

Adsorption of water vapour from humid air by selected carbon adsorbents

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Abstract

The water uptake by carbon molecular sieves (CMS) and graphitized carbons, all of which are used to determine volatile organic compounds in air, was investigated using a direct experimental approach. CMS, e.g. Carboxen 1002, Carboxen 1003 and Anasorb CMS adsorb substantial amounts of water, in the range 400 to 450 mg per gram of adsorbent. Graphitized carbons, e.g. Carbograph 5TD and Carbopack X show low water trapping, less than 30 mg g⁻¹ and Carbopack Y as little as 5 mg g⁻¹ or less. The water sorption capacity for graphitized carbons is strongly dependent on the relative humidity (RH). The change of RH from 95 to 90% decreases the amount of adsorbed water by more than a factor of 2. Two different water adsorption mechanisms are operative: adsorption on polar centers and micropore volume filling. For graphitized carbons and CMS at low RH, adsorption on polar centers is involved. For CMS, once the threshold value of relative humidity (RH_{th}) is surpassed, micropore volume filling becomes predominant. RH_{th} is 44 ± 3 and 42 ± 3% for Carboxen 1002 and 1003, respectively, and 32 ± 3% for Anasorb CMS. The CMS mass in the trap was found not to affect the mass of retained water under condition of incomplete saturation of adsorbent bed with water. Thus, the restrictions commonly imposed on the CMS mass are not necessary. The dry purging technique is suggested to remove adsorbed water. Carbograph 5TD and Carbopack X require only a few hundred ml of dry air to remove adsorbed water entirely. Water can also be purged out from CMS; however, much larger volumes of dry air are needed.

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1. Introduction

Recently, the use of adsorbents for preconcentration of organic contaminants of atmospheric air and water has vastly increased [1–3]. Especially carbon adsorbents: carbon molecular sieves (CMS) and graphitized carbons enjoy wide popularity [3]. One of the most serious problems in the use of these sorbents is coadsorption of water while sampling humid gases [4–8]. The water adsorbed can interfere with analysis in many different ways: it can decrease the safe sampling volume [9], it can lead to analyte degradation [10] and, when released during thermal desorption, it may thwart the analytical procedure completely. We have studied extensively the phenomenon of water coadsorption on the sorbents for some time. Our investigations were concerned with CMS (Carbosieve SIII, Carboxen 569, Carboxen 1000), polymeric

sorbents, and graphitized carbons as well [5–8]. Our aim was to determine to what extent the individual sorbent can be used for sampling in very humid environment. The main parameters to be reckoned with are the total mass of water sorbed by the bed and the so called threshold humidity, RH_{th}, a value of relative humidity that should not be surpassed in order to avoid a steep increase in the sorption of water [5,7]. In this work we want to conclude our studies extending experiments to the new graphitized carbons, Carbograph 5TD and Carbopack X. These sorbents are currently gaining favour with analysts at the expense of CMS. The former sorbents feature fairly large specific surface (200–600 m² g⁻¹), and were introduced as commercial products to fill a gap between CMS and traditional graphitized carbons that have small specific surface (Carbotrap B and C). Since there is strong correlation between specific surface and adsorption capacity, Carbograph 5TD and Carbopack X seem to be very promising as an intermediate layer in three layer samplers, to sorb at least a part of volatile compounds C₃–C₅.

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The aim of this work is to study adsorption of water vapour from humid air by carbon molecular sieves (Carboxen 1002, Carboxen 1003, Anasorb CMS) and graphitized carbons (Carbograph 5TD, Carbopack X and Carbopack Y). Carboxen 1000 which is very well characterized is used as a standard to control experiments.

2. Experimental

Experimental details have been described elsewhere [5–8]. Only salient features of experiments be reported here (see Fig. 1). A stream of humid air is passed through a thermostated stainless steel tube packed with the sorbent. A proper amount of the sorbent (100, 300 or 500 mg) is located in the middle of the tube and kept in position using wads of glass wool. A hygrometer probe (used to measure humidity and temperature) is placed at the outlet of the tube. In front of the tube inlet the pipe to admit dry air is attached. This way the relative humidity of the air passed through the tube can be adjusted within the range 0 ~ 95%. Two distinct modes were operative: (i) saturation of the adsorbent with air at constant humidity; (ii) desorption of adsorbed water in a stream of dry air. The amount of adsorbed water was determined both from the saturation and desorption curves. The detailed description of determination of the mass of adsorbed water is given elsewhere [6,7].

2.1. Chemicals

The adsorbents Carboxen 1000, Carboxen 1002, Carboxen 1003 (Supelco), Anasorb CMS (Alltech), Carbograph 5TD

(LARA), Carbopack X and Carbopack Y (Supelco) were activated for 5 h in a stream of helium at 350 °C prior to use. Adsorbent physical parameters are assembled in Table 1.

3. Results and discussion

Two parameters, water sorption capacity (WSC) and threshold relative humidity (RH_{thr}) are needed to assess the adsorbent performance in preconcentrating and sampling organic compounds from very humid air (or another gas). In what follows the experiments conducted to measure those two parameters are described.

3.1. Water sorption capacity

The total amount of water adsorbed on the sorbents was determined, according to a procedure described in detail elsewhere [6,7]. A reference saturation curve (saturation of the system without any sorbents), the saturation curves for the molecular sieves (Carboxen 1003 and Anasorb CMS), and the saturation curve for Carbograph 5TD are shown in Fig. 2 (upper section). The mass of water was determined from the area under the desorption curve. Water sorption capacity for all of the adsorbents is listed in Table 1. It is seen that while carbon molecular sieves exhibit a very large value for WSC, 400–450 $mg\ g^{-1}$, Carbograph 5TD and Carbopack X are much poorer sorbents, $25 \pm 5\ mg\ g^{-1}$, and Carbopack Y does not sorb water at all. The saturation curves for carbon molecular sieves and graphitized carbons are completely different. It is not surprising because we believe that two mechanisms of water adsorption are in effect. Firstly, water

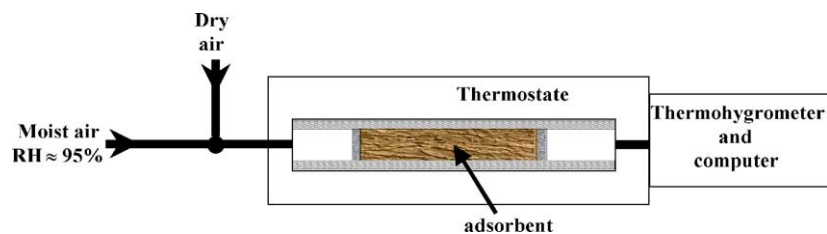


Fig. 1. Outline of experimental setup to study adsorption of water on carbon adsorbents.

Table 1
Physical properties of adsorbents studied and maximum amount of adsorbed water

Adsorbent	Specific surface ^a ($m^2\ g^{-1}$)	Micropore volume ^a ($cm^3\ g^{-1}$)	Size ^a (mesh)	$m_0(H_2O)$ ($RH \approx 90\%$) ($mg\ g^{-1}$)	$m_0(H_2O)$ ($RH \approx 95\%$) ($mg\ g^{-1}$)	RH_{pr} (%)
Carboxen 1000	1200	0.44	40/60	442	445 (450) ^b	45 ± 3^b
Carboxen 1002	1100	0.36	40/60	425	415	44 ± 3
Carboxen 1003	1000	0.38	40/60	436	435	42 ± 3
Anasorb-CMS	–	–	40/60	396	392	32 ± 3
Carbopack X	240	–	40/60	11	29	–
Carbograph 5TD	560 ^c	–	40/60	10	24	–
Carbopack Y	24	–	60/80	<5	<5	–

^a Manufacturer's specification.

^b [8].

^c Measured $260\ m^2\ g^{-1}$ [15].

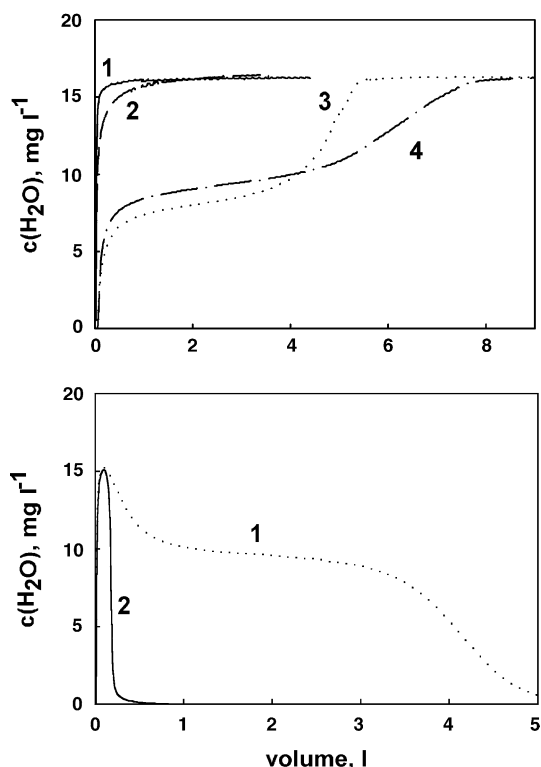


Fig. 2. Upper section: *saturation curves* (H_2O concentration in air at the outlet of the adsorbent trap vs. humid air volume); adsorbent mass – 100 mg; gas flow rate – 100 ml min^{-1} ; temperature 20°C . (1) – fundamental saturation curve; (2) – Carbograph 5TD; (3) – Anasorb CMS; (4) – Carboxen 1002. Bottom section: *desorption curves* (H_2O concentration in air at the outlet of the adsorbent trap vs. dry air volume); adsorbent mass – 100 mg; gas flow rate – 100 ml min^{-1} , temperature 20°C . (1) – Anasorb CMS; (2) – Carbograph 5TD.

undergoes adsorption on the polar centers always present on the carbon surface. This water is weakly bound and can be released easily. Such a mechanism is typical for graphitized carbons. Under saturation with humid air (see Fig. 1, upper section) water vapour appears in the detector practically instantaneously after the start of experiment; next, water concentration increases slowly to reach a maximum value corresponding to $\text{RH} \approx 95\%$ at a given temperature. All polar centers are saturated. The amount of adsorbed water is much smaller than the amount necessary to cover the adsorbent surface with a monomolecular layer of water. In the case of carbon molecular sieves, apart from adsorption on the polar centers, another mechanism is operative, a micropore filling [11]. Some part of water vapour undergoes condensation within the micropore volume, another part passes by freely. This process continues until the micropores are filled entirely, as is evidenced by a pseudo plateau visible on the CMS saturation curve (Fig. 2, upper section). Consequently, CMS sorb much more water per adsorbent gram than do graphitized carbons (Table 1). Such functioning of carbon molecular sieves and graphitized carbons agrees well with our former observations [5,8]. To conclude, Carboxen 1002 and Carboxen 1003 exhibit practically identical features, much similar to those of Carboxen

1000 [5]. However, the saturation curve for Anasorb CMS is different. The water vapour concentration in a gas leaving the trap is smaller – the plateau is located lower and is shorter. Anasorb CMS features a smaller value for the threshold humidity, which will be commented later on. This difference notwithstanding, all three adsorbents function as typical CMS and sorb substantial amounts of water ($400\text{--}450 \text{ mg g}^{-1}$).

The water adsorbed by CMS, massive as it is, undergoes reversible adsorption and can be expunged easily. Water desorption curves from Carboxen 1002 and Carbograph 5TD are shown in Fig. 2 (bottom section). Both sorbents were completely saturated with water. Water adsorbed on the polar centers adheres weakly to the surface [12], and can be removed by dry gas purging. 300 ml of dry air is enough to remove water from Carbograph 5TD (see Fig. 2, bottom section). However, the removal of water from Carboxen 1002 (and from other carbon molecular sieves as well) requires much larger volume of dry air, on the order of liters. A difference in water adsorption between CMS and graphitized carbons is best illustrated if saturation with humid air at two distinct RHs, 90 and 95%, is examined. As can be seen in Table 1, water sorption capacity of CMS does not depend on the air RH (within the range studied, RH either 90% or 95%). However, in the case of Carbograph 5TD and Carboxen X even such a slight change in RH, from 95 to 90%, results in a twofold decrease in the mass of adsorbed water. Water desorption curves for Carbograph 5TD are shown in Fig. 3. The volume of dry air needed to release the water is much smaller when the adsorbent was saturated with air at 90% relative humidity. The ease of water removal from the surface of graphitized carbons can readily be explained on the basis of adsorption mechanism. Water adsorbed on the polar centers is grouped in clusters, and the molecules are interlinked with each other. The number of molecules linked this way with one center depends very strongly on RH [12]. Thus, even a minute decrease in RH of saturating air results

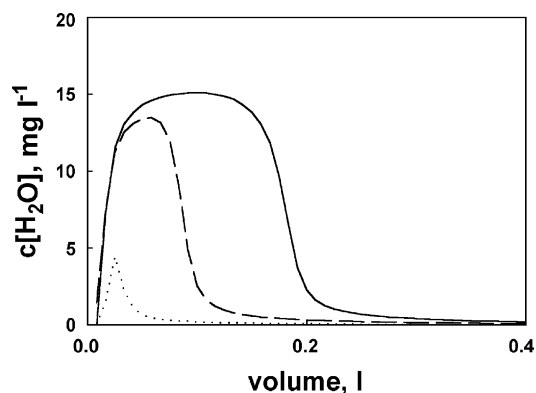


Fig. 3. Desorption curves: (H_2O concentration in air at the outlet of the adsorbent trap vs. dry air volume) adsorbent mass – 100 mg; gas flow rate – 100 ml min^{-1} ; temperature 20°C . Solid line – Carbograph 5TD; adsorption of water vapour from air at $\text{RH} \approx 95\%$; dashed line – Carbograph 5TD; adsorption of water vapour from air at $\text{RH} \approx 90\%$; dotted line – Carboxen Y; adsorption of water vapour from air at $\text{RH} \approx 95\%$.

in a significant decrease in the number of molecules adhering to the surface, and, consequently, in a decrease in the volume of dry air necessary for effective purging.

To conclude, the graphitized carbons studied, Carboxgraph 5TD and Carbopack X, adsorb small amounts of water from humid air (or another gas even at $RH \approx 95\%$), and dry purge is facile. Since in most cases sampling involves air at $RH < 90\%$, adsorption of water on Carboxgraph 5TD and Carbopack X does not occur for all practical purposes. If graphitized carbons are used in traps combined with carbon molecular sieves, the latter ones are responsible for all of the water adsorbed (Fig. 2 and Table 1).

The saturation and desorption curves for Carboxen 1000, Carboxen 1002 and Carbopack X are shown in the Supplementary data, Fig. S1 on the WWW, to save space.

3.2. Threshold relative humidity RH_{thr}

The introduction of threshold relative humidity was a novelty in investigations of water adsorption on CMS [5,7]. The idea originates from the mechanism of micropore volume filling, adopted by Stoeckli [11] to explain the adsorption of water on microporous activated carbons. Here, the essentials of this mechanism will be briefly reminded. For a more detailed explanation see our previous publication [7]. Water vapour adsorption on CMS could be understood as a condensation of some water vapour to the liquid phase in the micropores at RH higher than RH_{thr} . The threshold relative humidity for a given adsorbent practically does not depend on temperature and is related to the water vapour concentration being in equilibrium with liquid water inside micropores.

Eq. (1) was derived using this mechanism. The mass of water adsorbed on the CMS bed, $m(H_2O)$, can be estimated approximately depending on the sample volume, V_{air} , the water vapour concentration in the sampled air, c_{inp} , the relative threshold humidity for a given adsorbent, RH_{thr} , and the saturated water vapour concentration at adsorption temperature, c_{sat} .

$$m(H_2O) = V_{air}c_{sat} \left(\frac{c_{inp}}{c_{sat}} - \frac{RH_{thr}}{100\%} \right) \quad (1)$$

Eq. (1) can be written in a different form using the definition for relative air humidity $RH = (c_{inp}/c_{sat})100\%$.

$$m(H_2O) = V_{air}c_{sat} \left[\frac{(RH - RH_{thr})}{100\%} \right] \quad (2)$$

To estimate the threshold relative humidities for every adsorbent studied, the mass of water adsorbed from 51 of humid air was assessed at a trap temperature. Two water vapour concentrations were examined: 15 and 18 $mg\ l^{-1}$. Experimental dependence of the mass of adsorbed water on the trap temperature for Carboxen 1002 is shown in Fig. 4 (upper section). Solid lines were obtained by fitting experimental results to Eq. (1) on the assumption that $RH_{thr} = 44\%$. Taking into account

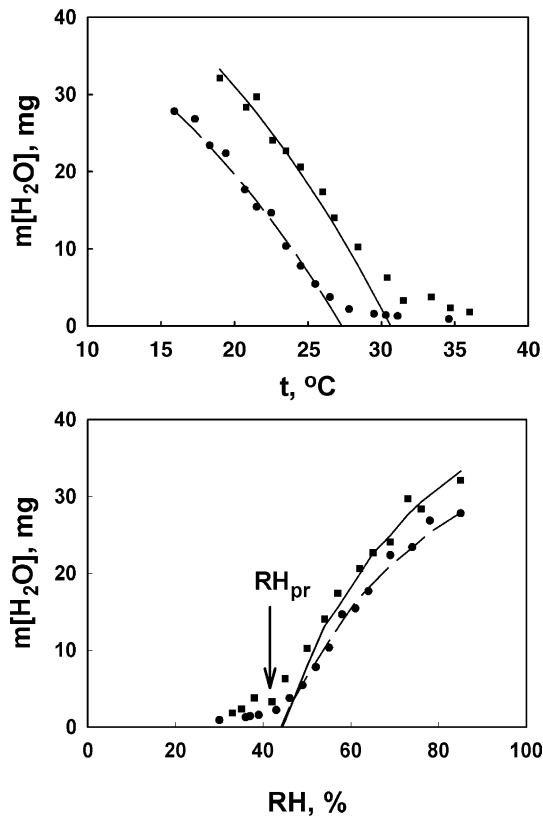


Fig. 4. Water vapour adsorption in Carboxen 1002. (300 mg adsorbent trap). Upper section: mass of adsorbed water from 51 of humid air vs. trap temperature at different water concentration; circles 15 $mg\ l^{-1}$; squares – 18 $mg\ l^{-1}$; solid and dashed lines estimated from Eq. (1) assuming $RH_{thr} = 44\%$. Bottom section: mass of adsorbed water vs. humidity of saturating gas; solid and dashed lines estimated from Eq. (2) assuming $RH_{thr} = 44\%$.

the adsorbent trap temperature, water vapour concentration in air can be recalculated yielding the relative humidity. This way the mass of adsorbed water vs. the relative humidity can be obtained, as shown in bottom section in Fig. 4. Solid lines the dependencies according to Eq. (2) at $RH_{thr} = 44\%$. It is clearly seen that up to a certain threshold value adsorption is very ineffective; in all likelihood it is adsorption on the polar centers. Once RH_{thr} has been exceeded, water adsorption exhibits a fast growth apparently due to micropore filling [11]. Fig. 4 is concerned with Carboxen 1002. To save space, much similar results for other two CMS are presented in the Supplementary data, Figs. S2 and S3, and Tables S1 and S2 on the WWW. RH_{thr} for all three adsorbents are listed in Table 1, and are seen to span the range from from $32 \pm 3\%$ for Anasorb CMS up to $44 \pm 3\%$ for Carboxen 1002. Such values agree very well with those for other CMS studied previously in this laboratory [7,8] (see RH_{thr} for Carboxen 1000 in Table 1).

Examination of Eq. (2) discloses some peculiarities. At $RH < RH_{thr}$, $m(H_2O)$ is negative which can be rationalized as the sink of water, as, for instance, during the dry purge. Further inspection of Eq. (2) reveals that dry purge is more

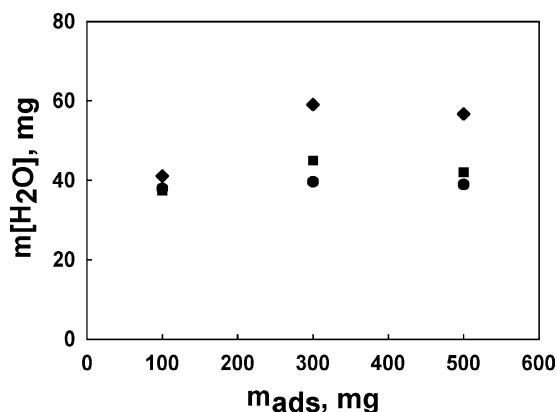


Fig. 5. Adsorbed water mass vs. CMS mass in the trap. Adsorbents saturated with 5 l of air at $\text{RH} \approx 95\%$. Circles – Carboxen 1002; squares – Carboxen 1003; diamonds – Anasorb CMS.

effective the smaller the RH of the purging gas, the most effective at $\text{RH} = 0$.

From an analytical point of view the existence of RH_{thr} is important: adsorption of water in CMS can be prevented by enhancing the trap temperature, a so called warm trap method [7]. Even a slight increase in trap temperature ($\Delta t = 3\text{--}15^\circ\text{C}$) above the temperature of sampled air results in RH decreasing below RH_{thr} , and, consequently, in a drastic diminishment of water adsorption. We have formerly presented dependencies of Δt on RH estimated for carbon molecular sieves at RH_{thr} 35 and 45% (see Fig. 5 in ref. [7]). These values can be used to estimate Δt for CMS studied in this work.

While RH_{thr} for Carboxen 1002 and 1003 is much similar to that for Carboxen 1000 (see Table 1 and ref. [8]) RH_{thr} for Anasorb CMS is much smaller. Since this adsorbent will start sorbing water at lesser RH we cannot advocate its use.

Carbon molecular sieves adsorb substantial amounts of water but only after RH_{thr} has been surpassed. In consequence, two problems important for analytical practice emerge: how the mass of adsorbent in the trap affects (i) the mass of adsorbed water, and (ii) the volume of dry gas necessary for purging.

- i) Dependence of the mass of adsorbed water on the mass of the adsorbent bed has, until recently, been controversial. It has been suggested to use minimum amounts of CMS in traps to avoid water interference [13]. This leads to a decrease in the volume of sampled gas and, consequently, to a deterioration of determination limits (the smaller the bed mass the smaller the breakthrough volume). The experimental dependence of adsorbed water mass on the CMS mass in the trap is shown in Fig. 5 (Supplementary data, Table S3). 100 mg adsorbent portions were saturated with 5 l of RH 95% air. The dependence is seen to be very weak, in agreement with our former work. Even a five-fold increase in Carboxen 1002 or Carboxen 1003 mass practically does not affect the mass of adsorbed water. Only does Anasorb CMS display some dependence but still a small one. A fivefold increase in Anasorb mass is

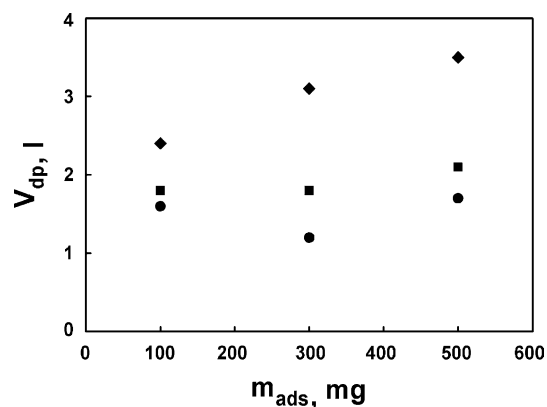


Fig. 6. Dry air volume needed to release water from CMS vs. adsorbent mass. CMS saturated with 1 l of air at $\text{RH} \approx 95\%$. Circles – Carboxen 1002; squares – Carboxen 1003; diamonds – Anasorb CMS.

accompanied by only about 30% increase in the mass of adsorbed water [8].

- ii) The dependence of the dry air volume necessary for successful purging on the adsorbent mass is shown in Fig. 6 (Supplementary data, Table S4). Different adsorbent masses (100, 300 and 500 mg) were saturated with 1 l of humid air at 95% RH (parallel experiments using 3 or 5 l of humid air are described in Table S4). The water adsorbed was released in a stream of dry air. The volume of dry air is seen (Fig. 6) to be practically independent of the adsorbent mass. This may cease to be true if the volume of humid air becomes larger. As many as 9 l of dry air are needed to remove water completely from 500 mg of Anasorb CMS saturated with 5 l of humid air ($\text{RH} \approx 95\%$). Under the same conditions Carboxen 1002 (or 1003) require 4 up to 6 l of dry air for thorough purging.

In conclusion, increase in the adsorbent mass do not affect the adsorbed water mass appreciably. To release the adsorbed water we advocate dry purge [6,14]. The level of water removal during dry purge can easily be monitored using a hygrometer located at the outlet from the sampler.

To sum up we want to emphasize that our results are concerned with only one facet of the analytical problem: coadsorption of water during sampling of organic compounds from humid air or other humid gases. Other features of the adsorbent may require paramount attention: breakthrough volumes, recoveries, degradation of analytes on the bed and adsorbent background.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.chroma.2005.04.096](https://doi.org/10.1016/j.chroma.2005.04.096).

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