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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. Carbrogaph 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.

Keywords: Air analysis; Sample preparation; Carbon molecular sieves; Graphitized carbon adsorbents; Water adsorption; Volatile organic compounds

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 m^2 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 C_3–C_5.

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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 will 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 ± 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

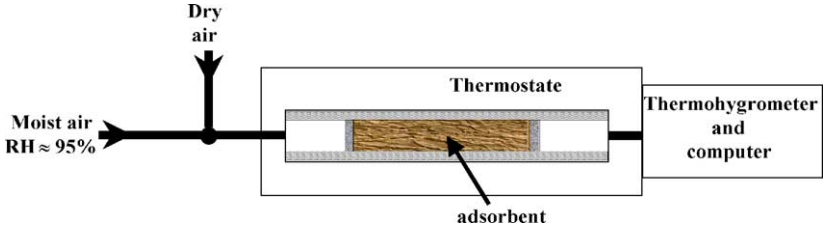

Fig. 1. Outline of experimental setup to study adsorption of water on carbon adsorbents.

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 ≈ 90%) (mg g^{-1})	$m_0(H_2O)$ (RH ≈ 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].