlier. In this case the resolution in Fig. 7b is much better than that in Fig. 7a.

Toxaphene

Similarly, in the aquatic environment, toxaphene (chlorinated camphene) presents a serious hazard because it is persistent, readily accumulated, toxic to fish at low concentration levels, and produces chronic effects in fish and wildlife.

A typical packed-column gas chromatogram suggests that a maximum of 30 principal constituents may be present in the commercial mixture. Since accurate identification and determination of toxaphene residues in environmental samples of fish and sediment have been very difficult to achieve, considerable effort has been expended to characterize and quantify toxaphene[23,24]. Toxaphene has 4380 theoretical congeners and 170 reported isomers[25]. Chromatograms of toxaphene residues are exceptionally complex and because toxaphene can undergo both chemical and biological alterations some means of establishing similarities in residue profiles are needed.

We are convinced that narrow-bore WCOT columns can provide fingerprints that would be applicable in principal component pattern recognition technique (SIMCA)[26]. This technique has been applied to the problem of establishing similarities among, and differences between, toxaphene residue profiles[27].

Fig. 8 shows the GC separation of toxaphene. Fig. 8a illustrates the packed column separation, and Fig. 8b the same sample separated with a 250-μm I.D. column; Fig. 8c shows 104-μm I.D. column. All columns were coated with OV-1. On 104-μm I.D. column over 210 peaks are resolved and the analysis is completed in approximately half the time.

Tetrachlorodibenzo-p-dioxins

Polychlorinated dibenzo-*p*-dioxins are environmental contaminants that have been identified at trace levels in our environment. Evidence to date concerning their biological activity indicates that the highest toxicity is observed for 2,3,7,8-tetrachloro-dibenzo-*p*-dioxin (TCDD). Problems involving quantitative determination of

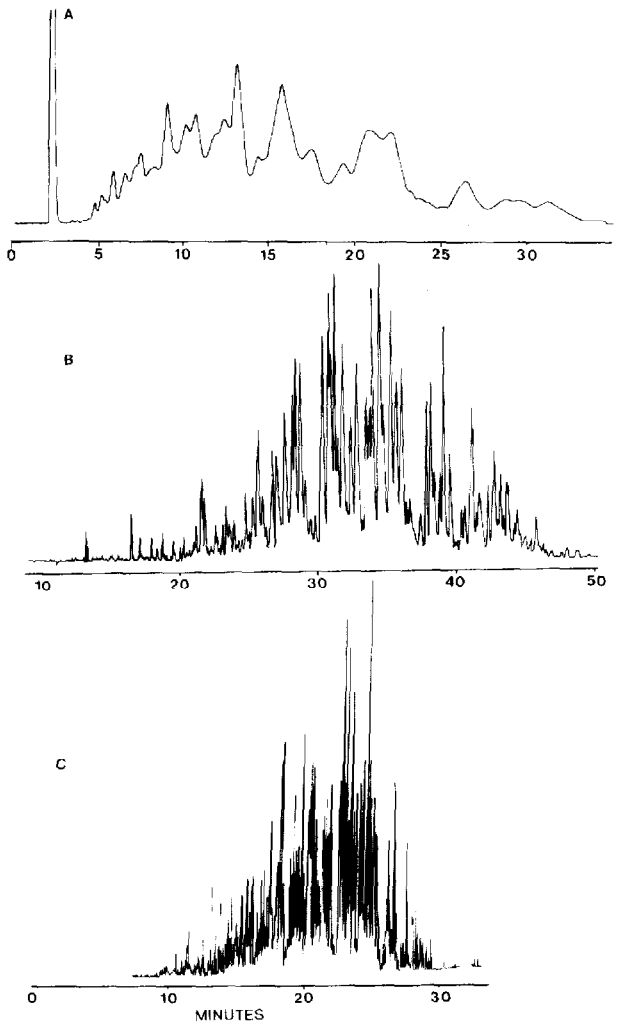

Fig. 8. Chromatograms showing separation of toxaphene at 2 ng/μl level. (A) 185 cm × 2 mm packed OV-1 on Chromosorb W (3%), silanized; isothermally at 200°C; argon–methane (5%) at 25 ml/min; (B) 30 m × 250 μm I.D. OV-1 WCOT column; cold on-column injection at 60°C; temperature programmed from 140°C (10 min hold) at 2°C/min to 230°C; hydrogen as a carrier gas at 350 kPa; (C) 25 m × 104 μm I.D. OV-1 column; cold on-column injection at 60°C; after 1 min balistically to 180°C at 40°C/min hold for 5 min; temperature programmed at 1°C/min to 225°C.

2,3,7,8-TCDD are related to the necessity of detecting very low amounts in the range of 10^{-12} g/g or less.

The technique involving WCOT column gas chromatography has been reported by Buser[28]. This author indicated that WCOT columns with efficiences of 140,000 theoretical plates can not accomplish the separation of all 22 TCDD isomers. The 2:2 type of TCDD substitution pattern contains two chlorine atoms in each carbon ring. The separation of this mixture has also been reported by Buser[29] indi-

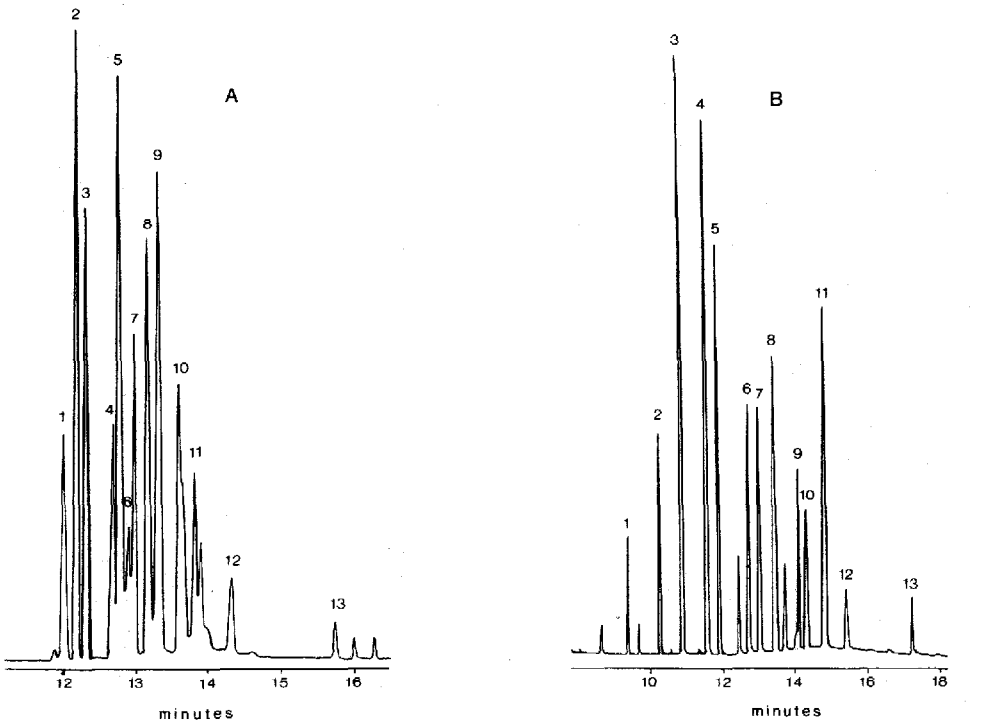

Fig. 9. Chromatograms of a 2:2-type tetrachlorodibenzo-*p*-dioxin mixture. (A) 25 m × 104 μm I.D. OV-1 column at 230°C; (B) 25 m × 100 μm I.D. Silar 10 C column at 200°C. Identification of peaks: Column A: 1 = 1368; 2 = 1379; 3 = 1369; 4 = 1469; 5 = 1378; 6 = 1268; 7 = 1478; 8 = 1279; 9 = 1269; 10 = 2378; 11 = 1278; 12 = 1267; 13 = 1289. Column B: 1 = 1368; 2 = 1379; 3 = 1378; 4 = 1369; 5 = 1268; 6 = 1478; 7 = 2378; 8 = 1279; 9 = 1278; 10 = 1468; 11 = 1269; 12 = 1267; 13 = 1289. Commas among numbers are omitted.

cating that only 8 congeners of the 13 could be separated on a 55 m × 310 μm I.D. WCOT column.

At present, column technology has reached the stage that it should be possible to separate all TCDD isomers using narrow-bore columns. Fig. 9 shows the separation of the standard 2:2 substituted TCDD isomers on 104-μm I.D. OV-1 and 100-μm I.D. Silar 10 C columns only 25 m in length. As illustrated in Fig. 9 all 13 isomers of the 2:2 substitution can be partially separated on the OV-1 column. Using a Silar 10 C stationary phase, as suggested by Buser and Rappe[30], we were able to separate all 13 2:2-type TCDD isomers on a 25 m × 100 μm I.D. WCOT column at 200°C. In addition, the excellent peak symmetry of all of these peaks should be noted. 2,3,7,8-TCDD isomer elutes at 13.26 min having $k' = 6.9$ at 200°C. The WCOT column exhibits 229,540 theoretical plates.

Using GC–MS–SIM, we have been able to determine 2,3,7,8-TCDD at 200 fg level with signal-to-noise ratio (S/N) better than 20:1 as shown in Fig. 10.

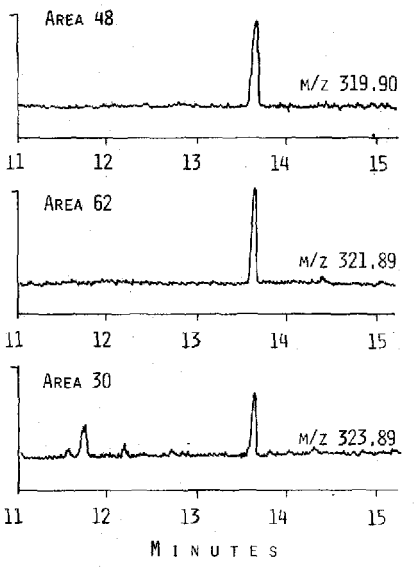

Fig. 10. Selected ion monitoring of 2,3,7,8-tetrachloro-dibenzo-*p*-dioxin (200 fg) on a 25 m × 100 μm I.D. Silar 10 C column at 200°C.

CONCLUSIONS

Narrow-bore WCOT columns with 100-μm I.D. have been shown to be applicable and efficient tools in environmental trace analysis. The present capillary column instrumentation allows the use of these columns with standard features and detection systems such as FID, ECD and MS, generally without modification, and probably with no more than minor replumbing or by replacing gauges in the pneumatic system, in less optimum cases.

Thus, the proven ability of 100-μm I.D. columns to greatly accelerate many GC separations is now routinely available. A number of questions have been raised previously concerning the ability of narrow bore columns to perform as well as theory predicts. Some of these questions have been examined here, and it has been shown that there is no reason to believe that 100-μm I.D. WCOT columns cannot closely approach the performance with current instrumentation as suggested by theory. Extra-column contributions do not affect or limit column efficiency at higher head pressures. Other studies have suggested that narrow-bore columns would become overloaded by samples larger than a few nanograms. Although we found in agreement with theory, that the maximum sample size decreases with decreasing I.D., it is still possible to introduce 10 ng of a sample on to 25 m × 100 μm I.D. columns without a significant decrease in plate number and overloading.

In conclusion, no fundamental impediments to the full exploitation of the potential of narrow bore columns were found. It is evident that the combination of narrow bore columns with laboratory data systems or personal computers opens up new horizons for the routine high-resolution GC and GC–MS separations with WCOT columns of 100 μm I.D. or even smaller-bore columns.

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