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RAPID PROCEDURE FOR PREPARATION OF SUPPORT-BONDED CARBOWAX 20M GAS CHROMATOGRAPHIC COLUMN PACKING

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SUMMARY

A rapid and simplified procedure is described for the preparation of support-bonded Carbowax 20M gas chromatographic column packings. The heat treatment process is carried out in a 100-ml volumetric pipet in a conventional gas chromatograph. Using the described procedure, column packing can be prepared in as little as three days. Representative chromatograms of intact carbamate pesticides and underivatized polar pesticide metabolites are illustrated.

INTRODUCTION

Several years ago it was shown that a common gas chromatographic (GC) liquid phase such as Carbowax 20M could be chemically bonded to diatomaceous earth supports[1]. This material was shown to be chromatographically active for compounds such as *n*-alkenes and alcohols. Shortly thereafter, Lorah and Hemphill[2] demonstrated the usefulness of this column packing for the GC of intact carbamate pesticides. In 1974 Hastings and Aue[3] described the use of Carbowax-modified Celite, both with and without conventional coatings of common liquid phases. Building upon this work, Winterlin and Moseman[4] chemically bonded Carbowax 20M to different solid supports and used them without further treatment or coated with OV-210 for the electron-capture GC of a variety of pesticide compounds and metabolites. Very recently, Daniewski and Aue[5] described an alternative method for bonding liquid phases to solid supports.

The advantage of these column packings are that they are reasonably selective, low bleed, and most importantly for our purposes, highly inert. This latter characteristic has allowed for the GC of many heat-labile compounds such as carbamate insecticides and other nitrogen-containing pesticides and the more polar metabolites. Interfaced with the recently developed highly selective and sensitive nitrogen detectors, a host of faster and simpler analytical schemes will become possible.

Support-bonded Carbowax 20M column packing has recently become available from several commercial sources. The cost of these materials is very high compared with that of conventional column packings, and variations in quality among batches and suppliers has been noted. Support-bonded packings can be made in the laboratory

by following the procedure of Aue *et al.*[1]. The time required for this preparation is several weeks, and probably considered too involved for most pesticide laboratories.

A form of support bonding Carbowax 20M was done by bleeding this liquid phase into conventional packed GC columns to make them more suitable for the GC of organophosphates[6]. This treatment, at best, provides only temporary deactivation of the column packing and must be repeated periodically.

In this article a much more rapid method is described for preparation of support-bonded Carbowax 20M column packing. A conventional gas chromatograph was used to heat treat the support. Although the acid washing and the extraction of the non-bonded Carbowax 20M is not as thorough as is described by Aue *et al.*[1,7], it appears to be sufficient to prepare a highly deactivated material. This packing has been used without further treatment for the GC of chlorinated hydrocarbon pesticides[8]. Coated with other liquid phases such as OV-101, it has been successfully used for polar and heat-labile compounds.

EXPERIMENTAL

Preparation of supports

Chromosorb W or Chromosorb G either acid washed or non-acid-washed was further acid washed with hot 6 *N* HCl. This operation was done in a 350-ml coarse frit Buchner funnel by simply slurrying the support with hot acid in the funnel. The acid was then drawn off with a vacuum supplied by a water aspirator. Usually no more than three or four washings were required to remove all traces of yellow color. The support in the funnel was then washed with several portions of distilled water to remove excess acid. The acid washed support was then oven dried at 100° overnight and coated with 3–5% Carbowax 20M using a vacuum filtration technique[9]. The coated support was air dried on aluminum foil in a fume hood, rather than with the fluidization apparatus[10].

The heat treatment process (support bonding) was done in a 100-ml volumetric pipet. The portion of the pipet below the bulb was packed with uncoated Chromosorb and held in place with glass wool plugs. This prevents back diffusion of oxygen into coated support. The remainder of the pipet was filled with the coated support. Using Swagelok fittings drilled out to the proper size, the pipet was connected to the inlet of a Tracor MT-222 gas chromatograph (see Fig. 1). A ferrule was fabricated with PTFE tape in order to obtain a gas-tight seal between the pipet and the Swagelok fitting. Nitrogen was swept through the column packing at a flow-rate of 60 ml/min for at least 2 h at room temperature. After this time the oven temperature was programmed to 270° at 1°/min and held for 16 h. At the end of the heat treatment period, the oven was cooled to room temperature while continuing to maintain the nitrogen flow. The pipet was removed and the contents emptied into a 350-ml coarse frit Buchner funnel.

The non-support-bonded Carbowax 20M was removed from the Chromosorb by slurrying with methylene chloride and drawing off the solvent with vacuum into a filter flask. This process was repeated four or five times or until two successive washes yielded no visible yellow color. The packing material was then transferred to a sheet of aluminum foil and allowed to air dry in a fume hood.

At this point the material could be packed into a gas chromatographic column, conditioned at 230°, and used. Special attention should be given to purge oxygen from

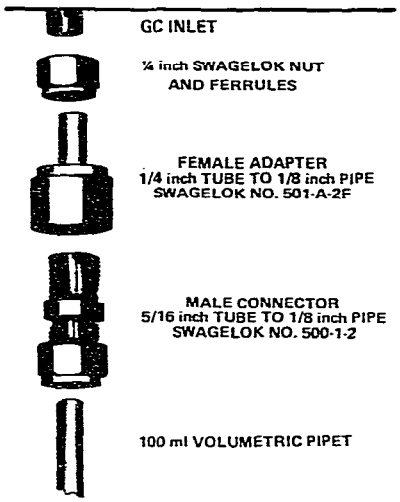

Fig. 1. Swagelok adapter for heat treating in a GC oven.

the column during the conditioning process before raising the oven temperature. This should also be done when installing a column for routine use.

Alternatively, the support-bonded material can be coated with any liquid phase desired. In this study, a vaccuum filtration technique was used primarily because of speed and simplicity. Other methods of coating should produce satisfactory packings. If fines appear to be a problem, the packing can be screened through the proper size mesh.

Apparatus

The gas chromatograph used for heat treatment of the coated supports was a Tracor MT-222. A Perkin-Elmer 3920 B gas chromatograph equipped with a flameless nitrogen–phosphorus detector was used for evaluation of the prepared column packings. All column materials were packed into 1.8 m × 4 mm I.D. glass columns and conditioned for at least 16 h at 230° prior to use.

RESULTS AND DISCUSSION

Using the described techniques, excellent support-bonded column packings could be prepared. Application of these laboratory-prepared packings for the GC determination of chlorinated hydrocarbon pesticides in human tissue extracts using a Hall conductivity detector system has been the subject of a recent publication[8].

Further coating of the support-bonded materials with OV-101 has provided a column packing which will allow for the GC of intact carbamate pesticides and other polar compounds such as chlorinated anilines and metabolites of triazine herbicides.

The investment of a little time in the preparation of these column materials can result in a savings of time and effort in the determination of many polar or heat-labile compounds. Since in many instances derivatization is not necessary, a potential source of error in the analytical procedure can be eliminated.

Fig. 2 shows the gas chromatogram obtained for a mixture of compounds on

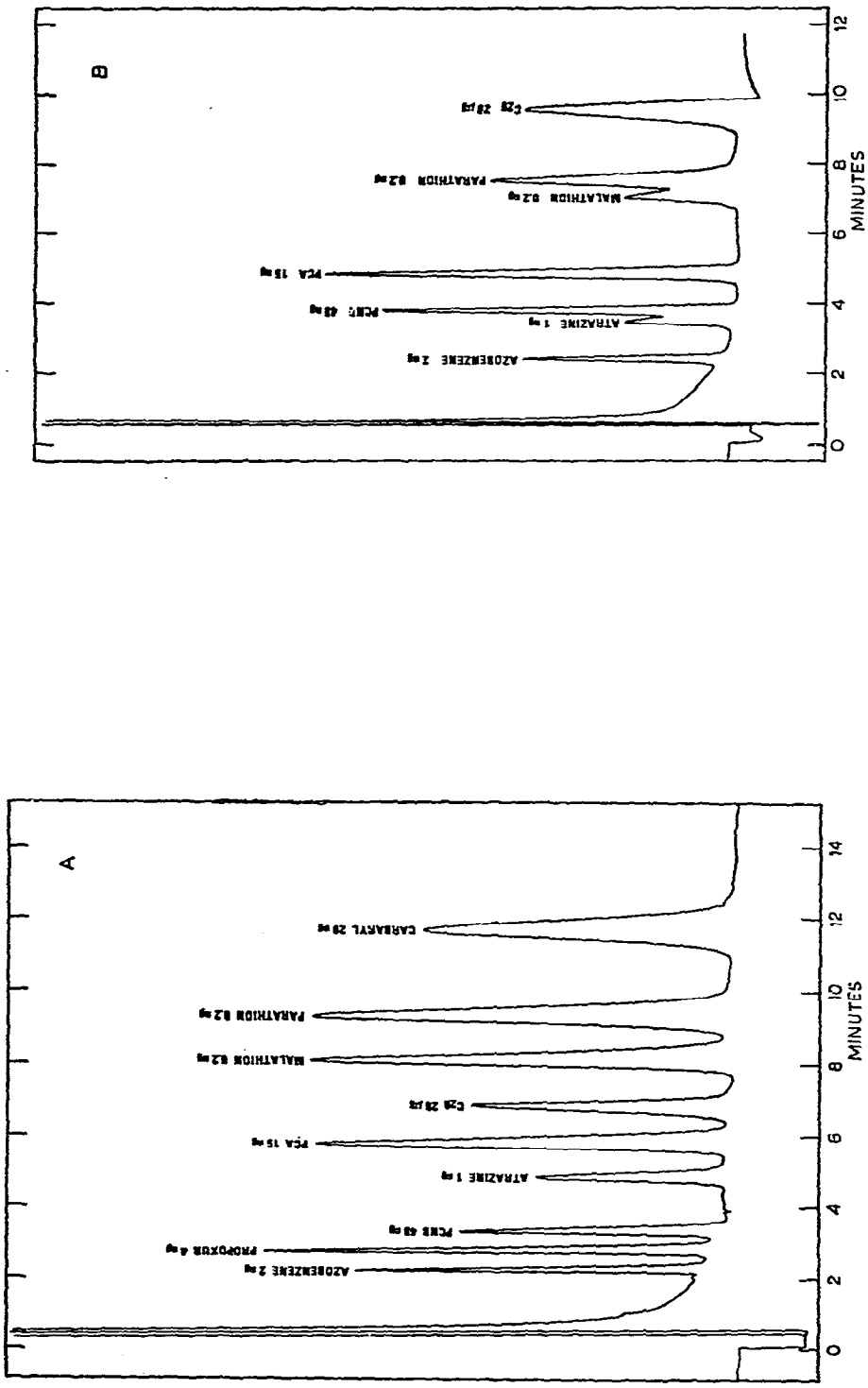

Fig. 2. (A) Gas chromatogram of nine-component mixture on 3% OV-101 coated on 80–100 mesh Chromosorb W support-bonded Carbowax 20M. (B) Same mixture on 3% OV-1 coated on 80–100 mesh Gas-Chrom Q. Column temperature, 185°; helium flow-rate, 57 ml/min. Perkin-Elmer N-P detector, nitrogen mode.

two nearly identical liquid phases. The important difference here is that both carbamate pesticides chromatograph nicely on the column prepared with Chromosorb W which has been support-bonded with Carbowax 20M. Neither propoxur nor carbaryl chromatographed on the conventional column. Other differences are the later elution of eicosane and the reversed elution order for atrazine and pentachloronitrobenzene. Thus the behavior of some compounds seems to be affected by the very small amount of Carbowax present. This was also recently observed by Aue and Daniewski[11]. Other carbamate pesticides which showed good chromatography include: carbofuran, aminocarb, and mexacarbate.

The gas chromatographic characteristics of two N-dealkyl metabolites of triazine herbicides is illustrated in Fig. 3. Neither of these compounds could be successfully gas chromatographed on conventional column packings. Only minor tailing of the peaks is evident. Use of this GC column will allow for the development of a sensitive residue method for these compounds in urine and water.

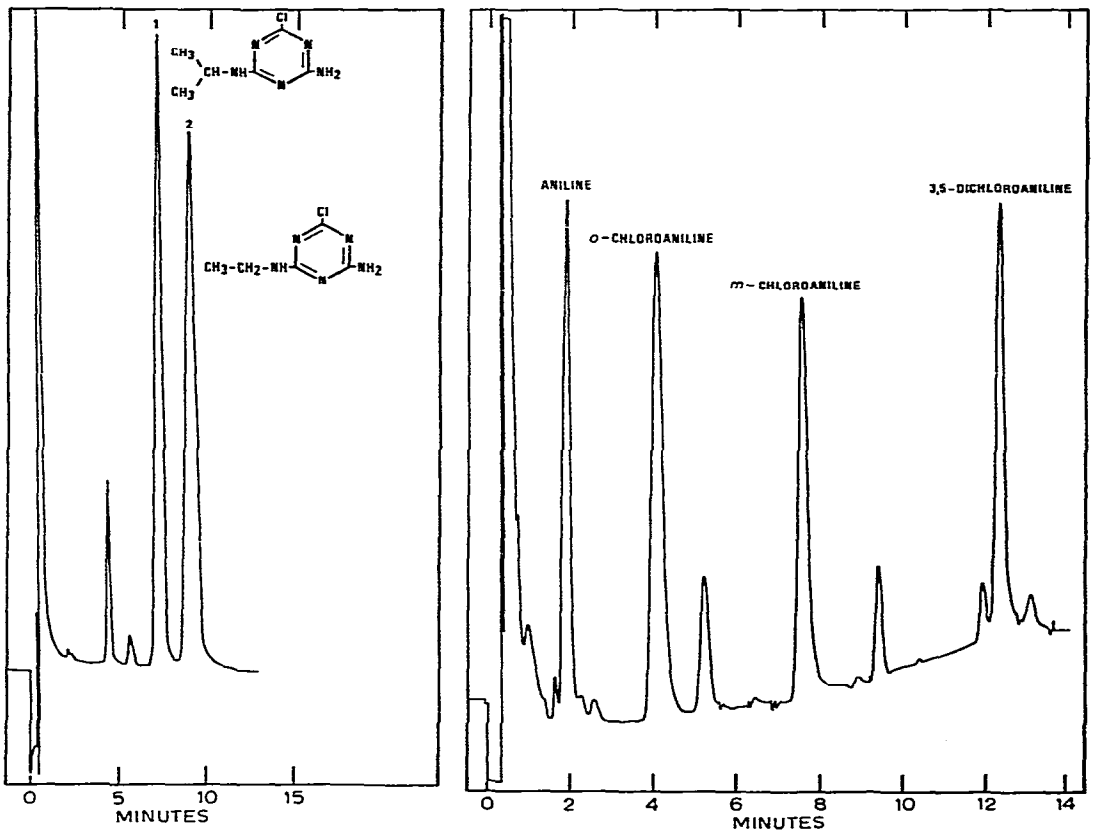

Fig. 3. Gas chromatogram of N-dealkyl metabolites of triazine herbicides. Same conditions as in Fig. 2A.

Fig. 4. Gas chromatogram of chlorinated anilines on 2% OV-101 coated on 80–100 mesh Chromosorb W support-bonded Carbowax 20M. Column temperature programmed from 100° to 160° at 8°/min; 4-min initial hold.

Fig. 4 demonstrates the capability of this support-bonded column packing for the GC of several chlorinated anilines. Ordinarily these compounds would require derivatization prior to GC on a methyl silicone liquid phase. As can be seen, good peak symmetry can be obtained. Temperature programming was used in order to achieve separation in a reasonable time. None of these compounds could be successfully chromatographed on a conventional silanized 3% OV- 1 column.

Several advantages of the technique described for preparation of support-bonded GC column materials can be realized. The most important of these is a saving in cost and time for preparation. In this laboratory it has been possible for one person to prepare support-bonded and coated column packings ready for use in analytical schemes in less than four days. This represents a saving of weeks over the original method described by Aue *et al.*[1]. Although support-bonded column packings are available from commercial sources, these materials are expensive and one must accept what is available in the time frame required.

Stability of the support-bonded column materials prepared in this labotatory has presented no particular problems. Months of useful analytical time have been realized from these columns in a variety of applications. A most important factor for preservation of these columns is exclusion of oxygen during conditioning and use at elevated temperatures. This is true for both laboratory-prepared packing and that purchased from commercial suppliers.

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