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Precisely deactivated adsorbents applied to the separation of chlorinated hydrocarbons

The active sites on silica or alumina adsorbents do not all have the same energy of interaction with a given solute species. The most energetic sites must be occupied (masked) with a molecular species that is not transported appreciably by the eluting solvent if the adsorption isotherm is to be reasonably linear in the range of solute concentration experienced during the separation. Water and less frequently, ethylene glycol have been used to occupy the most energetic sites which lowers R_F values and reduces tailing of solute bands. The degree of deactivation is specified by the weight percent of water added to the adsorbent. The method described here is applicable to adsorbents usually deactivated with water (silica gel, magnesia, alumina and Florisil) and involves the equilibration of the activated adsorbent with a solution of a strongly adsorbed material in an appropriate solvent. The degree of deactivation can be specified by the composition of the deactivating solution. Elution must be performed only with solvents incapable of removing the strongly adsorbed species from the adsorbent bed.

Silica gel and alumina adsorbents for the chromatography of molecular species which are extremely non-polar such as polychlorinated biphenyls (PCBs) and DDT and its metabolites (DDTs) must be very active. Columns for the separation of chlorinated hydrocarbons from interfering biological materials prior to gas chromatography and columns for the separation of PCBs from DDTs must both be of Brockmann Grade I[1]. However, the latter columns must be considerably more active and more reproducible than the former.

Experimental

Alumina columns. Due to its high column loading capacity, alumina has shown itself to be the best adsorbent for the separation of chlorinated hydrocarbons from biological materials prior to gas–liquid chromatography (GLC). Alumina (Baker No. 0536) is first activated at 400° for 4 h or longer and then forced into equilibrium with a 1% methanol in benzene solution. This is accomplished by the passage through a column of the adsorbent of 1.1 ml of deactivating solution per gram of alumina. The minimum amounts of solution necessary to deactivate columns having activities different from the one used in this example can be read from Fig. 1.

The adsorbent can be stored, covered by the deactivating solution, for several months in a tightly stoppered flask without change in its activity. Separation of chlorinated hydrocarbons from lipids is accomplished on a 5-mm diameter, 75-mm long column (a disposable Pasteur pipette 14.5 cm long plugged at the bottom with glass wool) containing 1.7 ± 0.1 g of alumina. The adsorbent is slurried into the column with deactivating solution, packed by vibration, and rinsed with 3 ml of hexane. Lipid samples as large as 45 mg extracted with acetone-hexane (50:50) from plankton and fish have been satisfactorily cleaned up for GLC with electron capture detection. However, sample size should be restricted to 15 mg of extractable lipid to guarantee that the column is not overloaded. The extract should be taken to dryness under vacuum to remove all traces of acetone. The concentration step should be performed at or below room temperature to minimize the volatilization

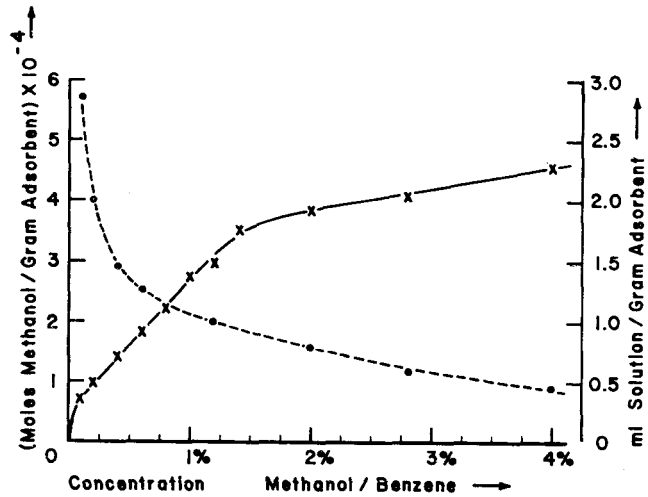

Fig. 1. The solid curve is the adsorption isotherm of methanol on Baker No. 0536 alumina from benzene solution. Isotherms were measured by frontal analysis with eluate fractions analyzed with GLC (DEGS column at 70° with thermal conductivity detection). The dashed curve and right-hand ordinate refer to the volume of methanol/benzene solution required to deactivate 1 g of alumina.

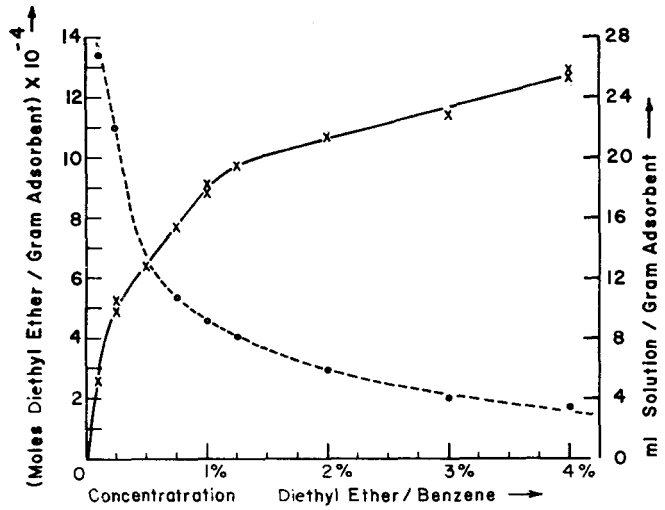

Fig. 2. Solid curve: The adsorption isotherm of diethyl ether on M.C. & B. SX-144-6 silica gel from benzene. Dashed curve and right ordinate: The volume of diethyl ether/benzene solution required to deactivate 1 g of silica gel.

of the pesticide residues. Complete recovery of PCB, polychlorinated naphthalenes, BHC, lindane, heptachlor, aldrin, heptachlor epoxide, dieldrin, endrin and DDT and its related compounds and metabolites can be expected in the first 3.5 ml of *n*-hexane. Short lengths (4 cm) of polytetrafluoroethylene tubing having 5-mm I.D. and 1-mm wall thickness are useful for coupling volumetric pipettes to the columns.

Silica gel columns. The separation on silica gel of the DDT metabolite, DDE, from the PCB isomer which interferes with it on most GLC columns is a very difficult task. The activity of silica gel reaches a maximum value at an activation temperature

of 185°. Silica gel activated at this temperature and used without deactivation exhibits an excessively small R_F value for DDE of about 0.015 with *n*-hexane as solvent. SNYDER AND REINERT[2] have utilized silica gel activated at 200°. This material is less active than the maximum possible and provides a reasonable R_F (DDE) of about 0.08.

A method that has shown itself to be reliable in our laboratory and which yields columns having R_F(DDE) = 0.08 consists of equilibration of silica gel (M. C. & B.* SX-144-6 activated at 180°) with a solution of 0.5 % diethyl ether in benzene. This is accomplished by the passage of the solution through the column until the ether concentration in the eluate equals that of the feed solution (12 ml of the solution per gram of silica gel is required, see Fig. 2 for minimum amounts of solution for columns having more or less activity). The column is then rinsed with 5 ml of hexane per gram of adsorbent to remove the benzene. A column having 4-mm I.D. and 230-mm length separates PCB in the first 10 ml of *n*-hexane. The DDTs are eluted with 5 ml of the 0.5 % diethyl ether in benzene solution. After a 10 ml *n*-hexane rinse the column is ready for re-use. Reproducibility can thus be enhanced by the use of the same column for standard and unknown solutions.

Discussion

If the eluting solvent removes some of the deactivating material from the column the adsorbent will become more active as the elution proceeds. Solute bands will be skewed and the retention volumes of the solutes will not be reproducible. Five consecutive *n*-hexane elutions from 1 % methanol/benzene deactivated alumina and from 0.5 % diethyl ether/benzene deactivated silica-gel yielded symmetric solute bands and constant retention volumes for various solutes for each series of consecutive elutions. Therefore, solvent activation of the adsorbents did not take place to a measurable extent.

If the adsorption isotherms of other substances on silica gel exhibit the abrupt change in slope found for diethyl ether at 5×10^{-4} mole/gram then columns not deactivated beyond this level will suffer from the effects of isotherm non-linearity if this level of surface coverage is reached during an elution. The strongly adsorbing sites responsible for the very steep portion of the diethyl ether adsorption isotherm on silica gel will also irreversibly adsorb impurities in the eluting solvent and reduce the activity of the column during the elution. On that portion of the isotherm where the slope is not as great, the tendency to irreversibly adsorb contaminants from the solvent was not so pronounced.

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* Matheson, Coleman & Bell.