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Thermal desorption of organic pollutants enriched on activated carbon

V^a. Desorption behaviour and temperature profile

L. SENF and H. FRANK*

Arbeitshygieneinspektion der Stadt Gera, Humboldtstrasse 11, DDR-6500 Gera (G.D.R.)

ABSTRACT

Thermal desorption of airborne contaminants sampled on charcoal is a useful alternative to solvent desorption. The temperature dependence of the desorption process was examined in a continuous-flow apparatus. It was found that the grain size of a given charcoal does not influence the desorption properties, that the maximum temperature needed for complete desorption is independent of the loading and that the members of homologous series obey some regularities.

INTRODUCTION

Activated carbon is a widely used adsorbent for passive and diffusion-controlled sampling of organic pollutants in the workplace atmosphere. The advantages and also the disadvantages of thermal desorption have been discussed and compared with solvent desorption, predominantly with carbon disulphide [1]. The principle of our procedure [2,3] is to heat the adsorbent and suck the released pollutants into an evacuated 500-ml gas sampling bulb. Therefore, temperature is the major parameter influencing recovery.

Few papers have treated the desorption behaviour of organics trapped on carbon. Rivin and Illinger [4] examined the desorption of acetone from soot and Scewald and Jüntgen [5] that of benzene and phenol from activated carbon. The course of non-isothermal reactions and their kinetics were discussed in detail by Jüntgen and Van Heek [6]. Cocheo *et al.* [7] described an apparatus for the thermal desorption of solvents sampled on charcoal and also studied the recovery of different adsorbates as a function of loading.

A continuous-flow apparatus equipped with a heating tube and a flame ionization detector was used here to examine the temperature profiles of this essential preanalytical step.

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a For IV, see L. Senf, F. Stapf, W. Müller and G. Schimmel, *Z. Gesamte Hyg.*, 35 (1989) 481.

EXPERIMENTAL

The design and the operating conditions of the continous-flow apparatus were similar to those in the analytical procedure described previously [2]. The activated charcoal used exclusively throughout the experiments was prepared from peat with zinc chloride (Aktivkohle AS; Kunstseidenwerk Premnitz, Premnitz, G.D.R.). A 150-mg amount of carbon was loaded with the pollutants by static adsorption via the gas phase [8]. Then the charcoal was placed in a desorption tube, purged with a continuous stream of purified nitrogen. Maintaining comparable desorption conditions in all experiments [2,3], the nitrogen stream was adjusted to a flow-rate of 175 ml/min. After switching on the heating tube (70 V, P_{max} 700 W), desorption began and the released organics were swept after splitting directly into a flame ionization detector (GC 18.3; Chromatron, Berlin, G.D.R.) operated with optimum flow-rates of carrier nitrogen 33 ml/min, hydrogen 23 ml/min and air 330 ml/min. The temperature was measured with an Ni/CrNi element within the adsorbent bed and recorded parallel to the detector signal. The heating rate was about $21 \pm 1°C$ from 80 to 250°C, and became less steep at higher temperatures. Provided that parameters such as nitrogen flow-rate, heating rate and geometric design were kept constant, the bed temperatures at the beginning, the maximum ($T_{D,max}$) and the end of the desorption profile were reproducible to within 10°C for a particular pollutant.

RESULTS AND DISCUSSION

Influence of grain size

It would be expected that after crushing large particles of charcoal and creating highly active fracture surfaces the sorption properties would change. The charcoal was ground in a mortar and the single sieve fractions were subjected to a standard loading and desorption procedure using trichloroethylene and benzene as indicators. No differences in the desorption profile and the temperature at the desorption maximum ($T_{D,max}$) could be found between the several size fractions. Additionally, neither thermal heating of blank charcoal up to 350°C nor repeated desorption procedures with different pollutants changed the properties of the adsorbent, indicated by a constant $T_{D,max}$. Therefore, all further investigations were carried out with the 0.4–1.0 mm fraction.

Influence of bed loading on desorption profile

It would be a problem in routine analysis if a higher loading necessitated more severe desorption conditions. To examine this, charcoal was loaded statically with 0.25, 0.75 and 1.25 μl of benzene or trichloroethylene. The desorption profiles of benzene are given in Fig. 1. Very similar results were obtained with trichloroethylene. It can be seen that with increasing loading, desorption starts at lower temperatures. Likewise, the maxima of the desorption profiles are shifted in the same direction, but the rear slope is not influenced by the degree of loading. This means that the temperature that is necessary for complete desorption is independent of the amount of pollutant adsorbed, which is the actual value of interest. Similar results were found for the desorption of phenol [5].

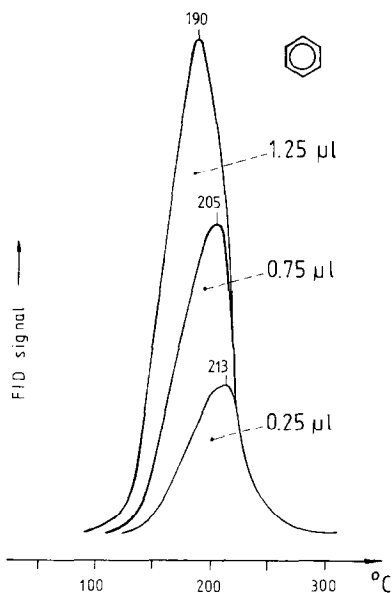This behaviour can be explained by microcrystalline regions and energetic het-

Fig. 1. Desorption profile as a function of loading with benzene.

erogeneities of the charcoal surface. There are diverse adsorption sites having different affinities for the adsorbate molecules. At the beginning of the desorption, molecules are released which are bonded less strongly. Finally molecules resistantly bonded to the surface are released. However, these most active sites are covered at the beginning of the adsorption process, so determining the rear slope of the desorption profile and the necessary temperature.

The charcoal used has a specific surface area (S_{BET}) of about 1200 m^2/g. Assuming a molecular size of benzene of about 30 Å^2, then a loading of 1.25 μl of benzene (14 μmol) represents only about 2% of the theoretical monolayer. Hence multi-layer effects can be regarded as insignificant.

Desorption profile and boiling temperature

It seemed of interest to examine the relationship between desorption and boiling temperature within homologous series to establish whether thermal desorption should be the method of choice for genuine samples of known composition.

Fig. 2 shows the desorption profiles of C_5–C_{11} n-alkanes. The higher the carbon number, the higher is $T_{D,max}$ and the broader is the temperature range. n-Alkanes with more than nine carbon atoms exhibit serious tailing in the high-temperature region, restricting the thermal desorption under the conditions used previously [2] for shorter chain hydrocarbons up to C_8.

In Fig. 3 it is demonstrated that with the n-alkanes the desorption temperature is linearly correlated with the boiling temperature, indicating a similar mechanism of interaction in the liquid and the combined state, which is caused by non-specific dispersive forces between the regular regions of the carbon surface and the hydrocarbon chain.
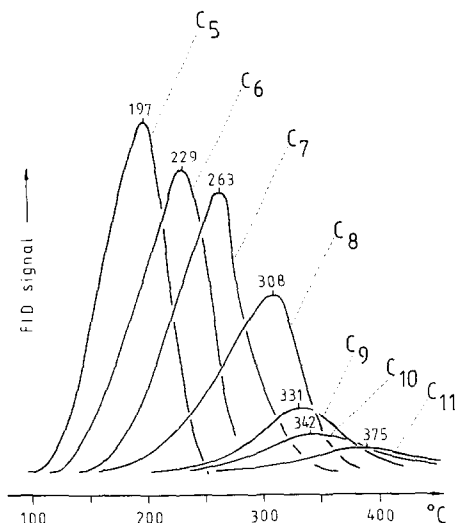
Fig. 2. Desorption profiles of homologous *n*-alkanes.

The homologous *n*-alkanols also show an increasing desorption maximum $T_{D,max}$ for the longer chain members (Fig. 4), as do the aromatic hydrocarbons benzene, toluene and *o*-xylene. However, in contrast to the hydrocarbons, a linear correlation between desorption and boiling temperature does not exist, owing to the graduated effect of additional interactions with polar surface groups. Using Fig. 3, a $T_{D,max}$ of 150°C for butane can be extrapolated. The difference of about 40°C for
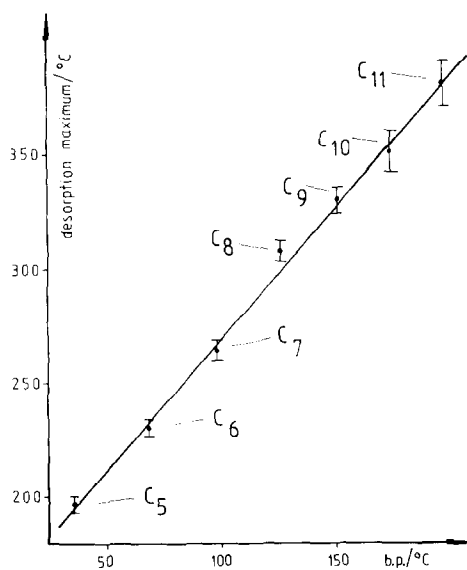

Fig. 3. Plot of the linear correlation between boiling and desorption temperatures for *n*-alkanes.
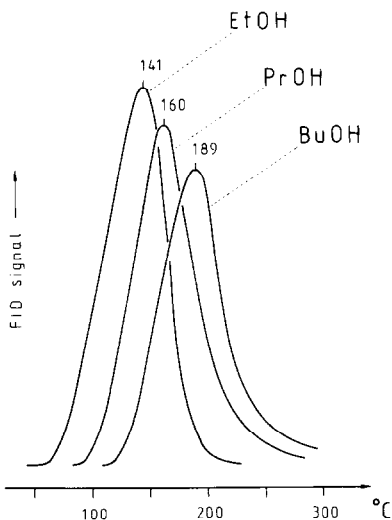
Fig. 4. Desorption profiles of homologous *n*-alkanols. Et = Ethyl; Pr = propyl; Bu = butyl.

butanol ($T_{D,max}$ = 189°C) expresses these specific interactions, *e.g.*, hydrogen bridges to oxygen-containing surface groups. These attractive forces cannot be overcome by non-polar solvents such as carbon disulphide, yielding a low recovery.

Our tests show that the method of thermal desorption [2] is well suited for airborne contaminants with boiling points up to 150°C and an advantagous alternative to the application of solvent modifiers. With higher boiling compounds some analytical problems arise, as indicated here. Obviously, the sorption behaviour of a given charcoal with respect to polar substances is affected by its origin and by its method of preparation. The results of suitability tests with different charcoals for routine analysis will be given elsewhere.

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