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## Prevention of water vapour adsorption by carbon molecular sieves in sampling humid gases

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### Abstract

The water uptake by the solid sorbents Carbosieve S-III, Carboxen 569, 1000 and 1001, all of which are used for sampling of volatile organic compounds from the atmosphere, was examined using a direct experimental approach. The content of retained water is affected both by the trap temperature and the initial water vapour concentration in the sampled gas. Two different adsorption mechanisms are operative. At low relative humidities (RH) only active polar centres are involved. This adsorption is so weak that negative water interferences can easily be managed. Another mechanism, the micropore volume filling, involves substantial amounts of water, becomes operative once the threshold value for relative humidity ( $RH_{th}$ ) is surpassed.  $RH_{th}$  is  $45 \pm 3\%$  for Carboxen 1000 decreasing to  $35 \pm 3\%$  for the three other sorbents studied. A novel but simple strategy was tested for water management: moderate heating of the trap during the sampling (a warm trap method). The temperature elevation required depends on the  $RH_{th}$  characteristic for the specific sorbent, and RH and the temperature of the sampled gas. Usually the 5–15°C elevation is sufficient; only under extreme RH conditions is an elevation of 20°C necessary. The diagrams are given to determine this elevation. Since the sample RH is significantly decreased at an elevated temperature the negative effect of water uptake on the safe sampling volume is alleviated. Consequently the sampled gas volume can be as large as desired which decreases detection limits. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Air analysis; Instrumentation; Sample preparation; Molecular sieves; Dubinin–Astakhov isotherm; Adsorption isotherms; Volatile organic compounds

### 1. Introduction

Carbon molecular sieves (CMSs), such as Carbo-sieve S-III and Carboxens, find ever widening uses in the analysis of airborne contaminants, trapping very volatile and highly polar organic compounds.

Unfortunately, apart from analytes, substantial amounts of water vapour are sorbed from the humid air [1,2]. This is a serious drawback. Water is released during thermal desorption, and interferes with the subsequent determination by gas chromatographic methods.

There are reports that water also blocks the sorbent surface which may result in less efficient interception of analytes. In this case, even more important than the concentration of water vapour in

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the air is the more general parameter, the relative humidity, RH:

$$\text{RH} = 100\% \frac{c}{c_{\text{sat}}} = 100\% \frac{p}{p_{\text{sat}}} \quad (1)$$

where  $p$  and  $c$  denote, respectively, the pressure and concentration of water vapour in contact with the sorbent at given temperature while  $p_{\text{sat}}$  and  $c_{\text{sat}}$  refer to the water vapour saturated at the same temperature.

If the RH of the sampled air exceeds 90%, up to a tenfold decrease in the safe sampling volume (SSV) can be observed [3,4].

Four methods to circumvent the negative effects of water adsorption are recommended for routine analyses: use of drying agents, use of different sorbents, reduction of the sample volume to the smallest allowable and removal of water from the sorbents by dry purging prior to the thermal desorption step with an inert dry gas at controlled flow and temperature [4,5]. None is completely satisfactory. Sorbents as effective as CMSs but resistant to water adsorption are currently unavailable. Investigations on new graphitized carbons that feature very large specific surfaces, such as Carbograph 5 [6,7] and Carbotrap X [8], revealed that although these sorbents are stronger than Carbotrap B and Tenax, they fail to intercept hydrocarbons more volatile than  $C_4$  as well as low-molecular-mass compounds of high polarity. Restrictions on the volume of sampled air, either by reduction of the sample volume or by splitting, results in deterioration of the detection limit. While dry purge is effective and easy for monitoring and automation [9], it cannot alleviate the negative, diminishing effects of water uptake on the safe sampling volume.

The best solution would be the substantial decrease in, or even total elimination of, water adsorption during sampling. Helmig and Vierling suggested heating of the CMSs traps as one of the methods for adsorption prevention [1]. Examples cited by these authors are an air sample at 20°C and RH of 80%; calculations are given indicating that heating of the Carbosieve S-III trap up to 40°C may result in a decrease in water vapour adsorption by as much as 98%. However, such estimates have not been verified experimentally.

In our earlier work we also considered different

methods for prevention of water vapour adsorption in traps filled with carbon molecular sieves [2]. Experimental data indicate that CMSs sorb water vapour by the same mechanism as microporous activated charcoals. Stoeckli has described the mechanism of such adsorption in detail [10,11]. Only a very brief account is given here. Two types of adsorption are observed. At low RH water molecules undergo adsorption on the polar centres exclusively. These centres are represented by the functional groups, carboxylic, hydroxylic, phenolic, basic, etc., linked with the carbon surface. Usually in activated carbons the number of such polar centres is limited; consequently, adsorption is also slight and the surface can be described as strongly hydrophobic. The polar centres seem also to be linked, more strongly or weakly, with the CMS surface as is evidenced by the gradual release of carbon dioxide with the increasing temperature of the sorbent [12].

To describe adsorption at high RH, Stoeckli adopted Dubinin's theory of micropore volume filling, originally developed to explain adsorption of hydrocarbons by microporous activated charcoals. It is not the usual physical adsorption on the surface. Rather, it is condensation of water vapour to a liquid or a liquid-like phase within the micropore area. Condensation can occur below the saturation point under the action of strong adsorption fields inside the micropores while available polar centres are likely candidates for condensation nuclei. A maximum mass of retained water corresponds approximately to the total filling of micropore volume. An isotherm for the micropore volume filling is given by the Dubinin–Astakhov equation, the D–A isotherm [10,11,13]. Using the definition for RH from Eq. (1) we suggest the form for the D–A isotherm convenient for the description of water vapour adsorption:

$$m(\text{H}_2\text{O}) = m(\text{H}_2\text{O})^\circ \times \exp \left[ - \left( \frac{RT \ln(100\%/\text{RH})}{E_a} \right)^n \right] \quad (2)$$

where  $m(\text{H}_2\text{O})$  is the mass of adsorbed water,  $\text{mg g}^{-1}$ ;  $m(\text{H}_2\text{O})^\circ$  is the maximum mass of adsorbed water also called the sorption capacity,  $\text{mg g}^{-1}$ ;  $E_a$  is the adsorption energy,  $\text{J mol}^{-1}$ ;  $R$  is the gas constant,  $\text{J K}^{-1} \text{mol}^{-1}$ ;  $T$  is the absolute temperature, K;  $n$  is the measure of the homogeneity of the system.

According to Eq. (2) the mass of adsorbed water depends on the RH and the parameters that characterize the sorbent,  $m(\text{H}_2\text{O})^0$ ,  $E_a$  and  $n$ .

The D–A isotherm is of the V-type, its shape resembles a slanted S letter. The tilt results from the nonhomogeneities of the surface. The more homogeneous the surface, the larger the  $n$  value.

The D–A isotherm exhibits two important features. First, adsorption is observed only after some critical value for RH has been surpassed. Henceforth, this value will be called the threshold relative humidity,  $\text{RH}_{\text{th}}$ . In other words, condensation will not occur in micropores as long as RH is smaller than  $\text{RH}_{\text{th}}$ .  $\text{RH}_{\text{th}}$  for the activated carbons is usually larger than 35% and depends on the carbon identity. The second important feature of the D–A isotherm is a very slight effect of temperature on the isotherm shape and location on the RH axis, hence on the value for  $\text{RH}_{\text{th}}$ .

Our experiments on Carbosieve S-III and Carboxens 569, 1000 and 1001 indicate that substantial adsorption of water vapour from the sampled humid air occurs [2]. Sorption capacity of the investigated CMS is very large, ranging from 170 mg for Carboxen 1001 up to 450 mg for Carboxen 1000 per gram of sorbent. Approximate values for  $\text{RH}_{\text{th}}$  fall within the range 35–50%. On the assumption of the micropore volume filling mechanism, the properties of the D–A isotherm discussed above lead to the obvious conclusion that adsorption can be prevented, even in the case of very humid samples of air [2]. It is enough to lower RH to a value smaller than  $\text{RH}_{\text{th}}$  of the used adsorbent, i.e. the condition  $\text{RH} < \text{RH}_{\text{th}}$  has to be obeyed. A number of methods can be suggested to decrease the relative humidity. Heating the trap filled with the sorbent, and, necessarily, the

air flowing through the trap seems to be the best choice. Temperature elevation leads to an exponential increase in  $c_{\text{sat}}$ , the denominator in Eq. (1); a concomitant fast decrease in the RH follows. Recall that  $\text{RH}_{\text{th}}$  for the specific adsorbent does not depend on temperature. Hence, proper elevation of the trap temperature will result in fulfillment of the condition  $\text{RH} < \text{RH}_{\text{th}}$ . Condensation in the micropore volume can no longer occur.

The aim of this work was to verify experimentally whether moderate elevation of the CMS trap temperature indeed prevents adsorption of water vapour from the samples of humid air. If so, an assumption of the micropore volume filling mechanism would be justified. Our goal was to provide guidelines for practical implementation of this method. Multilayer traps filled with carbon molecular sieves and graphitized carbons were used. Such traps find widespread use in real field measurements.

## 2. Experimental

### 2.1. Adsorbents and materials

A list of sorbents (Supelco, Bellefonte, PA, USA) supplemented with some sorbent properties is given in Table 1. The traps were filled consecutively with 100 mg of Carbotrap C, 150 mg of Carbotrap B, and 300 mg of investigated CMS. Adsorbents were placed in a stainless steel tube (115×5 mm I.D.). A bed in the tube was fixed using wads of glass wool; such wads served also to separate the layers of individual sorbents. The traps were activated at a temperature of 300°C for 1 h in a stream of helium flowing at a rate of 100 ml min<sup>-1</sup>. Such a procedure

Table 1  
Properties of the examined sorbents

Sorbent	Mesh size <sup>a</sup>	Surface area <sup>a</sup> (m <sup>2</sup> g <sup>-1</sup> )	Micropore volume <sup>a</sup> (ml g <sup>-1</sup> )	Water sorption capacity (mg g <sup>-1</sup> ) [2]
Carbotrap B	20/40	100	–	<5
Carbotrap C	60/80	10	–	<5
Carbosieve S-III	60/80	820	0.35	330
Carboxen 569	20/40	485	0.20	194
Carboxen 1000	20/45	1200	0.44	450
Carboxen 1001	20/45	500	0.22	170

<sup>a</sup> Manufacturers' specification.

was also conducted for 10 min directly prior to use. These multibed traps are used in our laboratory for different purposes, mostly to determine volatile polar organic contaminants of atmospheric air and water.

Dry synthetic air (<20 ppm v/v water) was used as a carrier gas; very pure helium (<1.6 ppm water, 1.2 ppm oxygen) was used for activation of sorbents. Water was Milli-Q (Millipore) grade.

## 2.2. Apparatus

The apparatus described previously was used [9]. An outline describing the work of the experimental system is shown in Fig. 1. The most important elements of the gas path are: a bottle with compressed dry air; a gas flow controller (VCD 1000, Porter Insert.); a Valco (Houston, TX, USA) four-port valve with attached moisture saturator (a glass tube; 40×1.1 cm I.D.; filled with ~8.9 g of Sterhamol 60–80 mesh, diatomaceous earth used as GC supporting material, moistened with 5 g of water); another Valco four-port valve with attached trap filled with tested sorbents. A thermohygrometer probe was put in a special glass tube at the end of the flow path. The first Valco valve is bypassed by an additional

gas path inserted at points D and M. The humid air that passed the saturator and the dry air from the additional flow path are mixed at the junction of the gas paths, point M. In both gas lines needle valves were used to control the gas flows, hence, the concentration of water vapour; 1/16 in. stainless steel and 1/8 in. PTFE tubes were used throughout (1 in. = 2.54 cm).

The saturator and the tube filled with the sorbent were thermostated separately; the first one in a water thermostat ( $20 \pm 0.1^\circ\text{C}$ ), the second one in a metallic block thermostated to within  $\pm 0.5^\circ\text{C}$ . The valves and gas connections were thermostated in air at a temperature of about  $60^\circ\text{C}$ . The thermohygrometer (LB-701H, LAB-EL, Warsaw, Poland) was connected to a computer through a RS 232 interface. The humidity and temperature of the gas were registered every 5 s, and converted to water vapour concentration. Laboratory-written programmes for data acquisition and conversion were used.

Depending on the position of the four-port valves, either humid air (simulation of the sampling) or dry air (dry purge) could be passed through the trap with sorbents. Adsorption and desorption of water vapour was monitored by continuous measurements of the

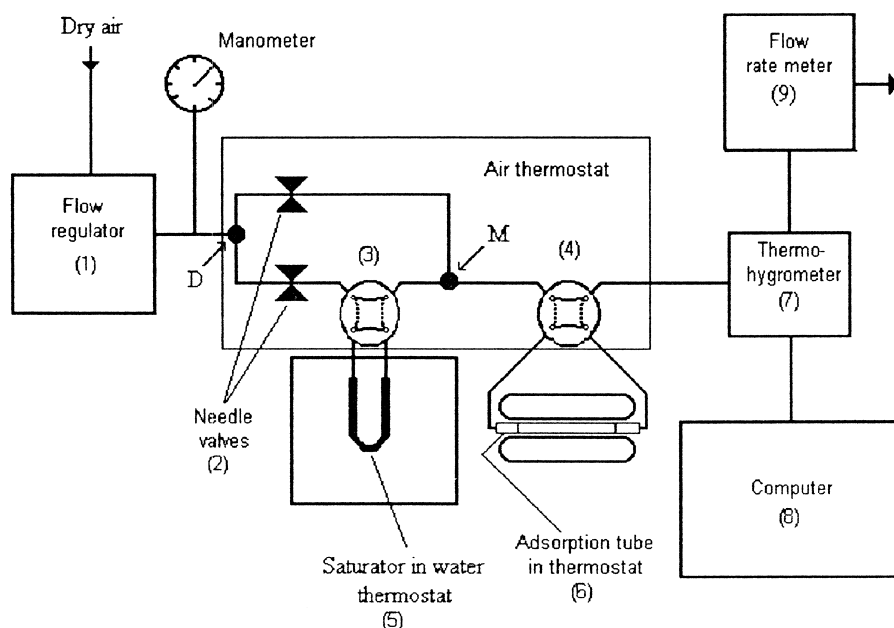


Fig. 1. Outline of the experimental set-up (details in the text).

water vapour concentration in air at the outlet of the system.

### 2.3. Description of experiments and results

The temperature dependence of the mass of adsorbed water was determined for four concentrations of water vapour in air: 6.1, 9.6, 11.5 and 13.8 mg l<sup>-1</sup>. These concentrations were selected to correspond to 90% RH at a temperatures of 5, 12, 15 and 18°C, respectively. The sample volume was 5 l in all experiments; the flow-rate was 100 ml min<sup>-1</sup>. The temperature of the trap filled with sorbents was varied.

Prior to every experiment, the trap underwent activation and was fixed in the apparatus. Once the gas flow-rate and the temperature were stabilized, the measurements of RH and temperature at the outlet of the system started. The examples of the changes in water vapour concentration for a trap filled with Carboxen 1000 are shown in Fig. 2 at 19.1°C (bottom figure) and at 34.9°C (upper figure). At the start of measurements the first four-port valve is closed and the second one is open. The saturator is detached and dry air flows through the trap, to remove the traces of moisture from the sorbents. The concentration of water vapour is nearly zero — the initial segment of the curve. At the point marked a, both the four-port valves are switched over. The air flows through the saturator while the trap is detached. The water vapour concentration increases quickly to attain a constant value, 13.8 mg l<sup>-1</sup> in this case. Once this value has been attained the second four-port valve is opened which corresponds to point b. The stream of humid air flows through the trap. This is a simulation of humid air sampling under real conditions. A measure of the adsorption rate at a given moment is the difference between water vapour concentration in air entering the trap,  $c_{\text{inp}}$ , shown as a broken line, and in air at the outlet of the trap,  $c_{\text{out}}$ , shown as a solid line.

After 50 min ( $V=5$  l) both the valves are closed, and the saturator and the trap are detached — point c. Dry air is passed through the line to remove water vapour from the gas phase and the walls. Then the second four-port valve is opened — point d. The stream of dry air desorbs water vapour by the usual dry purge technique. The initial increase in water

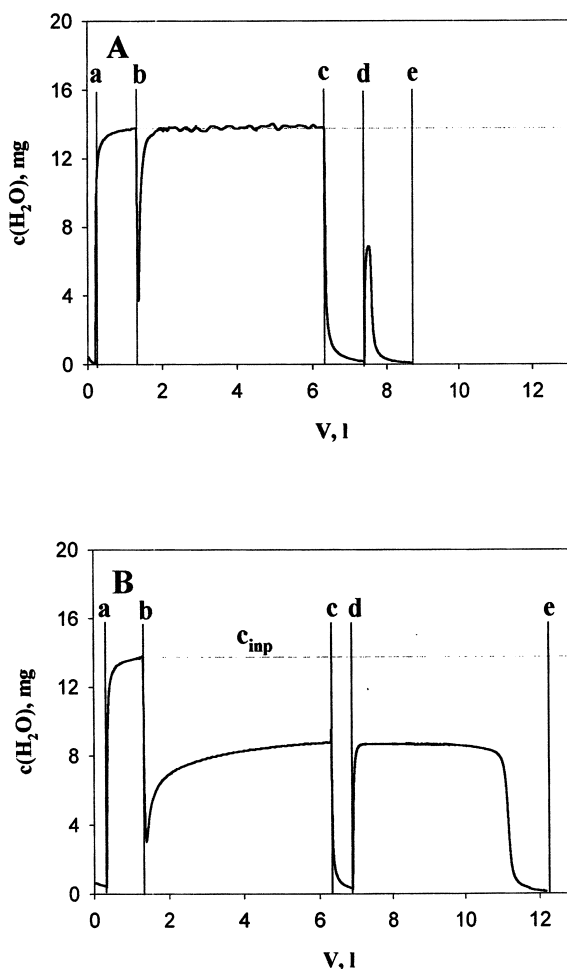


Fig. 2. Changes in water vapour concentration for experiments on the trap: 100 mg Carbotrap C/150 mg Carbotrap B/300 mg Carboxen 1000 Initial water vapour concentration 13.8 mg l<sup>-1</sup>; (A) trap temperature 34.9°C; (B) trap temperature 19.1°C. Detailed description in the text.

vapour concentration is very fast but decreases to zero once all the water has been removed. The experiment is terminated once the water vapour concentration approaches zero — point e. The b–c segment represents saturation and the d–e segment desorption. The mass of retained water can be estimated from the area of the surface limited from above by the broken line  $c_{\text{inp}}$ , from below by the solid line  $c_{\text{out}}$ , and at sides by the straight lines b and c. An alternative and simpler way is to integrate the area under the desorption curve, step d–e.

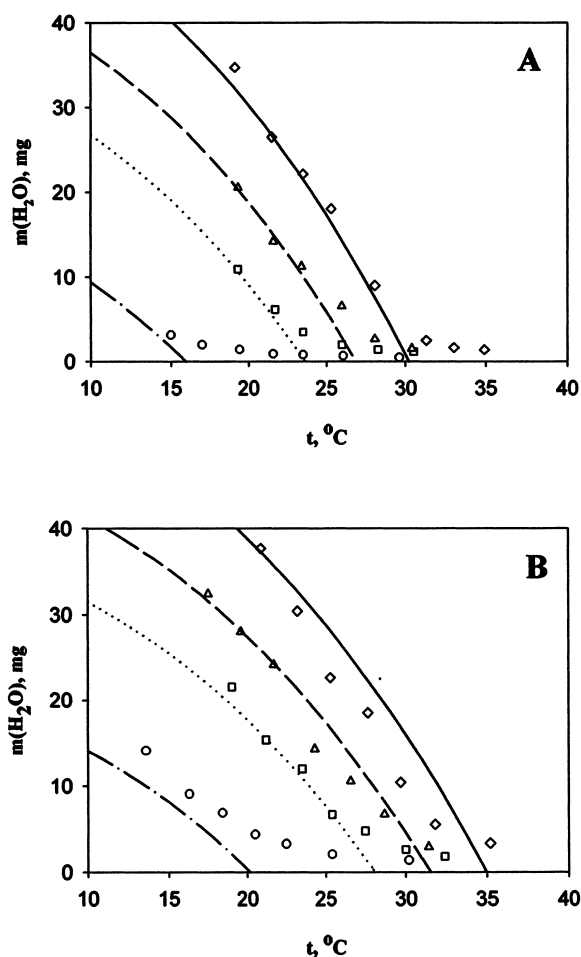


Fig. 3. Dependence of the adsorbed water mass on the trap temperature for different concentrations of water vapour in sampled air: circles  $6.1 \text{ mg l}^{-1}$ ; squares  $9.6 \text{ mg l}^{-1}$ ; triangles  $11.5 \text{ mg l}^{-1}$ ; diamonds  $13.8 \text{ mg l}^{-1}$ . Curves for the individual concentrations are drawn according to Eq. (4). (A) The trap: 100 mg Carbotrap C/150 mg Carbotrap B/300 mg Carboxen 1000; (B) the trap: 100 mg Carbotrap C/150 mg Carbotrap B/300 mg Carbosieve S-III.

The dependence of this mass on temperature is shown in Fig. 3 for Carboxen-1000 and Carbosieve S-III. The results for Carboxens 569 and 1001 are similar and were not reported to save space; these data are available from the authors on request.

### 3. Discussion

Even though multilayer samplers were used, only

carbon molecular sieves retain water vapour to a considerable degree (Table 1). Thus, discussion is restricted to the CMSs sorbents. Information on the course and kinetics of adsorption can be gained from the saturation curves, the b–c segments in Fig. 2. All of the traps examined exhibit a similar pattern. If moist air ( $c_{\text{inp}} = 13.8 \text{ mg l}^{-1}$ ) is flown through the trap, the measured water vapour concentration,  $c_{\text{out}}$ , initially exhibits an abrupt decrease to attain a sharp minimum, and next increases to level off at a plateau value.

At a temperature of  $19.1^\circ\text{C}$  (RH about 84%), the plateau value for the water vapour concentration is smaller than the input concentration (Fig. 2B); while only a part of the water entering the system is retained by the sorbents, the remainder flows freely through the trap. A slight slope of the plateau indicates that the adsorption rate decreases slowly with increasing volume. The total mass of water introduced to the trap was 69 mg (5 l at  $13.8 \text{ mg l}^{-1}$ ); integration of the area below the desorption curve gave 34.7 mg as the mass of adsorbed water. Hence, adsorption efficiency is about 50%. Since the Carboxen 1000 trap can retain as much as 135 mg of water (based on the Carboxen 1000 mass in the trap and sorption capacity — see Table 1), it is very far from saturation. Elevation of the trap temperature to  $34.9^\circ\text{C}$  alters radically the course of events (Fig. 2). While  $c_{\text{inp}} = 13.8 \text{ mg l}^{-1}$  remains the same, RH decreases to about 35%. The inlet and outlet water vapour concentrations in air from the trap are equal over the plateau region. Water vapour is sorbed only from the first volume of about 500 ml. Integration of the area under the desorption curve indicated that only 1.4 mg of water, about 2% of the water introduced into the trap, underwent adsorption.

The course of saturation curves at both temperatures can easily be explained assuming the Stoeckli mechanism described in the Introduction. A fast decrease in water vapour concentration at the start of the curve results from adsorption on the polar centres. After saturation of the available centres, water vapour appears at the outlet of the trap; an increase in concentration is registered, accompanied by a minimum on the saturation curve. The volume corresponding to the minimum represents approximately the breakthrough volume, BTV, of the water vapour, once the correction for the dead volume (about 4 ml) is accounted for. BTV is small for all of

the traps, within 100–250 ml, depending on the experimental conditions, the sorbent identity, the temperature and the concentration of water vapour.

At a temperature of 19.1°C the further shape of the saturation curve and the occurrence of the plateau, Fig. 2B, indicates adsorption according to the micropore volume filling mechanism. We begin with a simplified picture of the occurring phenomena. Since the relative humidity of the air introduced into the trap is large, about 84%, water vapour undergoes concentration inside the micropore area. Water vapour concentration decreases and so does the RH. At  $RH = RH_{th}$  further condensation becomes impossible; recall the properties of the D–A isotherm discussed in the Introduction. Water vapour remaining in the gas phase is in equilibrium with the liquid water inside micropores. Its concentration at the outlet of the trap,  $c_{out}$ , corresponds to  $RH_{th}$ , and should be constant (a flat plateau) until the micropore volume is filled completely. According to such a mechanism the rate of adsorption per unit of volume is given by  $c_{inp} - c_{out}$ . Hence, multiplication by the sample volume,  $V_{air}$ , gives the mass of adsorbed water:

$$m(H_2O) = V_{air} (c_{inp} - c_{out}) \quad (3)$$

Since the water vapour concentration at the outlet of the trap should correspond to the threshold relative humidity, according to Eq. (1) we can write  $c_{out} = c_{sat} RH_{th}/100\%$ . After substitution from Eq. (3) and some simple transformations we obtain the dependence of the retained water on the  $RH_{th}$ :

$$m(H_2O) = V_{air} c_{sat} (c_{inp}/c_{sat} - RH_{th}/100\%) \quad (4)$$

It is readily seen that the first term in brackets is associated directly with the RH of the air introduced to the trap,  $RH = 100\% c_{inp}/c_{sat}$ , which gives a direct relationship between RH of the sampled gas and the mass of retained water:

$$m(H_2O) = V_{air} c_{sat} [(RH - RH_{th})/100\%] \quad (5)$$

The experiment deviates somewhat from this idealized picture of events. Starting from the minimum (see Fig. 2B) we observe a sharp increase in  $c_{out}$  followed by a mild transition into the plateau region that is not completely flat, however. The small slope of the plateau indicates that the water vapour concentration in equilibrium with the liquid water inside the micropores increases slowly as the mass of

retained water increases. Eqs. (4) and (5) are not very accurate because the plateau is not completely flat; an approximate estimate of the mass of water retained in the micropores can be gained, however.

At a temperature of 34.9°C the minimum on the saturation curve occurs as well but it is followed by a fast increase in  $c_{out}$  up to a value of  $c_{inp}$ . Water vapour freely flows through the trap. The mechanism of micropore volume filling is not operative; apparently the RH of the passing air, about 35%, is below the threshold value for Carboxen 1000. The estimated mass of adsorbed water can be ascribed to adsorption on the polar centres.

The results of these two experiments convincingly show the strong effect of temperature on water vapour adsorption by Carboxen 1000. Elevation of the trap temperature from 19.1 to 34.9°C decreases the mass of retained water by about 96% (from 34.7 to 1.6 mg).

According to the results reported in Fig. 3, not only the trap temperature but also the initial water vapour concentration affect the extent of water vapour adsorption. Dependencies retained water vapour vs. temperature exhibit separate curves for individual concentrations. As the water vapour concentration increases, so does the temperature indispensable to reduce adsorption. It is convenient to use a more general parameter, the relative humidity (see the D–A isotherm, Eq. (2)). The results from Fig. 3 are recalculated for the new system of coordinates and are shown in Fig. 4. The direct effects of temperature are no longer visible; points obtained at different temperatures lie approximately along the same curve; two different adsorption processes are clearly discernible, however. At small RH adsorption is slight and increases slowly with increasing RH. Once the threshold value,  $RH_{th}$ , is surpassed, the increase becomes faster; apparently another adsorption mechanism starts contributing. The transition between both the mechanisms is diffuse, making accurate determination of  $RH_{th}$  difficult.  $RH_{th}$  for Carboxen S-III, Carboxen 569, and Carboxen 1001 is about  $35 \pm 3\%$ , but increases markedly, up to  $45 \pm 3\%$ , for Carboxen 1000. These values are in satisfactory agreement with our preliminary estimations [2]. The results are important both from the theoretical and practical point of view. Experiments confirm that dependence of the adsorbed water mass on RH exhibits a threshold behaviour, and the value

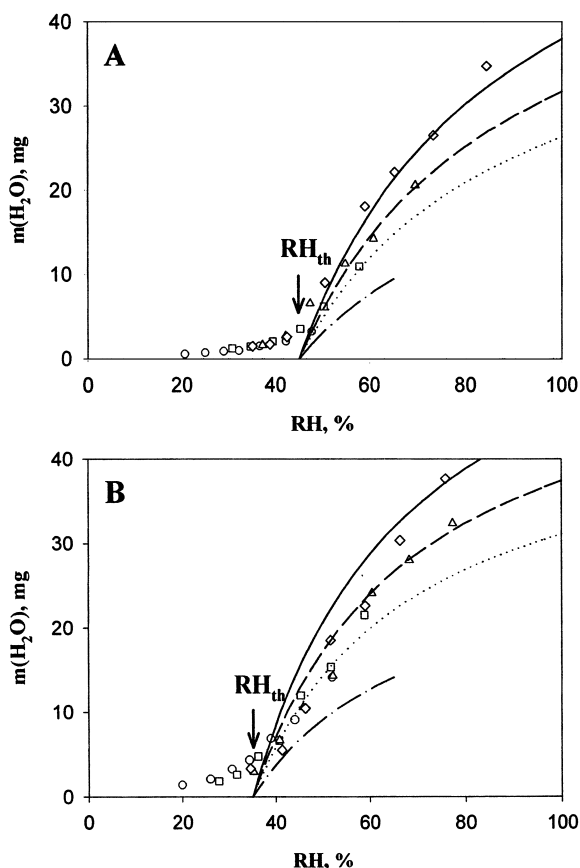


Fig. 4. Dependence of the mass of adsorbed water on the relative humidity of sampled air. Data taken from Fig. 3. Curves are drawn according to Eq. (5).

for  $\text{RH}_{\text{th}}$  is independent of temperature. Apparently, adsorption of water vapour by CMSs indeed occurs according to the mechanism suggested by Stoekli for the microporous active carbons [12], and both adsorption mechanisms can clearly be distinguished.

At  $\text{RH} < \text{RH}_{\text{th}}$  the adsorption observed can be ascribed to retention of water molecules on the polar centres. Under our experimental conditions about 1–5 mg of water is retained in the close vicinity of  $\text{RH}_{\text{th}}$ , the smallest value for a trap with Carboxen 1000 and the largest one for that with Carboxen S-III. Polar centres are also likely to be present on the surface of graphitized carbons being responsible for water vapour adsorption by Carbotrap B and C. The saturation curve shown in Fig. 2A describes this

type of adsorption under the sampling conditions. The initial adsorption rate is high but decreases quickly to zero. After passing about 500 ml of humid air, complete sorbent saturation is achieved. The desorption curve indicates that the retained water can easily be removed from the sorbent. A dry purge with about 500 ml of dry gas is completely satisfactory.

The mechanism of micropore volume filling becomes operative above  $\text{RH}_{\text{th}}$ . The mass of adsorbed water may be significant, up to tens of milligrams of water in our experiments (see Fig. 4). Figs. 3 and 4 show the dependencies of the mass of retained water on the temperature and RH of sampled air estimated from Eqs. (4) and (5), respectively, using the threshold values for RH estimated above.

The agreement between calculations and experiment is most satisfactory provided the mass of adsorbed water exceeds 8–10 mg. Over this range Eqs. (4) and (5) correctly predict the effects of temperature and concentration (Fig. 3) as well as of RH (Fig. 4) on the mass of retained water. This important observation gives additional weight to the assumptions of the micropore volume filling mechanism. At  $m(\text{H}_2\text{O})$  below about 8 mg, the calculated values are clearly underestimated, because the process of adsorption on the polar centres, that also occurs at RH smaller than  $\text{RH}_{\text{th}}$ , is not accounted for. The occurrence of such a process can be observed in Fig. 4; its contribution to the overall adsorption decreases markedly above  $\text{RH}_{\text{th}}$ , and can be ignored altogether when the RH surpasses the threshold value by about 10–15%.

Note that the mass of adsorbent does not appear as the parameter in Eqs. (4) and (5). If so, the sorbent mass should not affect the mass of retained water provided the condition  $m(\text{H}_2\text{O}) < m(\text{H}_2\text{O})^{\text{p}}$  is obeyed, i.e. the sorbent has not been completely saturated. This conclusion is not in accordance with the data of Helmig and Vierling who suggested that the mass of water retained by Carboxen S-III and Carboxen 569 is proportional to the sorbent mass. On the basis of this reasoning they advocated decreasing the mass of the sorbent bed in a trap to an absolute minimum [1]. Helmig and Vierling developed a set of equations to estimate the mass of water intercepted from the sample of humid air; the sorbent mass is one of the necessary parameters.



Unfortunately, the useful range of these equations (the sample volume  $\leq 5$  l per gram of the sorbent) does not overlap with the volumes used in our work ( $V=5$  l per 300 mg of the sorbent). Hence, a meaningful comparison is not feasible. It is important from the practical point of view to establish firmly whether or not the mass of retained water depends on the mass of the sorbent. This problem should be settled experimentally. Even though the form of Eqs. (4) and (5) does provide a useful guidance, the conclusions cannot be considered as final, since derivation of these equations involved approximations. To throw more light on this subject, further investigations are conducted in our laboratory.

Be as it may, the preliminary conclusions advanced in our former paper [2] are now fully confirmed: adsorption according to the micropore volume filling mechanism can be prevented even at large water vapour concentrations. It is enough to heat the trap up to a proper temperature. To estimate the temperature required, one needs the  $RH_{th}$  for the CMS used as well as the RH and temperature of the analysed air; the latter values are usually determined prior to sampling. On the basis of semiempirical dependence of the saturated water pressure on temperature one can fairly readily devise an empirical relationship. Impressive as such an equation might look, its practical use would have been cumbersome: the necessary calculations are involved and some numerical values of the parameters have to be included. Instead, we report the necessary elevation of the trap temperature depending on the RH (up to  $RH=100\%$ ) and the sampled air temperature over the range  $-20^{\circ}\text{C}$  up to  $+40^{\circ}\text{C}$ . The graphic representation is given for Carbosieve S-III, Carboxen 569 and Carboxen 1001 in Fig. 5A and for Carboxen 1000 in Fig. 5B. In practice, elevation of the trap temperature by 5–15 $^{\circ}\text{C}$  above the ambient temperature is frequently satisfactory. Under extreme conditions, large relative humidity and CMS with  $RH_{th}=35\%$ , the elevation approaches 20 $^{\circ}\text{C}$ . Hence, the method can be termed the warm trap method. Carboxen 1000 seems to be a sorbent of choice, since its  $RH_{th}$  is the largest from among the four sorbents investigated. Carboxen 1000 also exhibits the best effectiveness, when used in the dry purge technique [9]. Other criteria must not be overlooked,

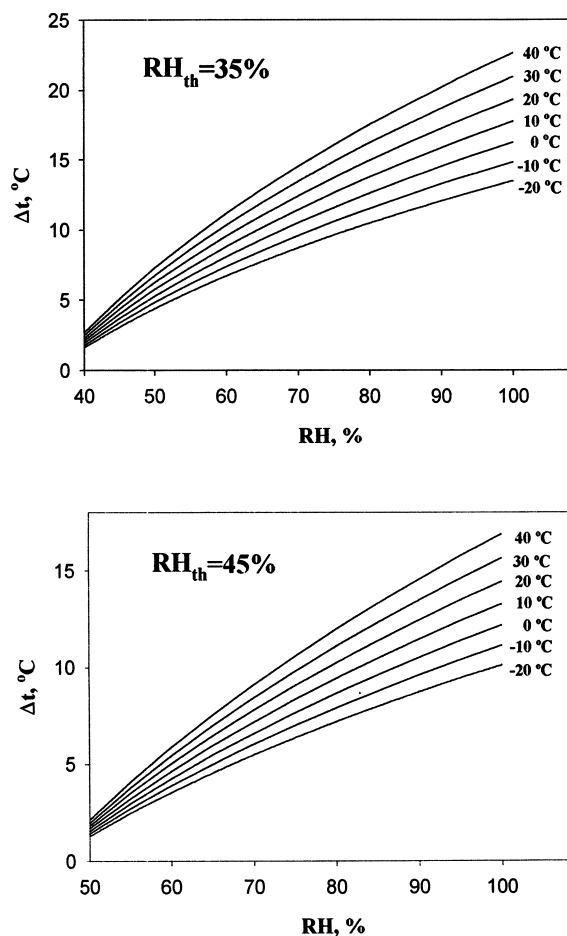


Fig. 5. Elevated trap temperature to be applied depending on the RH and temperature of the sampled gas. Upper figure: the trap, 100 mg Carbotrap C/150 mg Carbotrap B/300 mg Carboxen 1000; Bottom figure: the trap, 100 mg Carbotrap C/150 mg Carbotrap B/300 mg Carbosieve S-III.

however: breakthrough volume and recovery coefficient during thermal desorption.

The warm trap method for prevention of water vapour adsorption apart from serious merits exhibits some demerits as well.

1. Decrease in the RH of sampled gas eliminates the negative effect of large RH on the safe sampling volume, SSV. Water does not fill micropores that remain available to retain analytes. According to the literature data, as large as tenfold decrease in SSV may occur under  $RH>90\%$ , while an increase in temperature by 10 $^{\circ}\text{C}$  decreases SSV only

by a factor of 2 or less [3–5]. Thus, the overall effect is positive, even if the trap temperature has to be elevated by as much as 20–25°C.

2. The sampled air or gas volume can be as large as desired, even at very large RH. The SSV of the least sorbed analyte is the sole limitation. SSV becomes the larger the larger the mass of the CMS bed in a trap without any negative side effects. Obviously, large sample volume decreases detection limits.
3. Drying of the air prior to admission into the trap is not necessary. There are many reports in the literature warning against use of desiccants as well as Nafion membranes; the loss of polar analytes has frequently been reported.
4. Elevation of the trap temperature does not prevent water vapour adsorption entirely; adsorption on the polar centres persists.
5. Requirement for the proper equipment and the power source to heat and regulate the trap temperature is a serious drawback.

The warm trap method can find wide uses when the CMS traps are necessary and the RH exceeds 40–50%. The equipment factor rather precludes use under field conditions and for personal samplers at work places. However, stationary sampling points and laboratories using samples transported in canisters should experience no problems. Elevation of the trap temperature can easily be implemented determining volatile organic compounds (VOCs) in water by the purge-and-trap method.

As far as water management techniques require, the warm trap method should not be treated as competitive with the dry purge. Rather, it can supplement the latter method under specific conditions. The dry purge is universal, removes retained water completely, can be used for all carbon and polymeric sorbents. Difficulties arise when large volumes of humid gases have to be sampled, because substantial masses of water can block the sorbent surface. Removal of this water requires large volumes of dry gas, comparable with the sampled volume if not higher. Both the time needed for analysis and the risk of contamination increase [9]. Then the use of the warm trap method may be to the best advantage. Water will be adsorbed on the polar

centres exclusively and can be purged easily with the small volume of dry gas. These advantages can be appreciated readily comparing desorption curves shown in Fig. 2A and B.

In our laboratory the warm trap method is used for the determination of polar VOCs in water by the modified purge and trap technique. Also attempts to analyse polar VOCs in the atmosphere have met with full success. In earlier analyses we removed water from the traps by dry purge. The warm trap method can decrease the dry gas volume necessary to remove the adsorbed water by as much as a factor of 5. The total analysis time is shortened (compare the desorption curves shown in Fig. 2), and the danger of sample contamination is diminished.

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### References

- [1] D. Helmig, L. Vierling, *Anal. Chem.* 67 (1995) 4380.
- [2] J. Gawłowski, T. Gierczak, A. Jeżo, J. Niedzielski, *Analyst* 124 (1999) 1553.
- [3] MDHS 72. UK Health and Safety Executive. Her Majesty Stationary Office, London, 1992.
- [4] E. Woolfenden, *J. Air Waste Manag. Assoc.* 47 (1997) 20.
- [5] Compendium Method TO-17, US Environmental Protection Agency, Cincinnati, OH, 1999.
- [6] E. Brancaleoni, M. Scovaventi, M. Frattoni, R. Mabilia, P. Ciccioi, *J. Chromatogr. A* 845 (1999) 317.
- [7] L. Sampaolo, E. Pierini, A.R. Mastrogiacomo, *Chromatographia* 50 (1999) 680.
- [8] K. Dettmer, Th. Knobloch, W. Engewald, *Fresenius J. Anal. Chem.* 366 (2000) 70.
- [9] J. Gawłowski, T. Gierczak, E. Pietruszyńska, M. Gawryś, J. Niedzielski, *Analyst* 125 (2000) 2112.
- [10] F. Stoeckli, T.S. Jakubov, A. Lavanchy, *J. Chem. Soc. Faraday Trans.* 90 (1994) 783.
- [11] F. Stoeckli, *Carbon* 36 (1998) 363.
- [12] E. Koch, P. Woźniak, J. Gawłowski, J. Niedzielski, *Chem. Anal. (Warsaw)* 42 (1997) 49.
- [13] P. Lodewyckx, E.F. Vansant, *Carbon* 37 (1999) 1647.