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Use of a novel carbon sorbent for the adsorption of organic compounds from water

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Abstract

A porous carbon sorbent prepared by pyrolysis of cellulose in the presence of porogens was tested for the preconcentration of volatile organic pollutants (particularly hydrocarbons in the gasoline range) from water matrices by the purge-and-trap method. The trapped components were desorbed by carbon disulphide and measured by high-resolution capillary gas chromatography with on-column injection. The studied concentration range of individual hydrocarbons in water was 10 ppb–10 ppm. Drinking water, spring water and gasoline-contaminated water are given as examples of real sample analysis.

1. Introduction

The investigation of the contamination of water with low concentrations of compounds is a complex problem that can only be solved by using isolation and preconcentration procedures prior to the determination. There are many techniques that can be used for the isolation and preconcentration of the considered pollutants from environmental samples that have been described in several reviews [1–4]. One of the most commonly used techniques, especially for volatile organic compounds (VOCs), is the determination of the purgeable priority pollutants listed by the US Environmental Protection Agency (EPA) involving the purge-and-trap technique, first introduced by Bellar and Lichtenberg [5].

The commonly used sorbents for trace enrich-

ment purposes have been reviewed by Liška *et al.* [4]. In recent years, organic polymers of the Tenax variety and various carbon materials have mostly been used. Comparison between the collection efficiency of Carboxpack B and Tenax GC [6] and Tenax TA and Carbotrap [7] shows that for all VOCs additional adsorbents or methods must be considered. Therefore, volatile compounds are in many instances trapped on selective adsorbents connected in series, *e.g.*, Tenax TA–Chromosorb 106–Spherocarb [8], Tenax GC–silica gel–charcoal [9,10] or Carboxpack B–Carbosieve [11], or multi-bed carbonaceous sorbents such as Vocarb 4000 and Vocarb 3000 [12].

The development of new types of sorbents for solid-phase extraction (SPE) is growing rapidly. Among the materials that have been investigated in recent years are tailored sorbents. They have attracted attention because of their potential for the optimum solution of separation problems. Second-generation sorbents with a predominant-

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ly carbonaceous matrix should be mentioned in this context. The advantages of these materials are their thermal stability, chemical resistance and stability over a wide pH range. The method employed for the preparation of many porous carbons [13] is based on the pyrolysis of organic precursors on the surface and within the pores of macroparticulate silica gel. After pyrolysis the silica is removed by alkali digestion, leaving a carbonaceous material whose particle size, porosity and surface area are dependent on the silica gel used as a support.

The aim of this work was to evaluate the possibilities of trapping volatile organic compounds from water matrices on a novel porous carbon sorbent, prepared by pyrolysis of cellulose in the presence of porogens.

2. Experimental

All chemicals used were of the highest available purity and were obtained from different sources. A stock standard solution of the following *n*-alkanes and aromatic hydrocarbons was prepared in methanol: *n*-heptane, toluene, *n*-octane, ethylbenzene, *m*-xylene, *p*-xylene, *o*-xylene, *n*-nonane, 1,3,5-trimethylbenzene, *n*-decane, *n*-undecane, 2-methylnaphthalene and 1,6-dimethylnaphthalene (weighing of 10 μ l of standard per 10 ml of methanol). Working standard solutions of lower concentration were prepared by dilution of the stock standard solution in CS₂.

Test solutions containing 10 ppb, 0.2 ppm and 10 ppm of each component were prepared by dilution of aliquots of the mixtures in doubly distilled, deionized water.

The tested carbon sorbent (Carb II) was prepared by controlled pyrolysis of cellulose beads in the presence of porogens [14] and had the following characteristics: particle size 180–400 μ m, surface area 400 m²/g, spherical particles.

The nitrogen purge gas with a flow-rate of 20 ml/min was dried and purified using molecular sieve 5A and CaCl₂ and transferred through a custom-made purge vessel. Organic compounds

were stripped from 30 ml of water at 90°C for 15 min and the drying time was 5 min.

Adsorption cartridges were prepared by packing glass tubes (11 cm \times 3 mm I.D.) with 150 mg of carbon sorbent activated by heating under a CO₂ atmosphere at 750°C for 15 min. The trapped components were desorbed by the addition of 1 ml of carbon disulphide to the glass vial with the transferred sorbent and the vial was placed in an ultrasonic bath for 20 min. The eluates were then analysed by high-resolution capillary gas chromatography (HRcGC).

GC measurements were performed on a Fractovap 4160 capillary gas chromatograph (Carlo Erba, Milan, Italy) equipped with a Grob-type cold on-column injector and a flame ionization detector. The analyses were carried out using two capillary columns, as follows.

An HP-1 fused-silica capillary column (Hewlett-Packard, Avondale, PA, USA) with a dimethylsiloxane phase (25 m \times 0.2 mm I.D., 0.33- μ m film thickness) was connected with a 1.4-m retention gap (0.53 mm I.D.). The temperature programme was 1 min isothermal at 35°C, increased at 8°C/min to 180°C, held for 5 min. Hydrogen was used as the carrier gas with a linear velocity 50 cm/s.

An HP-PONA fused-silica capillary column (Hewlett-Packard) (50 m \times 0.2 mm I.D., 0.50- μ m film thickness) was connected with a 1-m retention gap (0.53 mm I.D.). The temperature programme was 15 min isothermal at 40°C, then increased at 1.6°C/min to 190°C, held for 10 min. Hydrogen was used as the carrier gas with a linear velocity 35 cm/s (at 40°C).

The detector temperature was 300°C and the sample volume injected was 1 μ l in both instances.

3. Results and discussion

In a recent paper [15] it was shown that a carbon sorbent prepared by pyrolysis of saccharose in a matrix of silica (Carb I) was suitable for the preconcentration of non-polar and slightly polar compounds from air samples. Preliminary experiments have shown the possibility of using

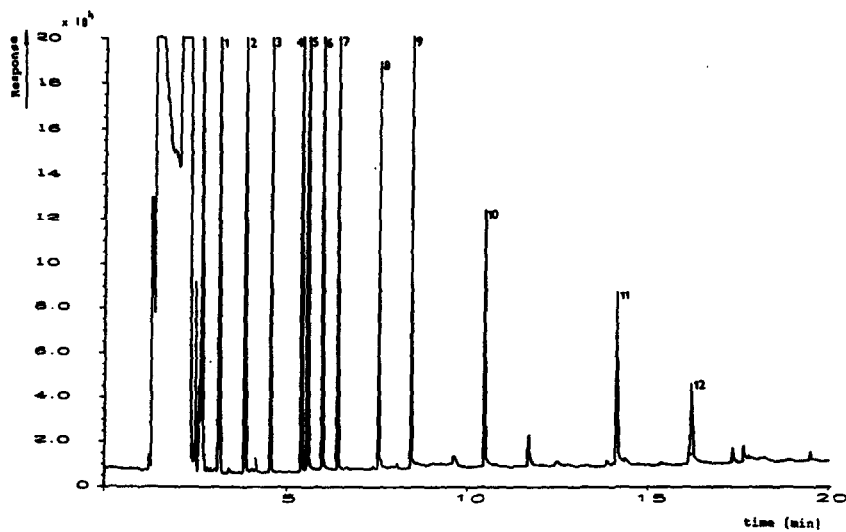


Fig. 1. Chromatogram of the separation of standard hydrocarbon mixture after preconcentration by the purge-and-trap method from water at a concentration of 0.2 ppm. Measurements were performed on the HP-1 column with hydrogen as carrier gas at 50 cm/s under temperature-programmed conditions: 35°C, held for 1 min, then increased at 8°C/min to 180°C, held for 5 min. On-column injection; flame ionization detection. Peaks: 1 = *n*-heptane; 2 = toluene; 3 = *n*-octane; 4 = ethylbenzene; 5 = *m*-, *p*-xylene; 6 = *o*-xylene; 7 = *n*-nonane; 8 = 1,3,5-trimethylbenzene; 9 = *n*-decane; 10 = *n*-undecane; 11 = 2-methylnaphthalene; 12 = 1,6-dimethylnaphthalene.

carbon sorbents prepared by pyrolysis of cellulose in the presence of porogens (Carb II) in the analysis of non-polar compounds trapped from air samples. In this work, we investigated the possibilities of using a carbon sorbent in the purge-and-trap technique and in the determi-

nation of volatile compounds in water samples, particularly hydrocarbons.

The sorbent was evaluated on the basis of calculated recoveries of the sorption-desorption procedure. Purge-and-trap recoveries of hydrocarbons were studied at concentrations of 10

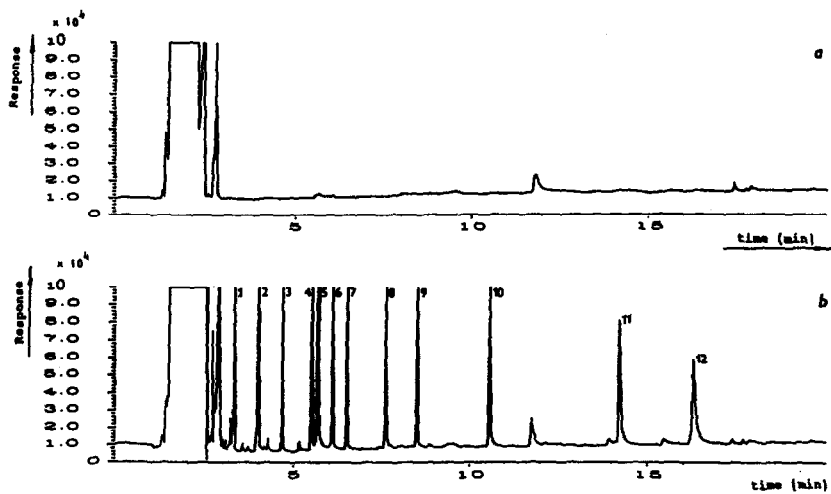


Fig. 2. Chromatogram of the separation of organic compounds after preconcentration by the purge-and-trap method from (a) spring water and (b) spring water with addition of standards (ca. 75 ppb). Chromatographic conditions and peak assignments as in Fig. 1.

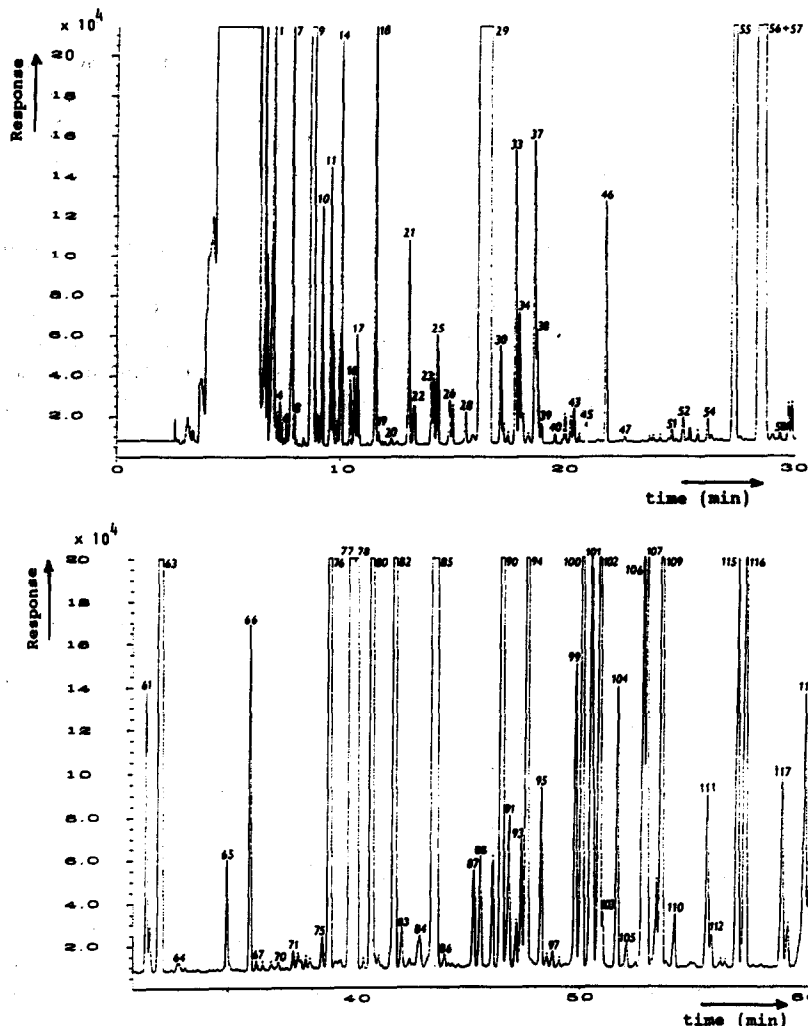
ppm, 0.2 mg/kg and 10 $\mu\text{g/kg}$. A chromatogram of the separation of a standard mixture at the 0.2 ppm level after preconcentration is given in Fig. 1; chromatographic measurements were performed on an HP-1 non-polar chemically bonded dimethylsilicone column. The recovery R was calculated from the GC peak-areas ratio:

$$R (\%) = (A_i/A_i') \cdot 100$$

where A_i is the peak area determined in eluates after the stripping procedure and A_i' is the peak area of the model mixture of corresponding dilution (without preconcentration).

The recoveries under the given experimental conditions for hydrocarbons up to C_{10} approached 100%; for higher boiling compounds, particularly naphthalenes, they were significantly lower. When measuring lower concentrations (ppb level) the signal profile was slightly disturbed by the signals of the solvent and the sorbent blank itself. The analysis of higher boiling components was problematic.

The tested carbon sorbent was also applied to the determination of hydrocarbons in real samples (drinking water, spring water and water contaminated by gasoline). In drinking water and



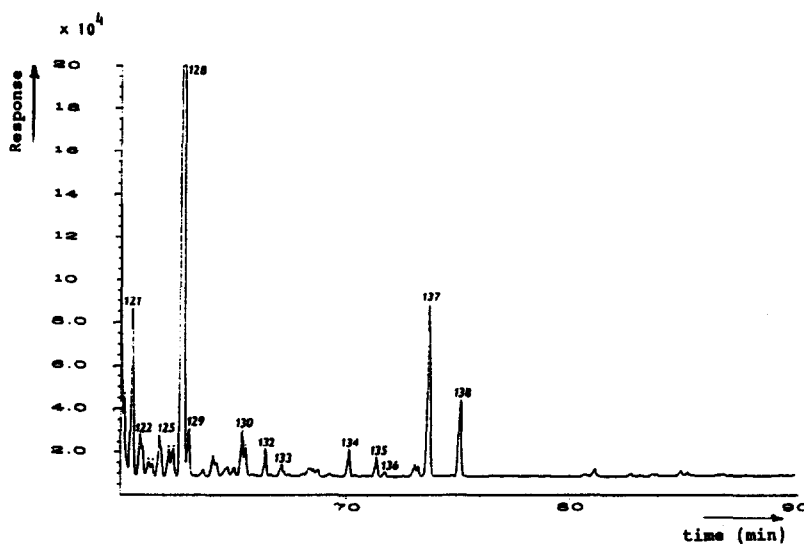


Fig. 3. Chromatogram of the separation of organic compounds stripped from gasoline-contaminated water. Measurements were performed on an HP-PONA column with hydrogen as carrier gas at 35 cm/s, under temperature-programmed conditions: 40°C, held for 15 min, then increased at 1.6°C/min to 190°C, held for 10 min. On-column injection; flame ionization detection. Peaks: 1 = *n*-hexane; 2 = *cis*-1-hexene/*trans*-2-hexene; 3 = 2-me-2-pentene; 4 = 3-me-cy-pentene; 5 = *cis*-2-hexene; 6 = 3-me-*trans*-2-pentene; 7 = me-cy-pentane; 8 = 2,2,3-tri-me-butane; 9 = benzene; 10 = cy-hexane; 11 = 2-me-hexane; 12 = 2,3-di-me-pentane; 13 = 1,1-di-me-cy-pentane; 14 = 3-me-hexane; 15 = 1-*cis*-3-di-me-cy-pentane; 16 = 1-*trans*-3-di-me-cy-pentane/3-et-pentane; 17 = 1-*trans*-2-di-me-cy-pentane; 18 = *n*-heptane; 19 = 3-me-*cis*-2-hexene/2-me-2-hexene; 20 = 3-me-*trans*-3-hexene; 21 = 1-*cis*-2-di-me-cy-pentane/me-cy-hexane; 22 = 2,2-di-me-hexane/1,1,3-tri-me-cy-pentane; 23 = et-cy-pentane; 24 = 2,5-di-me-hexane; 25 = 2,4-di-me-hexane/2,2,3-tri-me-pentane; 26 = 1-*trans*-2-*cis*-4-tri-me-cy-pentane; 27 = 3,3-di-me-hexane; 28 = 1-*trans*-2-*cis*-3-tri-me-cy-pentane; 29 = toluene; 30 = 1,1,2-tri-me-cy-pentane; 31 = 2-me-3-et-pentane; 32 = 2,5-di-me-2-hexene; 33 = 2-me-heptane; 34 = 4-me-heptane/3,4-di-me-hexane/3-me-3-et-pentane; 35 = 2,2,4,4-tetra-me-pentane; 36 = 1-*cis*-2-*trans*-4-tri-me-cy-pentane; 37 = 3-me-heptane; 38 = 3-et-hexane; 39 = 1-*trans*-4-di-me-cy-hexane; 40 = 1,1-di-me-cy-hexane; 41 = 1-me-*trans*-3-et-cy-pentane; 42 = 1-me-*cis*-3-et-cy-pentane; 43 = 1-me-*trans*-2-et-cy-pentane; 44 = 2,2,4-tri-me-hexane; 45 = 1-*trans*-2-di-me-cy-hexane; 46 = *n*-octane; 47 = iso-pro-cy-pentane; 48 = 2,3,5-tri-me-hexane/2,2,3,4-tetra-me-pentane; 49 = 1-me-*cis*-2-et-cy-pentane; 50 = 2,2-di-me-heptane; 51 = 2,4-di-me-heptane; 52 = *n*-pro-cy-pentane/et-cy-hexane; 53 = 1,1,3-tri-me-cy-hexane; 54 = 2,5-di-me-heptane/3,5-di-me-heptane; 55 = et-benzene; 56 = *m*-xylene; 57 = *p*-xylene; 58 = 4-et-heptane; 59 = 4-me-octane; 60 = 2-me-octane; 61 = 3-et-heptane; 62 = 3,3-di-et-pentane; 63 = *o*-xylene; 64 = 1-me-*cis*-3-et-cy-hexane; 65 = *n*-nonane; 66 = iso-pro-benzene; 67 = cy-nonane; 68 = 2-me-4-et-heptane/iso-pro-cy-hexane; 69 = cy-nonane; 70 = 2,2-di-me-octane; 71 = 3,5-di-me-octane; 72 = 2,5-di-me-octane; 73 = *n*-bu-cy-pentane; 74 = cy-decane; 75 = 3,3-di-me-octane/2,6-di-me-octane; 76 = *n*-pro-benzene; 77 = 3-et-toluene; 78 = 4-et-toluene; 79 = 1,1,3,4-tetra-me-cy-hexane; 80 = 1,3,5-tri-me-benzene; 81 = 4-et-octane; 82 = 2-et-toluene; 83 = 2-me-nonane; 84 = 3-me-nonane; 85 = 1,2,4-tri-me-benzene; 86 = iso-bu-cy-hexane/2,2,7-tri-me-octane/1,2,3,4-tetra-me-cy-hexane; 87 = iso-bu-benzene; 88 = *sec*-bu-benzene; 89 = *n*-decane; 90 = C₁₀ aromatic; 91 = 1-me-3-iso-pro-benzene; 92 = 1-me-4-iso-pro-benzene; 93 = 3,4,6-tri-me-octane; 94 = indane; 95 = 2,2-di-me-nonane/*sec*-bu-cy-hexane; 96 = 1-me-2-iso-pro-benzene; 97 = 2,6-di-me-nonane; 98 = *n*-bu-cy-hexane; 99 = 1,3-di-et-benzene; 100 = 1-me-3-*n*-pro-benzene; 101 = 1-me-4-*n*-pro-benzene/1,4-di-et-benzene/C₁₀ aromatic; 102 = 1,3-di-me-5-et-benzene; 103 = C₁₀ aromatic; 104 = 1-me-2-*n*-pro-benzene; 105 = 2,3-di-me-nonane; 106 = 1,4-di-me-2-et-benzene; 107 = 1,3-di-me-4-et-benzene; 108 = C₁₀ aromatic; 109 = 1,2-di-me-4-et-benzene; 110 = 3-me-decane; 111 = 1,2-di-me-3-et-benzene; 112 = 1-me-3-*sec*-bu-benzene/1-et-3-iso-pro-benzene; 113 = C₁₀ aromatic; 114 = 1-me-4-*sec*-bu-benzene/1-et-4-iso-pro-benzene; 115 = *n*-undecane/C₁₀ aromatic; 116 = C₁₁ aromatic; 117 = aromatic; 118 = C₁₁ aromatic; 119 = C₁₁ aromatic/alkane; 120 = C₁₁ aromatic; 121 = C₁₀ aromatic; 122 = C₁₁ aromatic/C₁₂ aromatic; 123 = C₁₁ aromatic; 124 = C₁₂ aromatic; 125 = C₁₂ aromatic; 126 = C₁₁ aromatic/C₁₂ aromatic; 127 = aromatic; 128 = naphthalene; 129 = C₁₁ aromatic/C₁₂ aromatic; 130 = C₁₁ aromatic; 131 = C₁₁ aromatic/C₁₂ aromatic; 132 = C₁₂ aromatic; 133 = *n*-dodecane; 134 = aromatic; 135 = aromatic; 136 = C₁₁ aromatic; 137 = me-naphthalene; 138 = me-naphthalene. Abbreviations: me = methyl; et = ethyl; pro = propyl; bu = butyl; cy = cyclo.

spring water the organic components sought were not found at the studied concentration level. Chromatograms for the analysis of spring water and spring water with the addition of standards (ca. 75 ppb) are shown in Fig. 2a and b, respectively.

To obtain a better resolution of larger numbers of hydrocarbons expected in gasoline-contaminated water, GC measurements were performed on an HP-PONA capillary column, which is specially designed for the analysis of multi-component hydrocarbon mixtures [16–18]. Qualitative analysis was done by comparing the retention times of sample components with those of hydrocarbon mixtures of known composition (gasoline for pyrolysis and reformat). All chromatographic measurements were carried out with the optimized temperature programme. A chromatogram of compounds stripped from contaminated water is given in Fig. 3, where 163 compounds were identified, predominately aromatic hydrocarbons, cycloalkanes and alkanes. Quantitative analysis was performed by the internal standard method. The concentrations of individual components were found to be in the range 7 ppb–3.5 ppm.

4. Conclusions

The possibilities of the accumulation of non-polar volatile organic compounds from water matrices on a novel porous carbon sorbent, Carb II (prepared by the controlled pyrolysis of cellulose in the presence of porogens), were studied. The trapped components (*n*-alkanes and aromatics), after stripping, were desorbed by CS₂ and subjected to HRcGC. Good recoveries with the adsorption–desorption procedure (purge-

and-trap method) were obtained at the studied concentration levels (10 ppb–10 ppm). The tested sorbent was also applied in the analysis of real samples (drinking water, spring water and gasoline-contaminated water).

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