

CHROM. 10,073

USE OF THE SORBENT SPHERON SE IN THE ANALYSIS OF TRACE AMOUNTS OF IMPURITIES IN WATER

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(Received March 8th, 1977)

SUMMARY

The determination of the capacity of the sorbent Spheron SE for comparable concentrations of toluene and *m*-cresol in comparison with Spheron MD is described and the advantages of the former in trapping low concentrations of pesticides are demonstrated. A description is also given of the determination of UV-absorbing aromatic hydrocarbons in the presence of phenols, and of the practical application of the method to the determination of trace amounts of hydrocarbons and phenols in surface waters.

INTRODUCTION

The contamination of water with organic substances has been widely studied in recent years using the adsorption of such substances on organic macroreticular sorbents with a certain degree of specificity. There are several types of contaminating compounds: (a) hydrocarbons, especially aromatic, in waste waters from the petrochemical industry; (b) aromatic amines and phenols in waste waters from the heavy organic chemicals industry; (c) pesticides; (d) waste products from the cellulose production; (e) waste waters from the food and pharmaceutical industries. In this work, attention was concentrated only on the first three types of contaminants, which contained a distinct lipophilic moiety in the molecule.

The basic aspects of the sorption of impurities from an aqueous solution on macroreticular sorbents were investigated by Junk *et al.*¹. In all instances a hydrophobic molecule or the hydrophobic moiety of an organic molecule is adsorbed on the non-polar surface of an organic copolymer. Analytical methods using polymer resins as a sorption material for removal of organic impurities from water, sea water and waste waters by means of commercial sorbents manufactured by Röhm and Haas (Philadelphia, Pa., U.S.A.), Amberlite XAD-2 and XAD-4, have also been described²⁻⁴.

Divinylbenzene copolymers possessing a high sorption capacity for a wide range of contaminants present in water have been used. The compounds thus trapped were desorbed with diethyl ether and the eluate was analysed by gas chromatography (GC) or GC combined with mass spectrometry (GC-MS)⁵.

Seidl⁶ reviewed organic copolymers, their properties and manufacturers, and discussed possible applications.

In a recent paper⁷ on the adsorption of hydrocarbons and phenols from water on a macroporous copolymer (Spheron MD), we reported the quantitative trapping of these compounds from aqueous solutions, the determination of the capacity of the sorbent for individual model compounds and the character of their adsorption or desorption curves. Although the properties of the sorbent were satisfactory, further work on interactions of dissolved compounds with the surface of a macroporous organic material led to the preparation of a series of sorbents with different chemical characters of the monomers used, specific surface areas, specific pore volumes and thus also the sorption capacities for the individual compounds under investigation.

From this series, the sorbent Spheron SE was selected, which, in addition to the uses described in this work, can also be applied as a column packing in reversed-phase liquid chromatography. In comparison with the sorbent Spheron MD described earlier, the capacity for comparable concentrations is approximately 5-fold with toluene and 2-fold with *m*-cresol. Moreover, the material can be used for trapping low concentrations of pesticides from water, as has been demonstrated with prometryne.

EXPERIMENTAL AND RESULTS

Materials

Spheron SE, a copolymer of styrene and ethylene dimethacrylate, particle size 32–40 μm , inner surface area 70 m^2/g , stable up to 280° and with an exclusion limit of molecular weight 300,000 daltons was used. The sorbent was prepared in the Research and Development Laboratory, Laboratory Instruments Works, Prague, Czechoslovakia.

Toluene and *m*-cresol (98%, purified product) were obtained from Lachema (Brno, Czechoslovakia).

Prometryne (Gesagard 50, Ciba-Geigy, Basle, Switzerland) (2-methylthio-4,6-bis(isopropylamino)-1,3,5-triazine) was used for the pesticide investigations. The elution mixture for desorption was methanol–diethyl ether (50:50, v/v).

Determination of the capacity of the sorbent for a model hydrocarbon, phenol and pesticide

The capacity is given in milligrams of compound adsorbed per gram of dry sorbent or in millilitres of solution of a given concentration per gram of dry sorbent which led to saturation of the sorbent. Saturation of the sorbent was defined as penetration of 50% concentration of the compound with respect to the entering solution, calculated from the adsorption curve.

The capacity of sorbent for individual compounds was determined on a glass column (40 mm \times 5 mm I.D.), connected with a stainless-steel capillary (350 mm \times

0.25 mm I.D.) to a double-action pump (modified Model MC 300, Mikrotechna, Prague, Czechoslovakia).

The column was packed with 100 mg of sorbent diluted with an inert non-adsorbing material, so that no by-passes could occur in the column, which would have markedly reduced the efficiency of the process. Crushed silica glass (particle size 50 μm) was used in this instance, the ratio of sorbent to inert silica packing being 1:1 (v/v).

The order of packing was as follows: quartz-wool, silica layer, sorbent + silica, silica layer; the column was closed with a small quartz-wool plug. The quartz-wool and crushed silica glass were extracted with methanol and distilled water before use.

Preparation of solutions and measurement of the capacity of the sorbent

Stock solutions were prepared by dissolving 1 ml of toluene (*m*-cresol) in 100 ml of methanol in calibrated glass vessels with ground-glass joints. The capacities were measured each time with freshly prepared solutions of the required concentration by dosing the respective volume of the stock solution into distilled water with a microsyringe. The measured solution was pumped through the column; the inlet and outlet concentrations in 10-ml fractions were followed spectrophotometrically (Pye Unicam SP 800 spectrophotometer, optical path length 4 cm, wavelength 259 nm for toluene and 254 nm for *m*-cresol, outlet recorded with a logarithmic recorder). In all experiments precautions were taken to prevent the solution from contacting any other material except stainless steel, silica and glass. Figs. 1–3 show adsorption curves for toluene and *m*-cresol, from which the capacity of sorbent can be read off. The concentration is given as c/c_0 ($c_{\text{max}} \rightarrow 1$), where c = outlet concentration and c_0 = concentration of solution entering the column (inlet concentration).

In the analysis of real samples of surface waters containing large amounts of impurities, the simultaneous determination of aromatic hydrocarbons in the presence of phenols is often required. Such a determination is feasible if distillation is introduced into the separation scheme, assuming that the pH of the sample has been adjusted so that volatile aromatic hydrocarbons could be removed by distillation.

The separation was carried out by using the following arrangement. A 500-ml distillation flask was connected by means of a glass bend with a 15-cm long helical cooler, at the outlet of which a deaerated cooled 40-ml receiver was fixed. A 70-mm long glass tube of I.D. 7 mm was sealed to the bottom; the tube ended with a 3-cm long glass capillary of I.D. 2.5 mm, which, on packing with 100 mg of sorbent served as the sorption column.

One part of the water sample was distilled into the distillation receiver cooled with a water-ice mixture; the receiver was disconnected from the distillation apparatus and a small overpressure of nitrogen was used to force the distillate through the column connected with the distillation receiver. Compounds trapped in the column were desorbed with methanol-diethyl ether, which at the same time provided regeneration of the column, which, on washing with distilled water, was prepared for further sorption. Compounds present in the desorbate were identified by GC or liquid chromatography.

Determination of aromatic hydrocarbons by gas chromatography

A Chrom 4 (Laboratory Instruments Works) apparatus with a modified recorder was used in the analysis under the following conditions: column, glass,

120 cm × 3 mm I.D.; packing, Chromosorb 102; column temperature, 200°; injection temperature, 270°; pressure of carrier gas (helium), 0.16 MPa; and amount injected, 2 μ l. Quantitative evaluation of the chromatograms was performed using calibration by means of a model mixture of benzene, toluene and xylene.

Determination of aromatic hydrocarbons and phenols by liquid chromatography

The following conditions were used: column, analytical, glass, 500 mm × 3 mm I.D.; packing, adsorbent based on crosslinked polystyrene (spherical particles, 25–32 μ m; exclusion limit, 40,000 weight units; prepared in Laboratory Instruments Works); eluent, water–diethyl ether–methanol (11:18:71, v/v/v); pump, ISCO Dialagrad, Model 384, with pulse-free delivery of solvent, maximum pressure 20 MPa; flow-rate, 40 ml/h; and detection, UV at 269 nm for toluene and 254 nm for *m*-cresol.

Solution of 1 ppm of toluene in water. A 300-ml volume of the sample plus 1.22 g of solid sodium hydroxide were placed in the distillation flask and 10% by volume (*i.e.*, 30 ml) was distilled off. The distillate was percolated through the column at a nitrogen pressure of 0.12 MPa. Desorption was carried out using methanol–diethyl ether; 1-ml fractions were analyzed by liquid chromatography.

Solution of 10 ppm of toluene in water. Distillation was carried out as above, except that another glass column (120 mm × 5 mm I.D.), packed with 100 mg of sorbent, was connected to the outlet of the deaerated distillation receiver. On completing the distillation, the column was desorbed and the fractions were analyzed by liquid chromatography.

Solution of 2 ppm of toluene + 1 ppm of m-cresol in water. From 300 ml of the sample, 10% by volume of distillate containing toluene was distilled after alkalization with 1.22 g of sodium hydroxide. The sample was then acidified with 6.5 ml of dilute sulphuric acid (1:1) and another fraction of 10% by volume containing *m*-cresol was obtained by distillation.

Practical measurement of low hydrocarbon and phenol concentrations in water

The practical application of the method to the determination of trace amounts of hydrocarbons and phenols in real samples of surface waters was studied. The contents of aromatic hydrocarbons and phenols were examined in six samples, taken once a month from a defined location in The North Bohemia basin. The samples, placed in dark bottles with ground-glass joints and kept in an ice-cooled storage tank, were transported to the laboratory and subjected to immediate treatment in order to eliminate losses of volatile hydrocarbons and interference from microorganisms between sampling and determination.

The capacity of Spheron SE for the sorption of toluene (30 ppm in water) was 150 mg of toluene per gram of dry sorbent. For such a concentration of toluene in water, the first penetration appears at 62% of the determined capacity. The adsorption curve, showing the dependence of the toluene concentration on the volume of the stock solution that has passed through the column, is given in Fig. 1. The free volume of the sorption column used (*ca.* 0.4 ml) was neglected in the calculations.

A detectable concentration of toluene (4.0 ppm) with a UV spectrophotometer as the detector was observed only when the volume of the eluate had reached 140 ml.

The model sorption of *m*-cresol was carried out in two experiments. The con-

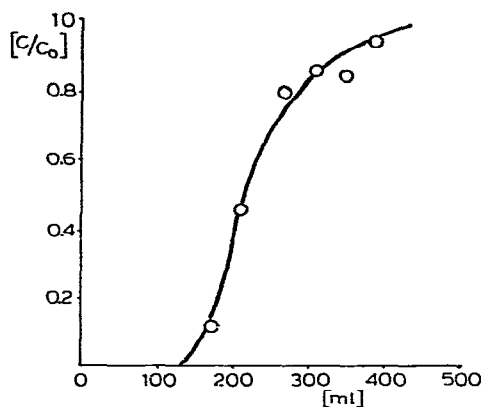


Fig. 1. Adsorption of toluene from aqueous solution (concentration 30 ppm).

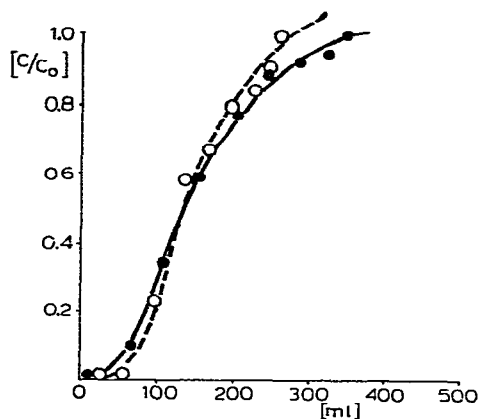


Fig. 2. Adsorption of *m*-cresol from aqueous solution (concentrations: ●, 5.8 ppm; ○, 7.7 ppm).

centrations of the inlet solutions of *m*-cresol were calculated from the UV spectra (279 nm), and were 5.8 and 7.7 ppm. The adsorption curves of these solutions of *m*-cresol in water are shown in Fig. 2.

m-Cresol can be determined with a UV spectrophotometer virtually from the beginning of elution. The theoretical capacity of the sorbent for a solution containing 5.8 ppm of *m*-cresol is 8.7 mg/g, and for a solution containing 7.7 ppm it is 10.3 mg/g. A 50% concentration in the eluate is reached at a level of *ca.* 1.5 l of effluent per gram of sorbent.

Prometryne (Fig. 3) was also detected very early with an inlet concentration of solution of 10 ppm. The capacity for this solution is 47 mg of prometryne per gram of sorbent, and a 50% concentration in the eluate is reached at a level of 4.7 l of effluent per gram of sorbent.

As in earlier work⁷, the desorption was carried out with methanol-diethyl ether (1:1). About 2 ml of this mixture is sufficient to achieve complete elution of adsorbed contaminants from the 40 × 5 mm column.

Hydrocarbons were determined in water in the presence of phenol by using distillation after alkalization followed by acidification. Optimal conditions were determined that enable one to obtain from an alkalized sample the maximum amount of volatile hydrocarbons if phenols are present as phenoxides. Phenols can be removed from water after acidification.

The sodium hydroxide concentration used was chosen on the basis of several experiments, in which the maximum yield of toluene and *m*-cresol depending on the concentration of sodium hydroxide was followed. The effect of the arrangement of the apparatus on the yield was followed simultaneously with the amount of the standard distilled from the mixture. The most suitable arrangement is as described above.

To preclude possible losses of part of the hydrocarbons, the apparatus was fitted with a sorption column to trap vapours of uncondensed components. After the analysis had been completed the column was subjected to desorption of the solvent mixtures in a similar manner to the liquid column. About 15% of volatile hydrocarbons from the sample being determined was found to be trapped. This finding justifies the measures applied in transportation (cooled storage tank), as described above.

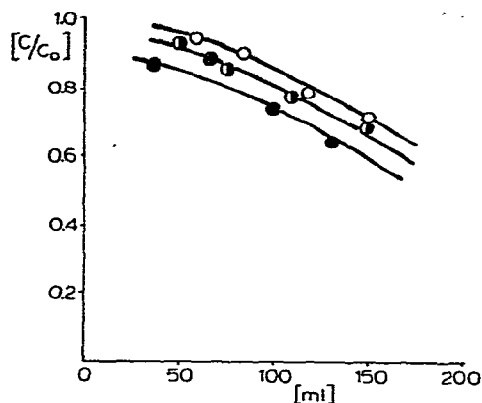
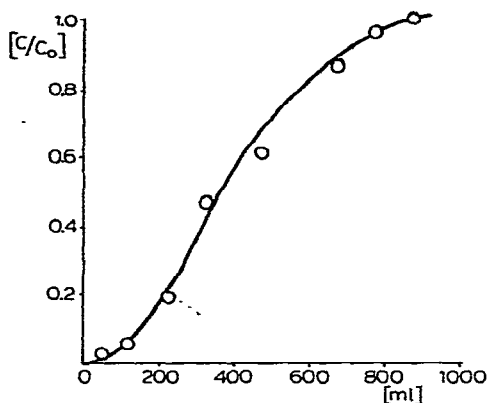


Fig. 3. Adsorption of prometryne from aqueous solution (concentration 10 ppm).

Fig. 4. Loss of toluene from methanol-diethyl ether solution depending on the free volume of the test-tube. Concentration, 70 ppm; total volume of test-tube, 7 ml. Volume of solution in the test-tube: ○, 5 ml; ◐, 3 ml; ●, 1 ml.

The following recoveries were found in model analyses: 1 ppm of toluene in water, 85.7% (without sorption of vapours); 10 ppm of toluene in water, 75% (15% sorption of vapours); 2 ppm of toluene + 1 ppm of *m*-cresol in water, toluene 72% and *m*-cresol 83% (without sorption of vapours).

Both gas and liquid chromatographic determinations of the desorbate are very sensitive. The result is influenced not only by losses involved in the sampling and in the transportation of the sample, but also by fraction sampling in the desorption.

A solution of 70 ppm of toluene in the solvent methanol-diethyl ether (1:1) was placed in amounts of 1.3 and 5 ml in 5-ml test-tubes, provided with ground-glass plugs. The samples were kept at 0°; the dependence of the toluene content in solution on time was measured by liquid chromatography. The dependence of the loss due to the transition into the gas state in the free volume of the test-tube on time is shown in Fig. 4.

CONCLUSIONS

Spheron SE, a sorbent for reversed-phase liquid chromatography, was used to trap trace amounts of aromatic hydrocarbons, phenols and pesticides. The material exhibits a sufficiently high capacity for such compounds, which were determined quantitatively after desorption with a mixture of solvents.

When treating solutions containing volatile aromatic hydrocarbons in low concentrations, it is necessary to eliminate as far as possible losses due to sampling, transportation, storage and intervals between the operations (the time between the desorption and analysis of the desorbate must be as short as possible). The errors thus arising are such that the overall result may be distorted by several tens percent. The losses in the determination of phenols are considerably smaller.

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