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IRREVERSIBILITY EFFECTS IN LIQUID DESORPTION OF ORGANIC SOLVENTS FROM ACTIVATED CARBON

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SUMMARY

Two methods for the determination of recoveries in the desorption step have been studied: spiking the carbon with subsequent desorption and mixing the sample with the desorbing agent. The former method gave lower recoveries and equilibrium was not reached (irreversible adsorption). Differences between the two methods depended on the sample load and were more pronounced when carbon disulphide was used for desorption than dimethylformamide. These effects seem to be related to the pore size distribution and the chemical nature of the adsorption sites.

INTRODUCTION

The analysis of samples of organic solvents collected on activated carbon from workplace air is usually carried out by liquid desorption followed by gas chromatography[1]. Common desorbing agents are carbon disulphide (CS_2), dichloromethane and dimethylformamide (DMF). In order to determine recoveries in the desorption step, known amounts of solvent in the liquid or vapour state have to be added to the carbon before desorption is carried out.

The recovery, or desorption efficiency, is defined as the amount desorbed divided by the amount of sample. It is still a controversial question how these recoveries should be determined. The closest means of mimicking the actual sampling situation is the generation of vapours of known concentrations in dynamic systems and to collect an air sample of well defined volume ensuring that no breakthrough occurs. This requires equipment and experience not found in many laboratories and, moreover, is a very time-consuming procedure. It therefore cannot be used in routine work. A simpler method is to add a known amount of vapour as described by Severs *et al.*[2] (the U-tube method). A charcoal tube is connected to a pump and the solvent is injected into the airstream in a U-tube. The solvent thereby enters the carbon as a highly concentrated vapour. A similar method has been used by other workers[3].

In an extensive study conducted by the National Institute for Occupational Safety and Health (NIOSH), the procedure adopted was first to spike the carbon with the analyte using a microlitre syringe. Then, after a delay of at least 24 h, the samples were desorbed and analysed[1]. A good correspondence between this technique

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and vapour generation was established. The inherent assumption is that equilibrium between the gas-phase and the adsorbent is reached within this time period.

Dommer and Melcher[4] proposed a simplified method, denoted the "phase equilibrium technique". We prefer to call it adsorption from solution. The analyte is mixed with the desorbing agent and is then added to the carbon and agitated. The advantage is that the sample preparation is easier and systematic errors due to additions of small volumes with microlitre syringes are minimized. It is assumed that the same concentration in the solution as for the spike technique is reached within 1 h (this equilibration time is usually used for CS_2), *i.e.*, equilibrium is reached "from the other side". Dommer and Melcher made a comparison with the NIOSH spike technique for pentane, trichloroethylene and methyl ethyl ketone using CS_2 as desorbing agent, and a good correspondence was obtained.

Johansen and Wendelboe[5] made a similar comparison between the two techniques for two desorbing agents, CS_2 and DMF, and found differences in recovery (up to 10% for alcohols, ethers and esters). In another work[6] where a slight modification of the NIOSH techniques was used (vapourization of a liquid spike), a divergence between the two techniques was seen for chloroethane and isobutanol (dichloromethane for desorption).

Krajewski *et al.*[7] compared four techniques for determining desorption efficiencies with CS_2; (i) generation of vapours in dynamic systems, (ii) the NIOSH spike technique, (iii) spikes with the analyte diluted with CS_2 and (iv) the "phase equilibrium technique". They compared method (i) with the other techniques and found the best agreement between (i) and (iii). Method (iv) gave the poorest correspondence with method (i). However, no explanation of the results were given and the absence of an adequate description of the experimental procedure makes it impossible to repeat the study or draw any definite conclusions.

All four studies cited were made on different carbons and hence no valid conclusions can be drawn. The carbons were not characterized in any of the work cited, a weak point that is shared by almost all other papers concerning the use of activated carbon for air sampling.

In our opinion, it is therefore impossible to settle the question of whether differences exist between proposed methods for the determination of recoveries without more detailed information concerning the carbons used. This paper is an attempt to explain observed irreversibility phenomena and to relate them to carbon parameters.

THEORETICAL

The amount of organic solvent collected from an air sample on a charcoal tube containing 100 mg of carbon is often within the range 0.1–10 μl (as a liquid), although for some compounds with low hygienic limits the amount collected could be less than 0.1 μl. A volume of 1 μl corresponds roughly to an average concentration of 150 mg/m^3 collected in a 5 l air sample.

Fairly accurate prediction of equilibrium between the gas phase and the adsorbent can be made by the use of the Dubinin–Radushkevich equation[8], provided a good estimate of the fundamental parameters w_0 and κ_s is available. This equation can be expressed as

$$\ln W = \ln W_0 - (\kappa_s/\beta^2)[RT\ln (P_0/P)]^2$$

where W is volume adsorbed per unit weight of adsorbent, W_0 is the limiting amount of adsorption, usually equal to the micropore volume, β is the "affinity coefficient", often calculated as the ratio of molar volumes or parachors[8], κ_s is a parameter for each adsorbent, P_0 and P are the saturated vapour pressure and the equilibrium pressure of the adsorbate, respectively, R is the gas constant and T the absolute temperature.

For the carbons used in this study, $W_0 = 0.481$ ml/g, $\kappa_s = 2.5 \cdot 10^{-9}\mathrm{mol}^2/\mathrm{J}^2$ (SKC 120) and $W_0 = 0.422$ ml/g and $\kappa_s = 2.6 \cdot 10^{-9}$ $\mathrm{mol}^2/\mathrm{J}^2$ (Merck). These estimations are based on adsorption from liquid nitrogen at 77 K and some preliminary determinations of the adsorption of hexane and toluene in the gas phase.

The amounts of butanol adsorbed at equilibrium calculated according to the Dubinin–Radushkevich equation for an air concentration of 150 mg/m^3 (about 50 ppm) are 33 μl per 100 mg of carbon (SKC) and 28 μl per 100 mg of carbon (Merck). A sample of 1 μl butanol is therefore far below the maximum capacity. If the adsorption is irreversible or the desorption–adsorption kinetics are slow, the sample is therefore concentrated on the front of the sampling tube. Suppose only the first 20% of the tube is occupied by the sample. The theoretical equilibrium concentrations on this part of the tube would then be about 0.04 ppm (SKC) and 0.07 ppm (Merck). To transfer 80% of the sample to the remainder of the tube would require large volumes of air containing low concentrations of butanol.

This crude calculation is well justified by the results obtained by Rasmusson[9]. He studied the adsorption of sub-ppm levels of butanol and toluene and found that the time required to reach equilibrium was extremely long and required forced circulation of the gas phase. For compounds with higher vapour pressures such as acetone or ethanol, equilibrium would be reached much faster and the distribution of a sample of 1 μl more uniform compared with butanol. Some calculations of equilibrium concentrations for different amounts adsorbed are shown in Table I.

The most important point in the preceding discussion is that with the exception of very volatile solvents the sample is far from being uniformly distributed on the sampling tube. If an adsorbent consists of homogeneous adsorption sites of equal energy the distribution is unimportant as all molecules are adsorbed on the same type of sites. However, activated carbon is a heterogeneous adsorbent with regard to the chemical nature of the adsorption sites and to the size and shape of the micropores where most of the adsorption takes place. A carbon that contains a significant fraction of sites capable of retaining adsorbed molecules for a long time would be expected to have a larger number of these sites occupied in the case of a uniform distribution, compared with the situation where the sample is concentrated. In the latter instance a redistribution will take place during storage, although for non-volatile samples this will hardly be noticeable.

Factors that could influence the distribution in the charcoal tube are concentration of the sample, sample volume, competing solvents and water vapour. If the sample distribution has an effect on the recovery in the subsequent desorption, the method involves an inherent uncertainty that is difficult to cope with in practice.

In the absence of sites capable of strong interaction, equilibrium is expected to be reached rapidly in the desorption step, provided that no chemisorption or

TABLE I

CALCULATED EQUILIBRIUM CONCENTRATIONS IN THE GAS PHASE

Calculations for different adsorbed volumes (μl per 100 mg of carbon) based on the Dubinin–Radushkevich equation[8] (P_{sat} = saturated vapour pressure at 20°C). Values for β (affinity coefficient) taken or calculated from ref. 8.

Compound	*Carbon*	P_{sat} *(mmHg)*	β	*Equilibrium concentration (ppm) for adsorbed volume (μl per 100 mg of carbon)*			
				0.3	*1*	*3*	*10*
Acetone	SKC	160	0.77	0.14	0.82	5.6	76
Acetone	Merck	160	0.77	0.21	1.3	8.8	120
Butanol	SKC	5.6	0.99	$8.1 \cdot 10^{-5}$	$8.2 \cdot 10^{-4}$	$9.6 \cdot 10^{-3}$	0.28
Butanol	Merck	5.6	0.99	$1.5 \cdot 10^{-4}$	$1.5 \cdot 10^{-3}$	$1.7 \cdot 10^{-2}$	0.51
Dichloromethane	SKC	341	0.69	1.3	6.4	36	370
Dichloromethane	Merck	341	0.69	1.9	9.6	53	570
Ethanol	SKC	41	0.64	0.39	1.7	8.5	74
Ethanol	Merck	41	0.64	0.56	2.5	12	110
Hexane	SKC	107	1.26	$1.0 \cdot 10^{-5}$	$2.0 \cdot 10^{-4}$	$4.6 \cdot 10^{-3}$	0.33
Hexane	Merck	107	1.26	$2.2 \cdot 10^{-5}$	$4.2 \cdot 10^{-4}$	$9.6 \cdot 10^{-3}$	0.72
Propanol	SKC	14.6	0.80	$6.8 \cdot 10^{-3}$	$4.4 \cdot 10^{-2}$	0.32	4.9
Propanol	Merck	14.6	0.80	$1.1 \cdot 10^{-2}$	$7.1 \cdot 10^{-2}$	0.52	8.1
Toluene	SKC	20.9	1.19	$7.5 \cdot 10^{-6}$	$1.2 \cdot 10^{-4}$	$2.3 \cdot 10^{-3}$	0.13
Toluene	Merck	20.9	1.19	$1.5 \cdot 10^{-5}$	$2.4 \cdot 10^{-4}$	$4.7 \cdot 10^{-3}$	0.28

catalytic oxidation takes place[10]. No difference between desorption (the spike technique) and adsorption from solution ("phase equilibrium") would then be seen. When the spike technique is used, solvent molecules are not surrounded by a vast excess of desorber molecules (the desorbing agent/analyte ratio is usually in the range 100–100 000) which means that the solvent molecules have access to sites that could be blocked by desorber molecules or sites located inside constrictions in the pore system. If such effects are present, the time to reach equilibrium could be very long and not be reached in a reasonable time (irreversible adsorption). As adsorption sites are limited in number, such effects are likely to be more pronounced at low loadings.

Ways to obtain a more uniform distribution are to heat the sample (heating can cause changes in the adsorbent) or to prepare concentrated solutions (of a volume not exceeding the micropore volume) of the analyte in a desorbing agent that does not compete for the same type of sites. For example, if the analyte is polar, dilution with CS_2 or hexane could be expected to distribute the polar analyte more uniformly. If recovery in the desorption step then decreases, it is likely that equilibrium between the gas phase and the sample is not reached and that irreversible adsorption occurs in the liquid state.

EXPERIMENTAL

The characteristics of the carbons used SKC 120 (SKC, Eightyfour, PA, U.S.A.) and Nr. 9624 (Merck, Darmstadt, F.R.G.) have been described previously[11,12]. The pore size distribution is given in Fig. 1.

Carbon (100 mg) previously dried at 100°C was placed in a 3-ml screw-capped

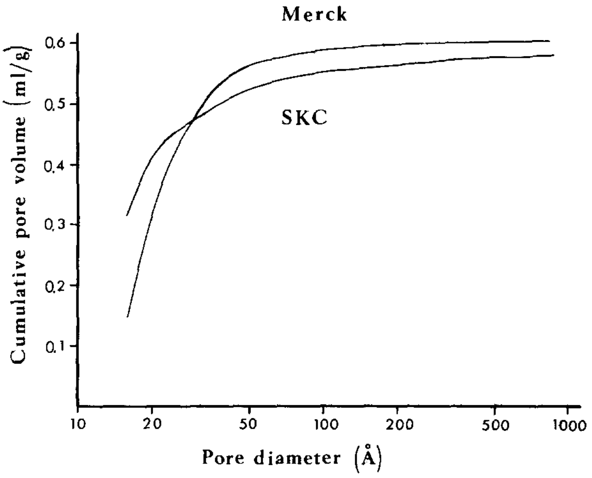

Fig. 1. Pore size distribution for SKC and Merck carbons.

vessel. For the spike technique, the analyte was added to the carbon from a microlitre syringe. The samples were stored for 1 day and then, with a few stated exceptions, desorbed using 1 ml of CS_2 or DMF and shaken for *ca.* 1 h (CS_2) or 24 h (DMF). The agitation time chosen for CS_2 corresponds to general practice and that for DMF is according to Johansen and Wendelboe[5].

Samples for studies of adsorption from solution ("phase equilibrium" technique) were prepared by adding the analyte to a known volume of desorbing agent and thereafter adding the carbon. The same syringes were used for both techniques and for the preparation of standards. This was done to minimize the effect of systematic errors due to the problems associated with the addition of small volumes. The agitation time was the same as above. Submicrolitre samples were prepared as mixtures with hexane (total addition 1 μl). All samples were duplicated.

Samples (duplicates) for the study of the kinetics of desorption and adsorption (concentration in the solution as a function of time) were prepared in the same way. At certain intervals small aliquots were withdrawn and analysed. The sample vials were weighed periodically to ensure that no evaporation occurred and a correction was made for the aliquots removed.

Gas chromatographic analysis was carried out with a Varian 3400 gas chromatograph equipped with a flame ionization detector and an Altex Chromatopak integrator for calculation of peak areas. Most separations were made on capillary columns (25 m × 0.22 mm I.D.) after split injections. As internal standard a suitable aliphatic hydrocarbon was chosen (no adsorption). When DMF was used for desorption, an aliquot (usually 0.50 ml) was withdrawn after the agitation of the sample and to this aliquot the internal standard was added. Samples for the kinetic studies were analysed on packed columns with external standards.

Calorimetric studies were carried out using an LKB 2277 microcalorimeter. Carbon (100 mg) was placed in an ampoule. After addition of the analyte as a liquid and thermostating for *ca.* 30 min, measurements were started. Heat flows down to 0.1 μW can be studied with this equipment.

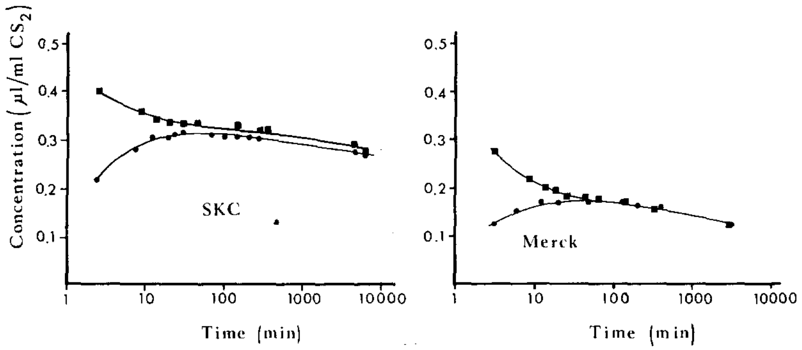

Fig. 2. Kinetics of adsorption from solution, "phase equilibrium" (upper curve) and desorption after spiking the carbon (lower curve). Experiments made with 0.5 µl of butanol, 1 ml of CS_2 and 100 mg of carbon. Results given as concentration in solution *vs.* time.

RESULTS AND DISCUSSION

The kinetic experiments (Fig. 2) with CS_2 as a desorbing agent show that no equilibrium is reached within the period studied (3 days). The concentration in the solution decreases steadily although at a slow rate after a maximum for the spike technique has occurred. The quasi-equilibrium reached after 1 h is fairly stable and reproducible and on the Merck carbon there is no difference between the two techniques. In contrast, DMF (Fig. 3) seems to produce a stable concentration after a few hours of desorption. However, there is a small discrepancy between the two methods for SKC carbon; even after 3 days the curves have not merged.

The difference (irreversible adsorption) between the two techniques seems to be related to the carbon, the amount of analyte and the desorbing agent (Figs. 4 and 5). Irreversible adsorption is smaller for the polar desorbing agent, DMF, than for CS_2. As can be seen from Fig. 4, non-polar or weakly polar compounds display very little irreversibility, whereas alcohols and glycol ethers are significantly affected. As the recoveries for these compounds are incomplete, the relative difference between

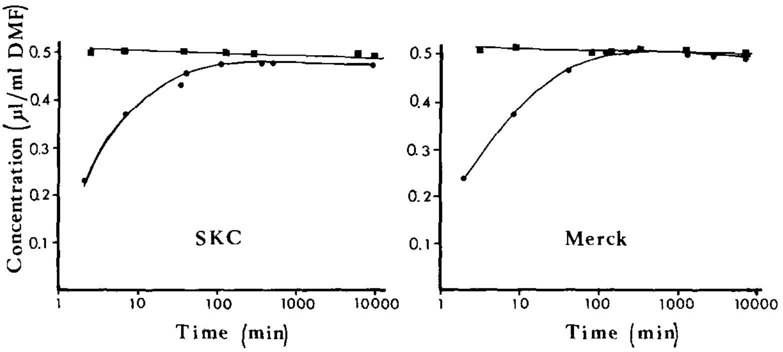

Fig. 3. Kinetics of adsorption from solution, "phase equilibrium" (upper curve) and desorption after spiking the carbon (lower curve). Experiments made with 0.5 µl of butanol, 1 ml of DMF and 100 mg of carbon. Results given as concentration in solution *vs.* time.

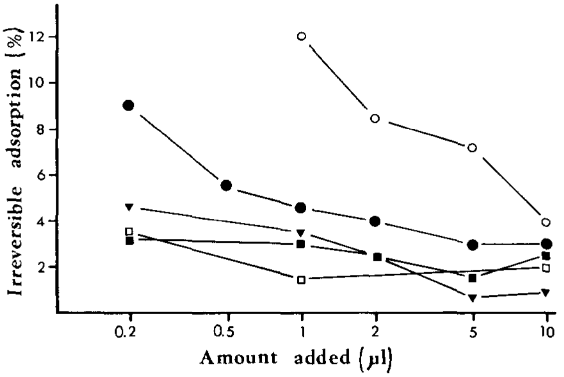

Fig. 4. Irreversible adsorption *vs.* amount added (μl) for various adsorbates on SKC and Merck carbons (1 ml of CS_2, equilibration time 1 h). Irreversible adsorption is given as the difference in adsorption between the two techniques divided by the amount added. ●, Alcohols (SKC); ▼, dioxane, propyl acetate (SKC); ○, ethyl Cellosolve (SKC); □, toluene, octane; ■, propanol (Merck).

"phase equilibrium" and the spike technique becomes larger here. In accordance with Figs. 2 and 3, the effect is more pronounced for SKC carbon. Moreover, for the polar analytes there is a dependence on the loading; at lower loadings the irreversibility effects are more severe.

Spikes of various volumes (0.2–1 μl) of ethanol, propanol and butanol with the simultaneous addition of CS_2 (1–50 μl) or hexane gave less than a 2% change in recovery for the Merck carbon. The decrease in recovery (average for the three alcohols) for SKC was less than 2% for additions up to 10 μl, 3.9% for 20 μl and 6.4% for 50 μl. Heating a sample of 1 μl of butanol at 120°C for 2 h caused a decrease in recovery of 15% (SKC carbon).

This shows, in our opinion, that when a more homogeneous distribution is obtained (although heating can cause other reactions or changes in the adsorbent or make sites in narrow pores available), more sites capable of strong adsorption (ir-

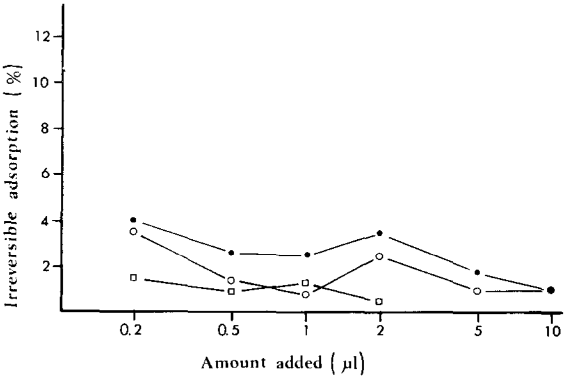

Fig. 5. Irreversible adsorption *vs.* amount added (μl) for various adsorbates on SKC and Merck carbons (1 ml of DMF, equilibration time 24 h). Irreversible adsorption is given as the difference in adsorption between the two techniques divided by the amount added. ●, Butanol (SKC); ○, butanol (Merck); □, toluene, octane.

reversible) are covered and consequently the recovery decreases. However, the effects are not drastic (hardly noticeable for the Merck carbon) and with 50 μl additions the whole micropore system is filled, which is not likely to occur during sampling. Another possibility is that the additions increases the adsorption due to lateral interactions of the adsorbed molecules or that some reaction takes place on the surface.

As small additions (a few microlitres) do not affect the recovery, the practice of increasing the accuracy of the spikes by dilution is justified. However, it must be pointed out that the diluent should be chosen so that it does not compete for the same sites as the analyte.

Calorimetric experiments with 10 μl spikes of butanol (Fig. 6) show that the heat of adsorption (integrated area under the curve) is higher for Merck carbon and that the mass transport due to diffusion is faster on this carbon. A redistribution still occurs 1 day after the addition of the analyte. Previous work[10] revealed no differences (less than a 5% decrease in recovery) for alcohols stored for up to 2 weeks in room temperature, which indicates that the redistribution, as expected, is a slow process for samples of low or modest volatility.

The two carbons differ in two respects, the pore size distribution and the number and nature of the oxygen complexes (surface oxides) present on the carbon. Adsorption of polar solvents is stronger on the Merck carbon and we have previously proposed a mechanism for this[12]. SKC 120 is a carbon made up almost entirely of micropores (diameter less than 20 Å) whereas the Merck carbon has a more developed mesopore (20–500 Å) and macropore region. Accordingly, the mass transfer rate due to pore diffusion should be higher for the Merck carbon, as can indeed be seen from Fig. 6.

Lacking a more detailed knowledge of the topography and the chemical nature of the adsorption sites, attempts to explain the results in Figs. 2 and 3 must be somewhat speculative. If adsorption from solution ("phase equilibrium") is considered, equilibrium is expected to be reached fairly rapidly in the larger pores. As CS_2 is a poor competitor with butanol for polar sites (surface oxides), the analyte is initially rapidly depleted from the solution. The time required to reach equilibrium in the narrow pores or pores located inside constrictions (diameter roughly equal to

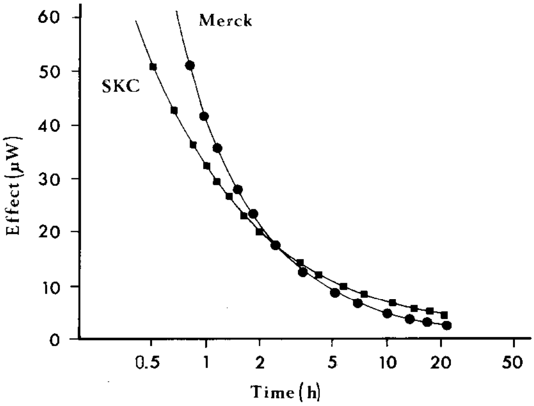

Fig. 6. Heat flow (μW) *vs.* time for 10 μl of butanol on 100 mg of carbon.

that of the molecules) is very long and this is seen as a very slow decrease in the butanol concentration in the solution (faster for Merck than SKC carbon owing to the pore size distribution). DMF competes strongly with butanol for polar sites, which can be seen from the almost constant concentration in the solution. However, there could be selective adsorption for butanol on the SKC carbon, as indicated by the slow change in concentration.

Desorption is more complicated. As previously mentioned, butanol is concentrated on a fraction of the carbon. As CS_2 is added, butanol is partly displaced from this part of the surface and adsorption on the "unused" part of the carbon will take place analogously to the mechanism described in the previous paragraph. One important difference is that the transiently occuring chemical potential gradients (which are the driving forces for diffusion from and to sites) must be different in the spike and "phase equilibrium" methods and therefore different kinetic effects may occur. It also seems reasonable to assume that on the SKC carbon there exist a number of sites with high binding energy located inside very small pores. Butanol initially adsorbed on these sites is irreversibly held and thus not desorbed. This is supported by the fact that the two curves in Fig. 2 do not coincide. When DMF is used, butanol is almost completely displaced from the Merck carbon and equilibrium is reached fairly fast. On SKC carbon a steady state is also quickly reached, but the irreversibility effects remain.

The steady decrease when CS_2 is used for desorption could be due to other mechanisms. Although no reaction products have been detected, it cannot be excluded that a slow surface reaction takes place. Andersson *et al.*[3] noticed such a reaction for epichlorohydrin when CS_2 was used for desorption, whereas no reaction took place when dichloromethane was used.

CONCLUSION

Irreversible adsorption can occur on activated carbon, compounds with high polarities, *e.g.*, alcohols, showing the strongest effects. The pore structure of the carbon and the chemical nature of the adsorption sites, in addition to the properties of the desorbing agent, seem to be important parameters. The distribution of the sample on the charcoal tube prior to analysis could therefore influence the recovery in the desorption step and introduce a systematic error that is difficult to control. However, this error is likely to be less than 10% in most instances. The preparation of standards by adsorption from solution ("phase equilibrium") should be avoided unless it is shown that no important irreversibility effects exist. For less volatile compounds, the use of more energetically homogeneous adsorbents such as porous polymers for sampling is often a good alternative[3,13]. Research efforts aimed at the preparation of carbons specially suited for the collection of organic vapours are needed. Desirable properties of a carbon are low catalytic activity, homogeneity of adsorption sites and a pore size distribution that favours rapid mass transport.

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