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RECOVERY OF VAPOURS FROM SOLID ADSORBENTS*

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SUMMARY

Losses due to polymerization of vapours collected from the atmosphere using a solid adsorbent (activated carbon), that catalyses this polymerization were examined. The losses of styrene vapour sampled on activated carbon that occur when elution is delayed were studied. Tests performed using an adsorbent treated with an inhibitor of the polymerization reaction (catechol), which is effective only when the granules remain in contact with the eluate, are described.

INTRODUCTION

For the efficient utilization of solid adsorbents for the sampling of organic vapours, several factors must be carefully controlled[1], in order to avoid possibilities of error.

When using a fixed adsorbent bed within which air containing the vapours flows, several parameters affecting the collection efficiency must be borne in mind, including the adsorption capacity, the particle size, the packing of the adsorbent, the size of the spaces between the particles with respect to the mean free path of the molecules, which determines whether viscous or molecular flow predominates, and the contact time between gas and solid[2,3].

Other errors may occur in the vapour phase. The tenacity with which the surface of the solid retains the vapour molecules varies greatly, depending on the characteristics of the different molecules (*e.g.*, polarizability) and on the fraction of the adsorbent covered, so that the recovery is never completely quantitative. The error is smaller with near-saturation of the retention capacity of the adsorbent for the vapours being considered, because the fraction retained (not desorbed) is negligible.

These are factors of a general nature, although their incidence is different in the various instances and they require a careful preliminary calibration. However, there can also be specific causes, linked to particular properties of a substance, that can have a pronounced effect on the recovery process, such as transformations undergone by the vapours on the adsorbent.

The possibility that some molecules may be polymerized or oxidized, favoured in these processes by the adsorbent, is of practical importance. This may occur particularly with activated carbon, with a consequent loss of sampled vapours.

The tests described in this paper were carried out in order to study this important practical aspect of vapour sampling on a bed of activated granular carbon.

EXPERIMENTAL

Materials

Activated carbon of surface area $1400 \text{ m}^2/\text{g}$ and particle size 15–30 mesh (some tests were performed using a particle size between 30 and 100 mesh) was used.

Styrene vapour was obtained by heating polystyrene at 600°C.

Procedure

For sampling styrene vapour, the apparatus shown in Fig. 1 was used. It consisted of a cylindrical copper reactor with capillary holes at the base, a copper tube connected with the outside which, after immersion in melting ice, was divided into two parallel lines, each consisting of a small tube containing 1 g of granular carbon, a flow meter and a suction pump.
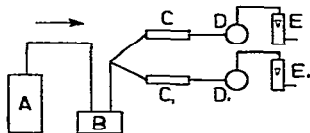

Fig. 1. Schematic diagram of apparatus. A = Reactor; B = refrigerator; C, C_1 = adsorbent beds; D, D_1 = suction pumps; E, E_1 = flow meters.

A 200-mg amount of expanded polystyrene was placed in the reactor and inserted in a muffle furnace at 600°C. The vapour produced was aspirated by the pump at a flow-rate of 0.5 l/min in equal proportions into the two small tubes containing carbon, one of which served as a reference standard (a reference standard had to be used for each test because the composition of the products resulting from the thermal degradation of polystyrene is influenced by the secondary reactions, which are affected by various factors, such as the time the vapour remains in the hottest zone and the thickness and compactness of the sample). The volatile products of pyrolysis of polystyrene in an inert atmosphere are monomer (44%), dimer (22%), trimer (27%), toluene and carbon monoxide[4]. The products vary, depending on the operating conditions, particularly in the presence of oxygen. At 400°C the degradation should be complete; at higher temperatures toluene, styrene, benzene and ethylene are produced. Between 400 and 700°C the highest percentage of styrene is obtained[5].

After the reaction, the standard tube was immediately eluted with carbon

dioxide (5 ml), whereas the other tube was eluted, using the same amount of solvent, after a time t which varied from test to test. The elution was effected by immersing the adsorbent in the solvent for a fixed period (30 min), then the carbon granules were removed by filtration. This method was preferred to percolation because it is more practical and easier to repeat.

The amount of styrene present in the eluate was determined by means of a DANI Model 3400 gas chromatograph using a 2 m × 1/4 in I.D. column packed with 3% SE-30 on Chromosorb and a flame-ionization detector. The number of theoretical plates was 3500 at 60°C, calculated on the styrene, with a retention time of 5.3 min; the carrier gas (nitrogen) flow-rate was 6 cm/sec. The calculations were carried out based on the toluene peak as internal standard, which is always present (t_R = 2.5 min) and which is not subject to variation with time.

RESULTS AND DISCUSSION

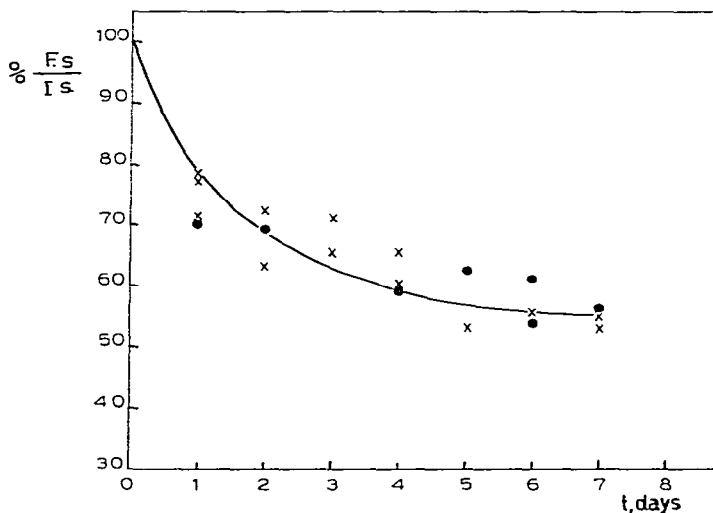The results obtained are presented in Fig. 2.

Fig. 2. Loss by polymerization of styrene vapour (percentage of final styrene, F.s., with respect to initial styrene, I.s.) with time. Adsorbent carbon size: ×, 15–30 mesh; ●, 30–100 mesh.

The reduction in the amount of styrene produced on delaying the time when the elution is carried out is fairly regular. The variations in the results, even though the tests were performed in a strictly standardized way, are inevitable because of the many factors that may affect the different tests.

The recovery losses are between 15% and 32% with elution after 24 h, and between 20% and 43% with elution after 48 h. These losses refer to an adsorbent bed of 1 g of carbon with an average total load of 50 µg of styrene, for tubes kept without special precautions with regard to light and at a temperature between 20 and 25°C.

Additional tests consisted of ascertaining the persistence of the vapour loss due to polymerization in the presence of carbon under different conditions, and of attempts to overcome this drawback by means of an inhibitor of the reaction.

Confirmation of the loss of styrene due to the catalysing effect of carbon on its polymerization was obtained by eluting the two tubes simultaneously, but leaving the eluate in one of them in the presence of carbon for various periods. The losses that occur in the eluate that is in the presence of carbon (compared with the control eluate) are of the same order as those which occur when the elution is delayed (Fig. 3).

To prevent the losses due to polymerization of the vapour, catechol was used as an inhibitor of the reaction, both in the liquid phase and in the vapour phase.
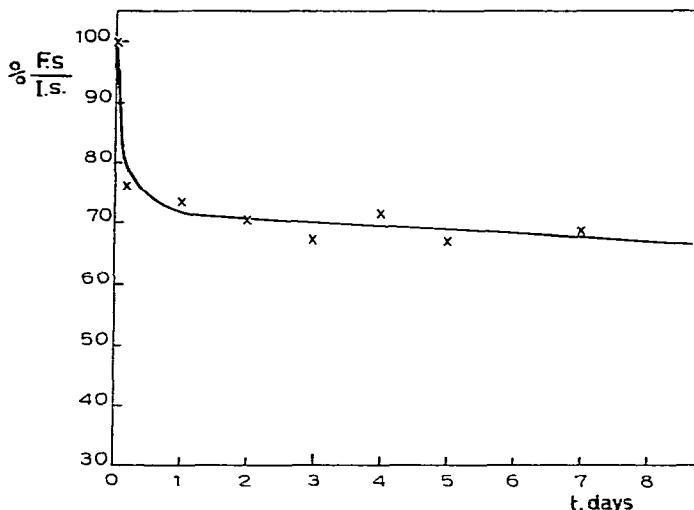

Fig. 3. Loss by polymerization of styrene in solution with time.

Liquid phase: solution of catechol in methanol

The granules of the adsorbent were treated with the solution; after evaporation of the solvent, the tubes were prepared and the tests described were performed. The amounts by weight of catechol, relative to the carbon, were 1:200 and 1:5.

With delayed elution there is in any case a reduction of the styrene produced comparable to that which occurs with the adsorbent untreated with the inhibitor. The behaviour is different if the carbon granules treated with catechol are left in the eluate; in this instance the amount of styrene produced remains constant with time.

Gaseous phase

Passing the catechol vapour over the carbon granules, both before and after adsorption of the styrene, does not lead to a suppression or decrease of the polymerization with time. On the contrary, the catechol vapour inhibits the reaction only when they pass through the adsorbent tube simultaneously with the styrene vapour, *i.e.*, during the sampling. In this instance there is a suppression of the polymerization and the amounts of styrene in the eluate remain constant, even if the elution is carried out after an interval of several days.

The behaviour of catechol can be explained as follows. When the catechol molecules are adsorbed on the surface of the adsorbent, they cannot perform their

inhibiting action because of their lack of mobility. The inhibition occurs when the catechol vapour is mixed with the styrene vapour before entering the tube and also when, on elution, the catechol regains its mobility in the eluate.

CONCLUSIONS

The tests performed with styrene show how the transformations undergone by the sampled vapour as a result of the action of the adsorbent can affect the final results. These results for styrene must be extended to all substances, *e.g.*, vinyl chloride and formaldehyde, that may also under transformation under the influence of carbon.

On the basis of the various tests, it is possible to conclude that prior treatment of the adsorbent with an inhibitor may prevent the loss with the monomer vapour sampled. In the specific case examined it was established that, if carbon granules previously treated with catechol (in solution or in the gaseous state) are left in the eluate, losses due to the catalytic action of carbon are prevented. In this way the analysis can be performed after an interval of time, with the certainty that the results obtained will not be affected by errors due to losses caused by the adsorbent.

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