

Magnitudes of Back Diffusion During Long-Term Diffusive Sampling of Volatile Organic Compounds Using Carbotrap and Chromosorb 106

Naciye KILIÇ

*University of Uludağ, Art and Science Faculty,
Chemistry Department, 16059 Bursa-TURKEY*

James A. BALLANTINE

*Monitoring Unit, Chemistry Department,
University of Wales, Swansea, SA2 8PP, UK.*

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The aim of the research was to investigate the magnitudes of the losses of some volatile organic compounds from the solid adsorbents, Carbotrap and Chromosorb 106 due to back diffusion during long-term diffusive sampling of volatile organic compounds in the environment. Experiments were performed by loading the compounds to be tested on the adsorbent tubes and leaving them in an outdoor environment to simulate the real life sampling conditions over a 14 day period. The losses due to back diffusion were investigated for both the high and the low initial concentrations of the fourteen compounds covering a wide range of volatilities namely acetone, dichloromethane, pentane, hexane, benzene, heptane, toluene, octane, ethylbenzene, m- xylene, o- xylene, nonane, decane and undecane.

Introduction

Carbotrap, a high purity graphitized carbon black adsorbent has no surface ions or active groups. Hence unlike other common adsorbents the entire surface of Carbotrap is accessible for interactions that depend solely on dispersion (London) forces.

The specific surface areas of graphitized carbon blacks range between 20 and 100 m^2/g .

In general porous polymers have a lower surface area and bigger pore sizes than carbon adsorbents. Therefore in comparison with carbon adsorbents they have lower adsorption capacity.

Chromosorb porous polymers are available in eight different types. The surface areas and pore sizes of each type differ considerably due to their method of synthesis and/or modification process. Their maximum temperature limits lie between 200°C and 350°C and they can all be used for pre-concentration purposes.

Chromosorb 106 is the one with the highest specific surface area and lowest pore size in this series and is classified as a medium strength adsorbent. It has quite high “blank” values during thermal desorption especially at the heavy ends, which limits the use of it for the sampling of high molecular weight compounds at low concentration levels. The maximum temperature limit of Chromosorb 106 is 250° and hence the thermal desorption of some high boiling compounds may not be complete.

Diffusive sampling using adsorbent tubes involves the diffusion of the gas or vapour phase compounds from the surrounding environment onto the adsorbent and the adsorption of the molecules which come into contact with the adsorbent. The adsorption of the gasses on solid adsorbents occurs as physical adsorption due to the operation of the forces between the solid surface and the adsorbate molecules that are similar to the van der Waals forces between molecules. Since the adsorption of the organic compounds on the solid adsorbents is a reversible physical adsorption, the compounds adsorbed on the adsorbent by diffusion from the surrounding can freely back diffuse from the adsorbent to the surrounding environment.

Back diffusion can be a major problem in long-term diffusive sampling causing decreases in uptake rates over time and losses of the adsorbed compounds in the case of fluctuating concentrations, if the adsorbent used does not match the adsorbates sampled.

The effect of decreases in uptake rates over time can be optimized by using calculated or experimentally determined effective uptake rates valid for the exposure periods used. The losses of adsorbed material due to back diffusion, after significant decreases in concentrations during the exposure period, causes negative bias in the results obtained. The magnitude of this sampling errors introduced by back diffusion is related to selection of the right adsorbent/ adsorbate combination. If the adsorbent is strong enough to hold the adsorbate, the losses from back diffusion will be low, but if the adsorbent is not strong enough the losses due to back diffusion will cause significant systematic errors in the final concentration calculations. Therefore it is important to measure the likely magnitude of the error introduced by the effect of back diffusion.

The effect of exposure to lower or zero concentrations after a high concentration of the pollutants during the sampling period can be examined by exposing the tubes to clean air following a period of exposure to a given pollutant¹.

The relative overall uncertainty calculated as precision (measured as twice of coefficient of variation) plus the absolute bias (given by the difference in the results for the tubes exposed to zero air relative to the unexposed tubes) in environmental measurements of benzene have been found to increase with concentration (ranging from 4 ppb to 220 ppb) and to be less than 50 % in each case². The losses due to the effect of back diffusion during a seven-day exposure period have been evaluated by exposing samplers loaded with known amounts of vapours to zero air and measuring the fraction retained. This study has shown that losses from Tenax TA were higher than those from Carbotrap for the compounds tested except 1- butanol which retained less on Carbotrap than on Tenax TA which agrees with the adsorption characteristics of these adsorbents³.

Experiment

To simulate a worst-case scenario of back diffusion effect with extreme changes in the exposed concentrations, the tubes were initially loaded with a certain amount of adsorbates and left in an outdoor environment containing zero or trace levels of the volatile organic compounds.

The analytes to be tested were loaded on adsorbent tubes by exposing the tubes to the vapour of the compounds in a sealed glass vessel. The tubes then were left in an outdoor environment for 14 days. Two of the tubes were removed and analysed every other day. The tube loading method and analytical methods for the analysis are given in the following sections.

Adsorbent Tube Loading

A mixture of the analytes, acetone, pentane, dichloromethane, hexane, benzene, heptane, toluene, octane, ethylbenzene, m-xylene, o-xylene, nonane, decane, and undecane were prepared by syringing 20 μ l of each these analytes into a vial fitted with a septum seal and weighing on a four decimal place analytical balance. This standard was used for high and low loading experiments.

Eight Perkin-Elmer stainless steel diffusion tubes (9 cm in length, with 0.188 cm² cross-sectional area) were packed with Carbotrap 20-40 mesh (Supelco), 100 m² g⁻¹ surface area and another eight tubes were packed with Chromosorb 106, 60-80 mesh (Supelco). The adsorbent length was 50 mm for each adsorbent. The tubes fitted with a Swagelok end-cap with a PTFE ferrula at the closed end and a diffusion cap with a silicon membrane at the sampling end were placed in an aluminium tube holder. The tubes held in the tube holder were placed inside the 5 litre volume Pyrex glass vessel.

A 4 mg aliquot of the standard mixture was syringed into the vessel for the high loading experiment and the tubes were exposed to this mixture for one hour. For the low loading experiment only 0.5 mg of the standard mixture was used with one hour exposure time.

The precision of the tube loading method was investigated for both high and low loading on Chromosorb 106 adsorbent by loading 16 tubes and desorbing them to obtain the % RSD between the tubes. The average % RSD for high loading was 8 \pm 3 ranging from 5 to 16 and for low loading 9 \pm 4 ranging from 5 to 22.

Back Diffusion Experiment

A total of 16 tubes for each experiment were loaded with the 14 compounds using the method described in the previous section. Two of the tubes were analysed to obtain the initial weight (ng) loaded on the tubes and the remaining fourteen tubes were placed at equal spaces in a rig and left in an outdoor environment. Two of the tubes were removed and analysed every two days during the 14-day back diffusion period. The background levels of volatile organic compounds present in the outdoor environment were also checked during this period by using an identical adsorbent tube which was changed at the same time that the tubes were removed.

Instrumentation and Analytical Parameters

A Perkin Elmer Model ATD 400 Automatic Thermal Desorption injector system and a Hewlett Packard 5890 II gas chromatograph fitted with a flame ionisation detector were used for the subsequent analysis of the collected samples. The results were plotted on a Hewlett Packard Model HP 3396A printer/plotter integrator and the data stored on an Elonex 286 M-120 PC using Hewlett Packard Peak 96 software.

ATD 400 Automatic Thermal Desorber parameters

Desorption Time: 10 min, Desorption Temperature: 250°C (for Chromosorb 106) and 320°C (for Carbotrap), Trap hold: 5 min, Trap high: 250°C, Trap low: -30°C, Trap packing: Tenax TA, Split factor: 5.6 (17.85 % to GC).

GC Conditions

A 25 x 0.3 mm id WCOT column with a 1 μ m film thickness of polydimethylsiloxane was used with a flow rate of the carrier gas (helium) of 1.8 ml/min. The column temperature was held for 2 min at 40°C, then increased at 10°C /min to 200°C, which was held for 5 min.

Calibration of analytes

Individual analytes in the standard mixture were identified by GC retention times. A four level external calibration of the analytes of interest was carried out by spiking adsorption tubes in a flowing stream of nitrogen with a multi-component standard mixture made up in methanol. The solvent (methanol) was purged with nitrogen flow to avoid overloading the cold trap and column. Since methanol has a low retention volume on Tenax TA, most of it broke through whereas the other compounds were adsorbed. The possible breakthrough of the compounds during nitrogen purging was checked and the optimum flow rate and volume were used. Nitrogen was purged through the adsorbent tube at 33 ml min^{-1} for 5 min to ensure the adsorption of the compounds of interest and removal of methanol.

Results

The analysis of two tubes at two day intervals during 14 days gave the ng amounts of the analytes retained on the tubes. The percentage of the analytes retained on the tubes on the day which they were sampled, relative to the initial concentration was calculated. The results of these calculations are given graphically by plotting the percentage of the analytes retained after losses in the amounts of analytes from the tubes during the 14-day period due to back diffusion against time. Figures 1 and 2 show the results obtained for high and low loading on Chromosorb 106. The results obtained for high and low loading on Carbotrap are shown in Figures 3 and 4.

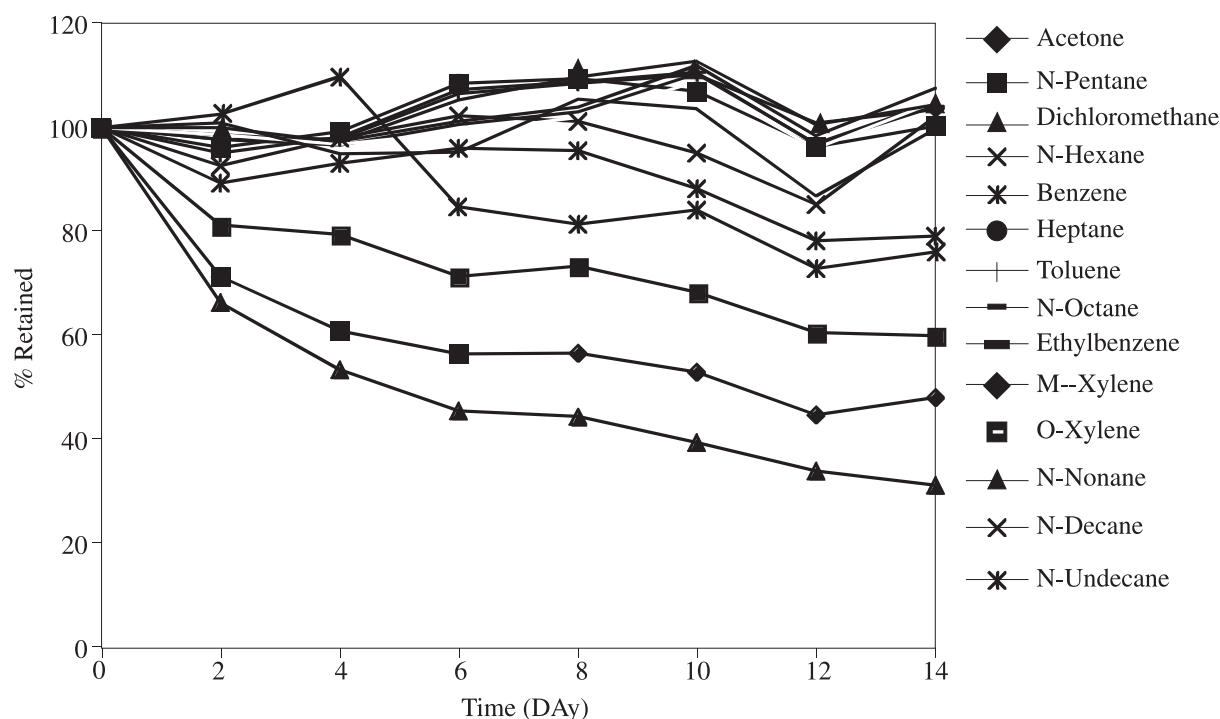


Figure 1. Percentage of the compounds retained on Chromosorb 106 during the 14-day period for a high loading case.

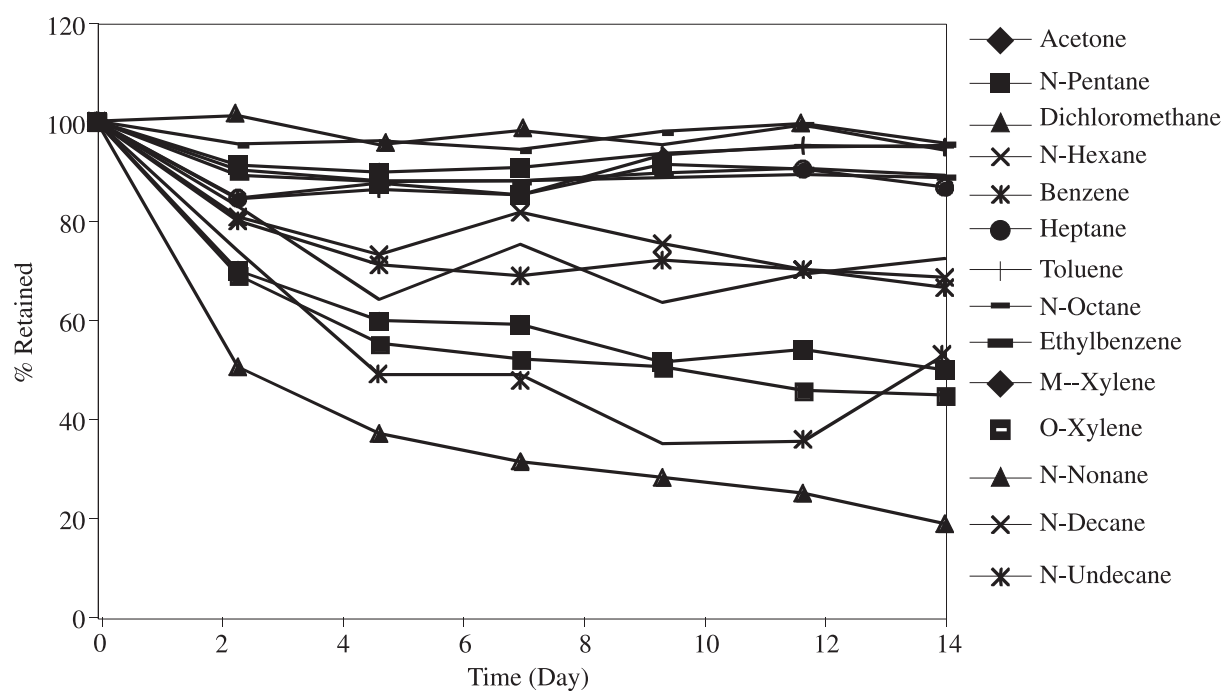


Figure 2. Percentage of the compounds retained on Chromosorb 106 during the 14-day period for a low loading case.

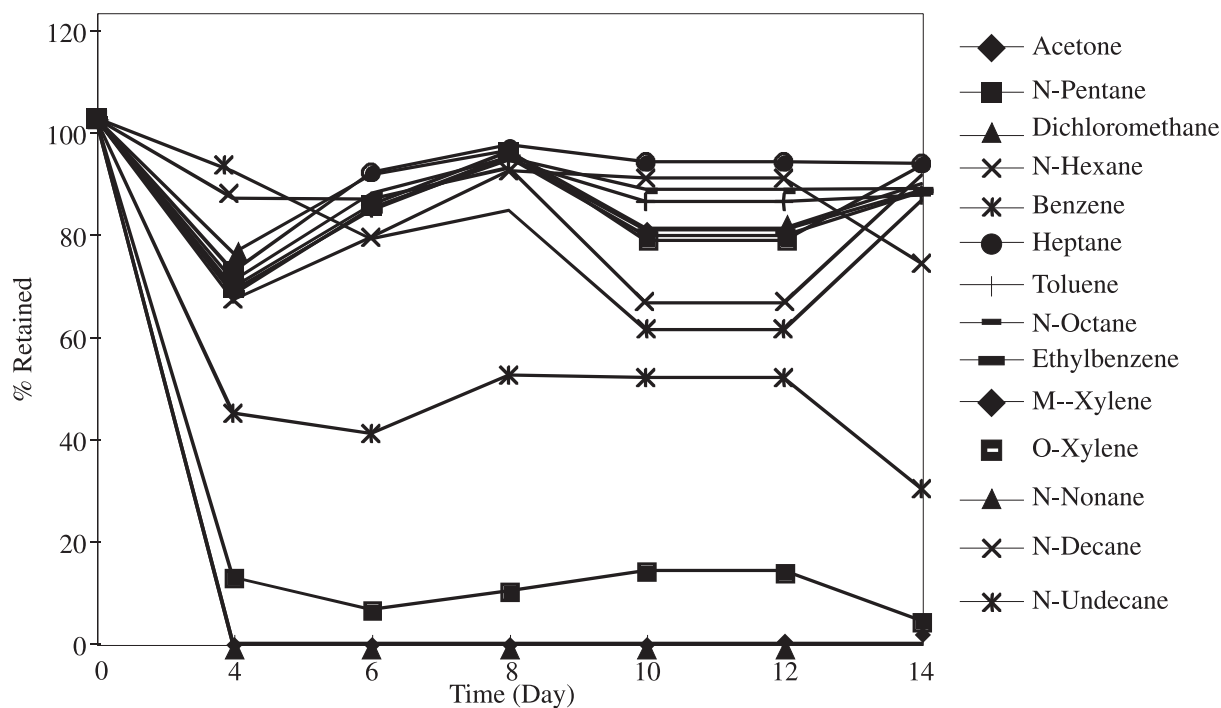


Figure 3. Percentage of the compounds retained on Carbotrap during the 14-day period for a high loading case.

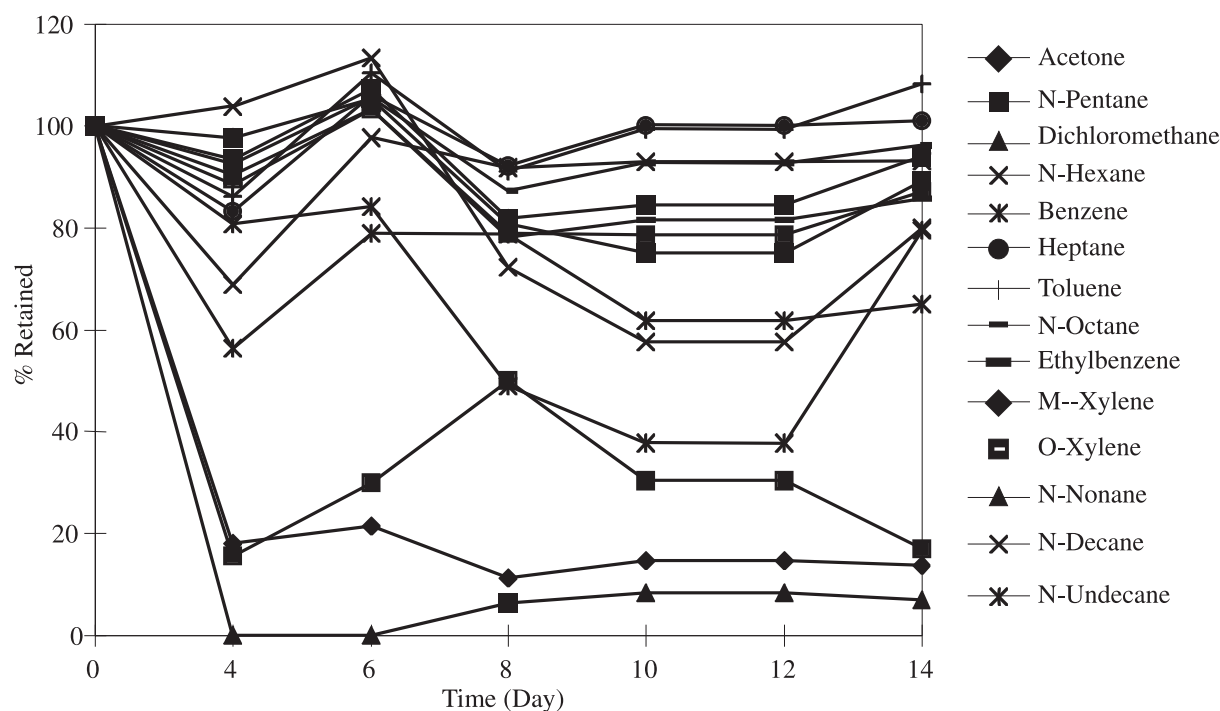


Figure 4. Percentage of the compounds retained on Carbotrap during the 14-day period for a low loading case.

As can be seen from the graphical results, the losses due to back diffusion are significantly high for low boiling analytes, on both adsorbents and decrease with decreasing volatility of the analytes.

The bias (systematic error) that could be introduced due to back diffusion if such extreme concentration changes are seen in a real sampling situation were calculated using the equation below⁴.

$$Bias = \frac{|x - x_{ref}|}{x_{ref}}$$

In this equation x is the mean value of a number of repeated measurements whereas x_{ref} is the true or accepted reference value for that measurement.

In the calculations of the bias for the data obtained in this experiment:

x = the weight of the analyte left on the tube after the 14th day (day 14).

x_{ref} = the initial weight of the analyte loaded on the tube (day 0).

Relative % biases calculated for low and high loadings on Chromosorb 106 are given in Table 1 and the % bias values calculated for high and low loading cases on Carbotrap adsorbent are given in Table 2.

The high negative values obtained for low boiling compounds illustrate the significant losses in amounts of analytes adsorbed in this worst-case scenario with a dramatic decrease in concentration.

The bias values obtained for Carbotrap are higher than those obtained for Chromosorb 106 for low boiling compounds. The high loading case showed higher negative bias values than the low loading case for Carbotrap, but same was not true for Chromosorb 106.

The experimental results are subject to random errors due to a number of reasons, such as between tube variations during loading and the effect of uncontrolled outdoor conditions such as humidity, temperature, rainfall and wind velocity during the 14-day back diffusion period. The precision of the experiments

were calculated to give percentage relative standard deviations for the two tubes analysed every two days during 14 days.

Table 1. Table 1 A comparison of % bias due to back diffusion from Chromosorb 106 during 14 days for low and high loading cases.

| CHROMOSORB 106 | | | | | | |
|-----------------|------------------|--------|--------|-------------------|--------|--------|
| COMPOUND | Low Loading (ng) | | | High Loading (ng) | | |
| | Day 0 | Day 14 | % Bias | Day 0 | Day 14 | % Bias |
| Acetone | 686 | 342 | -50 | 2213 | 1067 | -52 |
| N-Pentane | 809 | 362 | -55 | 2273 | 1272 | -44 |
| Dichloromethane | 928 | 175 | -81 | 2629 | 819 | -69 |
| N-Hexane | 327 | 225 | -31 | 1231 | 1195 | -3 |
| Benzene | 395 | 263 | -33 | 1807 | 1308 | -28 |
| Heptane | 320 | 277 | -13 | 1223 | 1217 | 0 |
| Toluene | 322 | 305 | -5 | 1577 | 1484 | -6 |
| N-Octane | 238 | 227 | -4 | 1078 | 1089 | 1 |
| Ethylbenzene | 275 | 245 | -11 | 1352 | 1373 | 2 |
| M-Xylene | 257 | 245 | -5 | 1336 | 1366 | 2 |
| O-Xylene | 271 | 241 | -11 | 1334 | 1367 | 2 |
| N-Nonane | 198 | 186 | -6 | 928 | 952 | 3 |
| N-Decane | 200 | 145 | -28 | 690 | 584 | -15 |
| N-Undecane | 202 | 107 | -47 | 425 | 249 | -41 |

Table 2. A comparison of % bias due to back diffusion from Carbotrap during 14-days for low and high loading cases.

| CARBOTRAP | | | | | | |
|-----------------|------------------|--------|--------|-------------------|--------|--------|
| COMPOUND | Low Loading (ng) | | | High Loading (ng) | | |
| | Day 0 | Day 14 | % Bias | Day 0 | Day 14 | % Bias |
| Acetone | 279 | 38 | -86 | 2305 | 0 | -100 |
| N-Pentane | 479 | 81 | -83 | 3122 | 140 | -96 |
| Dichloromethane | 204 | 14 | -93 | 1862 | 0 | -100 |
| N-Hexane | 274 | 255 | -7 | 1753 | 1269 | -28 |
| Benzene | 346 | 225 | -35 | 3073 | 902 | -71 |
| Heptane | 254 | 257 | 1 | 1728 | 1576 | -9 |
| Toluene | 273 | 296 | 8 | 2765 | 2357 | -15 |
| N-Octane | 203 | 195 | -4 | 1784 | 1541 | -14 |
| Ethylbenzene | 224 | 191 | -14 | 2400 | 2066 | -14 |
| M-Xylene | 226 | 212 | -6 | 2424 | 2118 | -13 |
| O-Xylene | 218 | 190 | -13 | 2323 | 1993 | -14 |
| N-Nonane | 135 | 121 | -11 | 1460 | 1326 | -9 |
| N-Decane | 108 | 86 | -20 | 1069 | 951 | -11 |
| N-Undecane | 62 | 49 | -21 | 525 | 442 | -16 |

The averaged % RSD values obtained for each analyte during the experiments are given in Table 3.

The averaged % RSD values obtained for Chromosorb 106 are low for both low and high loading cases. The relatively high % RSD values for high boiling compounds decane and undecane are found in every experiment during this research. This is perhaps due to incomplete desorption during the thermal desorption step.

Although the % RSD values obtained for Carbotrap were found to be relatively high, in general the results are reasonable. The % bias values for Carbotrap shown in Table 2 are in agreement with the known low retention of the analytes with a functional group on graphitized carbon adsorbent Carbotrap.

Table 3. Averaged % RSD values for the compounds

| COMPOUND | AVERAGED % RSD | | | |
|-----------------|----------------|--------------|-------------|--------------|
| | CHROMOSORB 106 | | CARBOTRAP | |
| | Low Loading | High Loading | Low Loading | High Loading |
| Acetone | 4±2 | 7±4 | 7±5 | 2± |
| N-Pentane | 8±4 | 9±3 | 36±30 | 54±31 |
| Dichloromethane | 6±4 | 7±4 | 9± | 1± |
| N-Hexane | 5±3 | 3±3 | 12±10 | 14±10 |
| Benzene | 5±3 | 4±3 | 18±12 | 29±19 |
| Heptane | 4±2 | 4±3 | 7±8 | 4±5 |
| Toluene | 3±2 | 6±4 | 7±9 | 7±9 |
| N-Octane | 5±4 | 5±3 | 5±5 | 5±6 |
| Ethylbenzene | 4±1 | 6±4 | 5±6 | 7±8 |
| M-Xylene | 4±1 | 6±3 | 5±5 | 7±7 |
| O-Xylene | 4±1 | 5±3 | 5±6 | 7±7 |
| N-Nonane | 7±4 | 4±2 | 5±4 | 7±7 |
| N-Decane | 11±8 | 4±2 | 12±14 | 9±9 |
| N-Undecane | 18±15 | 8±6 | 23±21 | 14±16 |

Conclusions

The adsorption of the gasses on solid adsorbents occurs as physical adsorption due to the operation of the forces between the solid surface and the adsorbate molecules that are similar to the van der Waals forces between molecules. Since the adsorption of the organic compounds on the solid adsorbents is a reversible physical adsorption, the compounds adsorbed on the adsorbent by diffusion from the surrounding can freely back diffuse from the adsorbent to the surrounding environment. This will cause the vapour pressure of the adsorbate to built up on the surface of the adsorbent and, thus decrease in the uptake rates over time. The degree of back diffusion will be depend on the match of the adsorbent adsorbate pair and the uptake rate of each adsorbate on a particular adsorbent will be different. The magnitude of the sampling error introduced by back diffusion is related to the selection of right adsorbent/adsorbate combination. If the adsorbent is strong enough to hold the adsorbate, the losses from back diffusion will be low, but if the adsorbent is not strong enough the losses due to back diffusion will cause significant systematic errors in the final concentration calculations.

This study showed that significant losses in the amount of low boiling compounds occurred during long-term diffusive sampling due to back diffusion of the adsorbed compounds in this worst-case scenario after a dramatic decrease in the atmospheric concentration of the analytes.

The losses from the Chromosorb 106 are much lower than those from Carbotrap, about 50 % loss for acetone, pentane and dichloromethane in both high and low loading cases. The losses decrease with the decreasing volatility of the compounds as expected.

Although the results of these experiments are subject to random errors due to a number of reasons, such as between tube variations during loading and the effect of uncontrolled outdoor conditions such as humidity, temperature, rainfall and wind velocity during 14 day back diffusion period, in general, the results obtained are meaningful and simulate the a real sampling conditions.

The adsorbent loading method used to load the analytes on the adsorbent tubes was very quick and practical and simulates the adsorption of the compounds onto the adsorbents a in real sampling situation. The between tube variations (%RSD) obtained for trial loading of 16 Chromosorb 106 tubes are 8 ± 3 for high loading and 9 ± 4 for low loading which are slightly higher than normally obtained % RSD (3 to 5) for introduction of the analytes on adsorbent tubes by syringing.

Clearly these results show that for the monitoring of environmental air it is more satisfactory to use Chromosorb 106 than Carbotrap in diffusion experiments where the identity of the analytes are unknown. Back diffusion in a worst-case scenario has given a maximum negative bias of 50% using Chromosorb 106, except for the case of dichloromethane where negative bias values of 81 and 69 % were observed. Where the analytes are known, and their adsorbate/adsorbent adsorption isotherm constants are also available, it is possible to calculate the effective uptake rates using the computer program of Nordstrand and Kristensson⁵ and hence achieve much better precision in the analysis over long-term environmental low level monitoring.

References

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